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REPRINTS

DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF WISCONSIN

Volume 1

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AN EXPERIMENTAL STUDY OF THE CORROSION OF IRON UNDER DIFFERENT CONDITIONS

BY

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WITH AN INTRODUCTION BY PROFESSOR C. F. BURGESS

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INTRODUCTORY NOTE.

BY PROFESSOR C. F. BURGESS.

The services which the engineer has rendered mankind during the century just completed are perhaps best illustrated by the extensive use to which iron has been put for industrial purposes as a result of his efforts. Structures which existed only in the imagination of the most venturesome engineers of a hundred years ago have, in this "age of iron," become commonplace realities.

The work of the engineer however, does not end with the design and erection of such structures, but it devolves upon him to see that they shall be permanent. While the importance of the problem of preserving iron from corrosion and decay has long been fully appreciated, a solution of the problem seems to belong to the future rather than to the past. In solving this problem the engineer must contend with a number of foes the most formidable of which is Nature, who seems to demand that decay and continual alteration shall supersede permanence. As a consequence, there appears to be little hope that the corrosion of iron can be completely prevented, and all that can be done is to reduce the rate of corrosion as much as possible. The many ways in which corrosion occurs and the many factors which influence it, make the problem one which is anything but simple and one which calls for a broad range of engineering and scientific knowledge.

It is becoming generally recognized that methods involving "main strength and awkwardness" avail but little in preventing corrosion, and the importance of careful and scientific study of the phenomena pertaining to the corrosion of metals is becoming more universally appreciated.

The bulletin here presented sets forth the results of an experimental study of this question made by Mr. Carl Hambuechen in the laboratory of applied electrochemistry in the University of Wisconsin, the work having been carried on continuously from September, 1898, to July, 1899, and presented as a thesis for the degree of Bachelor of Science in the Electrical Engineering course. While many of the observations made and the conclusions drawn are similar to those which have been previously set forth, it appears that sufficient original work and new information upon the subject are here presented to warrant a publication of the thesis in full.

The probability is pointed out that deductions as to physical and chemical structure of iron may be derived from corrosion effects produced by the electric current, and that by this means, information additional to that furnished by chemical analyses and physical tests may be available.

The work done here on the measurement of electromotive force of strained metals leads to some important conclusions which would tend to overthrow some of the commonly accepted ideas. It has been shown experimentally that iron under stress is more liable to corrosion than when in its normal condition, and, assuming the electrical potential as proportional to the tendency to corrosion, a "stress-corrosion" diagram may be constructed which has the same general appearance as the well-known stress-strain diagram.

It seems to be a common belief that the work which is expended upon a piece of iron in pulling it apart is wholly transformed into heat, such energy being made manifest by a heating of the metal. That the energy is transformed to a certain extent into heat cannot be denied, but that the increase of temperature will account for all the energy expended seems, in the light of these experiments, quite improbable. The experiments seem to show that a portion at least of the work done upon an iron test piece when subjected to stress, is transformed into chemical potential energy, as manifested by a change of electrical potential. Experimental work was not carried on with the object of determining quantitatively this property, but from observations which had been made, a calculation of the work done upon a test piece as obtained from a stress-strain diagram, and of the amount of chemical energy imparted to the iron as calculated from the electromotive force readings, showed that the two amounts are of the same order. A much closer agreement could undoubtedly be obtained by carrying on the experiments with this object definitely in view, in which case the test piece could be designed so as to eliminate the error involved in the approximation which necessarily had to be made in the calculation. This could also be checked by measuring the energy expended upon a test piece and simultaneously measuring the heating effect by means of a suitably designed calorimeter, the difference of the two giving the energy which is stored up as potential energy. It is expected that this work will be continued in the near future.

AN EXPERIMENTAL STUDY OF THE CORROSION OF IRON UNDER VARIOUS CONDITIONS.*

Introduction.—The rapidity with which iron corrodes under ordinary conditions is a question of great importance in the industries, and it involves a large proportion of the civilized people, since upon it depends the security of life, which is affected by the durability and safety of metallic structures, not to mention the item of expenditure of many millions of dollars yearly for depreciation, and expense of renewals. The rate and mode of decay of iron structures has received considerable theoretical and experimental study, but there is still much to be revealed upon this important question through the application of rational scientific methods which have hitherto been little applied.

It has been observed, for instance, that some particular qualities of iron have very different rates of corrosion from others when exposed to similar conditions; that equal amounts of metal removed by corrosion will weaken one kind of iron more than another; that iron containing graphite or carbon in uncombined state corrodes differently from iron in which the carbon is in the combined state. Whether it is the physical character, or the chemical character of the material, or a combination of the two, which influences the rates and effect of corrosion, is a matter of considerable doubt. The influence of silicon, manganese, sulphur and other impurities on the tendency to corrosion has been studied experimentally, but in such a way that little light has been thrown upon the subject.

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* A thesis submitted for the degree of Bachelor of Science in Electrical Engineering, University of Wisconsin, June, 1899. This thesis was awarded the Science Club Medal as the most meritorious thesis in pure or applied science for the year 1899. It was also awarded special honors by the Faculty of the University of Wisconsin.

Many peculiar cases of corrosion have been noted; as, for example, a more rapid corrosion in different parts of the same iron plate; marked pittings at certain places; that cast iron on exposure to sea water is changed into soft carbonaceous material within a period of two and one-half years,* and satisfactory explanations for such phenomena have not been forthcoming.

An attempt is made in this thesis to indicate a promising path for scientific investigation of the phenomena involved in the corrosion of iron, and to set forth the results of some experimental studies that have an immediate application to the proper theory of the action.

The most plausible explanation of the corrosion of iron is an electrolytic one, for it has been determined that the conditions necessary for corrosion are the same as the conditions which are necessary for electrolytic action.

The Conditions of Electrolytic Corrosion.—1. Two or more conducting substances in contact with an electrolyte.

2. A difference of electrical potential set up between such bodies.

3. Connection between the conducting substances furnishing a path for the flow of current.

These conditions are all found to be coexistent with the corrosion of iron. The electrolyte consists of moisture, which may be in contact with the iron body. It is known that iron in dry air will not rust, this being due presumably to lack of an electrolyte.

The difference of potential mav be set up in various ways. The iron which is never absolutely pure, may have in electrical contact on its surface foreign materials such as particles of carbon, graphite, various metals, and some metallic oxides which will conduct. Each of these substances sets up an electric potential peculiar to itself when immersed in an electrolyte, and as these potentials are different for different substances, differences of potential exist between the particles of the various foreign

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* **Trans. Am. Soc. Mech. Eng., 1895, p. 350.**

substances and the iron. These differently charged bodies being in contact, a flow of electricity is set up, the circuit being completed through the electrolyte. An electric current thus set up, flowing from the iron to the electrolyte, causes the eating away of the iron.

We may have metals in contact with iron, which, instead of promoting, will actually prevent corrosion of the iron by reversing the direction of the flow of current. This fact has often been noted, and some laboratory experiments which were carried out during the progress of this investigation confirm this explanation.

Cast iron plates three inches in diameter and three-fourths of an inch thick were polished on one face by a fine emery wheel and the remaining surface was lacquered. In the center of the polished surface a hole five-eights of an inch in diameter was drilled, and plugs of either copper, zinc, lead or carbon were firmly inserted. The specimens were then placed in sand, saturated with a solution of ammonium chloride. After an exposure of one month the specimens were examined and it was found that the polished iron surface had been badly corroded excepting in the case where the zinc plug had been inserted, the surface here having its original bright appearance.

The reason for this difference is that in each case with the one exception, the current flows from the iron to the solution, as explained above, and the iron is corroded, while in the exceptional case where the zinc plug was used the direction of the current is from the solution to the iron, and corrosion, therefore, does not take place.

In general it may be stated that any substance in contact with iron which, in the electro-chemical series is more electro-positive than iron, will tend to protect it, while the more electro-negative substances will promote the corrosion of the iron. Among the former substances are: magnesium, aluminum, zinc, and cadmium, and among the latter: lead, antimony, tin, copper, silver, carbon, some of the metallic oxides, etc.

A marked example of corrosion thus increased by the presence of a foreign body in contact with iron is seen in "pitting" in steam boilers, where it is frequently observed that each corroded place has in its center a small piece of cinder or carbon, thus centralizing the location of corrosion around that particular point.

It has been found that other factors influence the rate of corrosion, such as the difference in the physical character of different parts of the same piece of iron, such differences being caused by differences in temperature, variations in homogeneity, and differences in strain to which the metal has been subjected.

Rapid Method of Studying Corrosion.—A hindrance to experimental investigation on the corrosion of iron is the length of time required to produce measurable results. By taking advantage, however, of the fact that corrosion is caused by current flowing from iron to electrolyte, the rate of corrosion may be greatly increased by causing a current generated externally to flow from the iron as anode, thus causing the corrosion to occur under what may be termed exaggerated or intense conditions.

By use of a suitable electrolyte the iron may be corroded as much by this means in a few hours as it would be corroded in as many years by exposure to the weather, the resultant surface being practically the same in either case. By this method the character of the corrosion in different qualities of iron was studied, and from the results obtained by these tests it is noted that the effects produced by ordinary corrosion and by electrolytic corrosion are similar.

The descriptions of experiments which are represented herein are in every case illustrative of a series which frequently occupied weeks of time in preparation and execution. In some of the work carried on the methods used for producing and observing results and eliminating errors are new, and the burden of the work was thus increased. The deductions are drawn from a large amount of data.

Experiments for studying the character of corrosion in different qualities of iron were performed by placing specimens, as anodes, in glass jars containing a solution of ammonium chloride. Then by connecting a number of jars in electrical series, and having the exposed anode areas the same, the effect of an electric current upon the different samples was directly compared. Tool steel, cast iron, and sheet iron were taken as representative grades of iron of different chemical composition and crystalline structure. To facilitate comparison of results obtained under different conditions of corrosion, various specimens were taken from the same bar, or sheet of metal. The results are given in Tables I–IV.*

Condition of Specimens After Corrosion by an Electric Current—The appearance of different test pieces of similar qualities of iron is very much alike after corrosion by the electric current, but different qualities of iron present marked differences in this respect, as is shown by the plates which accompany this paper.

The surface of the cast iron specimens in each case consisted of a soft carbonaceous material which under some circumstances adhered very firmly to the surface of the iron. In case the current density was carried beyond 0.025 amperes per square inch, this soft material was found to separate from the iron after attaining a certain thickness. (See plate 21, fig. 2, plate 22, fig. 1, and plate 24.)

The sheet iron specimens were covered with a soft spongy material which could be readily removed with a brush; the metal below this coating had a bright appearance. (See plate 16 and plate 17, fig. 1.

The tool steel specimens were also covered with a layer of spongy material, but below this layer was a thin layer of black carbonaceous material similar to that of cast iron. (See plate 17, fig. 2, plates 18–20, and plate 21, fig. 1.)

Discussion of Results—It will be noticed by comparing the results given in table 3 that the amount of corrosion is for most of the specimens greater per ampere hour than the theoretical amount given by Faraday's law (1.0448 g. per ampere hour);

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*See end of paper.

the cast iron specimens, however, appear to be an exception to the rule and show a much lower rate of corrosion than would theoretically be required. This is accounted for by the fact that cast iron, as previously described, becomes covered with an adhering coating which possesses some strength and which, if forcibly removed by mechanical means, would make the loss to the plate per ampere hour equal to 1.17 grams as shown in table 2. The exception is therefore more apparent than real.

A peculiar effect was noticed in the case of the cast iron anodes, in the liberation of a gas at that point. That this was not due to the flow of current directly was shown by interrupting the current, the liberation of gas continuing for some time. In just what this action consisted I was unable to determine.

The peculiar changes which cast iron undergoes when acting as the anode are worthy of note. If the current density is not excessive, the iron may not undergo any material change in appearance, even though subjected to the action of the current for a long time. But, although the general form and outward appearance may remain the same, the fact that its structure has been materially altered may be readily shown by cutting or scraping it with a knife. It will be found to be softened to a certain depth, and the material which may be removed by scraping has the appearance of fine iron filings and graphite. If allowed to stand for some time and become dry, the coating becomes much harder—so hard, in fact, that it is with difficulty cut by a knife. It must therefore impart a certain amount of strength to the iron, but this amount is much less than that which the iron originally possessed.

Such corrosion of cast iron has been frequently observed in cast iron pipes exposed to the action of electric railway currents, the pipe in many cases retaining its original form, but possessing little strength, as may be readily shown by the use of a hammer and chisel. Cast iron is usually credited with being much more durable than other forms of iron for under-ground pipes exposed to the action of leakage current from electric railways.

This may be due to several different causes, principal among which are the following:

1. The fact that the cast iron may not change its form and general appearance even though it has been weakened by electrolysis, might convey the erroneous impression that it is still intact, while a wrought iron pipe exposed to the same conditions would quickly reveal its weakness to casual inspection.
2. This graphite-like coating forming on the cast iron may become hard and impart a certain amount of strength to the corroded pipe, while a wrought iron pipe equally corroded is not similarly favored.
3. It may *seem* that a cast iron and a wrought iron pipe are equally subjected to the corrosive action of the electric current while this is not really the case, due to the formation of this layer over the cast iron, which must offer some resistence to the flow of the current, and therefore protect it to a certain degree. Or, in other words, other conditions being the same, a given potential difference between an iron pipe and railway track will cause less current to flow if the pipe is of cast iron than if it be of wrought iron.

The conclusion may be safely drawn from my experiments that a given amount of current flowing from normal cast iron and wrought iron will cause an equal amount of corrosion in the two.

The changing of iron to a sort of soft graphitic substance is not a phenomenon alone associated with the flow of electric current from an external source, but it may occur without the external application of current by immersing cast iron in sea water for a long time. There are cases on record where cast iron cannons have been raised out of the sea after being submerged for many years, this cast iron having undergone the same changes as have been noted of the specimens used in my experiments, and the evidence appears to show that the changes were caused by local electric action of the nature that I have already explained.

The effect of the presence of mill scale (oxides of iron—$Fe_3 O_4 + Fe_2 O_3$) on the rapidity of corrosion, is shown by examining plates 18, fig. 2, and 20, fig. 1, which exhibit the appearance of specimens of annealed tool steel. The only difference in the treatment accorded the two was that in one case the surface had been ground by an emery wheel before the specimen was subjected to the corroding influence (plate 18, fig. 2) while in the other the scale formed during the annealing was allowed to remain (plate 20, fig. 1.) Similar results are shown by two burned steel specimens (plates 19, fig. 1 and 20, fig. 2) where similar differences of initial surface conditions existed in the specimens.

Changing the crystalline structure of steel by hardening, annealing, or burning, causes the amount of corrosion to vary, according to the results given in tables 1 and 3. Here we find that the amount of corrosion, per ampere hour, of the hardened steel is considerably less than that of annealed or burned steel. The effect which the crystalline structure has upon the corroded surface is well shown in the plates (plate 17, fig. 2, plates 18–19, and plate 21, fig. 1.) The pitting of the annealed specimen (plate 18, fig. 2) is similar to that of sheet iron (plate 16, fig. 2), which would naturally be expected, as the only known difference between the specimens in the small percentage difference in carbon and other slight impurities. The corrugated surfaces of hardened steel (plate 18, fig. 1 and 19, fig. 2) and of steel burned and then hardened (plates 17, fig. 2, and 21, fig. 1) are here to be noted and an apparent reason for this peculiar corrosion will be given later.

Corrosion of Iron in Different Solutions.—The ammonium chloride solution alone had thus far been used and for the reason that it represents fairly well the salts that are apt to be found in the ground that may be expected to surround iron structures of various kinds. However, the question may arise whether the action of a nitrate, or sulphate or other solution is different from that of the chloride solution? According to the results of a study by Silber and Biefeld* a sulphate of nitrate is not as active as a chloride. To determine this again, experiments were performed by taking nine pieces of sheet iron of the same size, and placing three specimens each in corrosion cells containing respectively normal solutions of ammonium chloride, ammonium sulphate and potassium nitrate. The nine cells were connected in series so that the same current passed through each specimen. The decrease in weight, as given in table 5, shows that the losses in the different solutions are practically the same, and that whether the salts are sulphates, nitrates or chlorides does not materially affect the amount of corrosion. This would of course be expected, being in accordance with the requirements of Faraday's laws. In the work of Biefeld and Silber, referred to, the cells were filled with sand moistened with the solutions of the respective salts. This made diffusion of the salts difficult, and doubtless the differences between the activity of corrosion of the different salts which they observed may be thus explained.

An interesting effect is, however, shown by the variable pitting in the different solutions (plate 22, fig. 2 and plate 23). Here we have a round pitting as a result of the action of the chloride, an elongated pitting from the sulphate solution, and a more uniform corrosion by the nitrate solution. It may clearly be concluded from the numerous experiments that I have examined that the manner in which corrosion affects an iron surface depends not only upon the chemical and physical structure of the metal itself, but also upon the nature of the electrolyte.

Ordinary Corrosion of Iron.—In order to draw a comparison between electrolytic corrosion and ordinary corrosion of iron, specimens similar to those previously described were immersed in a large tank containing a normal ammonium chloride solution and left undisturbed for four months. The results obtained from this experiment, as given in table VI show that the amount and character of corrosion depend upon the quality of iron and

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* University of Wisconsin, 1894. *Cf.* The Corrosion of Iron Pipes by the Action of Electric Railway Currents. D. C. Jackson, Jour. Assn. Eng. Soc., 1894, vol. 13, p. 509.

to that extent confirms the conclusions derived from electrolytic corrosion. The time was too short, however, to observe any very marked pittings; nevertheless, traces of corrosion similar to electrolytic corrosion could be observed, a slightly corrugated surface on the hardened steel specimens and a streaky pitting on the burned steel being noted.

Corrosion of Strained Metal.—There is no difficulty in explaining how the presence of conducting material other than iron, when placed in contact with normal iron may cause its corrosion in spots, as heretofore explained, as foreign materials or impurities are likely to be unequally distributed. It would be more difficult to apply the same reasons in explaining the corrosion illustrated by such a case as the specimen which is exhibited in plate 17, fig. 2, for it would be unreasonable to suppose that the impurities are regularly distributed as indicated by the corrugations.

It is a fact known among the boiler manufacturers that boiler plates made by drilling the rivet holes are more durable than those made by punching the holes in the cold plate. In the latter case it has been found that corrosion sets up in the neighborhood of the rivets, thus weakening the boiler. The same phenomenon has been observed in ships' plates.

In Willoughby Smith's *Rise and Extension of Submarine Telegraphy*,* it is stated in an account of the recovery of the cable of 1858, that the "core" (the gutta percha insulating material) looked as new as when first made, but it was curious to see that the outer covering of iron wire was intact in places and looked as though it had just left the factory, while in other places not far away the wires were broken and corroded to sharp points, evidently showing that at some time the cable had been under great strain.

We evidently have in these illustrative cases conditions which caused corrosion of iron, the cause of which cannot wholly be ascribed to the presence of some substance other than iron which is more electronegative. There must be differences in the

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* Page 305.

iron itself, and these differences must be dependent upon the mechanical strains to which the iron has been subjected.

Andrews's Experiments —Mr. Thomas Andrews of the Royal Society has performed a series of interesting experiments in which he has shown that a difference of potential existed between the strained and unstrained iron. A description of his experiments is as follows:*

> "Pieces of iron and mild steel of known character were submitted to tension, torsion, and flexure strains. For tension, a bar was strained until an elongation was produced of 23 per cent. in three inches, and at the point of reduced area, the bar was cut in two."
>
> "The halves were then turned down in the lathe at the shackle or vise end, where they had been subjected to little or no stress, until they had an area equal to the end half at the point where contraction of area had occurred, both pieces being finished exactly alike, and each piece representing a section of strained and unstrained metal.
>
> "They were then placed at the same depth in a saturated solution of common salt to approximate the action of sea water on metal, the immersed ends representing strained and unstrained metal respectively. An electrical contact being made between the two pieces of metal, through the medium of a delicate galvanometer (Thomson's), the difference in potential or corrodibility could be observed. It was found that in each case a sensible current was set up between the two halves of the specimen; the unstrained portion was in every case found to be the electropositive element of the pair, corresponding to the zinc in a galvanic couple, indicating clearly that the 'unstrained' metal was acted upon more rapidly by the solution and thus more easily corroded than the 'strained' metal."

Relation of Electromotive Force to Stress.—If, according to the above results, the tendency to corrode, as indicated by the electromotive force, is changed by straining the metal, it would be of interest to know in what manner the difference of potential varies with the stress. To investigate this matter, I arranged an apparatus which would simultaneously record the variation in electromotive force, and the stress placed upon the specimen. This was accomplished by placing the test piece in a testing machine, surrounding a portion of it with an electrolyte, as

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*Trans. Amer. Soc. Mech. Engineers, 1894, p. 371.

shown in plate 15. By means of a normal electrode and potentiometer, the electromotive force was measured. The normal electrode used was of the form described in LeBlanc's Electrochemistry, * consisting of a pure mercury electrode covered with a layer of mercurous chloride and the electrolyte, which is a normal solution of potassium chloride. The value of electromotive force usually ascribed to this form of normal electrode is 0.56 volt, and in direction from the electrolyte to the mercury, i. e., the mercury is at the higher potential and this value was assumed to be correct and form the basis of the following measurements. It is quite certain that such electrode maintains a constant value of electromotive force even when roughly used, and the fact that there is some dispute as to just what value should be given to this electrode in no wise affects the following results.

The apparatus which I employed in making the measurements of electromotive force consisted of a capillary electrometer and potentiometer testing set of the form designed by Mr. C. F. Burgess. The electrometer had a degree of sensitiveness sufficient to respond to a change in electromotive force of about 0.00007 volt.

The electromotive force of iron in an aqueous solution of its salt being very nearly zero, my electrochemical chain, which consists of the iron specimen and the normal electrode, gives a total electromotive force of 0.56 volt. To allow the most sensitive arrangement of the instruments used, it was found desirable to oppose this electromotive force by the difference of electromotive force between a Clark standard cell (1.434 volt) and a Helmholtz standard cell (1.00 volt). In other words a device was used to reduce the voltage to be measured from about 0.56 volt to 0.126 volt.

A large amount of preliminary work was necessarily performed before reliable results were assured. Various arrangements of apparatus and forms of test pieces were used, and considerable labor and thought was expended upon the trials, but

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* Page 218.

the final arrangement for carrying on this investigation is shown by diagram (Fig. 1). The test piece T was placed in the testing machine and the desired stress placed upon it. The wooden cup C, which was thoroughly paraffined, contained the electrolyte ($Fe\ Cl_3$). The difference of potential between the iron and the solution was then determined by the aid of the normal electrode N, the two electrolytes being placed in contact through the tube a. The Clark cell S, and the Helmholtz cell H, were connected in the circuit so as to oppose the normal electrode by their difference in voltage. By means of the electrometer, E, and the potentiometer, P, the total or resultant electromotive force of the arrangement was measured.

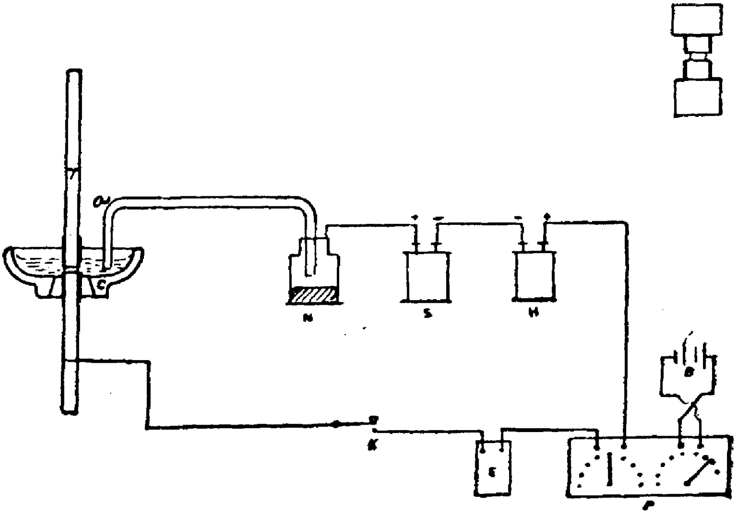

FIG. 1.

Before the adoption of this arrangement a number of devices were tried (as previously mentioned) but they were found to introduce errors and give unsatisfactory results. At first, a bottle with the bottom removed was used in place of the wooden cup, this being filled with a solution of ammonium chloride to a height of two inches. It was found that a variation in the position of the glass tube, *a* in figure 1, caused a difference in the reading of the potentiometer, and as the stress in the different parts of the test piece varied, local action was set up which again produced an unsteadiness in the readings.

It was thought that less unsteadiness in the readings would be introduced by reducing the area of contact of the electrolyte and the surface of iron, and to reduce the surface of the test piece in contact with the liquid, a trial was made by wrapping filter paper in a strip about three-eighths of an inch wide around the test piece, the filter paper being saturated with NH_4 Cl solution. Although this method gave improved results it was inconvenient to use, due to the evaporation, and in addition the contact surface was still too large for accurate readings. The wooden cup was then tried, and just enough liquid was introduced to allow only a narrow strip of metal to make contact with the liquid. Although this was found to be a more satisfactory arrangement, trouble was again caused by the creeping of the solution up the test piece, causing unsteady readings, the action of the air being thought to be the disturbing element. This was obviated by carefully covering the test piece with paraffine and scraping a narrow ring of paraffine away by placing the test piece in a lathe and cutting a small distance into the metal so as to bring the break within the distance being measured. There was thus only a small portion of the entire surface exposed to the electrolyte, and that portion was entirely immersed in the electrolyte. The coating of paraffine, being somewhat soft and pliable, was not injured by the elongation of the test piece. This method finally adopted after many trials gave very uniform results.

Results of Tension Tests —The results obtained, with various test pieces of iron, zinc, copper, and brass, are given in tables 7 to 25 and are also shown graphically by means of curves which were obtained by plotting stresses as ordinates and electromotive forces as abcissas. Hereafter I will refer to such curves as *stress electromotive force diagrams.* (See plates 6–14.)

It is seen that in nearly all the tests either of tension or compression the electromotive force rises with the stress. This increase in electromotive force is similar to the elongation produced by the stress. No marked changes of electromotive force occur until the elastic limit is reached, after which we have a rapid rise in the electromotive force, showing that the work which has been expended upon the piece, and stored up in it, is made evident by an increase in electromotive force and therefore an increased tendency to corrosion.

To compare directly a stress-strain diagram with a stress-electromotive force diagram, simultaneous readings were taken, using an automatically recording Riehle testing machine. The similarity of the two curves is shown by plate 10. In the stress-strain diagram we have at a certain point a, a sudden drop in the stress, which is accompanied by a similar drop of electromotive force, shown in the stress-electromotive force diagram by means of dotted lines, and shown better by means of table XVII. These two irregularities in the curves, occurring simultaneously, show how closely the electromotive force is dependent upon the stress.

It suggested itself that scraping the surface might have introduced serious error, as a surface is thereby produced which has already been strained. It is true that the electromotive force of a metal is increased by polishing or burnishing, but this effect is removed by scratching the surface with sand or emery cloth.* In the case of my test pieces I have at first what is equivalent to a burnished surface and the electromotive force is slightly higher than if perfectly unstrained metal were used. But upon subjecting the test piece to a strain and an elongation the surface is broken up and this effect removed.

Even assuming that the strained surface did introduce an error into the readings; from the fact that the electromotive force increased upon straining the metal, this error would be on the side to reduce the effect of the added strain, and a correction for the orror (if any exists) would show more marked results than those actually obtained.

By taking two pieces of iron from the same sample, one piece of which had been strained and one unstrained, and immersing the ends in an electrolyte, a measurement of electromotive force between these test pieces gave results agreeing very closely with the increase of electromotive force obtained in the testing machine.

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* Philosophical Magazine, 1898, Vol. 46, p. 82.

Tests were made with metals other than iron to see if analogous conditions existed, and for this purpose, rods of copper, brass, and zinc were used. It was found that the contact electromotive force between these metals and the electrolyte was increased by the stress (Tables VII, VIII, IX, X, XII). It will be noticed that brass does not seem to be affected materially until the breaking point is reached.

As the "strained" metal has a higher electromotive force than the unstrained metal, the conclusion would be drawn that a "strained" piece of iron will corrode faster than the unstrained piece; and this is borne out by experience. Assuming this statement to be correct, which seems undoubtedly to be the case, an explanation for many cases of corrosion of iron and steel is available. In the case of the punched rivet holes previously mentioned (page 244) the metal around the rivet has been subjected to a great stress, which causes it to assume a higher electromotive force toward an electrolyte than the surrounding metal and the rivets themselves. This condition favors the flow of a galvanic current, eating the strained metal away in the manner shown in actual practice. In the case of bored rivet holes, no inequality of electromotive force, and hence no inequality of corrosion exists.

In the illustration of the corroded cable armor, the corrosion of the strained places is similarly explainable.

We have here also an explanation of the peculiar corrosion which is exhibited in plates 17, fig. 2, 18, fig. 1, 19, fig. 2, and 21, fig. 1, all of hardened steel specimens. It is well known that during the process of hardening steel, stresses are set up within the metal, which may be sufficient in some cases to cause the steel to crack, and even fly in pieces. The stresses thus set up in the metal, causing certain parts to be more strained than others, will cause an unequal corrosion, the strained parts being corroded more rapidly than the unstrained.

Polished Surfaces.—It is a matter of common knowledge that an iron or steel surface which has been highly polished is far less liable to corrosion when exposed to the weather than a surface which has not been similarly treated. Among the explanations which have been offered for this fact are: that not so much surface is actually exposed; that a porous surface is more readily acted upon than a smooth one; that oil is used in polishing, and therefore affords protection, etc. I wish to add a further explanation, which seems to me to more fully fit the requirements.

In polishing a surface the particles of metal on the surface are subjected to a stress by the grinding or polishing materials, and the better the polish, the more nearly alike are the individual particles as regards their strained condition. A perfect polish would therefore mean a uniform state of strain in each particle and therefore a uniform condition over the entire surface. There would be no differences of potential and therefore no chance for galvanic action.

The results obtained in my experiments are diametrically opposed to those given by Mr. Andrews, and referred to heretofore, he making the statement that strained metal has a lower electromotive force toward the electrolyte than the unstrained. Mr. Andrews, in a discussion of his results, states that an *increase* of electromotive force ought to be expected and for its non-occurrence gives the following reasons:*

> "The experiments now recorded have afforded the additional information, that the corrosion of metals is considerably affected by the stress, varying according to the nature and extent of the strain applied. It might have been thought metals under stress would be more liable to increased corrosion than when in their normal state. The present experiments, however, indicate the opposite conclusion. This is when 'strained' is considered separately from 'unstrained' metal. When, however, the strained metal is in galvanic circuit or combination with the unstrained metal in any solution, an increased total corrosion ensues from galvanic action, which research has shown to arise consequent on the difference of potential between the two. The reason why the mere fact of a metal having become strained reduces its corrosibility, compared with the same metal in its normal unstrained condition, will be found in the results of a series of experiments undertaken by the author to investigate the influence of stress on railway axles. In that research it was demonstrated that the stress, whether tensile,

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* Transactions of the Institution of Civil Engineers of England, 1893-94, Vol. 118, p. 365.

flexional, torsional or any other kind, considerably alters the physical properties of iron and steel. Stress increases the rigidity of both iron and steel and renders the metal harder, also greatly reducing its properties of elongation and ductility. A higher tonnage is required to a 'strained' than an 'unstrained' portion of the same metal. A tensile stress applied to a wrought iron shaft, producing an elongation of only two per cent., increased the tensile resistance of the metal 2.66 per cent. Other investigators have also noticed a similar alteration in the properties of the metal referable to stress.

"From these observations it is manifest that the stress applied to the metal examined for corrosion, altered their structure, rendered them harder in nature, and hence less liable in the strained condition to be acted upon by sea water or other waters, than in their ordinary normal or soft condition."

From the fact that my results are contrary to those obtained by Mr. Andrews, who seems to have carried on quite an extensive investigation upon the subject, I was led to carefully study my results and the methods used for obtaining them, to see whether any serious error could have crept in; also to compare my methods of measurement with his methods of measurement. I am led to the conclusion that in my work greater precautions were used to insure against error than in the experiments of Mr. Andrews, as far as can be judged from the description given of his measurements. In the preparations of the samples under test, much greater care was used. The method which I used for obtaining the values of electromotive force is superior to his, embracing as it does the advantages of the potentiometer, or zero, method as opposed to the deflection galvanometer method for measuring electromotive forces. The requirement of the galvanometer method is the flow of an electric current, which causes alteration in the electromotive force due to polarization, while the potentiometer method depends upon the balanced system of electromotive forces.

As a check on the results which I have obtained, I prepared two specimens of iron in a manner similar to that used by Mr. Andrews; but instead of turning down the specimens in a lathe, I paraffined both pieces of iron, exposing only a small portion of the strained and unstrained metal. They were then placed as anodes in a solution of ferric chloride, and the exposed surfaces cleaned by electrolyzing the iron. By adopting this method of preparing the specimens, I avoided the error to which Mr. Andrews subjected himself of having a surface which was strained by the turning of the pieces in a lathe.

After the pieces were thus cleaned, the polarity was determined by means of the potentiometer and by the galvanometer, and both instruments indicated that the strained metal was the negative pole of a galvanic cell, again showing that strained metal would be corroded more rapidly than the unstrained.

In order to still further satisfy myself that my conclusions are not in error I repeated Mr. Andrews' experiments as nearly as I could from the description given by him. Two iron test pieces of the dimensions given by him were prepared and placed in a testing machine and subjected to a stress until an elongation of twenty-three per cent. in three inches was produced.

Immediately upon immersing both pieces simultaneously into a solution of sodium chloride, the strained metal was found to be the negative pole of the cell; but after one or two minutes the cell reversed, the unstrained iron becoming the negative pole of the cell, and this condition appeared to be stable. It was found, however, that upon shaking the cell, or by taking out one piece of iron and then replacing it, almost any result could be obtained. It appeared to me that this was due to a local action near the surface of the solution, and the top ends of the two specimens were then paraffined, thus preventing any creeping of the solution. This change appeared to reduce the unsteadiness to a considerable extent.

After allowing the test pieces to remain in solution for five hours, a measurement showed that the cell had again reversed and that the strained metal was again the negative pole. Upon again standing over night and then measuring the electromotive force it was found that the strained metal was still the negative pole, though the amount of the electromotive force had decreased slightly. Upon stirring the solution so as to remove the rust from the specimens, the electromotive force was increased threefold.

Such measurements readily show that almost any results may be obtained unless suitable precautions are taken. From the measurements it may be seen how results diametrically opposed to those I have previously described may be obtained by making measurements shortly after immersion and before stable conditions are reached.

Lord Kelvin in his experiments on Contact Electricity* found that by burnishing the metal the electromotive force increases, which would seem to confirm my results, as in this case the metal is strained, though, of course, only on the surface; and my results are further confirmed by the cases of corrosion to which I have referred and which may thus be readily explained.

It is well known that upon stretching or compressing a piece of metal in a testing machine beyond the elastic limit the temperature is increased, due to work which is done upon the metal. As a result, the question would naturally arise, is it not possible that the increase of electromotive force which has been observed is due to this increase of temperature, rather than to the strain of the metal directly? To determine whether this was actually the case the following experiments were carefully performed: An iron test piece about ten inches long was prepared as in the other experiments and placed in the apparatus as shown in the view of testing apparatus (plate 15), and the electromotive force carefully noted. The upper end was heated by a Bunsen flame, and, by conduction, the iron in the electrolyte was raised to a temperature much higher than would be produced in the testing machine. Measurements of potential showed that there was very little, if any, increase of electromotive force due to heating alone, there being sometimes a very slight negative and then a slight positive change; but in no case sufficient to account for the change in electromotive force observed when the metal was subjected to strain beyond the elastic limit, thus showing that the heating of the test piece had introduced no appreciable error.

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*Phil. Mag., 1898.

CONCLUSIONS.

A brief summary of the conclusions which may be drawn from the work embodied in this thesis should include the following points, some of which seem to be shown here for the first time, while some have previously been pointed out by others:

1. Nearly all, if not all cases of ordinary corrosion of iron and steel depend upon its physical and chemical properties. galvanic action due to differences in potential between different parts of the metal.

2. Electrolytic corrosion produced by the flow of current of moderate density from an external source produced results upon the metal which are similar to those produced by corrosion under ordinary conditions, thus affording a rapid method of studying the subject.

3. The character and rapidity of ordinary corrosion in iron and steel depends upon its physical and chemical properties.

4. Electrolytic corrosion of iron and steel where moderate current densities are employed does not give exactly the values which are called for by the application of Faraday's laws, and the divergence from these values depends upon the physical and chemical structure of the metals, and the impurities present.

5. The character of the corroded surface depends upon the physical and chemical properties of the metal, and also upon the electrolyte.

6. The application of stress to metals causes an increase in chemical activity, this increase being especially marked after the elastic limit has been reached.

7. It is possible to get a curve showing the relation of electromotive force to strain which is similar to that of stress to strain.

8. There is a definite relation between the electrical potential of iron toward an electrolyte and the amount of energy stored up in the metal through the application of stress.

9. Some peculiar cases of corrosion are explained through the application of these propositions for which no good explanations have hitherto been offered.

Evidences of Stored Energy.—A study of results such as have been shown in this work might have some important bearing upon electrochemical theories, but it has not been my purpose to deal especially with this side of the subject.

I do not attempt to explain just why a strain in a piece of iron will produce a change in its electrical pressure toward an electrolyte. That it does so seems to be demonstrated beyond question by the experiments.

The expression which Dr. Walter Nernst gives to show the value of electromotive force set up by a metal in an electrolyte is,

$$E = c \log \frac{p}{p'}$$

where c is a constant, p is the so-called "solution tension" of the metal, and p' is the osmotic pressure of the ion of that metal in the electrolyte. This formula does not take into account the fact that a certain metal may exert a different electromotive force when strained and when unstrained, and assuming this formula to hold, we must assume that the solution tension of the metal, p, must depend upon various conditions, and cannot be a constant for a given metal as is usually assumed to be the case.

Looking at the question from the thermo-chemical side, it is quite evident that the thermal effect of dissolving in an acid a steel spring which has been coiled up, must be different from what it would be if the uncoiled spring had been dissolved; else what would become of the energy stored up in the spring?

In straining a piece of iron, a certain amount of work must be expended upon it. It is true that a portion of this work is expended in heating the sample, but it must be only a small fraction of it, as shown by the fact that there is a very slight rise in temperature, and the remainder must thus be consumed in producing some other result. This stored up energy manifests itself in an increase of electromotive force, which in turn leads to the conclusion that the heat given off in dissolving a strained metal in an acid would be greater than it would were the same amount of unstrained metal dissolved.

In applying a tension to a metal, thereby causing an elongation of a certain amount, a certain amount of energy is expended upon the metal, namely:

$$W - \frac{TL}{12} \text{ ft. lbs.}$$

where T is the tension in pounds and L is the elongation in inches.

This energy is stored up in the metal, some of it manifesting itself in the form of heat. That only a small fraction of the energy is thus expended within the elastic limit, is shown by the fact that if the elastic limit has not been exceeded, the energy can be restored as mechanical energy. If the elastic limit has been exceeded, and if all the work done upon the body were transformed into heat, a rise in temperature would be observed which is beyond that actually obtainable. It must consequently be assumed that the energy is stored up in the metal itself, and this appears to be done in such a way that it becomes manifest when the body is submitted to chemical action, as has been shown quantitatively in the foregoing work by measurement of electromotive force.

Assuming that all the work done upon a body is stored up in this way, we should be able to calculate the amount of increase in electromotive force caused by performing a certain amount of work upon a given metal.

Let W = no. of calories expended upon the metal.
w = weight in grams of metal acted upon.
C = electro-chemical equivalent of the metal.
E = increase in electromotive force.

Then:

$$E = W \times \frac{C}{w} \times \frac{4.154}{96540}$$

Multiplying the total number of calories expended by the term C/w gives the number of calories associated with one electrochemical or gram equivalent of the metal. Multiplying this number of calories by 4.154 (the number of watt seconds in one calorie) gives the total number of watt seconds imparted to, and stored up in a gram equivalent of the body. It is known from Faraday's laws that 96,540 coulombs or ampere-seconds of electricity is asociated with one gram equivalent; and therefore dividing the total number of watt seconds stored up by the number of ampere-seconds associated with the material, the electromotive force will be given.

Table XVII gives the results obtained from a bar of wrought iron 10″ long and of a diameter of 0.635″ except at the middle of the bar where it had been turned down to .6″ for a length of 1/8″, at which point the measurements of electromotive force were taken. The total elongation of the piece was measured. The measurements were not made originally with the view of applying the above formula, and therefore contain insufficiently accurate data. Lack of time prevented a repetition of the experiments.

The metal at the point of smallest diameter received, of course, a greater expenditure of work than an equal amount of metal in other parts of the bar, and to find roughly the approximate relation between these amounts, the following experiment was performed: Four test bars were prepared exactly like the original ones, and subjected to the same stress. Prick punch marks had been made before the tests at distances of one inch along the bars, and a measurement between these marks after the application of stress gave the percentage of elongation. Similar measurements made upon the section of reduced diameter showed the percentage of elongation at that point. Now, by assuming that the work stored up in the metal is proportional to the elongation, which is only roughly the case, we have a means of getting at the amount of energy stored up in that part of the bar upon which measurements of electromotive force were made. From a number of measurements it was found that the percentage elongation at section of reduced area was 50%, and at other parts of the bar, 11%.

Letting n equal the number of calories stored up in a length of $\frac{1}{8}''$ of the bar where the diameter is largest, $\frac{50}{11}$ n = 4.55 n = the number of calories stored up in the section of reduced cross section. $8 \times 9\frac{7}{8}n + 4.55n = 83.55n$ = the total amount of energy stored up in the bar. This amount of energy may be derived from a measurement of the area inclosed by the upper curve on plate 19. At that point where the elongation had been 2.5″, the amount of work done, as shown by measurement of area is 2,643 foot pounds, or 861.6 calories. The number of calories applied to the $\frac{1}{8}''$ of reduced area is

$$\frac{4.55}{83.55} \times 861.6 = 46.9 \text{ calories.}$$

Now, assuming that all this energy had been stored up in such a way as to show itself in an increase of electromotive force, we can calculate what this increase of electromotive force should be, by substitution in the formula:

$$E = \text{Calories stored up} \times \frac{\text{elec. chem. equiv.}}{\text{grams affected}} \times \frac{4.154}{96540}$$

The number of gram calories affected by the 46.9 calories is constituted by the cylinder of iron .6″ in diameter and $\frac{1}{8}''$ long, whose volume is 0.0353 cubic inches. The weight of a cubic inch of wrought iron is about 0.28 pounds, and of 0.0353 cubic inches is .009884 pounds, or 4.483 grams, hence

$$E = 46.9 \times \frac{27.95}{4.483} \times \frac{4.154}{96540} = 0.0726 \text{ volt.}$$

The increase of electromotive force actually observed was more than double this amount, the discrepancy being due in all probability to the rough approximation which it was necessary to assume. One of the assumptions which it was necessary to make is that the stress equally affected the entire cross-section, which is by no means the case, for it is the outside layer which is affected the most, and would therefore give higher values for electromotive force than the calculated amounts. It is quite reasonable to expect, however, that more accurate observations would lead to a much closer agreement between the theoretical and observed amounts than here shown, and such work should offer a good field for future investigation.

The scientific and industrial value of my conclusions is something that I cannot estimate, but some suggestion of the importance of the questions involved has been made in the introduction to this thesis, and the following additional suggestions may properly be made here:

(a) From the conclusions numbered 1, 2, 3, 4, and 5, the deduction is evident that the protection of commercial iron and steel structures from decay requires their removal from electrolytic influences. The most complete means for doing this can only be determined after extended investigations that are beyond the scope of this thesis. Suffice it to say that the evidence clearly shows that ample care is not now provided for obtaining a satisfactorily uniform and homogeneous product in specifications for structural iron and steel.

(b) The sixth conclusion (which I can confidently say my experiments fully substantiate, though it is in conflict with the results of the experiments of Andrews which have heretofore been accepted as reliable) has an immediate valuable bearing upon various branches of scientific investigation. Thus, Prof. C. R. Van Hise lately said that he required a demonstration of an increase of chemical activity of a substance under pressure to fully substantiate his theories in regard to the transformation of rocks. The demonstration, as regards iron at ordinary temperatures is herein made.

(c) In the seventh and eighth conclusions are contained facts of value in substantiating the theories of electrochemical activity, and of the transformation of mechanical into electrical energy. Much valuable scientific information may apparently be obtained by an extended development of the quantitative method here set forth, using specimens of various metals. It is possible that through such additional investigations some light may be shed on the individual character of, or the character of the grouping of, molecules of different materials.

TABLES SHOWING THE CORROSION OF METALS UNDER DIFFERENT CONDITIONS.

TABLE I.

Material (surface polished.)	Weight before exposure.	Weight after exposure.	Loss in weight	Weight lost per amp. hr.
	Grams.	Grams.	Grams.	Grams.
Steel burned, not hardened	107.3	91.5	15.8	1.164
Steel burned, not hardened	120.5	104.9	15.6	1.147
Steel burned, not hardened	117.3	101.7	15.6	1.147
Annealed steel	118.9	103.2	15.7	1.155
Annealed steel	119.4	103.4	16.0	1.175
Annealed steel	121.4	105.4	16.0	1.175
Steel hardened	123.1	108.4	14.7	1.082
Steel hardened	123.3	108.8	14.5	1.067
Steel hardened	121.7	107.0	14.7	1.082

Ampere hours. = 13.6. Time = 23¾ hrs. Surface 10 sq. in.

TABLE II.

Material (surface polished.)	Area in square inches.	Weight before exposure.	Weight after exposure.	Loss in weight.	Loss in weight per amp. hr.
		Grams.	Grams.	Grams.	Grams.
Steel burned and hardened	10.72	122.71	109.80	12.91	1.15
Steel burned and hardened	10.39	119.64	106.80	12.84	1.145
Sheet iron	10.44	74.57	61.50	13.07	1.167
Sheet iron	10.31	77.00	64.00	13.00	1.16
Sheet iron	10.37	78.24	64.50	13.74	1.225
Cast iron	9.98	296.74	284.6	12.14	1.085
Cast iron	10.16	304.58	288.5	13.08	1.170
Cast iron	10.09	301.20	289.6	11.6	1.040

Ampere hours = 11.2. Time = 24¼ hrs.

TABLE III.

Material.	Area in square inches.	Weight before exposure.	Weight after exposure.	Loss in weight.	Weight lost per amp. hr.
		Grams.	Grams.	Grams.	Grams.
Sheet iron (scale partly removed)	9.95	77.43	63.07	14.36	1.08
Sheet iron (scale partly removed)	10.38	79.87	75.37	14.50	1.09
Sheet iron (scale partly removed)	10.46	79.54	75.01	14.53	1.092
Cast iron (scale partly removed)	10.55	344.64	334.55	10.09	0.755
Cast iron (scale partly removed)	10.66	343.19	332.90	10.29	0.775
Cast iron (scale partly removed)	10.67	337.56	327.95	9.61	0.722
Steel (burned not hardened, with scale)	10.59	121.32	105.80	15.52	1.16
Steel (burned not hardened, with scale)	10.01	121.96	106.45	15.51	1.155
Steel (annealed, with scale)	10.66	125.22	109.85	15.37	1.149
Steel (annealed, with scale)	10.52	124.58	109.30	15 28	1.15
Steel (annealed, with scale)	10.39	122.87	107.53	15.34	1.05
Steel (hardened, with scale)	10.71	124.57	100.60	13.97	1.057
Steel (hardened, with scale)	10.89	122.01	107.98	14.08	1.065
Steel (hardened, with scale)	10.34	123.17	109.00	14 17	1.045

Ampere hours = 13.3. Time = 19.5 hrs.

TABLE IV.

Material.	Area in square inches.	Weight before exposure.	Weight after exposure.	Loss in weight.
		Grams.	Grams.	Grams.
Steel (burned and hardened, with scale).	10.51	120.81	67.90	52.91
Steel (burned and hardened, with scale).	10.80	124.32	70.85	53.47
Sheet iron (scale on).....................	10.08	78.65	40.55	38.1
Sheet iron (scale on).....................	10.20	77.99	39.77	32.22
Sheet iron (scale on).....................	10.80	78.44	40.00	38.04

TABLE V.

Material.	Solution.	Weight before exposure.	Weight after exposure.	Loss in weight.
		Grams.	Grams.	Grams.
Mild steel............................	KNO_3	34.15	29.66	4.49
Mild steel............................	KNO_3	33.05	28.50	4.55
Mild steel............................	KNO_3	34.16	29.67	4.49
Mild steel............................	$(NH_4)_2 SO_4$	33.70	29.30	4.40
Mild steel............................	$(NH_4)_2 SO_4$	33.50	28.83	4.67
Mild steel............................	$(NH_4)_2 SO_4$	33.93	29.95	4.00
Mild steel............................	$NH_4 Cl$	34.17	29.33	4.74
Mild steel............................	$NH_4 Cl$	33.63	29.02	4.61
Mild steel............................	$NH_4 Cl$	33.58	28.95	4.63

TABLE VI.

Material.	Area in square inches.	Weight before exposure.	Weight after exposure.	Loss in weight.	Weight lost per sq. in.
		Grams.	Grams.	Grams.	Grams.
Sheet iron (surface polished).	10.33	75.15	74.40	0.75	0.072
Sheet iron (surface polished).	10.35	77.71	77.03	0.68	0.065
Sheet iron (surface polished).	10.63	79.60	78.93	0.67	0.063
Sheet iron (scale partly removed)	10.40	82.96	81.37	1.59	0.153
Sheet iron (scale partly removed)	10.40	84.17	82.55	1.62	0.155
Sheet iron (scale partly removed)	10.10	79.83	78.62	1.21	0.119
Sheet iron (with scale)	10.46	79.18	77.53	1.65	1.577
Sheet iron (with scale)	10.41	80.15	78.50	1.65	1.581
Sheet iron (with scale)	10.80	79.11	77.02	2.09	1.935
Cast iron (with scale)	14.03	374.52	372.75	1.73	0.1217
Cast iron (with scale)	14.19	379.70	378.00	1.59	0.1131
Cast iron (with scale)	14.13	376.87	375.05	1.67	0.1173
Cast iron (scale partly removed)	14.20	346.08	344.25	1.73	0.121
Cast iron (scale partly removed)	14.05	337.64	335.95	1.59	0.113
Cast iron (scale partly removed)	14.23	345.67	344.00	1.67	0.117
Steel burned not hardened (with scale)	10.07	121.38	117.28	4.10	0.4075
Steel burned not hardened (with scale)	10.47	126.57	123.27	3.30	0.3150
Cast iron (surface polished)	13.64	304.55	303.56	0.99	0.072
Cast iron (surface polished)	13.62	304.17	302.48	1.19	0.087
Cast iron (surface polished)	13.52	258.50	257.43	1.07	0.079
Annealed steel (scale partly removed)	10.85	124.35	123.22	1.13	0.104
Annealed steel (scale partly removed)	10.48	122.89	121.75	1.14	0.109
Annealed steel (scale partly removed)	10.48	121.55	120.58	0.97	0.093
Annealed steel (with scale)	10.41	122.88	121.05	1.83	0.176
Annealed steel (with scale)	10.28	121.72	119.66	2.06	0.200
Annealed steel (with scale)	10.32	123.20	121.09	2.11	0.202
Annealed steel (surface pol.)	10.47	121.80	121.10	0.70	0.0668
Annealed steel (surface pol.)	10.46	119.94	119.19	0.75	0.0717
Annealed steel (surface pol.)	10.18	117.95	117.20	0.75	0.0738
Hardened steel (with scale)	10.63	126.30	125.29	1.01	0.0950
Hardened steel (with scale)	10.43	123.05	122.09	0.96	0.921
Hardened steel (with scale)	10.65	125.80	124.68	1.22	1.1145

COPPER (TENSION).

TABLE VII.

P.	p.	P. R.	E. M. F.
0	0	.0090	—.5858
200	4,000	.0091	—.5861
400	8,000	.0091	—.5861
600	12,000	.0093	—.5867
800	16,000	.0091	—.5861
1,000	20,000	.0091	—.5861
1,200	24,000	.0090	—.5858
1,400	28,000	.0088	—.5853
1,600	32,000	.0082	—.5835
1,800	36,000	.0081	—.5833
2,000	40,000	.0080	—.5829
Break.	....	.0084	....

TABLE VIII.

P.	p.	P. R.	E. M F.
0	0	.0093	—.5867
200	4,000	.0095	—.5873
400	8,000	.0097	—.5878
600	12,000	.0097	—.5878
800	16,000	.0097	—.5878
1,000	20,000	.0097	—.5878
1,200	24,000	.0095	—.5873
1,400	28,000	.0093	—.5867
1,600	32,000	.0091	—.5861
1,800	36,000	.0091	—.5861
2,000	40,000	.0091	—.5861
2,100	42,000	.0090	—.5858
Break.	....	.0090	—.5858

ABBREVIATIONS USED.

P. = Load.
p. = Pounds per square inch.
P. R. = Potentiometer reading.

BRASS (TENSION).

TABLE IX.

P.	p.	P. R.	E. M. F.
0	0	.0094	—.5870
500	2,500	.0095	—.5873
1,000	5,000	.0095	—.5873
1,500	7,500	.0095	—.5873
2,000	10,000	.0095	—.5873
3,000	15,000	.0093	—.5867
3,500	17,500	.0093	—.5867
4,000	20,000	.0093	—.5867
5,000	25,000	.0093	—.5867
6,000	30,000	.0093	—.5867
7,000	35,000	.0093	—.5867
8,500	42,500	0093	—.5867
9,000	45,000	.0093	—.5867
10,000	50,000	.0093	—.5867
11,000	55,000	.0090	—.5858
Break.	....	.0085	—.5844

TABLE X.

P.	p.	P. R.	E. M. F.
0	0	.0090	—.5858
1,000	5,000	.0090	—.5858
3,000	15,000	.0090	—.5858
5,000	25,000	0090	—.5858
7,000	35,000	.0090	—.5858
10,000	50,000	.0090	—.5858
11,000	55,000	.0090	—.5858
Break.	....	.0076	—.5818

MACHINE STEEL (TENSION).

TABLE XI.

P.	p.	P R.	E. M. F.
0	0	.0478	+.0111
500	365	.0480	+.0118
200	1,460	.0480	+.0118
2,500	18,200	.0480	+.0118
4,000	29,000	.0475	+.0103
5,000	36,600	.0471	+.0090
6,000	43,800	.0540	+.0290
6,500	47,500	.0540	+.0298
7,000	51,000	.0550	+ 0319
7,500	54,700	.0560	+.0346
8,000	58,500	.0570	+.0375
8,500	62,000	.0590	+.0430

ZINC (TENSION).

TABLE XII.

P.	p.	P. R.	E. M. F.
0	0	.0280	+.5204
50	10,000	.0285	+.5218
80	16,000	.0285	+.5218
100	20,000	.0287	+.5225
150	30,000	.0290	+.5232
200	40,000	.0293	+.5242
300	60,000	.0300	+.5264
350	70,000	.0302	+.5266
360	72,000	.0303	+.5270

WROUGHT IRON (TENSION).

TABLE XIII.

P.	p.	P. R.	E. M. F.
0	0	.0400	—.0113
2,000	8,000	.0400	—.0113
4,000	16,000	.0410	—.0084
6,000	24,000	.0410	—.0084
8,000	32,000	.0410	—.0084
10,000	40,000	.0450	+.0030
11,000	44,000	.0470	+.0088
11,500	46,000	.0480	+.0116
12,000	48,000	.0490	+.0144
12,500	50,000	.0501	+.0175
13,000	52,000	.0536	+.0276
Break.	....	.0490	+.0144

TABLE XIV.

P.	p.	P. R.	E. M. F.
0	0	.0400	—.0113
2,000	8,000	.0400	—.0113
4,000	16,000	.0410	—.0084
6,000	24,000	.0410	—.0084
8,000	32,000	.0410	—.0084
10,000	40,000	.0410	—.0084
11,000	44,000	.0430	—.0026
12,000	48,000	.0450	+.0030
12,500	50,000	.0473	+.0098
12,750	51,000	.0478	+.0113
13,000	52,000	.0480	+.0116
13,250	53,000	.0490	+.0144
13,500	54,000	.0490	+.0144
13,750	55,000	.0500	+.0172
14,000	56,000	.0510	+.0194
Break.	....	.0495	+.0158

WROUGHT IRON (TENSION).

TABLE XV.

P.	p.	P. R.	E. M. F.
0	0	.0342	—.0278
2,000	4,000	.0344	—.0275
4,000	16,000	.0349	—.0273
6,000	24,000	.0350	—.0272
8,000	32,000	.0350	—.0272
10,000	40,000	.0351	—.0271
11,000	44,000	.0404	—.0110
11,750	47,000	.0430	—.0027
12,250	49.000	.0432	—.0025
12,500	50,000	.0447	+.0020
12,750	51,000	.0460	+.0059
13,000	52,000	.0461	+.0062
13,250	53,000	.0479	+.0113
13,500	54,000	.0505	+.0187
Break.	....	.0400	+.0113

TABLE XVI.

P.	p.	P. R.	E. M. F.
0	0	.0242	—.0565
1,000	6,000	.0242	—.0564
1,500	9,000	.0242	—.0563
2,000	12,000	.0242	—.0563
2,500	15,000	.0243	—.0561
3,000	18,000	.0244	—.0559
3,500	21,000	.0244	—.0559
4,000	24,000	.0244	—.0559
4,500	27,000	.0245	—.0557
5,000	30,000	.0245	—.0557
5,500	33,000	.0245	—.0556
6,000	36,000	.0245	—.0555
6,500	39,000	.0242	—.0545
6,680	40,080	.0249	—.0544
7,360	44,160	.0250	—.0542
7,400	44,400	.0250	—.0542
8,000	48,000	.0251	—.0540
8,000	48,000	.0256	—.0525
Break.	....	....	....

WROUGHT IRON (TENSION).

Table XVII.

P.	p.	P. R.	E. M. F.
0	0	.0363	—.0220
500	1,560	.0375	—.0183
2,300	7,050	.0382	—.0164
4,100	12,600	.0385	—.0154
7,000	21,500	.0383	—.0160
9,400	29,800	.0382	—.0164
10,600	32,600	.0385	—.0156
11,800	36,200	.0388	—.0148
12,300	37,800	.0408	—.0089
13,300	40,800	.0425	—.0040
14,000	43,000	.0433	—.0018
13,600	41,800	.0431	—.0022
13,300	40,800	.0420	—.0065
15,000	46,000	.0440	+.0002
15,500	47,600	.0480	+.0118
15,900	48,900	.0490	+.0144
16,000	49,200	.0560	+.0348
Break.	....	....	....

Table XVIII.

P.	p.	P. D.	E. M. F.
0	0	.0335	—.0302
300	920	.0338	—.0289
800	2,400	.0343	—.0275
1,900	5,800	.0343	—.0275
3,100	9,500	.0343	—.0275
4,700	14,700	.0344	—.0273
6,200	19,000	.0344	—.0273
8,000	24,600	.0346	—.0266
10,000	30,700	.0346	—.0266
10,700	32,800	.0345	—.0270
11,600	35,600	.0360	—.0228
11,900	36,300	.0360	—.0228
12,800	39,400	.0368	—.0204
13,900	44,200	.0375	—.0183
15,000	46,000	.0386	—.0152
15,400	47,300	.0398	—.0118
15,600	48,000	.0413	—.0075
15,000	46,000	.0540	+.0029
Break.	....	....	....

TOOL STEEL (TENSION).

TABLE XIX.

P.	p.	P. R.	E. M. F.
0	0	.0224	—.0617
3,000	17,900	.0225	—.0615
6,000	35,800	.0226	—.0612
8,000	47,500	.0226	—.0610
9,000	53,500	.0268	—.0609
11,000	65,500	.0285	—.0604
13,000	77,500	.0285	—.0604
15,000	89,500	.0229	—.0603
18,500	110,000	.0228	—.0606
19,000	113,000	.0229	—.0601
20,000	119,000	.0229	—.0600
21,000	125,000	.0230	—.0599
Break.	....	....	....

CAST IRON (TENSION).

TABLE XX.

P.	p.	P. R.	E. M. F.
0	0	.0236	—.0580
500	1,600	.0238	—.0577
1,000	3,300	.0238	—.0577
1,500	5,000	.0238	—.0577
2,000	6,600	.0238	—.0595
3,000	10,000	.0239	—.0572
3,500	11,600	.0239	— 0572
4,000	13,300	.0240	—.0571
4,500	15,000	.0240	—.0571
5,000	16,700	.0241	—.0568
5,500	18,300	.0217	—.0566
6,000	20,000	.0242	—.0559
6,500	21,600	.0243	—.0558
7,000	23,300	.0248	—.0548
Break.	....	....	....

CAST IRON (TENSION).

TABLE XXI.

P.	p.	P. R.	E. M. F.
0	0	.0232	—.0592
1,000	3,300	.0235	—.0585
1,500	5,000	.0235	—.0585
2,000	6,600	.0236	—.0583
2,500	8,300	.0236	—.0581
3,000	10,000	.0237	—.0580
3,500	11,700	.0237	—.0579
4,000	13,300	.0237	—.0579
4,500	15,000	.0238	—.0577
5,000	16,700	.0238	— 0576
5,500	18,700	.0239	—.0575
6,000	20,000	.0239	—.0573
6,500	21,600	.0240	—.0571
7,000	24,300	.0240	—.0571
7,500	25,000	.0240	—.0570
Break.	....	....	....

TABLE XXII.

P.	p.	P. R.	E. M. P.
0	0	.0230	—.0600
500	1,670	.0233	—.0599
1,000	3,300	.0232	—.0598
1,500	5,000	.0234	—.0588
2,000	6,600	.0235	—.0585
2,500	8,300	.0236	—.0583
3,000	10,000	.0236	—.0583
3,500	11,700	.0237	—.0580
4,000	13,300	.0237	—.0580
4,500	15,000	.0238	—.0577
5,000	16,700	.0238	—.0577
5,500	18,700	.0238	—.0576
6,000	20,000	.0239	—.0574
6,500	21,600	.0239	—.0574
7,000	24,300	.2039	—.0573
Break.	....	....	....

TOOL STEEL (COMPRESSION).

TABLE XXIII.

P.	p.	P. R.	E. M. F.	P.	p.	P. R.	E. M. F.
0	0	.0115	—.0930	22,000	62,100	.0138	—.0862
1,000	2,700	.0118	—.0929	24,000	64,700	.0140	—.0857
2,000	5,400	.0120	—.0915	26,000	70,300	.0148	—.0836
3,000	8,100	.0121	—.0913	28,000	75,600	.0150	—.0830
4,000	10,800	.0123	—.0907	30,000	81,000	.0156	—.0811
6,000	16,200	.0126	—.0898	32,000	86,500	.0160	—.0802
8,000	21,600	.0126	—.0896	34,000	91,700	.0163	— 0779
10,000	27,000	.0129	—.0890	36,000	96,000	.0167	—.0779
12,000	32,400	.0130	—.0887	38,000	102,800	.0168	—.0777
14,000	37,800	.0131	—.0885	40,000	108,000	.0175	—.0758
16,000	43,200	.0131	—.0885	42,000	113,600	.0180	—.0744
18,00	48,600	.0134	—.0876	44,000	119,000	.0182	—.0737
20,000	54,000	.0137	—.0866				

CAST IRON (COMPRESSION.)

TABLE XXIV.

P.	p.	P. R.	E. M. F.
0	0	.0370	—.0199
2,000	6,500	.0388	—.0148
4,000	13,800	.0380	—.0170
6,000	20,000	.0387	—.0150
8,000	26,600	.0389	—.0147
10,000	33,300	.0389	—.0146
12,000	40,000	.0397	—.0115
14,000	46,700	.0400	—.0113
16,000	53,300	.0417	—.0062
18,000	60,000	.0417	—.0062
20,000	65,500	.0427	—.0032
24,000	80,000	.0430	—.0027
26,000	86,500	.0440	+.0002
28,000	93,200	.0460	+.0060
30,000	100,000	.0470	+.0088
31,000	103,000	.0530	+.0260

TABLE XXV.

P.	p.	P. R.	E. M. F.
0	0	.0320	—.0341
2,000	6,500	.0320	—.0341
4,000	13,800	.0320	—.0341
7,000	23,300	.0320	—.0341
10,000	33,300	.0320	—.0341
12,000	40,000	.0320	—.0341
14,000	46,700	.0321	—.0338
16,000	53,300	.0321	—.0338
18,000	60,000	.0321	—.0338
20,000	65,500	.0325	—.0326
22,000	73,300	.0330	—.0313
24,000	80,000	.0330	—.0313
26,000	86,500	.0340	—.0284
28,000	93,200	.0345	—.0270
30,000	100,000	.0350	—.0257
32,000	106,500	.0360	—.0328
33,000	110,000	.0377	—.0179

MACHINE STEEL (COMPRESSION).

TABLE XXVI.

P.	p.	P. R.	E. M. F.
0,	0	0440	+.0002
1,000	4,000	.0437	—.0304
2,000	8,000	.0425	—.0048
3,000	12,000	.0390	—.0148
4,000	16,000	.0401	—.0110
5,000	20,000	.0408	—.0088
6,000	24,000	.0395	—.0126
7,000	28,000	.0403	—.0102
8,000	32,000	.0398	—.0118
9,000	36,000	.0395	—.0126
11,000	44,000	.0410	—.0082
12,000	48,000	.0423	—.0045
14,000	56,000	.0425	—.0040
15,000	60,000	.0430	—.0025
16,000	64.000	.0430	—.0025
17,000	68,000	.0438	—.0000
18,000	72,000	.0445	+.0018
19,000	76,000	.0454	+.0042
20,000	80,000	.0460	+.0060

WROUGHT IRON (TENSION).

TABLE XXVII.

P.	p.	P. R.	E. M. F.
0	0	.0227	—.0608
1,000	4,000	.0229	—.0603
2,500	14,000	.0228	—.0605
4,000	22,200	.0228	—.0604
5,000	27,800	.0228	—.0604
5,500	30,600	.0229	—.0603
6,000	33,300	.0293	—.0602
6,500	36,000	.0229	—.0601
7,000	39,000	.0230	—.0598
7,100	39,500	.0230	—.0598
7,200	40,000	.0230	—.0597
7,400	41,200	.0231	—.0595
7,500	41,700	.0231	—.0596
7,740	43,000	.0231	—.0596
7,800	43,300	.0231	—.0595
8,000	44,500	.0231	—.0596
8,340	46,400	.0231	—.0596
8,600	47,800	.0231	—.0395
9,000	50,000	.0238	—.0577
Break.	....	....	....

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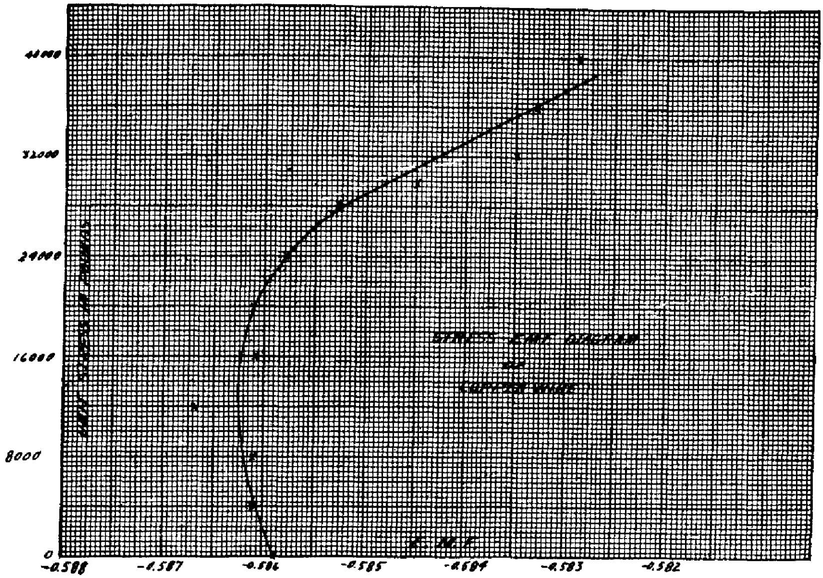
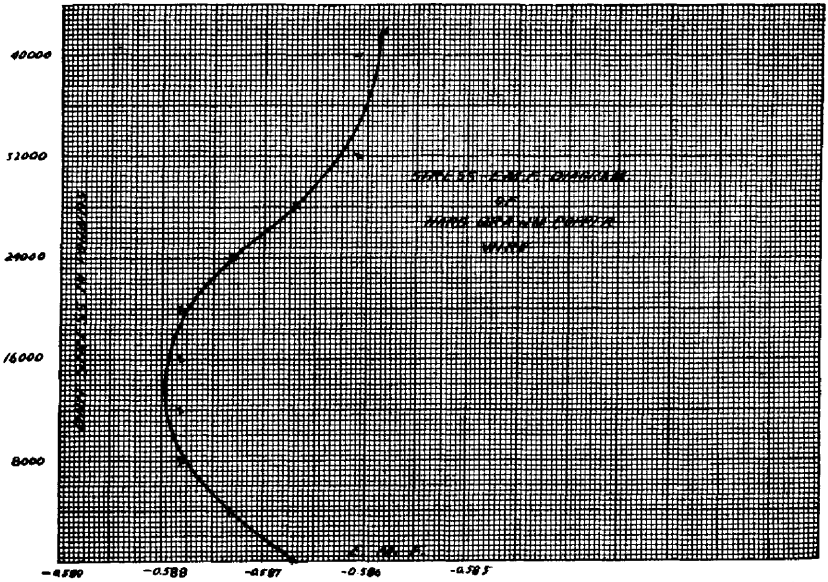
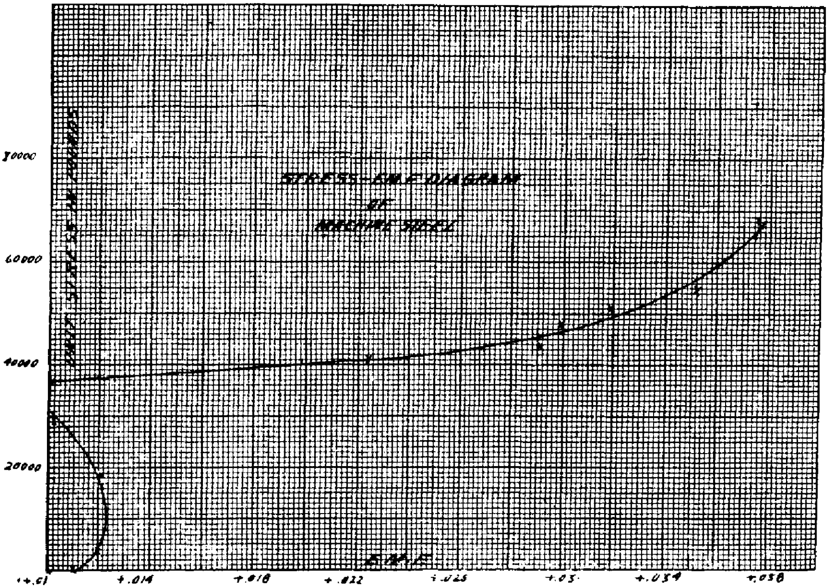


1. Copper Wire.



2. Hard Drawn Copper Wire.

STRESS ELECTROMOTIVE FORCE DIAGRAMS.



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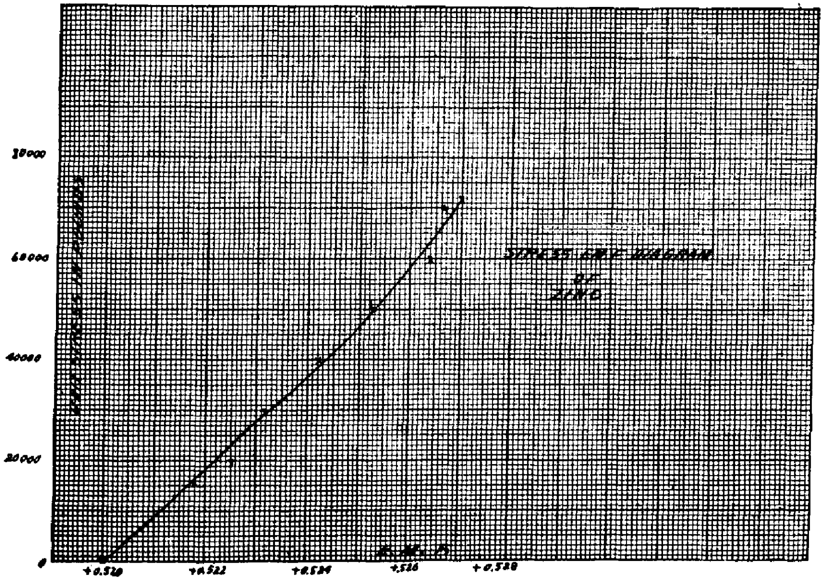
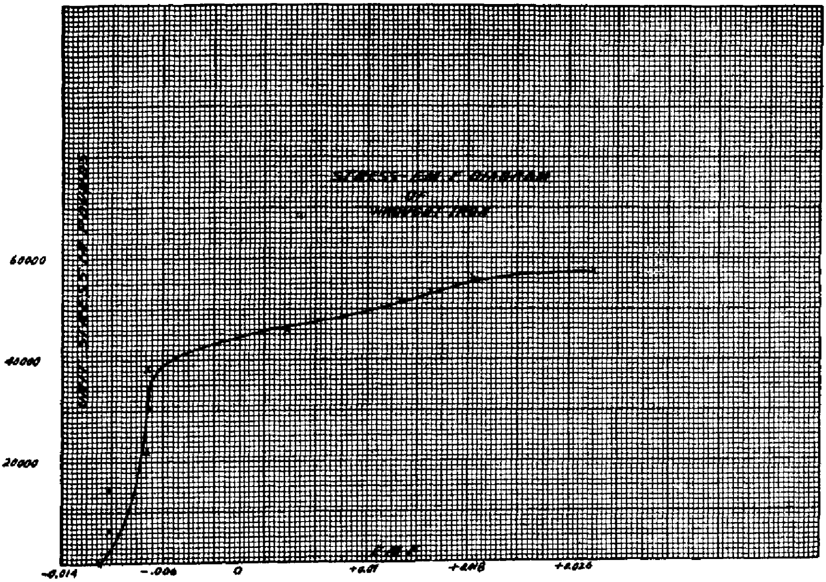


2. Zinc.

STRESS ELECTROMOTIVE FORCE DIAGRAMS.



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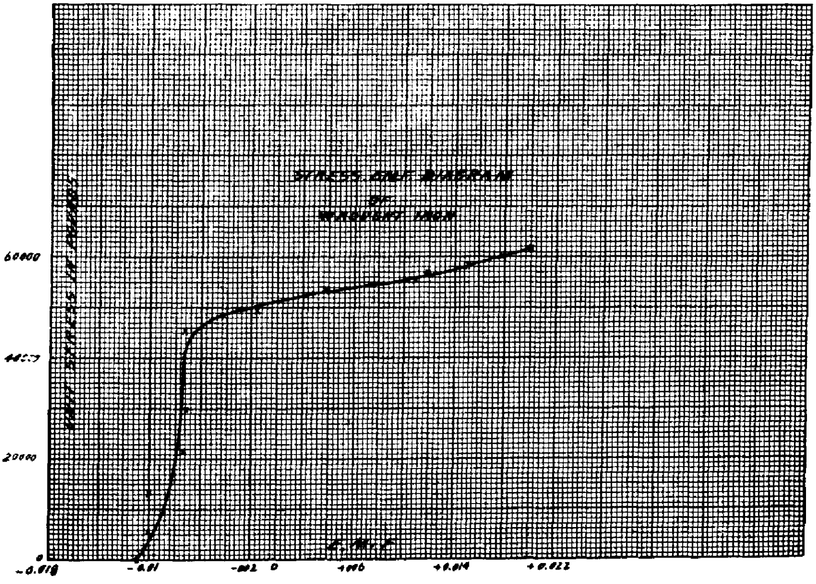
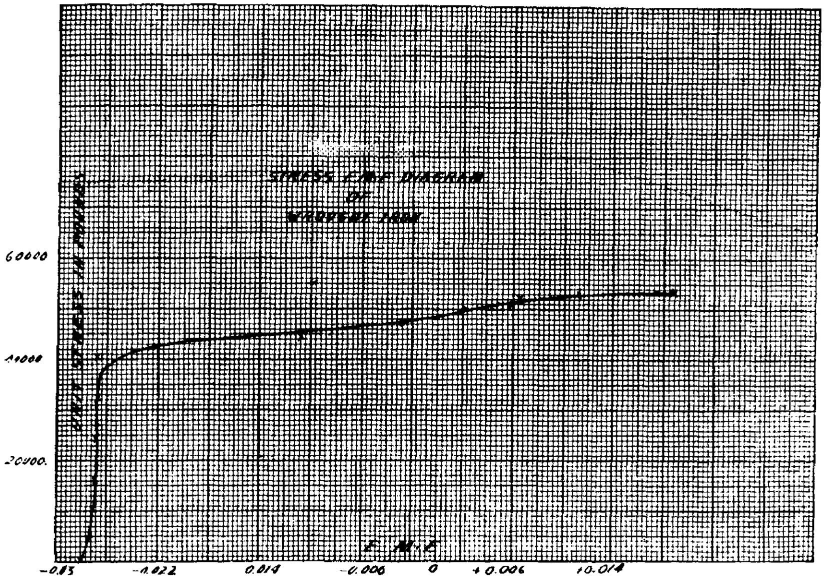
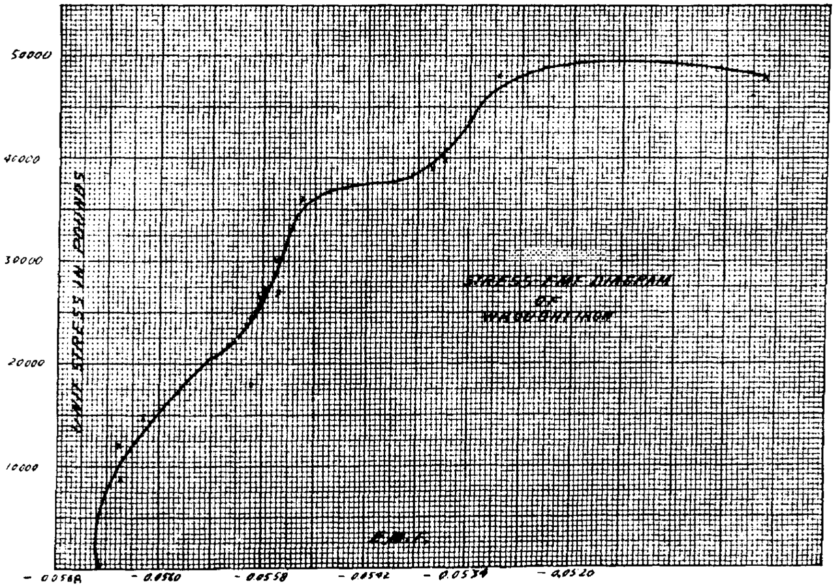


2. Wrought Iron.

STRESS ELECTROMOTIVE FORCE DIAGRAMS.

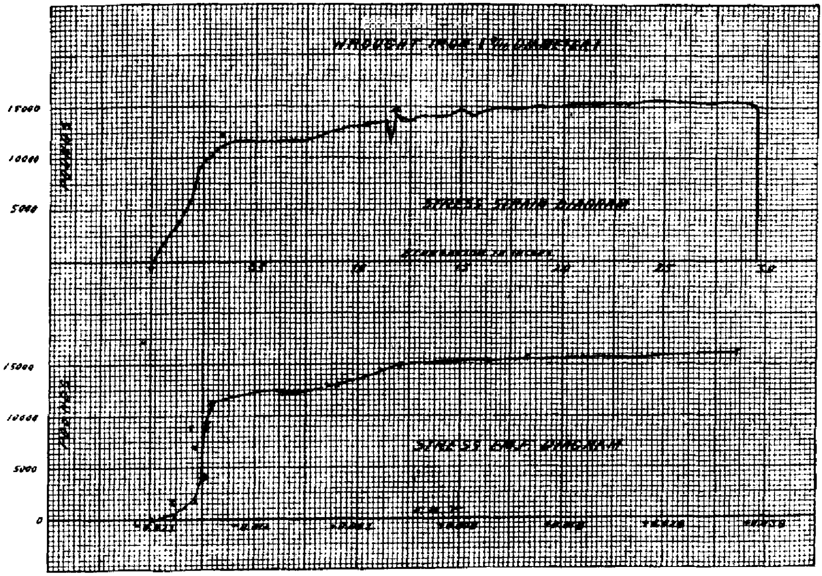


1. Wrought Iron.

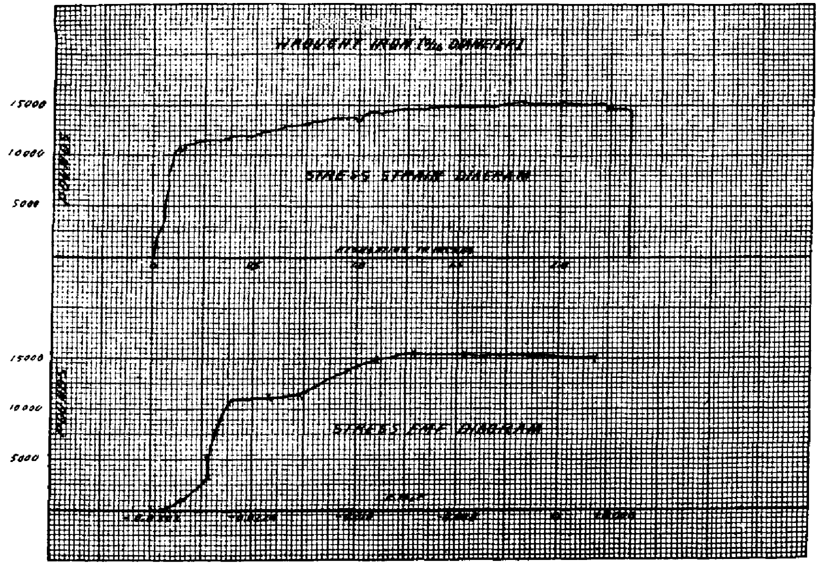


2. Wrought Iron.

STRESS ELECTROMOTIVE FORCE DIAGRAMS.

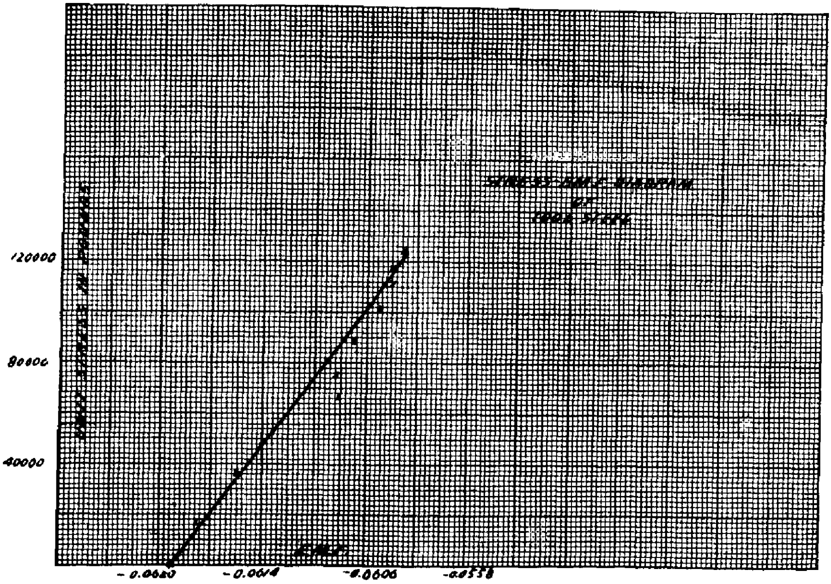


1. Wrought Iron.

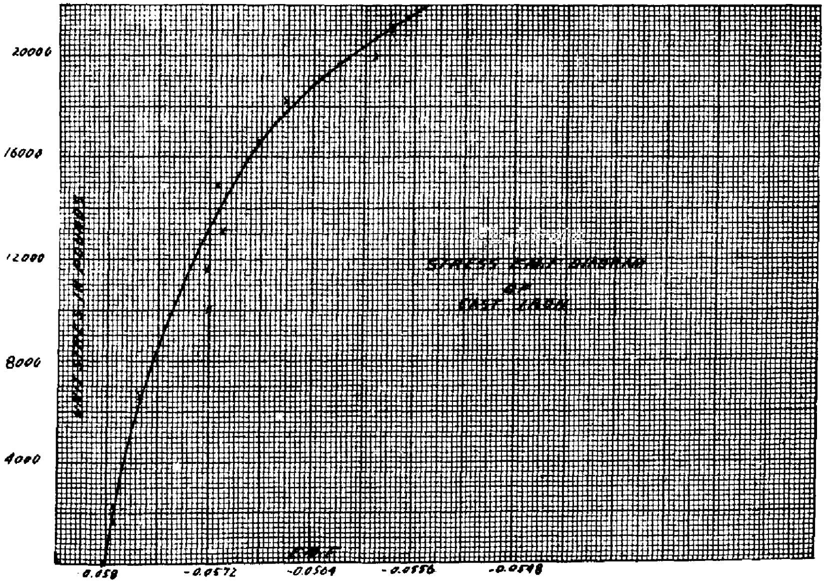


2. Wrought Iron.

COMPARISON OF STRESS STRAIN AND STRESS ELECTROMOTIVE FORCE DIAGRAMS.

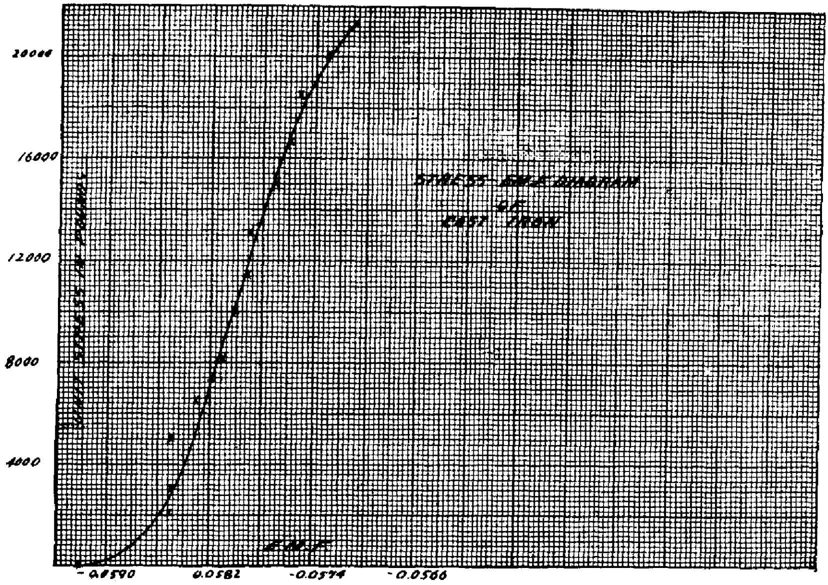


1. Tool Steel.

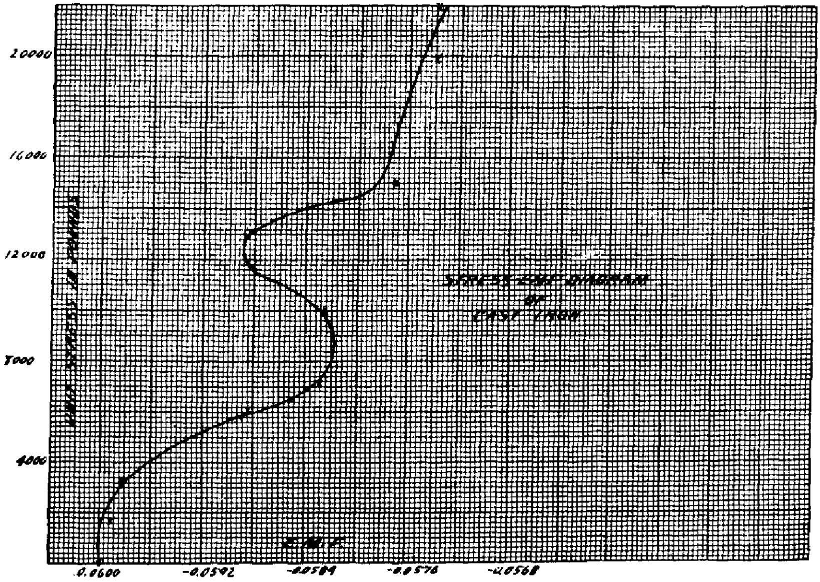


2. Cast Steel.

STRESS ELECTROMOTIVE FORCE DIAGRAMS.

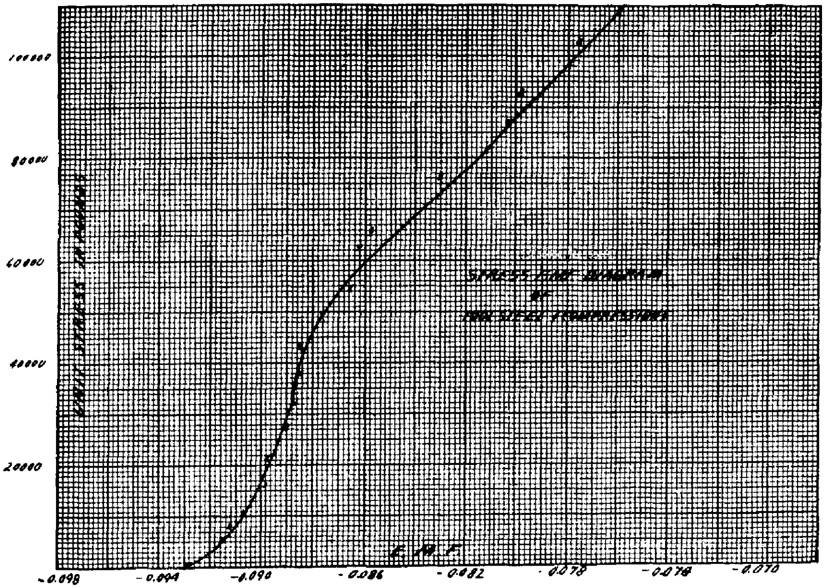


1. Cast Iron.

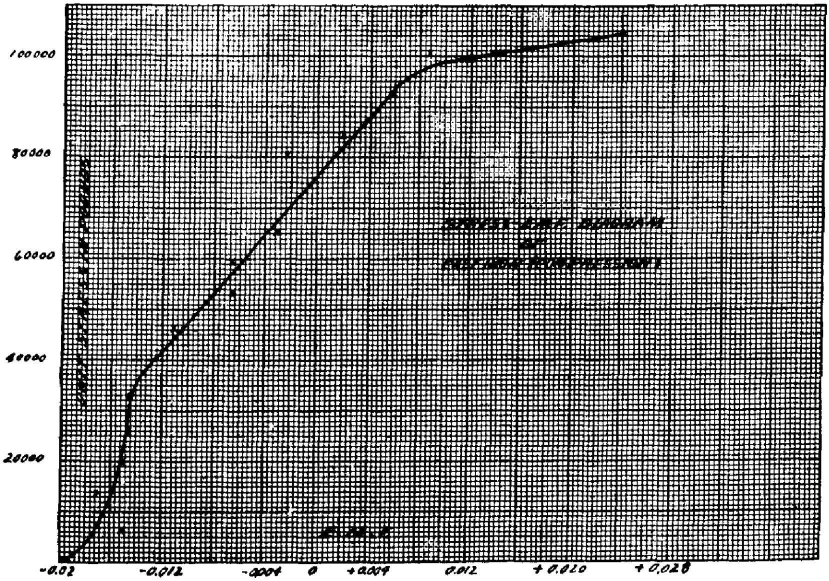


2. Cast Iron.

STRESS ELECTROMOTIVE FORCE DIAGRAMS.

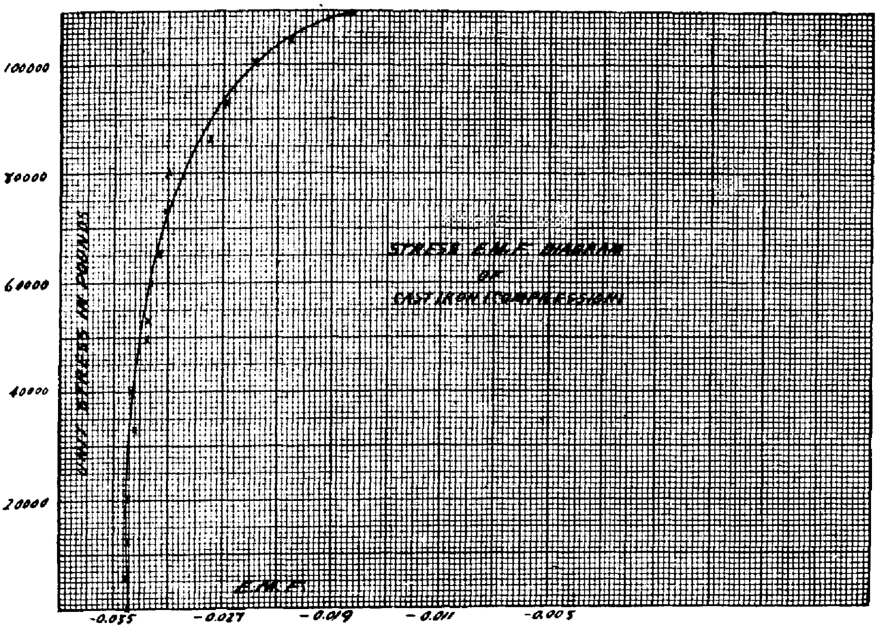


1. Tool Steel (Compression).

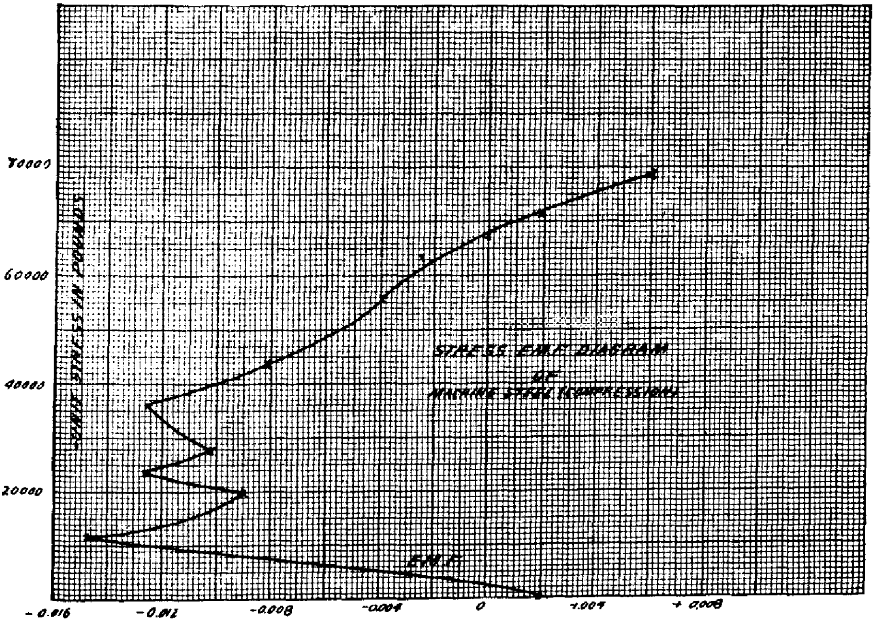


2. Tool Steel (Compression).

STRESS ELECTROMOTIVE FORCE DIAGRAMS.

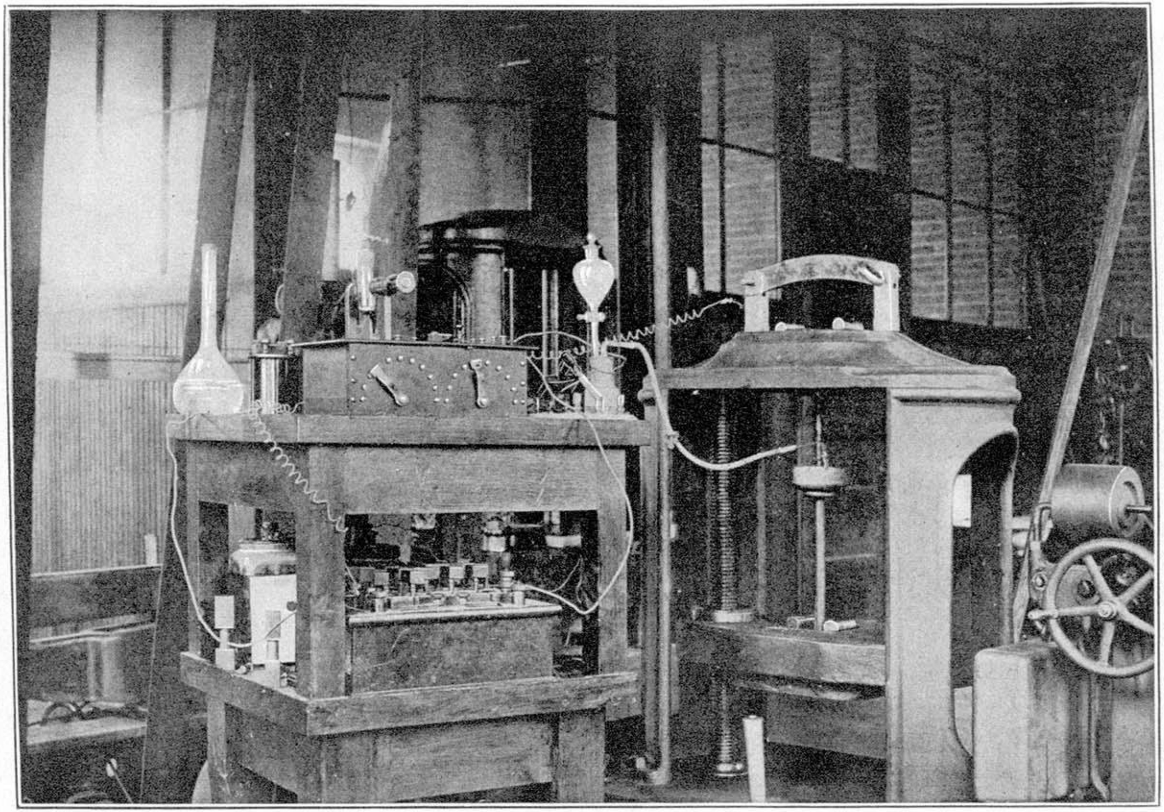


1. Cast Iron (Compression).



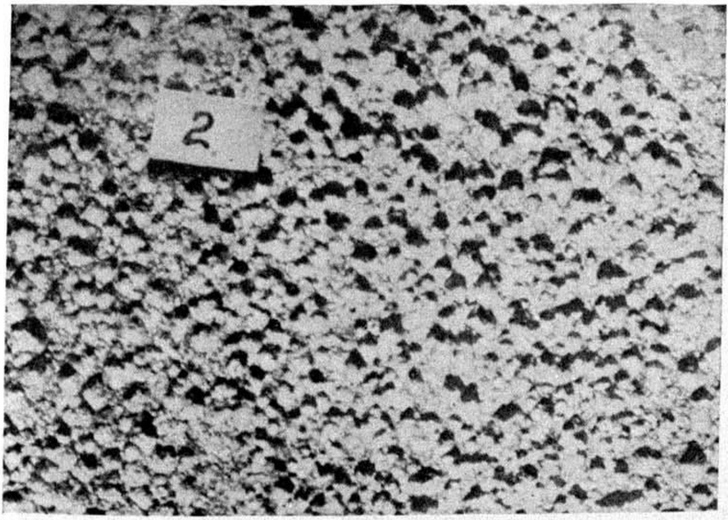
2. Machine Steel (Compression).

STRESS ELECTROMOTIVE FORCE DIAGRAMS.

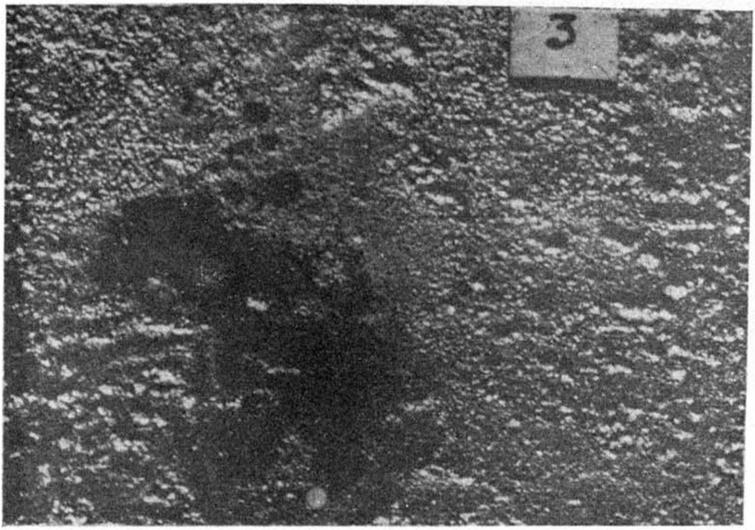


TESTING APPARATUS EMPLOYED.

1. SHEET IRON (POLISHED).
Magnified 2⅛ diameters.

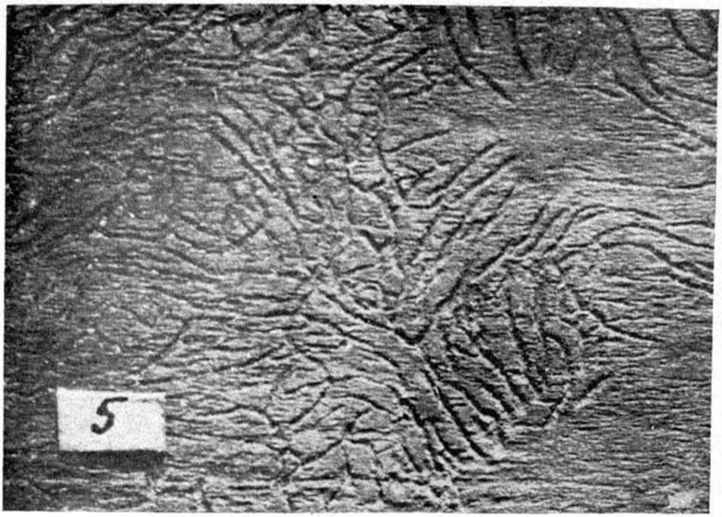


2. SHEET IRON.
Magnified 2⅛ diameters.

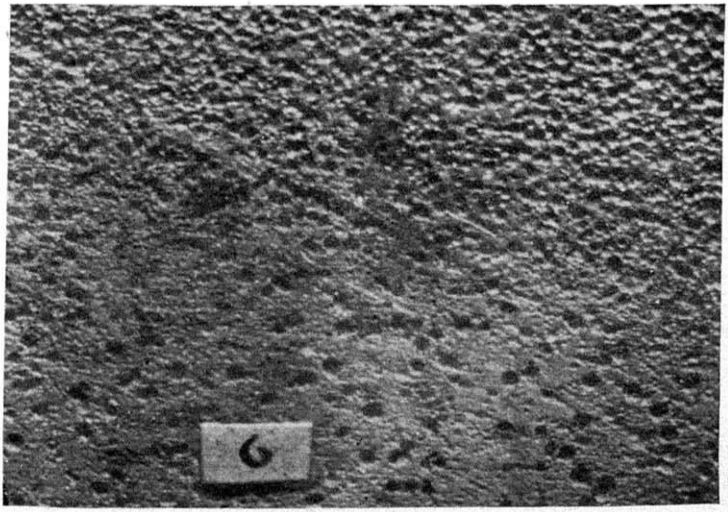


1. **SHEET IRON (WITH SCALE).**
Magnified 2⅛ diameters.

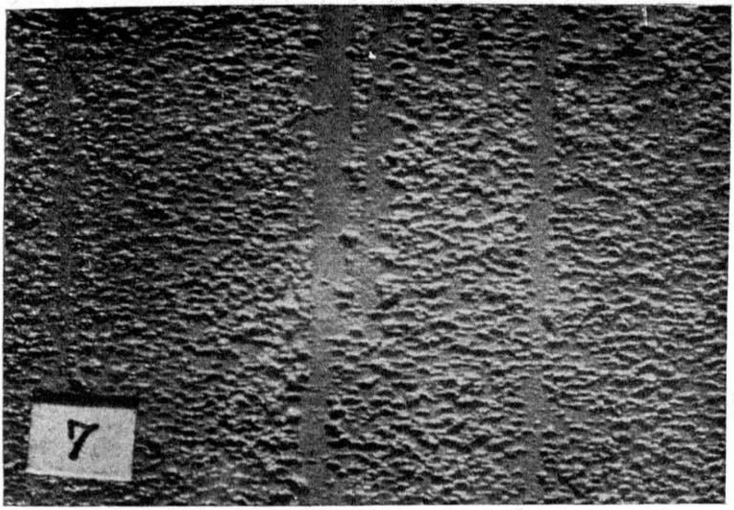
2. **BURNED AND HARDENED STEEL.**
Magnified 2⅛ diameters.



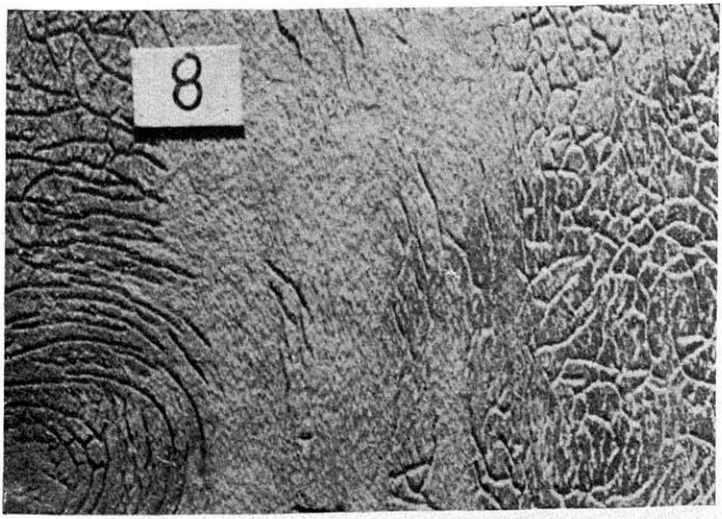
1. **HARDENED STEEL (POLISHED).**
Magnified 2⅛ diameters.



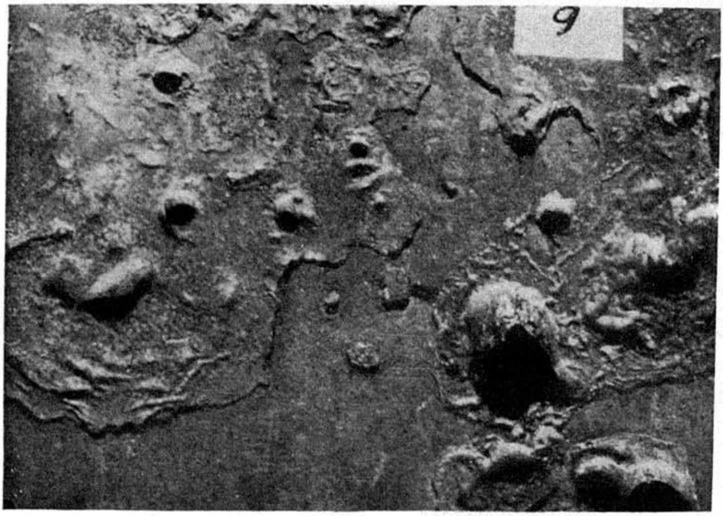
2. **ANNEALED STEEL (POLISHED).**
Magnified 2⅛ diameters.



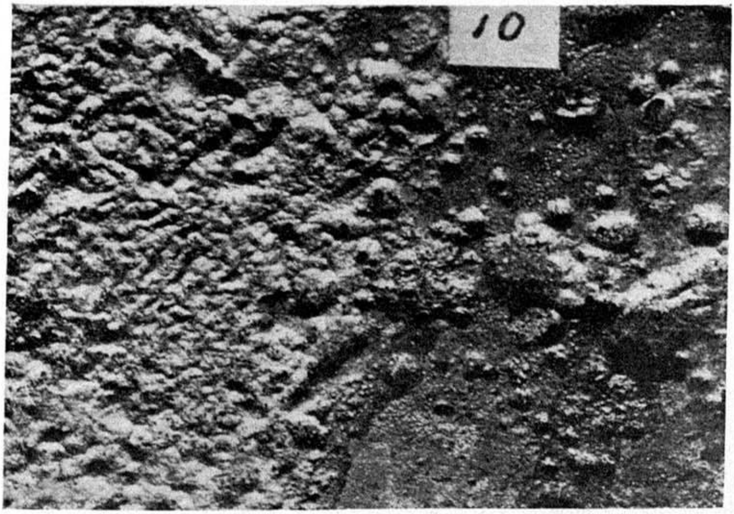
1. **STEEL BURNED BUT NOT HARDENED (POLISHED).**
Magnified 2⅛ diameters.



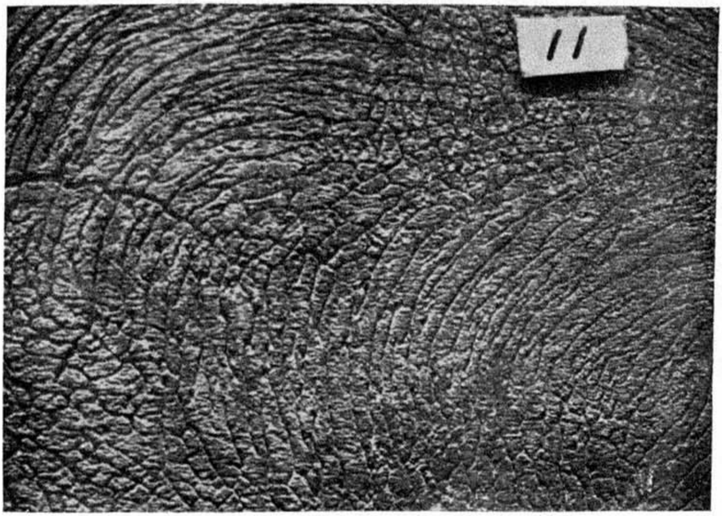
2. **HARDENED STEEL (WITH SCALE).**
Magnified 2⅛ diameters.



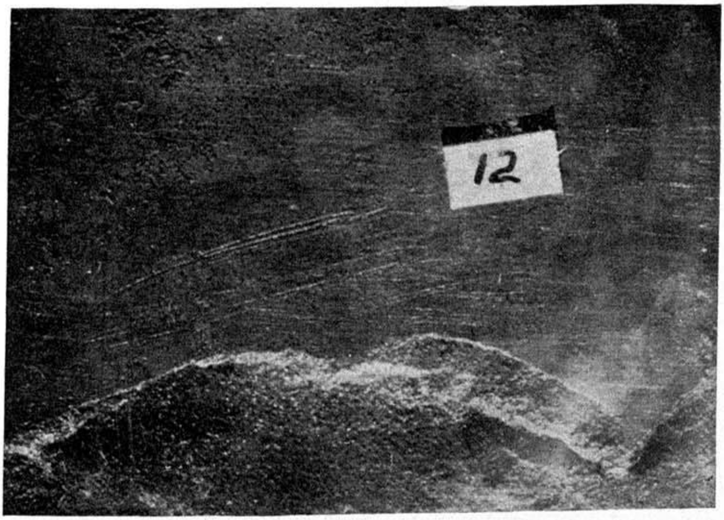
1. **ANNEALED STEEL (WITH SCALE).**
Magnified 2⅛ diameters.



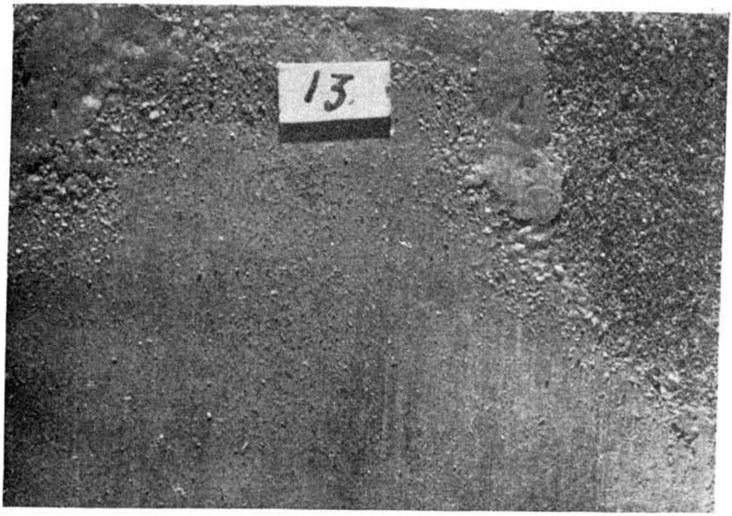
2. **BURNED STEEL NOT HARDENED (WITH SCALE).**
Magnified 2⅛ diameters.



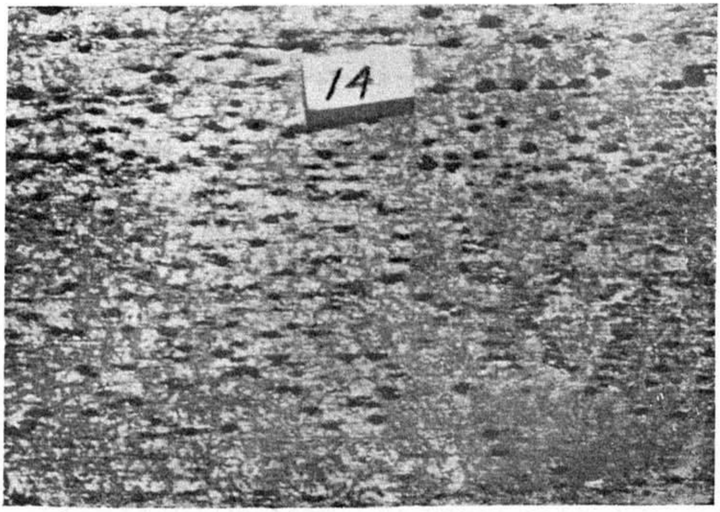
1. **STEEL BURNED AND HARDENED (POLISHED).**
Magnified 2⅛ diameters.



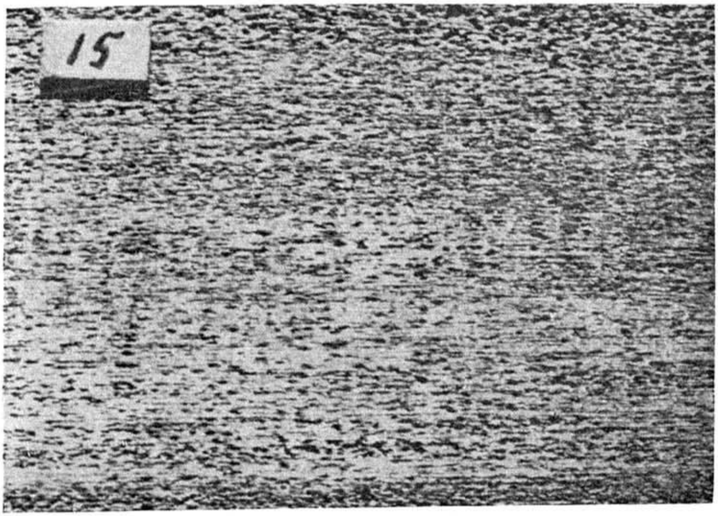
2. **CAST IRON (POLISHED) SHOWING FRACTURE.**
Magnified 2⅛ diameters.



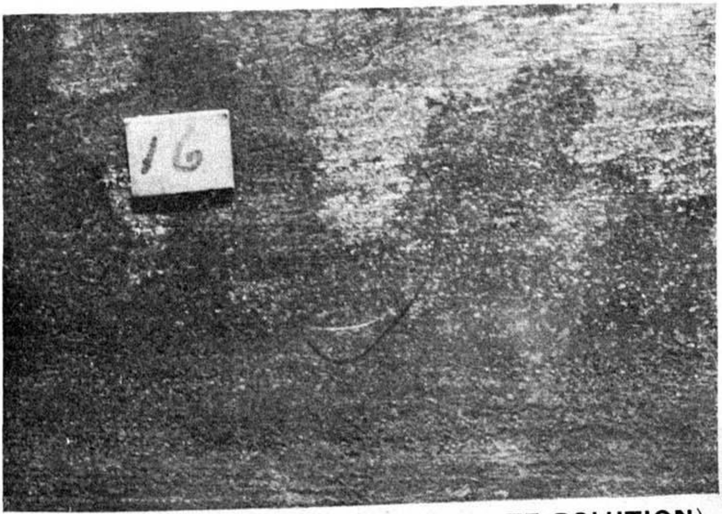
1. CAST IRON (POLISHED).
Magnified 2⅛ diameters.



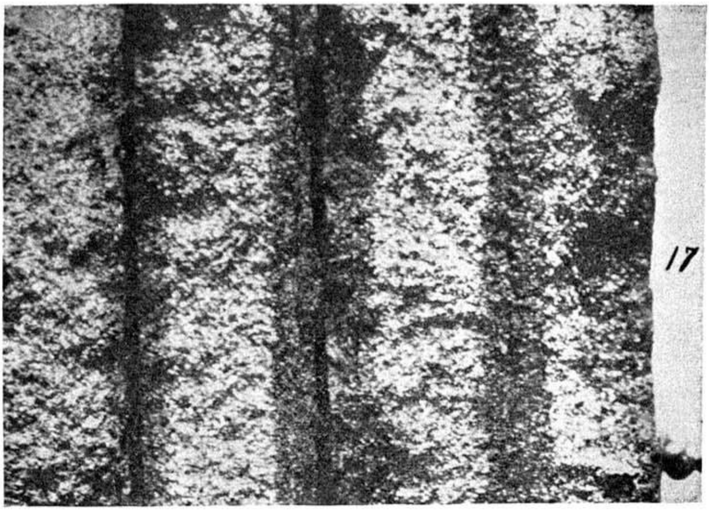
2. MILD STEEL (AMMONIUM CHLORIDE SOLUTION).
Magnified 2⅛ diameters.



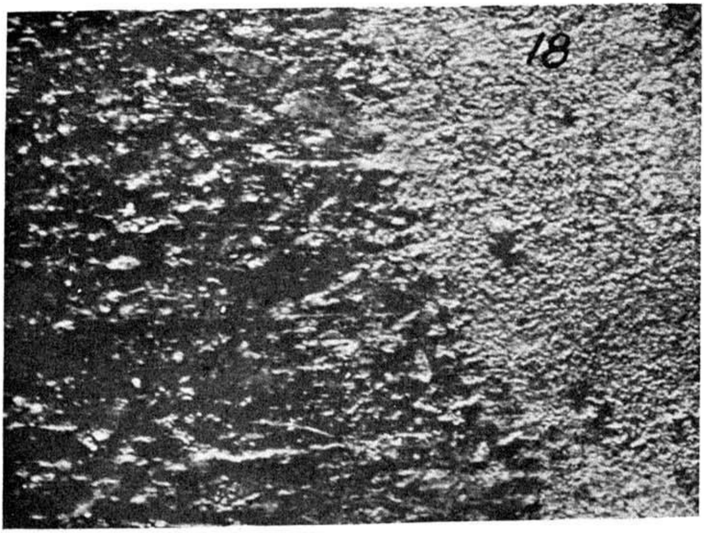
1. **MILD STEEL (AMMONIUM CHLORIDE SOLUTION).**
Magnified 2⅛ diameters.



2. **MILD STEEL (POTASSIUM NITRATE SOLUTION).**
Magnified 2⅛ diameters.



1. **FRACTURES OF CAST IRON (AFTER CORROSION).**
Magnified 2⅛ diameters.



2. **CAST IRON (WITH SCALE).**
Magnified 2⅛ diameters.

2

[Reprinted from the PROCEEDINGS OF THE SOCIETY FOR THE PROMOTION OF ENGINEERING EDUCATION, Vol. X., 1902.]

ELECTROCHEMISTRY AS AN ENGINEERING COURSE.

BY C. F. BURGESS,

Assistant Professor of Electrical Engineering, University of Wisconsin.

The justification of establishing a new course of study in engineering schools lies in the demand which the industries make for men having training which such courses offer. The rapid development in the application of electrical energy in producing chemical transformations which has taken place during the past decade has given rise to the new course of study which some or our engineering schools have recently organized or are about to institute, *i. e.*, applied electrochemistry.

Electrochemistry may be considered the pioneer among the various branches of electrical engineering, antedating and making possible telegraphy and other subsequent developments. The popular impression that electrochemistry is distinctly a new field arises from the renewed interest which has recently been attached to it through modern scientific and experimental study, with subsequent evolution of new theories, but more especially from the meteoric growth of what may be called our electrochemical and electrometallurgical industries. Scientific progress in electrochemistry and industrial progress in the same line have not been of the "hand-in-hand" variety, but there has been a considerable degree of independence of one upon the other and the industrial side has undoubtedly made the greater advances.

Modern theoretical electrochemistry as based upon modern research is in a very unsettled and uncertain state, and no theory has been set forth which will satisfactorily classify known electrolytic phenomena or afford a basis for calculation.

The industrial side, on the other hand, has made distinct, material and permanent advance, not so much through our new scientific discoveries as through the application of engineering knowledge to the many and long-known scientific facts which the pioneers have previously pointed out. Many of the laboratory experiments have, through such application, been advanced to the position of industrial processes.

While we cannot deny that scientific discovery is the basis of most industrial progress, we might reasonably expect industrial progress in electrochemistry to continue in the future, even though no new scientific discoveries be made; such progress to consist in the practical application of many discoveries which lie dormant, recorded in the technical and scientific literature and awaiting only engineering development to make them of direct utility to mankind.

In this field we have many illustrations of the fact that it is not the original discoverer to whom greatest credit is due, but it is he who makes such discoveries of direct utility that reaps not only the pecuniary reward but usually has associated with his name the honor of both discovery and of development. The Castner process for the production of metallic sodium is but a reproduction on a large scale of the experiment which Sir Humphry Davy performed nearly a century ago in separating metallic sodium from the fused sodium hydroxide. The McArthur-Forrest process for extracting gold by means of cyanide solutions is based upon the discovery of many years ago that potassium cyanide is a solvent for gold. Many other similar instances might be cited.

The pioneers of electrochemistry include such honored names as Davy and Faraday. Among the more modern ones, perhaps the most noted is that of Moissan, for his extensive work on the electric furnace. Such pioneers have furnished many discoveries which might be worked out to industrial advantage. In the fact that most of the scientific discoveries have not been worked out industrially by the originators we have a striking proof of the saying that "good pioneers do not make good settlers," and in considering the workers in electrochemistry we may regard the pioneers and the settlers as two distinct classes of workers.

The question may arise, "Should our colleges offer instruction with the view of developing pioneers, or of developing settlers?" The answer is, of course, "Both." If the question were to read, "Should our technical schools offer engineering courses in electrochemistry for the purpose of training pioneers or settlers?" the answer would properly be, "The training of the settlers is the primary object."

A considerable amount of discussion has been waged as to what the training of the electrochemist should be, and there has been a great diversity of opinion. The chemist maintains that he should be instructed primarily and most extensively in chemistry, together with various side lines including electrical subjects. The engineer says that he should be trained primarily in engineering with chemistry as a side line. The disciple of physical chemistry says his training should consist in a thorough grounding in modern theories of electrochemistry preferably in the German schools, or next best, by study under a graduate of such schools. The work which is offered in various institutions in this country shows the results of such differences of opinion. One institution places its instruction in electrochemistry in charge of the chemical department and the major part of the work is covered by the field of electrochemical analysis. Another institution places it in charge of the department of physics, holding it to be a branch of science. Another institution has a four years' course in electrometallurgy, assuming that as a broad and inclusive field in electrochemical application in connection with the metallurgical industries. Still another has instituted a four years' course in applied electrochemistry, included as an engineering course and parallel with a course in electrical engineering to a considerable degree. This wide divergence in opinion and practice arises largely through differences of opinion as to what the finished product of such a course should be and through differences of opinion as to what the term electrochemistry comprehends.

There are certain cases where the chemist's view is perhaps best, where the electrochemist's work consists most largely in chemical manipulation in which the electric current is used as an auxiliary agent and in which chemical knowledge is preëminently required.

It appears that, inasmuch as the warrant for establishing courses in electrochemistry arises from the present needs of the electrochemical industries, the courses of study should be such as will best supply men to meet such requirements. This calls for an engineering training; a familiarity with the various forms of energy, hydraulic, mechanical, electrical and thermal; the transmission, transformation and utilization of each, coupled with a sufficient knowledge of chemistry to enable such engineering information to be utilized with the best efficiency.

It was not many years ago that the chemical manufacturing industries were considered as independent of electrical or mechanical power, and chemical processes were supposed to be at the highest state of development when they were simplified to such a degree that machinery and power could be dispensed with, everything being accomplished by purely chemical reaction. The remarkable improvement in the efficiency and operation of the machinery as a substitute or as an aid for chemical reaction, cheapening of processes as regards both labor and material, and the utilization of electrical energy in very many chemical operations, have put the chemical industries on an entirely different basis. They are now preëminently power-using industries. It is this condition which has placed many engineers having a mechanical or electrical training at the head of our largest chemical industries, endowing them with the title of chemical engineers.

In discussing this question as to what the training in electrochemistry should be we must realize that there is the same difference between the term "electrochemist" and "electrochemical engineer" as between the terms "chemist" and "chemical engineer." It is the training of the electrochemical engineer with which I wish to deal.

Electrochemistry is a term which, in its popular conception, may include only a limited field, such for example as electrolytic decomposition. For our purpose it may be given a much broader and more comprehensive meaning, including the following divisions:

Electrolysis of aqueous and non-aqueous electrolytes, transforming chemical into electrical energy, or the reverse.

Electrothermal effects, or electrothermistry, as it has recently been called. This includes all forms of electrical furnace work.

Influence of the electrical discharge upon the decomposition or synthesis of gases.

Electrolytic osmosis, etc.

Electrometallurgy is really a more limited term than electrochemistry, inasmuch as it deals with one or more of the above divisions as related particularly to metallurgical industries.

It is not my purpose to go into detail in the citation of the industries related to the above divisions. Suffice it to say that the various applications make a diversified knowledge a necessity, and the most difficult question in designing a course of study is to get all the apparently necessary studies into the four years, which seems to be the maximum time which our colleges can well set aside for a course of study under present conditions.

In the electrical engineering department of the University of Wisconsin, instruction under the term applied electrochemistry has been offered as an elective for the engineering students during the past eight years. Something over a year ago a four years' course was instituted which has followed to some extent the plan as suggested by the electrical engineering course. A number of students have registered in this course and the various inquiries which have been received from various parts of the country indicate that it is going to be a popular one, and a considerable number of inquiries and requests for graduates from this course have already been received.

The following is the outline of work given the University of Wisconsin in the four years' course in applied electrochemistry.

FRESHMAN YEAR.

First Semester.

	Hours per Week.
German or French	4
English composition	3
Algebra	4
Descriptive geometry	5
Chemistry, general	3

Second Semester.

German or French	4
English composition	3
Trigonometry and analytical geometry	5
Descriptive geometry	1
Surveying	2
Shop work	1

SOPHOMORE YEAR.

First Semester.

Analytical geometry and calculus	5
Physics	5

Machine design kinematics	3
German or French, technical	3
Chemistry, qualitative and quantitive	4

Second Semester.

Calculus	5
Physics	5
Analytic mechanics	5
Machine design	2
Chemistry, quantitative analysis	3

JUNIOR YEAR.

First Semester.

Mechanics	5
Physics, precision of measurements	2
Electromagnetism, dynamos, etc	3
Chemistry, chemical analysis	5
Physical chemistry	5

Second Semester.

Applied electromagnetism	5
Materials of construction	3
Chemical preparations	5
Physical chemistry	5
Elective	3
Inspection tour of industrial establishments	

SENIOR YEAR.

First Semester.

Applied electrochemistry	5
Alternating currents	5
Organic chemistry	5
Steam engineering	3
Testing materials	2
Thesis and elective	2

Second Semester.

Applied electrochemistry	5
Alternating currents	3
Electric lighting and power	3
Chemical machinery	2
Elective	4
Contracts and specifications	1
Thesis	4

The first two years' work is practically that required in other branches of engineering, with more chemical work required during the sophomore year, this taking the place of shop work and drafting of the other courses. A considerable amount of physics and physical chemistry appears quite important, physical chemistry including the study of the elements of electrochemistry, together with the theory, as treated in the view of modern discovery.

The above is not set forth as an ideal course, but rather as one which will as nearly fulfill requirements as the present conditions in our university will allow. It is proposed to make some changes in the future and among such changes appearing desirable are the following.

General chemistry should be given as a daily study throughout the freshman year. Surveying is not an essential study and is included in the above list on account of the desirability of making the freshman work of all the courses alike.

During the sophomore year an improvement would consist in making qualitative and quantitative analysis a daily study throughout the year, the chemistry of the junior year to consist in organic chemistry for the first semester and in chemical preparations and industrial chemistry as a daily study for the second semester. Chemical engineering and chemical machinery and appliances might properly be a suitable branch to be followed throughout the senior year.

All of the work in chemistry, physical chemistry and applied electrochemistry consists largely in laboratory practice and it is the time necessary for this work that makes it difficult to include all the studies which seem desirable.

The course in chemical preparations and industrial chemistry as now given is designed with the view of impressing upon the student the matter of cost. Each student makes on a fairly good scale many common chemical products. He is supplied with the necessary raw materials which are charged up to him at current market prices, and the finished product is weighed, analyzed for purity, and the value of this same is credited to his account, at the market rates of this material. He is required to make a report giving a statement of the efficiency of the process, materials consumed, materials produced, waste products, methods of procedure on a large scale, the machinery and apparatus necessary, and an estimate of labor and power. In this manner it is sought to impress the economic questions which enter into chemical work.

It is proposed to assign similar experimental and laboratory work in applied electrochemistry, in which electrical energy becomes one of the important factors to be considered.

[Reprinted from the Transactions of the American Electrochemical Society,
Volume I, No. 1.]

A paper read at the Inaugural Meeting of the American Electrochemical Society, Philadelphia, April 4, 1902, President Richards in the Chair.

THE ELECTROLYTIC RECTIFIER.

By C. F. Burgess and Carl Hambuechen.

The facility with which the alternating current lends itself to voltage transformation is making this form of current the standard for electric power transmission purposes. This condition together with the difficulty of applying the alternating current directly for certain purposes such as series arc lighting and traction work, and the impossibility of employing it for electrolytic work, including the charging of storage cells, makes the transformation of an alternating into a direct current an operation of increasing importance.

That this problem has not received a satisfactory solution is evidenced by the disadvantages attendant upon existing commercial means of obtaining unidirectional current from alternating current lines. The synchronous rectifier or revolving reversing switch, while of considerable simplicity and high efficiency, has the apparently insuperable disadvantage that adjustment for minimum sparking is almost impossible to attain on account of the varying relation between inductance and capacity on the line. With rotary converters we have among other disadvantages the low weight and energy efficiencies, especially with smaller sizes, and the great cost.

The equivalent of the static pressure transformer which is used on alternating circuits would be an ideal solution of this problem, and among various devices having no moving parts which have been suggested, the electrolytic rectifier gives the greatest promise of commercial success.

From some of the claims which have in the past been made for the electrolytic rectifier we are led to doubt the justification of such claims or to wonder why apparatus embodying them has not begun to replace the more expensive, less efficient, more cumbrous methods of common practice. Such condition justifies the statement of the practical man that the utilization of the electrolytic cell as a rectifier possesses considerably more interest than value.

To determine if possible the practicability of successfully utilizing the electrolytic cell for this purpose the writers undertook an experimental investigation, some of the results and conclusions of which are here given. Attention was confined largely to the utilization of that remarkable property which various metals, particularly aluminum, possess in certain electrolytes of allowing current to flow freely in one direction and offering great resistance to its flow in the opposite direction. This phenomenon, which seems to have been first discovered in 1855 by Wheatstone, has been the basis of a considerable amount of speculation and of experimental investigation ever since. The commonly accepted view is that aluminum by means of its property of being easily oxidized (this term being used in its general sense) in certain electrolytes becomes so thoroughly covered with a continuous oxide coating that it effectively insulates the plate from the surrounding electrolyte and prevents any flow of current as long as this coating is maintained. When the pressure is in such direction as to make the aluminum the anode the effect is to maintain this insulating coating unless the pressure be high enough for disruption. When the aluminum is the cathode this insulating coating offers little or no barrier to the flow.

A question which is suggested by the above explanation is, if the insulating coating prevents the flow of current in one direction why is it not an insulator for the opposite direction? Further, the protective coating of the aluminum plate is formed at the expense of a certain amount of corrosion of aluminum by oxidation and this coating is destroyed or removed when current flows toward the plate, which must be done without the redeposition of aluminum, for as far as is known this cannot be done from aqueous solutions. The aluminum coating must be of a certain appreciable thickness to prevent flow of current and if this coating is formed and destroyed 60 times a second it ought not to take long before the aluminum plate is completely oxidized, which is found to be contrary to fact. Observations which were made lead to the following conclusion upon these points. The coating on the aluminum does not absolutely insulate but offers a resistance so high that only a small current (sometimes immeasurably so) flows when the aluminum is the anode. The leakage current does not flow uniformly from the surface but only from portions of it having lowest resistance and thinnest coatings. These portions are small openings or points distributed somewhat irregularly over the surface and the current flowing through these points produces enough heat to give the well-known sparking effect if pressure is sufficiently high. On reversing the direction of the pressure the current flows through these small openings and in so doing enlarges them, the resistance being thereby greatly decreased. On again reversing, this opening is immediately closed or contracted, which process may be considered as continuing at a rate equal to the frequency employed. The sparking seems to be the result of the leakage current, and from the general appearance of the sparks the amount of leakage may be estimated. When sparking is sharp, bright, distinct and occurring in fine sparks, the leakage is of a low value, and where sparks are larger and duller and in the nature of flashes, the leakage is greater.

The entire surface of the aluminum then does not act as the active electrode, but only those parts upon it at which the sparking or leakage takes place. It is undoubtedly the case that the expansion and contraction of the openings which takes place at these discharge points is due to the formation and destruction of the aluminum oxide coating, and, as before indicated, results in the continual oxidation of aluminum. This oxidation or wearing away does not, however, occur uniformly over the entire surface, but only at those localities (constituting a small proportion of the surface) at which the sparking occurs. This results in a gradual wearing away at these points, as evidenced by the marked pitting of the electrodes which may be observed after a considerable length of time of operation.

Some idea of the relative proportion of an aluminum surface which is active in a rectifier consisting of aluminum and lead electrodes in a potassium phosphate solution may be obtained from Fig. 1. This is a photograph of an aluminum electrode magnified 21 diameters, which had been in operation on an alternating pressure and which was subsequently immersed as cathode in a copper sulphate solution and a current of low density caused to flow. This produced a deposit of copper at various points on the aluminum surface not protected by the insulating coating, or, in other words, the spots showing the copper deposition indicate the position of the electrolytic valves. By taking a similar aluminum electrode and causing it to receive a very low current density as cathode in the phosphate solution for one-half minute, and then repeating the copper deposition process, the active surface is seen to be greatly increased. This is shown by Fig. 2, and bears evidence to the statement that the electrolytic valves consist of openings in the protective coating which expand and contract, according to the direction of the flow of current.

Reports of efficiency for the electrolytic rectifier have appeared in engineering and scientific publications from time to time, giving values of current and energy transformations of 90 and even 95 per cent., but such claims appear to have been made without considering all the factors or the conditions which have to be met in practice. Estimates for efficiency have been based upon the single factor, *internal resistance* of the apparatus. The statement that an aluminum rectifier "will give an efficiency of 95 per cent. provided the electrodes be made large enough," assumes erroneously that the direct heating effect of the current flowing through the resistance is the only loss in the cell.

The losses in the rectifier may be divided as follows : C^2R loss, C being the current flowing toward the aluminum and R being the resistance of the electrodes and electrolyte.

CE', where C is the current flowing toward the aluminum electrodes and E' is the counter electromotive force which is developed by the decomposition of the electrolyte.

$C'E$ where C is the leakage current flowing from the aluminum to electrolyte and E is the applied pressure.

The direct heating effect of the current while flowing in the useful direction may be made as small as desirable by decreasing the current density and by placing the electrodes in close proximity. The former is limited only by convenience of size and the cost of cell for given output, and the latter by mechanical construction consistent with freedom of circulation and the avoidance of short circuits. If this loss were the only one to consider, the question of efficiency of electrolytic rectification would be practically solved. An electrolyte having a resistance as low as ten ohms per cubic centimeter can be readily obtained, and with such electrolyte and with electrodes one centimeter apart, the resistance of a cell per square decimeter would be one-tenth of an ohm. This would produce, with a current density of 5 amperes,

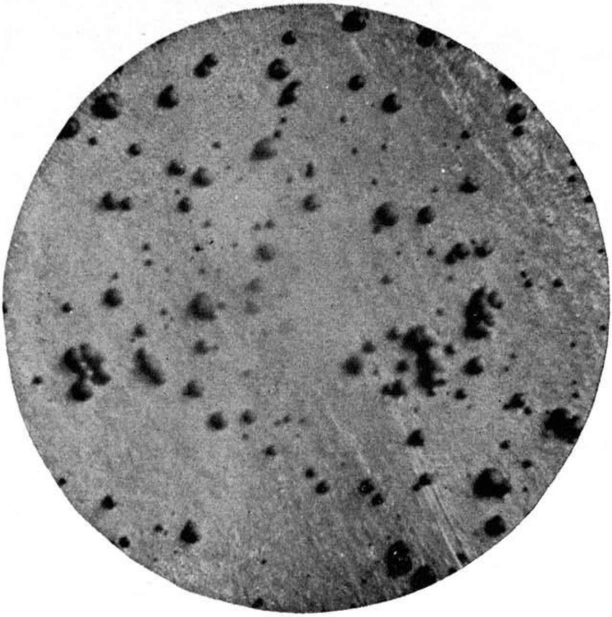


FIG. 1.

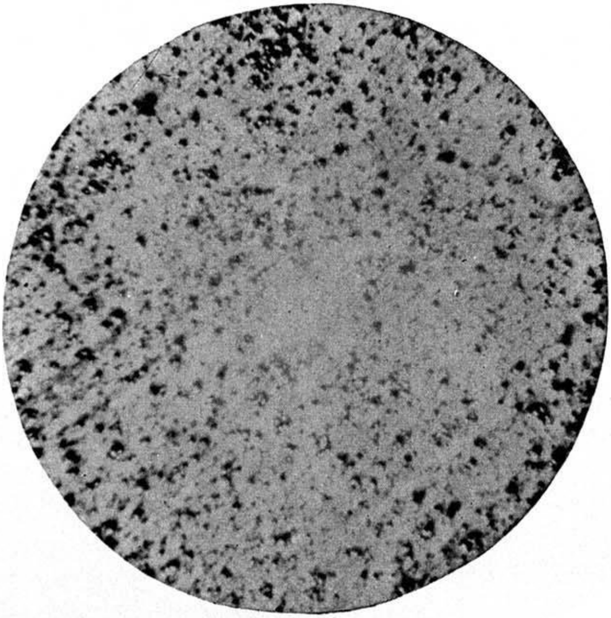


FIG. 2.

a drop of only one-half volt which, with an applied pressure of 25 volts, would mean a loss of 2 per cent.

It should be borne in mind, however, that the resistance of the electrolytic cell cannot be accurately figured from the specific resistance and the volume of the electrolyte inasmuch as only a small proportion of the aluminum plate is an active electrode surface and the resistance between the electrodes may, therefore, have a much higher value than calculations will show. The internal resistance is a variable quantity, being least when maximum current has flowed toward the aluminum and greatest after the maximum pressure has been applied with aluminum as the anode. The fact that the reduced area of the active aluminum surface has the effect of reducing the cross-section of the electrolyte was shown by measuring the resistance of an electrolyte with an aluminum cathode, and again with a carbon cathode. In the latter case the resistance was found to be 2.5 ohms as against 5.5 ohms in the former. This resistance of the electrolyte is not reduced proportionally as the electrodes are brought nearer together inasmuch as the greater part of the resistance exists near the aluminum electrode.

The current flowing through the electrolyte causes decomposition which cannot be avoided, inasmuch as most of the current flows in one direction. This, of course, requires a certain amount of energy, depending upon the current passing and the counter electromotive force. The counter electromotive force within the cell has a value depending upon the electrolyte and the electrodes. If the anode be a corrodible metal this pressure may be lower than where an insoluble metal, such as platinum, is used, but this lowering of counter electromotive force would be at the expense of corrosion of the electrode, which would probably be undesirable for commercial purposes. E' may have a value varying from 1 to 3 or 4 volts. This loss of energy shows itself primarily by a change of the composition of the electrolyte, and if the substances produced thereby recombine within the electrolyte, heat is produced. For a commercial rectifier the electrolyte should be so chosen that it produces a minimum pressure of decomposition and it should be sufficiently cheap that the waste of material by decomposition is a small amount. To reduce this source of expense to a minimum it may be desirable to construct the cell so that the liberated materials will recombine as completely as possible. The decomposition of the electrolyte, which cannot be avoided, offers the possibility of being the source of profit rather than expense if the products of decomposition are of greater value than the original material and provided they can be collected economically. This, however, from the commercial standpoint is a possibility rather than a probability.

The fact that a portion of the current flows in the wrong direction is probably the greater source of the difficulty with the electrolytic rectifier, and it is upon limitation of this leakage that commercial success depends. The leakage current may be made visible by the brilliant sparking which occurs over the surface of the aluminum, and it is evident that the energy thus expended, which may be of very considerable amount, is concentrated almost entirely upon the aluminum surface and manifests itself in the form of heat.

It will be observed that nearly all losses cause a liberation of heat, which tends to raise the temperature of the apparatus to such a point that it breaks down or becomes inefficient. The output of the apparatus is, therefore, limited to the rate at which the heat may be dissipated and to the maximum temperature allowable ; a large output means small losses, method of cooling, and a high allowable temperature.

To find the relations between these losses, a number of tests were made under various conditions, the results of some of which are here given. The method of studying the problem was by means of current and pressure curves obtained with an instantaneous contact maker.

The curves on Fig. 3 show something of the operation of an arrangement consisting of an electrolyte of potassium phosphate having a density of 1.27 sp. gr. and slightly acidified, in which were placed an aluminum sheet electrode having an immersed area of 45.5 square inches and a lead electrode of similar size. The aluminum electrode was previously cleaned and immersed for some time in a sodium hydroxide solution and then "formed" in the phosphate solution by applying a pressure from a direct current circuit with the aluminum as the anode.

The cell was then connected in series with a non-inductive resistance to the brushes of an alternator, and current and pressure curves were obtained. The method of connection is shown in Fig. 4.

The portion of the current curve (*a*), Fig. 3, below the base

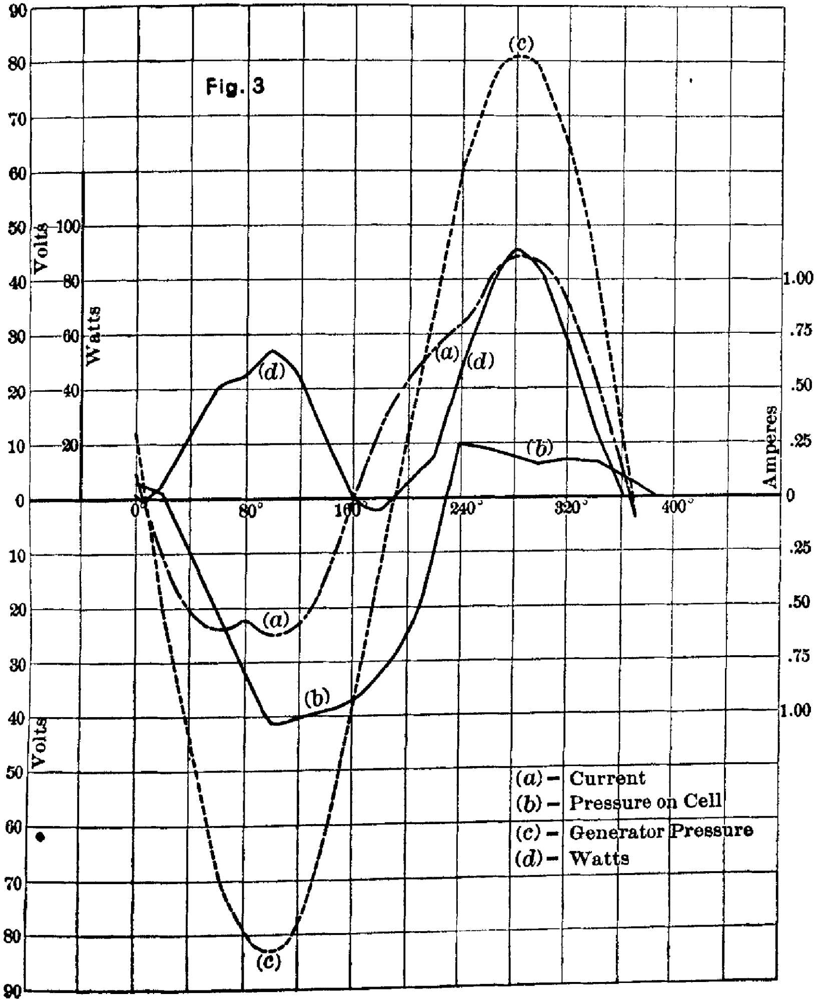


Fig. 3

line indicates the current which flows from the aluminum plate to the electrolyte, or the leakage current, and the remainder of the curve shows the current in desired direction. The pressure curve across the rectifying cell is shown by curve (*b*), the negative part being the pressure at which the leakage current flows through the cell and the positive part representing the CR + E′ in the cell where C is current flowing, R is internal resistance, and E′ is the counter electromotive force of polarization. The pressure applied to the circuit by the generator is indicated by the sine curve (*c*).

It is to be noted from these curves that there is a very considerable leakage current: the loss due to CR + E′ is seen to be much smaller than that due to leakage. The current curve being in advance of the pressure at the center of the cycle shows that there is some capacity effect.

The curve (*d*) showing the watts delivered to the circuit gives an idea as to the loss due to leakage as compared with the watts delivered during the remainder of the cycle. The average watts delivered to the circuit is 33.9. The average watts lost in leakage is 13.9.

In making the above tests we attempted to use the solution and electrodes as recommended by Pollak,[1] following his description as closely as possible in setting up the cell. The best efficiency, however, which we succeeded in attaining was so low as to lead to the belief that some essentail detail was omitted in the published descriptions or that errors in interpreting the same were made by us. The efficiency here shown is not sufficient to guarantee any extended commercial applications, and especially so as the electrolyte must be kept below 40° C., which means low size and weight output.

The leakage seems to be the principal subject for study in bringing the electrolytic rectifier to commercial efficiency. The leakage depends upon various factors including the following:

Electrolyte—as to composition and temperature.
Aluminum electrode—as to composition and surface exposed.
Pressure.
Frequency.

That the proper choice of electrolyte is important is shown by the fact that comparatively few substances will give satisfactory results. Among electrolytes which have been proposed are aqueous solutions of sulphuric acid, sodium and potassium phosphate, sodium potassium tartrate, and alum.

The temperature plays an important part as shown by the fact that if the temperature rises beyond a certain point low efficiency or complete failure of the cell results. Pollak gives 40° C. as the maximum allowable rise of temperature for potassium phosphate solution.

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[1] Bulletin Soc. Int. Electric, July, 1901. Paper by M. J. Blondin.

The leakage seems to depend upon, if not actually proportional to, the area of the aluminum surface immersed in the electrolyte and this being the case we are led to the use of high current densities. This is antagonistic to reducing the C^2R loss to a minimum which requires as low a current density as possible. A suitable balance between these two losses will have to be determined upon. It has been our observation that when the aluminum electrode becomes grooved or pitted by continued action of the current the leakage increases, due probably to increased area of surface, and smoothing down by hammering or polishing or grinding will increase the efficiency of such electrodes.

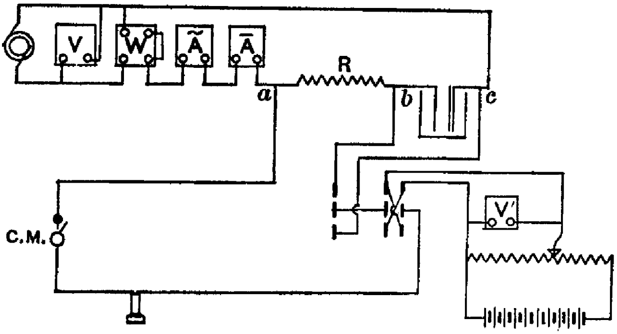

Fig. 4

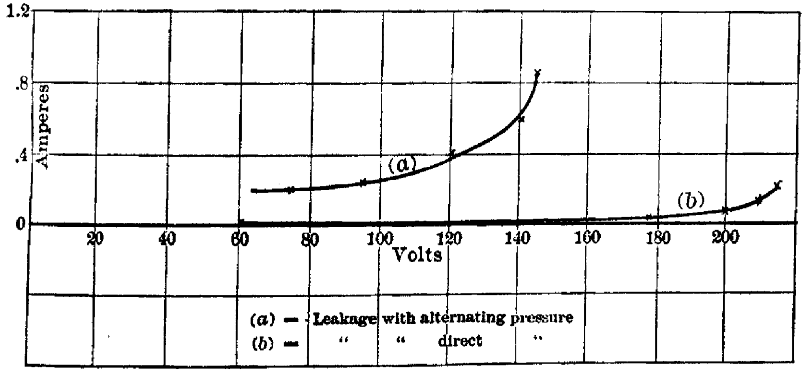

Fig. 5

The purity of the aluminum will have some considerable influence upon the leakage, inasmuch as the presence of another metal either as an alloy or in metallic contact reduces or destroys the rectifying action of the aluminum. It is possible, however, that some alloy of aluminum may be discovered which will have a more efficient action than does pure aluminum. The writers found that a small amount of chromium in the aluminum appeared to give it some slight advantage in efficiency, in addition to making it somewhat harder and more durable than the pure aluminum.

That leakage will depend upon the pressure applied is evident upon taking the characteristic of a cell having two aluminum electrodes, using either direct or alternating pressures. The leakage increases proportionally with the pressure to a certain point when the rate of increase becomes much greater. This is shown in Fig. 5 where curve (*a*) is for two aluminum electrodes in a sodium potassium tartrate solution using an alternating pressure, and curve (*b*) is for the same plates with unidirectional pressure. It will be seen from these curves that the behavior on alternating and on direct current circuits is very different and that the amount of leakage in one case is not a direct indication of the amount of leakage in the other. An aluminum electrode may successfully withstand 200 volts unidirectional pressure and not operate successfully on 120 volts alternating pressure. It will also be noted that with direct pressure up to 150 volts the leakage was almost a negligible amount, while with an alternating pressure of 75 volts the leakage was many times greater. This difference was probably due, at least, to a considerable extent, to the condenser effect which the aluminum electrode shows, allowing a capacity current to flow with the alternating pressure.

The sparking which occurs in both cases had very much the same appearance but there was this difference to be noted, that with equal values of leakage of the current, the sparking with the direct current seemed to be more violent than with the alternating.

It will thus be seen that no exact conclusions as to the action of the aluminum electrodes on alternating pressures can be drawn from observations made with unidirectional pressure as some experiments have evidently assumed.

The influence of frequency upon the leakage and the efficiency of the electrolytic rectifier is a question in regard to which we are unable to draw definite conclusions although a number of tests were made for the purpose of determining this point. Frequencies from 7 to 125 per second were used and in some cases higher efficiency was obtained with higher frequencies and in some cases the reverse condition held. The difference, however, was slight with the frequencies worked upon which represents the range of present practice and the conclusion may safely be made that the question of frequency is one of minor importance as far as efficiency is concerned. This is a subject, however, deserving of further investigation.

The frequency may, however, have an important influence upon the condenser action of the rectifier in producing a low power factor. To reduce this capacity effect, the remedy is evidently a decrease of the aluminum surface or an increase in current density.

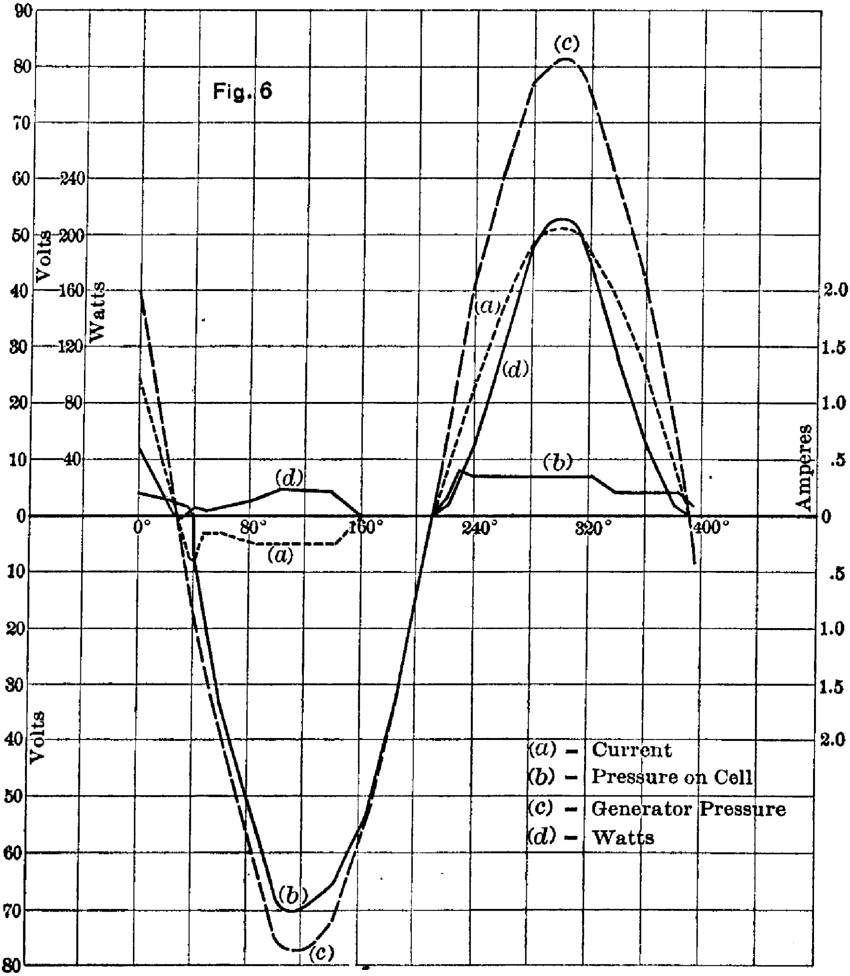
Fig. 6

For the purpose of increasing the efficiency of operation we have used a large number of electrolytes, but with indifferent results until the idea of using a fused electrolyte presented itself. Certain molten salts gave such decided improvement in results that extensive investigation was made in this field, and from a great many curves taken, Fig. 6 gives some typical results, such being obtained by use of an aluminum and an iron electrode in molten sodium nitrate.

Curve (*a*) represents instantaneous valves of current, the negative values indicating leakage. Curve (*b*) gives values of pressure at terminals of rectifier and curve (*c*) shows form of pressure wave delivered by the alternator at a frequency of 58. These curves compared with those of Fig. 3 and obtained under similar conditions as to pressure, frequency, and output show decided differences in operation between aqueous and fused electrolytes. The leakage is seen to be a much smaller percentage of the total current flowing.

The loss due to internal resistance and counter pressure is smaller in spite of the fact that the aluminum electrode in the fused salt was about one-fortieth the area of the aluminum in the aqueous solution.

The portion of the curve (*a*) between 30° and 50° demonstrates, we believe for the first time, the interesting fact that at the instant of reversal of aluminum from cathode to anode it offers little resistance to the flow of current, but that it quickly recovers itself and closes the current valve. The rapidity with which this action takes place is seen to be somewhere in the neighborhood of $^1/_{1100}$ of a second at the beginning of a sine pressure wave. After applied pressure has reached its maximum negative value the leakage current rapidly decreases to nearly zero where it remains until reversal of applied pressure again takes place.

The rapid increase, and slight elevation of curve (*b*) at the point 230° shows that the "formed" aluminum plate offers considerable resistance to the flow of current toward it but the resistance almost instantly diminishes. The portion of curve (*b*) from 340° to 400° consists mainly of the counter pressure which maintains its value even after direction of applied pressure has changed as shown by the fact that (*b*) becomes negative *after* (*a*) has reversed in direction.

A further observation is the fact that there is no evidence of capacity effect or difference of phase between pressure and current, which is so noticeable in curves in Fig. 3. This is undoubtedly due to the much smaller area of the electrode surface acting as condenser plates.

Curve (*d*) shows instantaneous values of watts delivered to the circuit, the portion from 30° to 160° representing the loss due to the leakage and from 200° to 380° the watts delivered during remainder of cycle. This curve shows an energy efficiency of over 80 per cent.

It will be observed that at a point at about 40° the value of the watts is negative to a very slight extent indicating that energy is being restored to the circuit. This is undoubtedly caused by the aluminum plate acting in conjunction with the iron as a voltaic cell, delivering energy at the expense of corrosion of aluminum. This delivery of energy, however, at the expense of the aluminum continues only for a very short part of the cycle, or until the "valves" begin to work. While having no figures to demonstrate this fact it seems reasonable to suppose that the small amount of corrosion of aluminum which takes place when used in a rectifier is due to, and proportional to, this energy delivered to the circuit.

Among the advantages which may be claimed for the fused electrolytes in comparison with aqueous solutions in addition to sharper and more clearly defined action, higher efficiency, and low inductive capacity effect, are large output per unit weight of cell, which is attained through ability of the cell to stand a high temperature in addition to the much greater conductivity which a fused salt may show over an aqueous electrolyte.

A difficulty in carrying on an experimental investigation upon electrolytic rectification is in the uncertain error which is introduced by the use of ordinary electrical measuring instruments. The amount of error depends upon the type of instrument used and form of current or pressure curve. A complete investigation of the subject of measuring interrupted, fluctuating or pulsating currents was not attempted, but a number of observations will show something of the order of the errors which may be expected.

A circuit carrying a current of the form indicated by curve (*a*), Fig. 6, had in series, three amperemeters of various types together with a copper voltameter. The three instruments represented the hot wire type, the Hoyt alternating current and the Weston direct current type. It was assumed that the voltameter would give a correct indication of the amount of current rectification and upon that supposition the Weston instrument gave a reading of 94 per cent. of correct value, or 6 per cent. low. The hot wire instrument gave a value 55 per cent. high, and the Hoyt instrument was 64 per cent. high. Using a combination of rectifying cells so as to obtain a pulsating current which did not reverse during any part of the cycle it was found that the Weston instrument still indicated too low a value by $5\frac{1}{2}$ per cent. ; the hot wire instrument was 17 per cent. high and the Hoyt instrument 23 per cent. high.

One of the chief uses mentioned for the electrolytic rectifier is the charging of storage cells, and the question will naturally arise as to whether the form of current which is furnished to the battery will be advantageous or disadvantageous to it. Mr. A. B. Marvin, who has been conducting extensive storage battery tests in the electrochemistry laboratories of the University of Wisconsin, took up the investigation of this question. A number of tests consisted in comparing the capacity and efficiency of the storage battery when charged from a steady, and from a pulsating or rectified current. Two storage cells were repeatedly charged and discharged under normal conditions and with steady charging current with the object of ascertaining as accurately as possible the capacity and efficiency of the cells. A rectified current was then substituted for the steady one in charging, and the capacity as shown by the discharge together with the efficiency was in all cases almost identical with the values obtained with the steady current. These tests seemed to show almost conclusively that the pulsating current, even if it has not a marked beneficial action upon the cell, as some writers claim, at least has no harmful action.

The question as to the influence of a pulsating current upon the character of electro-deposited metals or for other electrolytic purposes, is a subject which appears worthy of investigation and might lead to some new commercial applications of the same.

From the results of our investigations the possibility of commercial development of electrolytic rectification seems promising. With the present known means of rectifying with an efficiency of over 80 per cent. competition with the rotary converter, especially in the smaller sizes, is in favor of the electrolytic rectifier while in weight and cost, the balance is very decidedly in its favor.

We have no reason for assuming that further discoveries and improvements will not be made in the electrolytic rectifier and its application to practical use, and with such development its importance would proportionally increase. It may be possible to discover a better electrode than is furnished by pure aluminum, as regards leakage and maximum pressure at which it will operate. That we are not limited to aluminum as the active electrode has been shown by the same phenomena which some of the common metals, such as lead and copper, may show under proper conditions of electrolyte and current density. Lead in concentrated sulphuric acid into which a small amount of sodium bichromate had been dissolved was made to show an interrupting effect, a pressure of 65 volts having been opposed.

Similar possibilities are open for the discovery of new and improved electrolytes. We are not limited to fused or aqueous liquids but may be able to find advantages in the use of solutions in organic solvents.

The form of current obtained by use of a single pair of electrodes, as shown in curves in Figs. 3 and 6, is not suitable for most commercial purposes. The large degree of fluctuation and the slight reversal in direction would be disadvantageous on the operation of motors, and while storage batteries placed on such circuit become charged, the efficiency would not be high inasmuch as the pressure of the cells is added to the pressure applied to increase the amount of leakage. The commercial rectified current should always be in one direction and as near a steady current as possible. There are various combinations of cells and apparatus to accomplish this result but it is not the purpose of this paper to take up this branch of the question. As an illustration of one method for accomplishing this may be mentioned the well-known Pollak and Graetz method of joining four cells in such a way as to give a current which flows continually in one direction though of pulsating value. We deem it undesirable to present at this time the arrangements and devices for accomplishing similar results on account of protection which is expected from the Patent Office. We hope, however, to be able to present a description of such methods and improvements before this Society at a future date.

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DISCUSSION.

Mr. E. A. Sperry: Mr. Chairman, I have done considerable work in attempting to adapt the ordinary aluminum rectifier to practical service without success. It is not a commercial apparatus, at all. In a few hours it breaks down, and its efficiency as has been stated by Mr. Steinmetz is only about 20 per cent. when working at its best. As to the comparative results obtained in charging a storage battery by interrupted current, I might say that using a mechanical interrupter or rectifier, such as a synchronous motor working a turbine interrupter, giving off only a pulsating current cutting the tops of the waves with intervening spaces of rest, and measuring the energy through an ordinary Thomson watt-meter, we have data to show that a battery gives higher efficiency when so charged, this being somewhat different from the statements made by the reader. This might be explained by the indifferent action of the watt-meter itself; there, however, being no iron present in the watt-meter, I see no reason why a pulsating current of the kind described, especially of as low frequency as sixty cycles, would interfere in the slightest with its accuracy. The results that I speak of were repeated in different hands, and I think they are reliable. They showed an advantage of somewhere near 9 per cent.—not a very large percentage, but decidedly on the right side.

Mr. C. Hering: I would like to add my admiration of the excellent work of Professor Burgess and the results obtained by him.

Dr. H. S. Carhart: I notice in the first electrolyte the size of the voltage is very much smaller than in the other. That would account for the smaller watt capacity.

Professor Burgess: I would like to say I am not responsible for the discovery of the value of fused salts in rectification. Any credit which may be given for the same is due to my assistant, Mr. Hambuechen, who is the discoverer of this property. We subsequently carried on the experimental and development work together.

In regard to measuring the rectified current by means of ampere meters, we found that meters of various types gave various errors.

In checking such instruments with the copper voltameter we found that errors of 10 per cent. might always be expected. Similar errors were also found with watt-meters. Measurements of the efficiency of such current in charging a storage cell were made by the use of voltameters, and we have been unable to find much advantage in the use of pulsating over steady currents for this purpose.

President Richards: I would like to ask how you would determine the watt efficiency by the copper voltameter.

Professor Burgess: This may be done by using two voltameters, one for determining the current passing into the storage cells, and the other, connected in series with a non-inductive resistance of known value, for determining the pressure.

A paper read at the Third General Meeting of the American Electrochemical Society, at New York City, April 17, 1903, President Richards in the Chair.

V.3. pp 300-316

ELECTROLYTIC PRODUCTION OF METALLIC COMPOUNDS.

BY C. F. BURGESS AND CARL HAMBUECHEN.

An accurate estimate of the importance and extent of industrial development of electrochemistry is difficult to make. It is interesting and important to note that an estimate based upon achievements as recorded in the literature, is materially different from that based upon the capital invested in successful industrial enterprise. If all that is claimed in print could be realized in practice, the electric current, through its electrolytic and thermal properties of producing chemical change, would be of much greater service to mankind than it is now, even after the enormous strides have been made in this direction. Progress will be made in the near future through the realization of published though at present unpracticed claims, as is self-evident from a study of achievements of the past two decades. Advancement of known laboratory experiments to industrial processes affords ample room for a continuation of development in electrochemical lines even though no new scientific discoveries be made.

The voluminous literature in this comparatively new field is a most useful tool for the student of applied electrochemistry, provided it is properly used. The knowledge, however, as to how it should be used is most difficult to acquire. A statement might be warranted that an investigator will make almost as much progress by neglecting the literature as by following its guidance implicitly. The ability to use this tool properly lies in the power of discriminating as to the truth of published statements, which, in turn, requires a thorough knowledge of the laws of nature.

There is probably no field of industrial activity in which such a large percentage of the literature relating to it possesses the properties of inaccuracy, incompleteness, and absolute untruth as does applied electrochemistry. This condition arises through various characteristics of the writers, including excessive enthusiasm leading to premature declaration, incomplete knowledge of the subject under treatment and even the apparent intent to mislead the public. The patent literature is especially characterized in the exhibition of these traits, and as printed frequently bears internal evidence of the leading scientific and technical societies. Erroneous statements published, perhaps in all sincerety, by over-enthusiastic or insufficiently informed observers are almost invariably allowed to stand uncorrected, largely through the natural reluctance which one has of admitting that he was wrong, and by reason of that same trait of humanity which causes a man, after he emerges from the tent of a side-show where he has been swindled, to allow his neighbor to pay his money and enter without a word of warning.

One of the greatest advantages which could accrue to this industry in which we are all interested would be the placing of the literature on a basis of greater reliability. The difficulties, however, in accomplishing it are comparable in extent to those which must be overcome in the deposition of aluminum from aqueous solutions, which problem has been solved so many times on paper but not in practice.

Electrochemistry being a new and little understood field, has been a fertile one for fraudulent schemes. A list of such would be a lengthy, interesting, though perhaps a familiar one. A similar list of electrochemical applications which have been published through no fraudulent motives, but which have failed through unforeseen conditions, would be much larger; and it is a noteworthy fact that our literature is almost entirely lacking in publications setting forth the reasons for failure of previously supposed successful processes. Such publications would be of especial value as a guidance to others and would be of advantage in promoting industrial progress by calling attention to problems which need solution, such problems as an experimenter could discover otherwise only by lengthy preliminary research.

This somewhat extended introduction has been entered into not only for the purpose of calling attention to some unfortunate conditions in which we are interested, but also as a justification for the paper on the subject here presented, on the electrolytic production of metallic compounds.

It is not the purpose of this discussion to present an ideal or even an improved process for producing metallic compounds, but rather to point out the limitation of the methods at present available and to deal with some of the difficulties which must be encountered in large scale working.

The use of electricity in producing compounds of the metals seems to have been alluring to experimenters. Appended hereto is a partial bibliography of the literature of the past ten years relating to this matter, but there are few statements giving the reasons for the failure of many of the processes to attain commercial importance.

Electrical energy suitably applied to a soluble sulphate, chloride, nitrate or similar salt of one of the alkali metals, may produce a dissolving action upon a metal anode with a consequent production of a salt of that metal similar to that which would be produced by ordinary chemical corrosion by a corresponding acid. It is from this fact that arises the commercial possibility of replacing acids commonly used, by cheaper substances. Thus in the production of metal sulphate or chloride it is cheaper to obtain the SO_4 or Cl from a sodium salt than from the acid, especially in such localities where, by reason of freight rates or other circumstances, the acid may be of relatively high price.

A metal nitrate may be produced much more economically from sodium nitrate than from the nitric acid as far as cost of material is concerned. Figured on the basis of NO_3 content, 1.35 pounds of sodium nitrate is equivalent to 1 pound of nitric acid and, at present market values, represents a relative cost of 2.7 cents and 8 cents. Similar relative values might be shown in other cases.

Compensating for this saving in the cost of materials is the cost of power necessary in electrolytic operations, but where the process can be carried out on a large scale, this cost can be made insignificant. The amount of energy necessary to decompose 1.35 pounds of sodium nitrate in the production of a metal compound will be in the neighborhood of one-quarter horse-power-hour, which, at a cost of 0.5 cent, makes the cost per pound about 0.15 cent. A further advantage for the electrolytic process is the possibility of recovery of valuable cathode products, one of which, in the case above considered, is 0.6 pound sodium hydroxide, representing a value considerably more than the cost of power.

To realize the advantages for electrolytic methods which such reasoning makes apparent, requires suitable design of electrolytic apparatus, and it is on this point that the ingenuity and skill of the designer is required, inasmuch as each case presents individual characteristics and demands special treatment. The necessary complications of such apparatus may, with justice, be urged as favoring the purely chemical methods; but as partially or even more than offsetting this disadvantage is the fact that from a given metal surface corrosion may usually be caused to take place with much greater rapidity through the aid of electric current than without. This produces economy of floor space and volume of apparatus.

The metal compounds which may be produced may be classified as soluble or insoluble in accordance with the dissolving power of water for them. The chemical method for producing soluble metal compounds is typified in the action of an acid on a metal, either directly or indirectly, and the insoluble metal compounds may be produced from solutions of the former by precipitation by a carbonate, hydroxide or other precipitating agent. The double decomposition thus taking place results in the formation of a soluble salt as a by-product, which is usually of such a nature as to be difficult to recover in a pure state with an expenditure of energy sufficiently low to warrant it.

As compared with such chemical method, the advantages which can be obtained by the electrical current are the following: The dissolving acid and the precipitating base may be replaced by a cheaper salt, which is made by the electrical current to exert the dissolving action at the anode with the simultaneous formation of an alkali product at the cathode and the subsequent union of these two products producing a precipitate with a regeneration of the original salt. This salt may be used over again and does not represent a waste product. There is, therefore, no expensive material required to be consumed. While the electrical energy is a factor which must be taken into account, it is a comparatively unimportant one in figuring the cost of production on a large scale.

To the corrosion of lead and the production of various lead compounds much attention has been given, from the electrochem-compartments is practically the same and to maintain a given rate of flow requires a definite difference of level, depending on the character of the diaphragm. After electrolysis takes place for some time, the density of the solution in the anode compartment increases and that in the cathode compartment decreases or remains practically the same. The effect of the increase of density in the anode solution results in an equality of pressure toward the bottom of the cell, although there may be a difference of level at the surface of the solutions. This results in the diffusion of the anode solution into the intermediate and thus into the cathode compartment. To obviate this, an adjustment of the levels of the solutions to correspond with the relative density should be made. Another variable factor is the change of the character of the diaphragm due to the influences of the solution and the chemical products upon the same. A light, firm canvas has been found to give very satisfactory results, but the alkaline cathode solution and

FIG. 1.

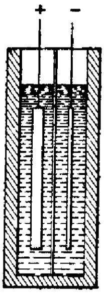


FIG. 2.

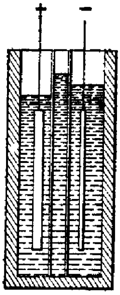
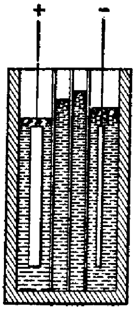


FIG. 3.



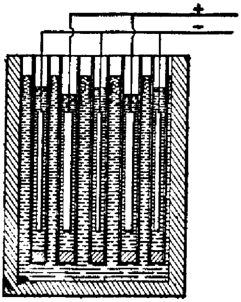


FIG. 4.

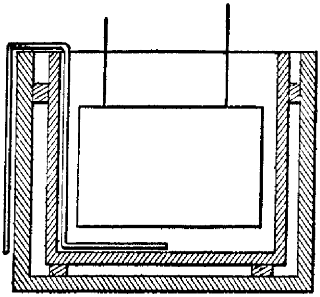


FIG. 5.

the acidified anode solution act in different degrees upon the two diaphragms in changing the porosity and the rate of diffusion. Temperature and current density also influence this diffusion. The maintaining of a definite fixed difference of level of solution between various compartments is hardly a satisfactory method of operation.

The writers have found that by a very simple method this difference of levels can be automatically adjusted by keeping the level of the solution in the intermediate compartment constant and drawing from the electrode compartments a certain definite *volume* of solution per unit of time. If the rate of diffusion with a given difference of level is not sufficient to supply this volume, the difference of level increases to such an extent that the flow through the diaphragm will be sufficient.

The fact that the lead solution in the anode has a higher density than the solution in any other of the compartments, makes it necessary either to maintain a very large difference in the level of the anode and the intermediate compartment, or the construction of the electrolytic cell with a limited depth. Our experience has shown that an anode plate about 8 inches in depth was the largest that could be used with the kind of diaphragms described.

Anode compartments being limited in depth in the manner shown, and the width, by the construction of the cell and the diaphragm, to about 2 feet, and the anode current density being limited for reasons of satisfactory corrosion and economy of power to about 10 amperes per square foot, the solution which should be drawn from every compartment is, in an hour's time, a comparatively small quantity. One liter per hour is a rate found desirable and for a uniform flow of this amount requires a very small opening in the discharge tube. On account of the difficulty of entirely preventing the formation of insoluble particles in the solutions, these openings gave a great deal of trouble from clogging, requiring constant attention until another method of regulating the discharge was devised.

In Fig. 6 is illustrated the manner in which the outflow can be satisfactorily regulated. Instead of regulating the flow by the size of the opening of the siphon tube O, the opening is made large enough to allow any precipitated particles to readily pass through. This outlet, normally closed by a piece of rubber pressing against it by a spring S, is opened periodically by an eccentric, H, rotating

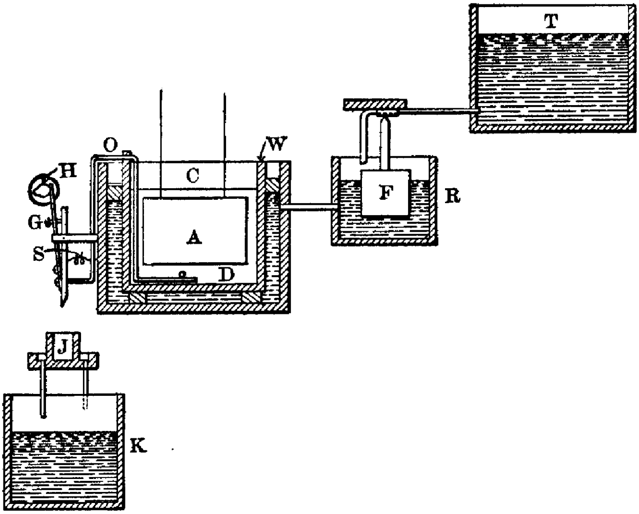


FIG. 6.

at a fixed speed. The quantity of solution drawn off is regulated by adjusting the screw G. Fig 7 illustrates a number of such

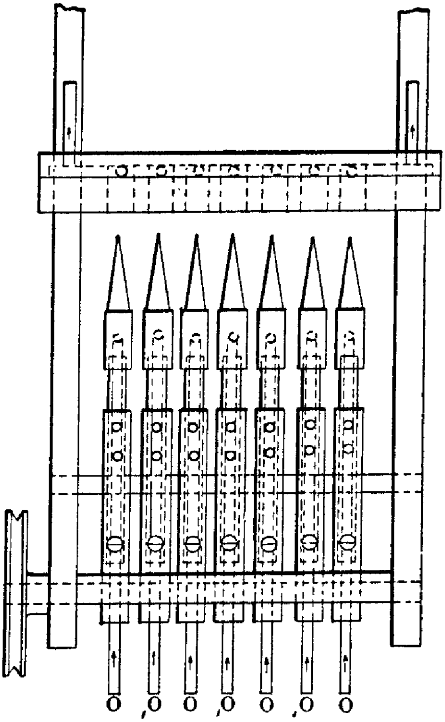


FIG. 7.

outlets arranged on a tank having three anode and four cathode compartments. This method of regulation proved satisfactory, and may be advantageously used in various other electrolytic processes. It was found that in the operation of a solution of sodium nitrate having a density of 1.12 sp. gr., 0.6 per cent. of free nitric acid was desirable to insure satisfactory anode corrosion. This free acid can be introduced either in the stock solution flowing between the two diaphragms, or directly into the anode solution. In the former method there is more uniform distribution of this acid than in the latter, but where the stock solution is acidified there is involved the disadvantage that more acid is required by some of it going into the cathode compartment and thereby being neutralized. To overcome this disadvantage a third diaphragm may be introduced, as shown in Fig. 3, the stock solution flowing into compartment E being acidified to the proper amount, and the stock solution flowing into compartment F being neutral. This prevents the unnecessary consumption of acid.

Figure 8 is a photograph taken from a small laboratory plant for the corrosion of lead. The electrolytic tank has three anode and four cathode compartments and is capable of corroding about 10 pounds of lead per twenty-four hours. Fig. 6 is a diagrammatic representation of the same equipment, where T is the tank containing the stock solution, R the regulating device for maintaining a constant level of solution in the electrolyzing tank, A a lead anode, and D a canvas diaphragm placed around a wooden frame, W. The top part of each diaphragm is paraffined to prevent a flow of the solution through the portion not completely immersed. O is a siphon tube for drawing off the lead nitrate solution as it is formed. The solution flows into trough J, which is so constructed that the anode and cathode solutions are kept separated, and thence it flows into tank K.

With this construction the diaphragms can be readily removed from the electrolytic cell when renewal and cleaning is necessary.

By the above method continuous operation can be effected with high percentage of corrosion, no clogging of diaphragms, and with uniformity of composition of solution running from the cell. The electromotive force found necessary is about 1.4 volts, representing an expenditure of energy of 0.22 horse-power-hour per pound of lead corroded.

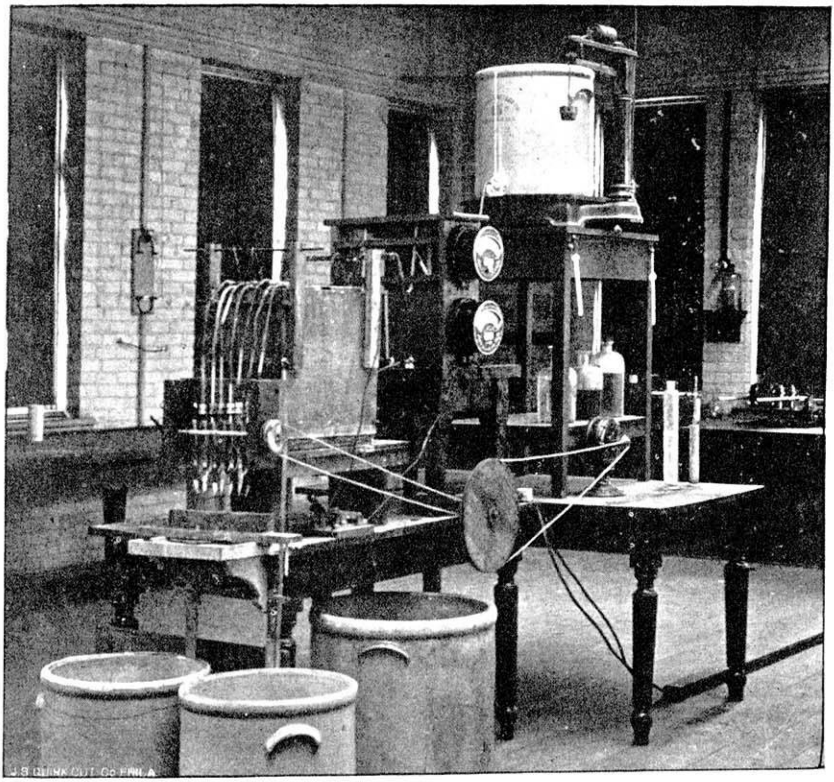


FIG. 8.

tions at such a rate that about one-half the sodium nitrate passes through without undergoing electrolysis.

Some of the disadvantages attendant upon the use of sodium nitrate, as the electrolyte material, can be avoided by the use of sodium acetate. The amount of alkali produced at the cathode is equivalent to the lead acetate formed at the anode and the chemical reactions are, therefore, simpler. The relative advantage of the acetate is not determined by this factor alone. The cost of sodium acetate is much greater than that of the nitrate, calling for great care in the prevention of waste from leakage, and washing the precipitate. The acetate requires to be used in a considerable degree of purity, while the ordinary commercial grade of sodium nitrate is sufficiently pure. The voltage necessary is considerably higher and the difficulty in effecting clean anode corrosion is decidedly against the acetate.

The experiments here described were carried out in an attempt to test, on a laboratory scale, various processes which have been described for the production of white lead. The work was carried on for several months, and we have found that it is entirely possible to produce a white lead of exactly the same composition, as far as the relative amount of hydroxide and carbonate of lead are concerned, as in the old Dutch process. The physical properties can also be duplicated. The conclusion seems to be justified, however, that there is little chance for the electrolytic process replacing the chemical methods for the production of this useful pigment, at least along the lines referred to. From the present market values of pure lead and the white lead made therefrom, it is seen that there is very little margin to pay the cost of the electrical energy, the necessary losses in the electrolyte, the cost of casting the lead into shape suitable for anode purposes, labor and depreciation of the electrolytic tanks and leave anything for a profit.

In the production of various other lead compounds, however, there seems to be greater opportunity for commercial application of the electrolytic method. The acetate of lead may be produced in a manner similar to that suggested for the production of the nitrate; lead chloride may be produced from the electrolysis of a hot sodium chloride solution, the lead chloride separating out on cooling; lead chromate, which is a pigment used in large quantities, can be made by precipitating the anode solution by sodium bichromate, thereby regenerating the original solution and furnishing the free acid necessary for effecting uniform corrosion of the lead anode.

It will be noted that in all of the proposed processes for the electrolytic production of metallic compounds, electricity plays only an incidental and sometimes very minor part in the operation. There are undoubtedly many places where the electrolytic step might be advantageously introduced into the present purely chemical operations. Not only may the electrolytic effect of the current be utilized, but the heat effect may also be employed. A process for the production of metallic compounds utilizing the heat properties of the current consists in volatilizing the metal either in a resistance or arc furnace and exposing the vapors or the fine metal particles thereby produced to the action of chemical reagents which will produce the desired chemical compound. The controlling factor in this case is the cost of electrical energy, the amount of energy required to treat a pound of metal in this way being much greater than in the electrolytic methods.

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DISCUSSION.

Pres. Richards: I have done some experimenting myself in producing insoluble metallic compounds from the metals used as anodes. I have tried the manufacture of white lead and found that one of the great difficulties in manufacturing a fine quality of white lead is the dropping of metallic particles from the anodes in with the precipitates; and this is dependent very largely upon the current density used at the anodes. If too high a current density is used the action is similar to that of a concentrated acid upon an easily soluble metal, tearing it to pieces, and small particles of metal then drop in and contaminate the product which is being obtained. I find, by regulating properly the current density, that the white lead can be obtained without any specks of metallic lead in it, whereas, by using too high a current density, it is contaminated with specks of metallic lead. I would also call attention to the easy manner of making a metallic sulphide by means of using the metal as an anode, in a solution of sodium hyposulphite. It makes a very pretty lecture experiment to use a cadmium anode in a solution of sodium hyposulphite; after passing the current for a little while, cadmium sulphide commences to form, with its beautiful golden yellow color. At first there is very little precipitate because cadmium sulphide is soluble to a certain extent in the electrolyte; but after passing the current for some time the electrolyte becomes saturated with cadmium sulphide and then a precipitate forms very abundantly. It is a quick and easy way of making sulphides. I do not know to how many metals it may be applicable. I have tried it with four or five. I think there is a great field for manufacturing the insoluble compounds of metals by the use of appropriate solutions; at least there is a great field for experimenting in that line.

Mr. Carl Hering: I have been very much interested in this paper, as I think there is a great future in the manufacturing of some chemical products by means of electrochemical reactions as distinguished from chemical reaction. I also agree with Professor Richards in regard to the current density, only I would rather put it in this way: that it is very important to keep the solution which you wish to have acted upon in actual molecular contact with the electrode and not let it be separated from them by an exhausted molecular layer; that is to say, if you want to use a strong current density you must have very strong circulation. I think this is a very important factor in a great many of these reactions, and that it is not fully appreciated. I have made some experiments in that direction myself and I have been surprised to see what great improvements are produced by very rapid circulation.

PROF. W. D. BANCROFT: I am sorry that this paper could not have been discussed more in detail by some of our technical friends. It would be of great assistance to those of us who are connected with the universities if our efforts at teaching our students something about applied electrochemistry could be subjected to friendly criticism by those who have had an opportunity to test these things on a large scale.

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A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

EFFICIENCY OF THE NICKEL-PLATING TANK.

BY OLIVER W. BROWN.

Although the nickel-plating tank is one of the best-known examples of an electrolytic cell, having been used in practical work for many years, there are certain peculiarities and factors about it which are not understood, and which are of such a nature as to leave considerable room for improvement in the process for electroplating with nickel.

The design of the present nickel-plating solution has been the result of the "cut-and-try" process, and few attempts have been made to give a good scientific explanation of why some solutions give better results than do others. The double nickel-ammonium sulphate electrolytes must be carefully watched during operation to insure satisfactory products, and the plater knows that his success depends upon keeping the solution at a chemical composition having somewhat narrow limits. It is known that a small percentage of certain impurities may ruin the solution, and that the electrolyte must not become appreciably acid or alkaline. It is to counteract such tendencies that his attention is principally directed.

An ideal electroplating cell is one which operates at a current efficiency of 100 per cent, and has a resistance sufficiently low that an electromotive force not exceeding five or six volts may send the proper current through it. A current efficiency of 100 per cent. means that the anode shall corrode at exactly the same rate that the metal is deposited at the cathode, this amount being equal to that calculated from the quantity of current and the electrochemical equivalent of the metal. With a current efficiency of 100 per cent., no change in composition of electrolyte will occur, and the greatest of simplicity in the operation will thereby be attained. That the nickel-plating cell, as at present used, is notably inefficient, when viewed from this standpoint, is apparent. It was for the purpose of determining some of the factors which influence this efficiency that a study was taken up, the results of which are given herein.

Inasmuch as the discharge potentials and polarization pressures are important factors in the study of the operation of the electrolytic cell, these were taken into account for the purpose of throwing some additional light upon the question. If the nickel-plating cell could be made to operate at a maximum efficiency, the electromotive force required to send a current through would be only that necessary to overcome the resistance of the electrolyte, a condition which is almost completely realized in the copper-plating cell using an acidified copper sulphate solution. In nickel plating, however, there is additional pressure which has to be overcome, amounting in some cases to over two volts. This polarization pressure is produced as a result of the fact that the current efficiency is less than 100 per cent, and is the summation of the values at the anode and at the cathode. To determine the variation of these two values and their summation, measurements of discharge potential at the two electrodes were made in the ordinary manner, employing the auxiliary electrode of the "calomel" type, the electromotive force of which was taken as — .56 volts. It was on this value that the measurements recorded herein are based.

The discharge potentials were measured by means of a specially-designed make-and-break switch, which interrupted the current and instantly thereafter made contact with the normal electrode circuit, in which the pressure to be measured was balanced against a pressure of known value. A galvanometer was used as a zero instrument in balancing these two values.

Measurements were first made upon a slightly acid nickel ammonium sulphate solution, taken from a 30-gallon nickel-plating tank. The ordinary cast nickel anodes were used as electrodes. The area of one side of each electrode exposed to the solution was 0.25 square foot. The area of only one side of the electrodes was taken into account in the calculation of the current density, as they were placed flat against the side of a large battery jar. The electrodes were thoroughly cleaned in acid before placing them in the nickel-plating solution.

The discharge potentials of the electrodes and the polarization electromotive force, at different current densities, are given in Table I:

TABLE I

Time at which measurement was made after starting the current at the given current density.	Ampères per square foot	Electrode tension Volts	Discharge potential in volts		Polarization Volts
			Cathode	Anode	
. . . .	no current	. .	—0.184	—0.154	. . . . .
25 Minutes	1.00	0.8	+0.074	—0 290	—0.388
55 "	1.60	1.1	0.164	—0.339	—0.524
25 "	2.80	1.5	0.202	—0 422	—0.650
20 "	4.40	2.3	0.239	—0.474	—0.730
7 "	5.60	. .	0.245	—0.486	—0.750
100 "	6.40	4.2	0.325	—1.725	—2 089
30 "	10.00	4.7	0.403	—1.650	—2.119

It will be noted that the sum of the cathode and anode discharge potentials given in this table does not quite agree with the polarization value obtained. This is due to the unavoidable experimental error in these determinations.

The results in this table are plotted in Curves I, II and III of Plate I. Curve I shows the change of cathode, and Curve II of the anode discharge potential with the change in current density. The polarization at different current densities is shown in Curve III. The anode and polarization curves make a very sudden bend at about 5.6 to 6.4 amp per square foot, the voltage in each case increasing more than one volt. The cathode curve also shows a slight increase in voltage at this current density.

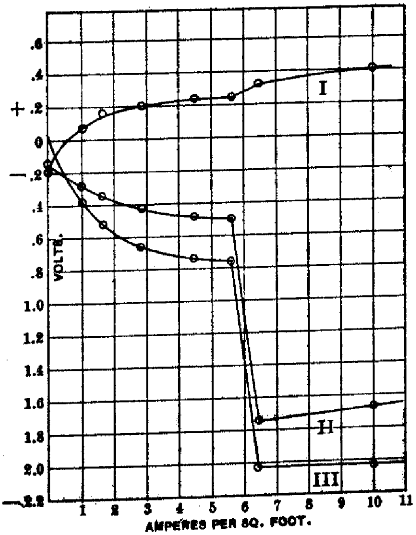

PLATE I.

A high current efficiency is generally supposed to be obtained only when the discharge potential at the electrode is near the single potential of the electrode. If this be true, the current efficiency of corrosion would naturally be expected to decrease to a low value when a current density of about 5.6 amp per square foot is reached. It will be noted from later determinations just how much the efficiency of anode corrosion is lowered by this sudden change in anode potential. A vigorous evolution of gas immediately begins at the anode, when its potential suddenly increases, and the amount of gas evolution increases with the increase in anode potential. No gas is seen at the anode when its potential is — .4 volt. Vigorous stirring of the electrolyte, when the potential first suddenly rises, has no perceptible effect on the potential. In many cases the anode is found to be coated with a thin layer of nickelic oxide when the potential suddenly changes.

In the nickel anode first employed copper was found as an impurity. The nickel dissolved away, leaving the copper on the surface. The presence of the copper, rather than being a detriment, seemed to be advantageous, in allowing a high anode current density to be used without producing a high increase of anode discharge potential. In one set of experiments, where the surface of the anode was found to be covered with a few spots of metallic copper, the anode discharge potential was only — 0.485 volt, and the polarization — 0.816 volt, with a current density of 16.8 amp per square foot. The anode and cathode were removed and thoroughly cleaned with acid, dissolving off the spots of metallic copper. After replacing the electrodes in the solution and passing a current of 14 amp per square foot for twenty minutes, the anode potential had risen to — 0.824 volt and the polarization to 1.964 volts.

A small cell of about 300 cc capacity and two small electrodes, placed about 1.5 inches apart and flat against the sides of the cell, were used in all of the following experiments. The electrodes were weighed on an analytical balance, and the current efficiency of corrosion and deposition determined. The electrolyte used contained 75 grams of nickel ammonium sulphate per liter. This solution had a slightly acid reaction. A fresh sample of electrolyte was used in every experiment, except where noted. The small cast-nickel anodes used were cut from a large cast nickel-plating anode. Cathodes of pure rolled sheet nickel were used. In some of the experiments these rolled sheets of pure nickel were used as anode. The area of the cathodes in most of the experiments was a little more than 9 square inches (counting one side only). The active surface of the cast anodes, however, was only about 5 square inches.

Table II shows the current efficiency obtained with cast, rolled and electrolytic nickel anodes:

TABLE II.

Nickel anode	Ampère hrs. used	Ampères per square foot		Discharge potential in volts		Current efficiency	
		Anode	Cathode	Anode	Cathode	Corrosion of anode	Dep. of nickel on cathode
Cast, surface gr'nd smooth	0.45	4.12	2.21	—1.834	+0.208	46.29%	75.42%
Cast, surface roughened in acid	0.45	4.12	2.21	—0.44	0.252	91.32	92.06
Rolled, pure . . .	0.45	4.42	4.42	—1.889	0.145	8.47	63.27
Electrolytic . . .	0.45	4.42	4.42	—1.883	0.143	12.65	61.61

These results show that electrolytic nickel anodes corrode very poorly as compared with the cast anodes; also, that pure rolled anodes are no better than the electrolytic. The different efficiencies obtained with cast anodes of smooth and rough surface are of interest. This difference in efficiency between the cast anodes may be due to the difference in current density, caused by the very great increase of *actual* surface of the roughened electrode over the smooth; formation of oxide on the surface of the smooth electrode, or to the electrode assuming a passive state in this experiment. The very high anode potential of the smooth electrodes indicates one of the latter reasons. The cause of this high anode potential will be considered in connection with data given later.

The relative efficiency of the cathode and anode is shown by the results in Table II. The cathode efficiency is affected to a marked degree by the anode efficiency. When the anode efficiency is only about 10 per cent, the cathode efficiency is near 62 per cent, while the cathode efficiency is 92 per cent when the anode efficiency reaches 91.32 per cent. This is an additional reason why rolled or electrolytic nickel anodes cannot be satisfactorily used in plating. The low anode efficiency reduces the efficiency at the cathode, and and the poor efficiency at both electrodes causes a change in the composition of the electrolyte.

Table III shows the effect of current density on the efficiency of corrosion of a rolled anode:

TABLE III.

Ampère hours used	Ampéres per square foot	Discharge potential of anode	Polarization Volts	Current efficiency	
				Anode corrosion	Nickel deposition
0.10	0.74	—1.829	—2.07	18.64%	64.71%
0.45	2.95	—1.869	—2.10	19.43	62.79
0.45	4.42	—1.889	—2.143	8.47	63.27

Discharge potent'l, cathode =

A very poor efficiency at the anode is obtained even with a current density as low as 0.74 amp per square foot. When rolled anodes are used, the corrosion increases slowly as a larger number of coulombs are passed through the solution, while the cathode efficiency decreases.

When the anode corrosion is as low as 19 per cent, the cathode efficiency is as high as 62 per cent. This means that the electrolyte becomes more acid as the number of coulombs passed through the solution increases. The acidity of the solution naturally decreases the amount of metal precipitated at the cathode, and increases the rate of corrosion of the anode. This is shown in Table IV:

TABLE IV.*

Ampère hours	Ampères per square foot	Anode potential	Polarization	Current efficiency	
				Anode	Cathode
0.45	4.42	—1.889	2.050	8.47%	63.27%
0.75	4.42	—1.820	2.052	12.28	51.14
1.531	4.57	—1.858	2.003	15.72	37.88
3.01	3.17	—1.883	2.028	27.08	33.18

From Table IV we see that the polarization and the anode potential change very little with increase in acidity.

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* The electrodes were removed from the solution at intervals, weighed, replaced in the electrolyte, and the electrolysis continued.

The ampère hours and efficiencies of Table IV are plotted in Curves I and II of Plate II.

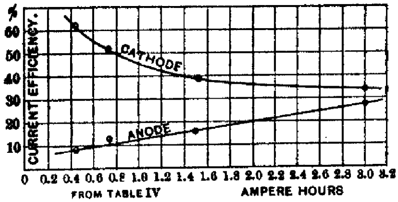


PLATE II.

Table V shows the influence of current density on the corrosion of a cast anode:

TABLE V.

Ampère hours used	Ampères per square foot		Current efficiency		Anode Voltage
	Anode	Cathode	Anode	Cathode	
0.40	7.25	4.42	62.93%	93.51%	—1.87
0.45	5.50	2.95	72.92	90.02	—1.60
0.45	4.12	2.21	91.32	92.06	—0.44
0.40	3.52	2.00	92.17	91.65	—0.30

The efficiency of corrosion of the anode is plotted with the current density in Curve I of Plate III. It is seen that the anode efficiency decreases quite rapidly with increase in current density.

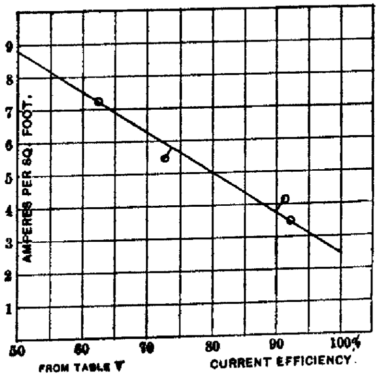


PLATE III.

The relations between the electrode discharge potentials and the efficiencies is shown by a comparison of the data in Table VI:

TABLE VI.

Nature of anode	Ampère hours used	Ampères per square foot		Current efficiency		Discharge potential in volts	
		Anode	Cathode	Anode	Cathode	Anode	Cathode
Cast	1.10	2.75	1.48	88.77%	90.37%	—0.387	+0.252
"	1.76	2.75	1.48	91.00	83.49	—0.337	0.212
"	0.39	2.75	1.48	82.80	94.29	—1.237	0.252
"	2.3	4.12	4.12	89.77	94.62	—0.290	0.273
"	3.29	4.12	4.47	92.61	88.94	—0.463	0.246
"	.4	7.25	4.42	62.93	93.51	—1.580	0.228
"	.3	4.12	2.21	82.96	91.10	—0.360	0.253
Rolled	.43	3.10	3.10	9.01	57.39	—1.880	0.142
"	3.01	3.17	3.17	27.08	33.18	—1.883	0.118

The cathode and anode efficiencies of Table VI are plotted, with their respective electrode potentials, in Curves I and II of Plate IV.

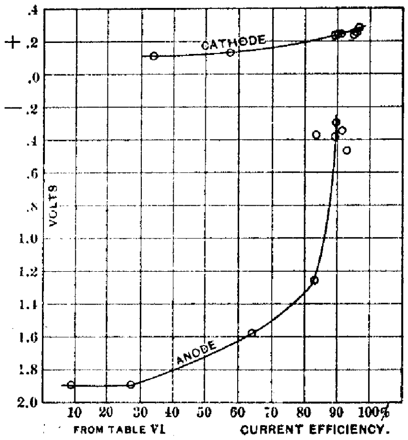
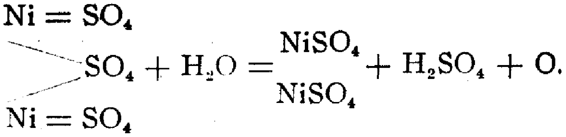


PLATE IV.

It seems that the highest cathode efficiency is obtained when the cathode discharge potential lies between + 0.22 and + 0.29 volt.

The anode voltage increases very fast as the anode efficiency begins to diminish. The results show that an efficiency of corrosion exceeding 90 per cent cannot be expected if the anode voltage is allowed to get much above — 0.46 volt.

Pfanhauser* states that nickel ammonium sulphate between nickel electrodes can be decomposed with a bath tension of about one volt; but that in a short time the current strength falls very fast to almost nothing, while the bath tension rises to two volts. He also states that there are two polarizations, one of about one volt and the other near two volts. He ascribes this high electrode tension and polarization to the formation of a coating of nickelic hydroxide on the anode. He has shown that nickel ammonium sulphate is a complex salt, and that in concentrated solutions $Ni(SO_4)_2$ ions are liberated at the anode. These $Ni(SO_4)_2$ ions may attack the nickel electrode and form two molecules of $NiSO_4$, or they may react with water, forming sulphuric acid, nickelous sulphate and oxygen. The $Ni(SO_4)_2$ ions may also unite with $NiSO_4$, forming $Ni_2(SO_4)_3$. He thinks that the nickelic sulphate is then decomposed by hydrolysis, yielding nickelic hydroxide, sulphuric acid and oxygen. He says that in strong acid solutions, however, the nickelic sulphate decomposes as follows:



$$\begin{matrix} Ni = SO_4 & \\ & SO_4 + H_2O = \begin{matrix} NiSO_4 \\ NiSO_4 \end{matrix} + H_2SO_4 + O. \\ Ni = SO_4 & \end{matrix}$$

He has tested the chain

$$Ni/(NH_4)_2\,Ni(SO_4)_2/Ni(OH)_3,$$

and finds that it gives 1.075 volt. For this reason he believes that the high polarization is due to the nickelic hydroxide on the anode.

In all of Pfanhauser's measurements either electrolytic or rolled nickel anodes were used. His explanation seems to fit the facts very well when these electrodes are used, but they do not explain the data obtained with cast-nickel anodes. In one experiment with a cast anode, after electrolysis at an anode density of 4.12 amp. per square foot for seventeen hours, the discharge potential was only — 0.47 volt, the polarization only .74 volt and the electrode tension 1.19 volts. In this experiment the anode efficiency was 92.6 per cent. This seems to show that with proper conditions, when cast anodes are used, the electrolysis may be

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* Pfanhauser, Zeitschrift für Elektrochemie, 7, 698 (1901).

continued for any length of time (especially when the solution is occasionally stirred) with a polarization considerably below one volt and with an electrode tension of about 1.2 volts.

Under certain conditions the cast-nickel anodes seem to become passive (possibly due to the formation of a coating of oxide, as suggested by Pfanhauser), and in all these cases the efficiency of corrosion immediately drops to a low value. This is not always due to the current density or to the composition of the electrolyte. The following is an experiment showing this passive state: A current was passed through the small plating cell for three hours. During this time the anode density was 4.12 amp per square foot. The anode potential at the beginning was — 0.439 volt, and at the end — 0.447 volt. The electrode tension was 1.1 volts throughout the run, and the polarization remained near — 0.721 volt. At the end of three hours the electrodes were removed, washed in distilled water, dried and weighed. An anode efficiency of 91.3 per cent was obtained. After the electrodes were weighed, they were replaced in the same electrolyte, and the current started at the same current density as before. The electrode tension rose to 2.2 volts, the anode potential to — 1.5 volts and the polarization to — 1.84 volts within fifteen minutes. After three hours the electrode tension was 2.3 volts; anode potential, — 1.68, and polarization, — 1.987 volts. The anode efficiency had dropped to 65 per cent.

When the anode potential suddenly rises, it may generally be brought back to its former value by removing it from the electrolyte, cleaning in a mixture of sulphuric and nitric acids, rinsing in distilled water and then replacing it in the cell. After the electrolysis has continued for thirty minutes, with an anode discharge potential of — 0.45 volt or lower, I have never known it to change to a much higher value at the same current density.

The rise in anode potential in these experiments must, then, be due to some treatment it received outside the cell, while washing in distilled water, drying in an air bath, cooling in a dessicator and weighing. One would at once say that the passive state of the electrode was caused by the formation of a film of oxide on its surface during the process of drying and weighing. This is possibly true, but the following experiment is not explained by this assumption.

The average electrode tension was 2.2 volts, the anode potential remained near — 1.78 volts and the polarization — 2.03 volts. A current density of 2.75 amp per square foot was used. After two hours' electrolysis, the electrodes were removed and weighed. An anode efficiency of 87.88 per cent was obtained. The electrodes were then replaced in the electrolyte, and a current of the same density started through the cell.

The electrode tension was surprisingly only 0.9 volt, the polarization 0.606 volt and the anode potential — 0.331 volt. The temperature of the electrolyte at this time was 28.5° C, but cooling it to 15° only raised the electrode tension 0.1 volt. After continuing the electrolysis sixteen hours, the electrode tension was 1.0 volt, polarization — 0.729 and anode discharge potential only — 0.444 volt. The anode efficiency was about 89 per cent. After the electrodes had been removed, rinsed in distilled water, dried and weighed, they were again placed in the same electrolyte. In a very few minutes the electrode tension was 2.1 volts, the polarization — 1.87 and the anode potential — 1.6 volts. After four hours' run the anode efficiency was 78 per cent.

From the results of these measurements the fact is shown that satisfactory operation of a nickel-plating solution depends to a large extent on the character of the anode employed. This is a fact which has been recognized by platers as a result of practical operation. It might be a natural supposition that the best results should be expected with the purest anode material, but this apparently is not the case. It appears that the presence of copper is advantageous to a certain extent, and it is quite likely that certain other impurities which are usually present in cast nickel may be equally advantageous. It has been shown that rolled nickel or electrolytic nickel are decidedly unsatisfactory for anode service, and the reason that the cast nickel shows a superiority may be due to the impurities or to a different physical structure, which gives rise to a great porosity and roughness of the surface, and thereby a greater actual surface area.

In electroplating operations the cathode has naturally been the point to which most attention has been given in the production of certain qualities of deposit, but a study of the conditions at the anode is equally important, for if the corrosion at that point is satisfactory the cathode will largely take care of itself. The lack of efficient corrosion at the anode results in an excess of acid being formed, which, diffusing to the cathode, causes a lower efficiency at that point as well. A change of efficiency at the anode is in a very short time made apparent by a similar change at the cathode. In instructions which have been published from time to time for operating nickel-plating tanks, the voltage which is necessary for plating is referred to in an indefinite way. This is probably due to the fact that the electromotive force required under different conditions is of a considerably different value, so that no definite rules can be laid down. The electroplater can obtain an efficiency of 90 per cent or more if cast anodes are used, with an anode density of about 5 amp per square foot. The best method of obtaining a check on his efficiency is by the determination of the anode discharge potential. This should not be allowed to reach a greater value than — 0.45 volt.

It is possible, however, that the study of such single potential is too much of a laboratory test, and requires apparatus which is not at his disposal. A study of the total polarization pressure, however, while not being as definite in the indications as a study of the individual electromotive force at the electrodes, will serve as a means for determining whether the cell is operating properly. When the polarization goes much above 0.75 volt, the assumption is justified that the anode is not corroding properly, and, on the other hand, if the polarization is below 0.70 volt the efficiency at the anode is as high as can be obtained. The means for measuring this polarization is at the disposal of most electroplaters, the method consisting in connecting a voltmeter to the anode and cathode terminals while the current is flowing and then suddenly interrupting the current and noting the pressure between the electrodes immediately after. This reading should be made as quickly as possible, as the polarization decreases rapidly after interrupting the current.

In conclusion, I wish to thank Prof. C. F. Burgess for his valuable suggestions and assistance throughout this work, which was proposed by him.

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DISCUSSION.

Mr. McA. Johnson: This article is interesting to me, for it follows along lines which I have worked on in the past, namely, the study of the anode potential and the cathode potential by means of a standard electrode in determining the factors of electrolytic work. I doubt though that the ordinary electroplater is going to install an Ostwald calomel standard electrode and a $150 potentiometer to determine electrode potentials. However, the way pointed out in the last page of Professor Brown's paper is a fairly accurate method and a practical one. This article, in my opinion, could be criticized in the following way: that not enough analyses were made of the electrolyte.

The current efficiency at the cathode is dependent upon the percentage of nickel at the cathode and also the percentage of free hydrogen ions. If the percentage of free hydrogen ions increases to a certain limit, we do not get metallic nickel, but we get pure hydrogen. As the percentage of hydrogen ions decreases we get an increasing percentage of nickel and a decreasing percentage of hydrogen; but, nevertheless, we always get hydrogen at every potential, under every condition, as can be shown by the fact that we have a low current efficiency at the cathode. To investigate on electroplating work I think about 250 analytical determinations would be necessary. I have had a good many more than that made on electro-refining work, where the conditions are entirely different—the nickel contents of electrolyte, instead of being 30 grams to the liter is 150 to 200 grams of metallic nickel per liter; the current density is 10 to 30 ampères per square foot, and the temperature as high as possible within practical limits. Nevertheless this article is of much value, even though it is imperfect in the fact that it gives little analytical data.

Prof. C. J. Burgess: The addition of analytical data such as Mr. Johnson recommends would undoubtedly make this paper more complete. If such completeness had been aimed at, however, this paper could not have been prepared in the time which has been available, as it would be an investigation of very considerable length.

Mr. Johnson does not think that the "calomel" electrode as a standard for the measurements of simple potentials is a practical instrument for technical men, but upon this point I am inclined to disagree with him; we have found it of great use in the laboratory on account of its simplicity of construction and operation. A potentiometer arrangement which we have employed in connection with this electrode was made in our laboratory and at a cost less than one-tenth the amount which Mr. Johnson names.

The measurements described in this paper were made on a nickel-plating solution, such as is used every day by the electroplater and no chemical analysis of such solutions were made. The approximate composition was known, however, inasmuch as after each run a solution freshly made up was employed. The only chemical tests which were made during the operation of the cells were such as are commonly made by the electroplater to determine the acidity or the alkalinity of the bath.

PRES. RICHARDS: The statement made on page 93 of Dr. Brown's paper is very interesting: "It appears that the presence of copper is advantageous to a certain extent, and it is likely that certain other impurities which are usually present may be equally advantageous." The idea that the presence of an impurity in the anode may be advantageous is odd at first, but I think may be explained by the fact of local action—the increase of local action upon the anode; that where copper is mixed with the nickel the local action of the solution will probably cause the nickel to dissolve in larger proportion than it would by electrical action alone. We find, for instance, that pure zinc is very slightly attacked by acids, but attacked rapidly if there is a small amount of another metal present to facilitate the solution, so I think the chemical solution of the anode is probably facilitated by the presence of copper or other impurity.

DR. RUDOLPH GAHL: I should not think that the impurities of the nickel could cause much local action. Nickel causes strong local action on account of its low overvoltage on metals of higher overvoltage; for example, on copper. But the metals which are generally contained in nickel as impurities have a higher overvoltage than nickel has, and, therefore, I do not think that they can cause local action.

PRES. RICHARDS: You state that they have a lower overvoltage effect?

DR. GAHL: Yes, sir.

Pres. Richards: Platinum with zinc intensifies the local action, but platinum has a lower overvoltage effect than zinc, so that it is rather the short-circuit effect of which I am thinking that the presence of the impurity in the body of the anode may have.

Dr. Gahl: It depends on the amount of the overvoltage. Platinum has a very low overvoltage, and, therefore, causes an especially great local action; the other metals of higher overvoltage than platinum when deposited on zinc do not cause so much local action as platinum does. For example, the local action caused by copper is less than that caused by nickel, and the local action of nickel is much less than that of platinum, therefore, you cannot cause local action on nickel at all by copper, nor by lead nor by zinc, if these metals are deposited upon nickel.

Mr. C. J. Reed: How is the overvoltage determined? The overvoltage of platinum, for instance, or nickel?

Dr. Gahl: Overvoltage of a metal is the excess of voltage which is required for developing hydrogen on this metal over that required for developing hydrogen on platinized platinum.

Mr. Reed: It is based, then, upon platinized platinum as a standard?

Dr. Gahl: Yes; we have no other standard. It is theoretically possible that there is another metal which requires a still lower voltage than platinum does for the electrolytic development of hydrogen. But we do not know such a metal and therefore take that metal which requires the lowest voltage of all known metals.

Mr. Reed: I have never been able to find two pieces of platinized platinum that acted alike, so I do not see that there is any standard if that is the case. If that is the only standard we have, it seems to me there is none.

Dr. Gahl: Yes, there are differences, but they are not so very great, the difference between platinized platinum and common unplatinized platinum is not more than 0.09 volt. On the other hand, the difference between zinc and platinum is 0.7 volt, and, therefore, great, compared with the variations of platinum. So, though platinum is not a perfect standard, it is a useful one for many purposes.

Mr. Reed: I have found the same differences in platinum depending upon the conditions under which it is used; for instance, with platinum electrodes in sulphuric acid, the overvoltage (voltage required to produce gas on the platinum) would depend on how you apply the current. If you begin with a very small electromotive force, you can gradually increase it up to two volts or in that neighborhood before you get any appreciable current. Then after the film of gas on the surface of the platinum has once broken, the voltage will drop down at once to one and a half volts, and you can continue to deposit hydrogen at one and a half volts. Now, what is the overvoltage of platinum in that case? A theoretical requirement of the electrochemical electromotive force would be 1.47 volts. Now, you can get gas at one and one-half volts, or you can get it at two volts under those two different conditions. Which is the overvoltage of platinum, .03 volt or .53?

DR. GAHL: I do not know this experiment which Mr. Reed refers to, but I have made similar experiments with different kinds of lead and almost the same conditions. I have electrolyzed, for example, two cells with sulphuric acid, one with a pure lead, the other one with an antimonious lead cathode, and always obtained higher voltages for the cell with pure lead. The difference between the two voltages is about the same for all densities of current; therefore, I should think the difference in the overvoltage for these two kinds of metal is the difference you find here, and I do not see why in replacing the one metal by platinum there should be much difference in the behavior, but I should like to make that experiment myself.

MR. REED: That is a very interesting experiment, and it is one that I think ought to be considered in discussing this question of voltage. The facts are as I have stated, that if you electrolyze platinum electrodes in dilute sulphuric acid, beginning with a very low electromotive force and gradually increasing it, not by large steps, but by continuous increments, as, for instance, by using a dynamo in which you gradually increase the electromotive force up to two volts, you can increase it to nearly two volts without getting any perceptible current, that is, without getting more than what is generally called "residual currents." Then suddenly the current will apparently break through a film of gas and gas will appear in spots or patches on the platinum electrode.

Then the voltage goes down immediately. You can continue then to get an evolution of gas with one and one-half volts.

PRES. RICHARDS: Mr. Reed has brought up the question of overvoltage. In a paper which I have prepared to read to-day, I show some experiments where the voltage was increased on platinum electrodes to 110 volts without any evolution of gas, so that we have in that case an overvoltage of perhaps 108.5 volts.

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A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 17, 1903, President Richards in the Chair.

A PRACTICAL UTILIZATION OF THE PASSIVE STATE OF IRON.

BY CHARLES F. BURGESS

In what may be considered the ancient literature of electrochemistry the fact was pointed out that iron and steel may be made to assume that peculiar condition known as the passive state by employing the material as an anode in suitable electrolytes. Among such solutions are sodium nitrate and various other soluble nitrates.

Upon assuming the passive condition, the iron no longer becomes attacked by the anode products, oxygen being liberated, and the metal acting towards the solution as would an anode of platinum. The passive state thus produced was held to be, and probably is, the same condition which iron assumes when immersed in concentrated nitric acid, the passivity probably being due to the same causes in both instances. Whether this peculiar condition is the result of the formation of a coating of iron oxide or of nitrogen oxide, or of some other material, is a disputed question, a discussion of which is foreign to this paper.

While this peculiar behavior of iron, when used as an anode material, has been known for many years, it is only quite recently that it has been made use of in an industrial way.

Some years ago we developed in our laboratory a process for removing brass from steel tubing, the brass having been left on the outside of the tubing as a superfluous material during the brazing process. An improvement in the method of brazing employed extensively in the manufacture of bicycles consisted in dipping bodily a portion of the frame to be brazed into a bath of melted spelter, which was covered by a suitable flux. By this operation not only was the brazing effected within the joints, but a thin layer of brass adhered to the outer walls of the tubing, so that it became necessary to remove this layer in preparing the frames for receiving a coating of enamel. This was effected for some time by filing, a process which had the disadvantage of entailing a large amount of labor and frequently of damaging the thin tubing, as some of the iron was removed as well as the brass.

An attempt was made to employ an electrolytic stripping process for removing this brass, but, upon trying a great many electrolytes, it was found that the iron itself tended to corrode much more readily than did the copper which enters into the constitution of the brazing spelter; and the problem resolved itself into finding a solution which would dissolve the copper, but in which the iron would not corrode.

Iron has a position considerably above copper in the electrochemical series of elements, and where two different metals are in contact the natural tendency is for the more electropositive one to go into solution with the greater ease. The idea presented itself of making the iron more electronegative than the copper by causing it to assume the passive state, and upon using the sodium nitrate solution in which this state could be developed it was found that the brass could be completely removed and the iron left intact.

This method of electrolytic stripping was installed and operated with success in various factories, and is now an important adjunct to the dip-brazing method. This same electrolytic stripping process may be applied equally well in removing silver, lead, tin and other metals more electronegative than iron from an iron surface. Nickel cannot be removed in this way, however, since nickel, as well as the iron, assumes the electronegative or passive state.

In some correspondence with the Patent Office it was claimed that while the iron might assume a passive condition, becoming coated with a resistant film of iron oxide, it could not be considered as becoming electronegative. For the purpose of determining this question, some measurements of single potentials were made upon iron before and after it had assumed its passive condition, and the results showed clearly the manner in which these metals behaved while being subjected to the action of the current. The measurements were made by means of a normal electrode of the "calomel" type, the potential of which was taken as — .56 volt. The metal whose single potential was to be tested was placed in the electrolyte and the potential measured before applying an electrical pressure, and also after currents of different values had been caused to flow. It was found that up to a certain limit the single potential varied in accordance with the current density. These values at different current densities were determined by a specially-constructed switch, which broke the current and immediately connected the electrode with the normal electrode circuit for an instant, long enough to determine the direction of the movement of the meniscus of a capillary electrometer used as a zero potentiometer instrument. In the following tables are given the results of some of these measurements:

I.

Solution = normal sodium nitrate.

Anode = iron, — area = 3½ sq. in.

E. M. F. between iron and solution before passage of current = + .07.

Applied Pressure Volts	Current Amp.	Single Potential Volt
.2	.006	+ .06
.4	.022	+ .032
.5	.032	— .01
.8	.085	— .053
1.2	.175	— .11

The above test was made in solution containing no $NaNO_2$. Measurements made as rapidly as possible.

II.

Solution = normal sodium nitrate.

Iron anode = area 3.5 sq. in.

E. M. F. between iron and solution before passage of current = + .002.

Applied Pressure Volts	Current Amp.	Single Potential Volts
.3	.005	— .138
.5	.015	— .138
.7	.034	— .138
1.	.080	— .138
1.3	.130	— .166
2.2	*.160	— 1.89
2.8	.130	— 1.97

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* When pressure of 2.2 volts was first applied, current was .16 ampères, but it quickly dropped to .026 ampères, due to assumption of passive state by the anode as shown by the great change in E. M. F. of the plate.

III.

Solution = normal sodium nitrate, into which was placed a small amount of $NaNO_2$.

Anode = iron plate, area = 3.5 sq. in.

E. M. F. between iron and pure nitrate solution = + .28 volt.

E. M. F. between iron and pure nitrate solution, with addition of $NaNO_2$, = + .23 volt.

E. M. F. of same after standing five minutes = .09 volt.

Applied Pressure Volts	Current Amp.	Single Potential Volts
.3	.0005	— .221
.5	.001	— .452
.7	.002	— .645
1.0	.003	— 1.04
1.3	.004	— 1.21
2.2	.070	— 1.46
2.9	.172	— 1.63

On remaining some time with this current flowing, the E. M. F. of anode rose to — 1.94 volts.

IV.

Solution = same as above.

Anode = sheet copper 3.5 sq. in. area.

E. M. F. between copper and electrolyte = — .238 volt.

Applied Pressure Volts	Current Amp.	Single Potential Volts
.3	.0005	— .421
.5	.003	— .49
.7	.005	— .56
1.0	.023	— .67
1.2	.043	— .64
2.4	.300	— .658

It was noted that the single potential of iron immersed in a sodium nitrate solution before the current passed was in the neighborhood of + 0.2 volt. In other words, a potential was set up toward the solution in the same direction, but of less magnitude than would be produced by zinc. By causing the current to pass from the iron electrode, however, this potential quickly became negative, and increased rapidly in negative value until potential as high as — 2.0 volts could be obtained under certain conditions. This potential of iron, when in the passive condition, is considerably higher than the single potential of platinum, and consequently in this condition may be considered as electronegative to that metal. Its potential is approximately equal to that of the peroxide plate of the lead storage battery.

Copper, on the other hand, as shown in Table IV, does not change its contact electromotive force in anywhere near the same degree. The maximum electromotive force of copper was — .65 volt, and it will be seen that the iron may readily be made much more electronegative than this value.

It was found that the iron did not assume the passive condition when used in sodium nitrate solution freshly prepared, but that this condition was developed after the current had flowed for some time. This fact led to the conclusion that the solution underwent some chemical change which was favorable to the passive state. In the electrolysis of a sodium nitrate solution under the above conditions sodium is liberated at the cathode, uniting with the water to form sodium hydroxide, and the hydrogen which is thereby set free reduces the sodium nitrate to nitrite.

Table I gives the results of a test upon a sodium nitrate in which there was present none of the nitrite.

Table II gives the results of a test with sodium nitrate after operating some considerable time, and Table III gives the results of measurements upon a sodium nitrate solution in which had been added previously a small amount of nitrite. It will be seen in the last case that the iron assumes the electronegative condition with a greater rapidity and at much lower current density.

In removing brass from iron, the current should remove it at the approximate rate of 1 gram per ampère hour, provided that all of the current enters the solution from the brass and none of it utilizes the iron as an anode surface. To determine how nearly this is the case when iron and brass in contact are exposed simultaneously to the solution, an experiment, illustrated in the following diagram, was performed:

A brass and an iron anode, each having dimensions of 1 x 2.75 inches, were immersed in a sodium nitrate solution. Each was connected through the ammeter to the same source of current. It was found that on first closing the circuit almost all of the current passed through the iron anode, but after operating for a few seconds the iron became passive, after which the brass took all of the current, the amount passing through ammeter, A, being so small as to be hardly detected. The following table gives the results of measurements:

Time	A	A_1	V
11.50	.15	.75	3.7
11.51 : 30	.70	0	3.7
11.55	1.1	0	3.7
11.56	1.85	.12	5.4

Gas liberated on iron.

By using very high current densities, however, the iron may begin to conduct a small portion of the current, thus causing a liberation of oxygen on the iron surface. From these tests it was shown that the current has a high efficiency in the removal of the brass, and a practical trial has demonstrated that a small percentage only is wasted by flowing from the iron surface, provided the solution be maintained in good working condition and the applied electrical pressure be kept within suitable limits.

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DISCUSSION.

Mr. C. J. Reed: The position of lead is higher in the scale than iron, as far as its electropositive character is concerned. If we were to remove brass or copper from lead in a similar manner the result would be to cause the formation of lead peroxide, and then we should get the same result as you get with iron, the coating of lead peroxide being highly electropositive. I want to ask whether you would consider it proper to say that was due to a passive state of the lead?

PROF. C. F. BURGESS: I am of the opinion that the so-called passive state of iron is analagous to that condition which lead assumes when it becomes coated with a lead peroxide coating. A reasonable explanation of the passive condition of iron is that it becomes coated with a certain iron oxide, which is electronegative, just as is lead peroxide electronegative as compared with the lead. There is opposition to this view, from the fact that there is not apparent upon the iron surface such a film. If, however, the iron be used as the anode for a considerable length of time a black coating is formed which is readily visible to the eye.

7

A paper read at the Fourth General Meeting of the American Electrochemical Society, Niagara Falls, N. Y., September 18, 1903, President Richards in the Chair.

ELECTROLYSIS OF SODIUM HYDROXIDE BY ALTERNATING CURRENT.

By Carl Hambuechen.

The title of this paper may, perhaps, be considered a misnomer, inasmuch as it deals with a method for producing electrolysis by connecting an electrolytic cell directly to a source of alternating pressure rather than with the electrolytic effects of a symmetrical alternating current.

Electrical energy is being generated and distributed in large amounts in the form of alternating current, and the means for transforming it into a unidirectional current becomes a matter of moment to the electrochemist. Such transformation is usually effected by the rotary transformer type of apparatus, and it is proposed to point out here a method whereby such apparatus may be dispensed with. This may be done by the use of aluminium as one of the electrodes in a cell in which electrolytic decomposition is to be effected.

At the first meeting of this Society it was pointed out in a paper, submitted jointly by Professor Burgess and the writer, that aluminium in certain fused salts presents, in a marked degree, the property of readily permitting the passage of current toward it and interposing a high resistance to the flow in the opposite direction. Utilizing this property, an electrolytic rectifier, using aluminium and iron electrodes in a fused sodium nitrate electrolyte, has been developed. It was found also that aluminium could be used in a like manner in various other fused electrolytes, one of which is sodium hydroxide.

While aluminium is actively corroded by sodium hydroxide in the presence of water, the observation was made that it is almost completely stable in contact with a fused sodium hydroxide, and that consequently an aluminium vessel might readily serve for containing this substance. Not only is aluminium unattacked in this condition, but in attempting to use it as the anode it immediately strengthens its protective coating so as to oppose with a considerable resistance the passage of current.

Curve No. 1, plotted with the volts pressure applied to an aluminium anode as ordinates, and with current as abscissæ, shows that the aluminium allows almost no current to flow until the pressure has exceeded a value of 40 volts. After such pressure has been reached, the protective coating becomes broken down and the current flows readily.

By employing two aluminium electrodes in the same electrolyte, and applying an alternating pressure, curve No. 2, of a somewhat similar form, is derived. It will be seen that the breakdown pressure with an alternating current is less than with a direct, due largely to the fact that the pressures given are effective pressures, the maximum pressure being considerably higher than that indicated by the alternating-current voltmeter. Inasmuch as the electrolysis of sodium hydroxide requires a pressure of about four volts, it will be seen that such pressure is well within the range of the aluminium.

An experiment was performed to determine whether a combination of an aluminium and an iron electrode in fused sodium hydroxide could be employed simultaneously as a rectifying cell and as an electrolytic cell for the production of metallic sodium. The results which were obtained seem to indicate that sodium may be produced, and with almost as high an efficiency, when connected to an alternating-current circuit as to a direct-current circuit. The accompanying sketch illustrates the construction of the cell in which this process was carried out:

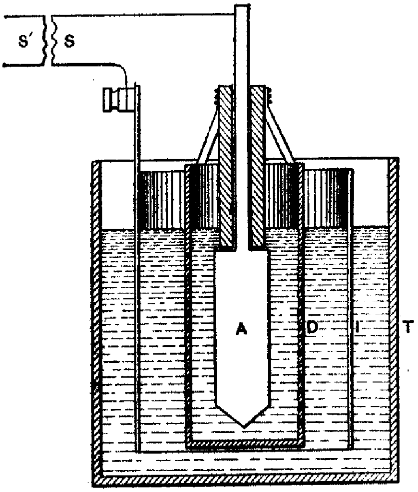

FIG. 1.

T is an aluminium vessel in which the salt is fused; I represents an iron electrode surrounding the aluminium electrode A; S represents the secondary of a step-down transformer, the pressure at its terminals being about six volts; S′ is the primary of the same transformer connected to a 110-volt circuit; D represents a diaphragm surrounding the aluminium electrode and insulated from it by a porcelain sleeve surrounding the upper portion of the aluminium electrode. This aluminium diaphragm was perforated so as to allow a communication of the electrolyte and the passage of the current through it.

A current of 9 ampères, as indicated by a direct-current instrument, was passed into this cell, and after some time globules of fused metallic sodium appeared on the surface. The cell was operated for several days, and a considerable quantity of metallic sodium was collected. It was found that careful regulation of the temperature was necessary to produce a large yield, but, other than this, the cell required no attention. At the end of the run the aluminium electrode showed almost no corrosion, the only indication of it being at the point where the aluminium was in contact with the porcelain.

As a result of a run to determine the amount of corrosion of the aluminium, it was found that an electrode 1.5 inches long and .5 inch in diameter lost about one-half gram during a run of 50 ampère hours. The sodium, upon being liberated, rose to the surface of the liquid, and was prevented from diffusing over to the cathode by means of the aluminium diaphragm. The short-circuiting between the aluminium anode and the diaphragm was prevented by the porcelain insulating sleeve.

To determine the effectiveness of the aluminium in preventing the current flowing from it to the electrolyte, current and pressure curves were obtained by means of a Blondel oscillograph. One of these curves is shown in Fig. 3, curve *(a)* being the current curve and *(b)* the pressure curve at the cell terminals. The portion of the current curve below the axis represents a leakage current, which may be due to the small particles of sodium adhering to the electrode and to a small leakage which naturally takes place from such an electrode. This portion of the curve represents a loss of energy which is wasted, unless its heating action is useful in maintaining the cell at the proper temperature. The portion of the curve above the axis represents the useful current. From a measurement of the areas of these curves, the current efficiency may be calculated. The efficiency, as computed in this manner, was about 73 per cent. The alternating pressure which was applied had a peaked wave form, and previous measurements showed that a sinusoidal or flatter wave form allowed a higher efficiency to be obtained, so that a value higher than that given can undoubtedly be realized.

What is apparently a new feature in the construction of electrolytic cells is embodied in the apparatus here described in the form of the aluminium diaphragm. The suggestion has been made by Professor Burgess that aluminium may be a suitable diaphragm material when used in electrolytes such that its property of opposing the flow of current from it may be utilized. The perforations in the aluminium diaphragm may be small and at the same time allow a high current density without the current passing through the aluminium conductor. The diaphragm will not,

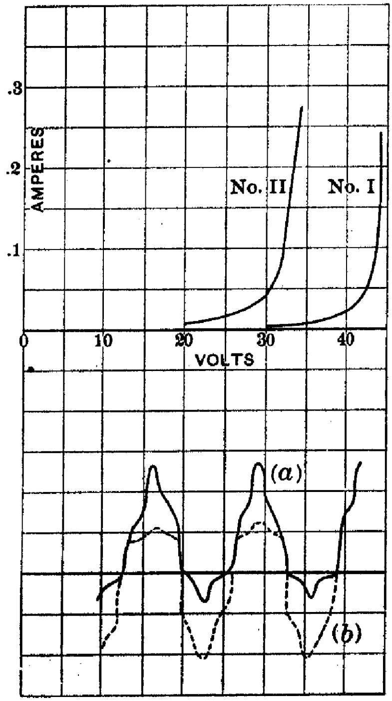

FIG. 2.

under such circumstances, take part in the conduction of the current, and the efficiency may therefore be higher than when iron or other similar metals are used. In the aluminium diaphragm employed in these experiments it was found that no corrosion occurred except at the surface of the electrolyte, where the diaphragm projected from the fused salt. There was a slight corrosion at this point, which could probably be accounted for by the absorption of moisture by the electrolyte when it was allowed to cool.

The same method of operation of an electrolytic cell might be applied in obtaining various electrolytic products other than sodium. While the current efficiency is less than if a direct current be employed, this loss may be partially balanced through avoiding the losses of a rotary converter. The additional loss caused by the leakage current is made manifest by the heating of the electrolyte, which may be an advantage or a disadvantage, depending upon the nature of the electrolyte.

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A paper to be read at the Fifth General Meeting of the American Electrochemical Society, at Washington, D. C., April 7, 8, 9, 1904.

ADVANCE SHEETS—SUBJECT TO REVISION.

SINGLE POTENTIALS OF THE HALOGEN ELEMENTS.

By William Roy Mott.

There are many points in the ionization theory not in harmony with some facts observed in the study of single potentials. The *impossible*[1,2,3] solution tensions assigned to metals tend to blind one to the fact that the *actual chemical reaction*[4] taking place and its free and bound energy are the essential points.

Dr. Patten and the author[5] have calculated the single potential of chlorine for *dilute aqueous* solution as —2.00 volts. By similar methods, the author has calculated the single potentials of the other halogen elements; iodine, —0.87 volts; bromine, —1.53 volts; fluorine, —2.53 volts, which values will be used in the reverse process of calculating the single potentials of metals.

In Table I, Column I contains the metals; Column II, the experimental values of the single potentials of the metals against their chlorides. All the single potentials, given* in this paper, are referred to Ostwald's zero[6]. These experimental values are Neumann's[7], except those given for the alkali metals[8]. The rest of the table consists of calculated decomposition voltages (D. V.) and calculated single potentials (S. P.) for dilute[9] aqueous solu-

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[1] The enormous magnitude of the solution tensions given to metals have been shown by Lehfeldt (Phil. Mag. [5] Vol. 48, 1899) to be incompatible with molecular physics.

[2] Kahlenberg has pointed out the important relation between heat of solution and single potential. See Jour. Phys. Chem., 1899, p. 379

[3] Compare F. Krüger Zeit. Phy. Chem., 1900, Vol. 35, p. 19.
Lehfeldt Zeit. Phy. Chem., 1900, Vol. 35, p. 257.

[4] The single potential observed with aluminum and magnesium is not that due to the formation of *normal* salts but of *basic* salts. It is well known that these metals dissolve in solutions of their own salts. See
Lemoine, Comptes Rend., 1899, 129, p. 291.
Kahlenberg, Jour. Amer. Chem. Soc., 1903, 25 : 380.
C. F. Roberts and L. Brown, Jour. Amer. Chem. Soc., 1903, 25 : 801.

[5] Electrochemical Industry, September, 1903, I : 450.

[6] Normal calomel electrode is taken as—0,56 volts. See Carveth, Jour. Phys. Chem., 1898, 2: 289.

[7] Zeit. Phys. Chem. 1894, 14: 229.

[8] Patten and Mott, Electrochemical Industry, September, 1903, and Jour. Phys. Chem., 1904.

[9] "Dilute" in thermal chemistry usually means normal to tenth normal.

tions. The original thermal data used is that given in Reyclor's "Outlines of Physical Chemistry." The calculated decomposition voltages do not include factors due to entropy, as the temperature co-efficients are practically unknown. The single potential of the metal is obtained by subtracting the single potential of the halogen from the total voltage.

TABLE I.

DECOMPOSITION VOLTAGES.

Col. I.	Col. II.	Flourides.		Chlorides.		Bromides.		Iodides.	
Metal.	Exp. Values	D. V.	S. P.	D. V.	S. P.	D. V.	S. P.	D. V.	S. P.
K^{I}	+2.38	4.98	+2.41	4.38	+2.38	3.93	+2.40	3.26	+2.40
Na^{I}	+2.18	4.80	+2.23	4.18	+2.18	3.73	+2.20	3.06	+2.20
Li^{I}	+2.45	5.04	+2.47	4.44	+2.44	3.98	+2.45	3.31	+2.45
Ca^{II}				4.08	+2.08	3.60	+2.07	2.93	+2.07
Si^{II}				4.26	+2.26	3.78	+2.25	3.12	+2.26
Mg^{II}	+1.231			4.07	+2.07	3.57	+2.04	2.91	+2.05
Mn^{II}	+0.824	3.36	+ .79	2.79	+0.79	2.32	+0.79	1.65	+0.79
Al^{III}	+1.015	4.03	+1.46	3.45	+1.45	3.00	+1.47	2.31	+1.45
Zn^{II}	+0.503	3.04	+0.47	2.46	+0.46	1.99	+0.46	1.32	+0.46
Cd^{II}	+0.174	2.69	+0.12	2.09	+0.09	1.65	+0.12	1.08	+0.22
Fe^{II}	+0.087	2.77	+0.20	2.18	+0.18	1.71	+0.18	1.04	+0.18
Fe^{III}		2.43	—0.14	1.85	—0.15	1.38	—0.15	.72	—0.14
Ni^{II}	—0.020	2.63	+0.06	2.04	+0.04	1.57	+0.04	.90	+0.04
Co^{II}	—0.015	2.66	+0.09	2.07	+0.07	1.60	+0.07	.89	+0.03
H^{I}	—0.249	2.18	—0.39	1.71	—0.29	1.24	—0.29	.57	—0.29
Cu^{II}	—0.550	1.95	—0.61	1.36	—0.64	.89	—0.64		
Hg^{II}				1.10	—0.90	.81	—0.62		
Pt^{IV}	—1.140			.87	—1.13	.57	—0.96		
Au^{III}	—1.356			.39	—1.61	.24	—1.29		

These values, given in Table I, are plotted on Plate I, with the voltages of decomposition as abscissæ and the single potentials of the metals as ordinates. This diagram represents the well-known additive law. In it, there will be noticed, that equal increments mark the displacement of one metal by another metal or one halogen element by another halogen element. This results in two sets of parallel lines. This diagram can be used in the calculation of any one of the three factors—the total decomposition voltage, single potential of the anion, or single potential of the cathion, when the other two factors are known. Some very useful results can be obtained in this way. It must, however, be remembered that the formation of *normal* salts in *dilute aqueous* solution is postulated.

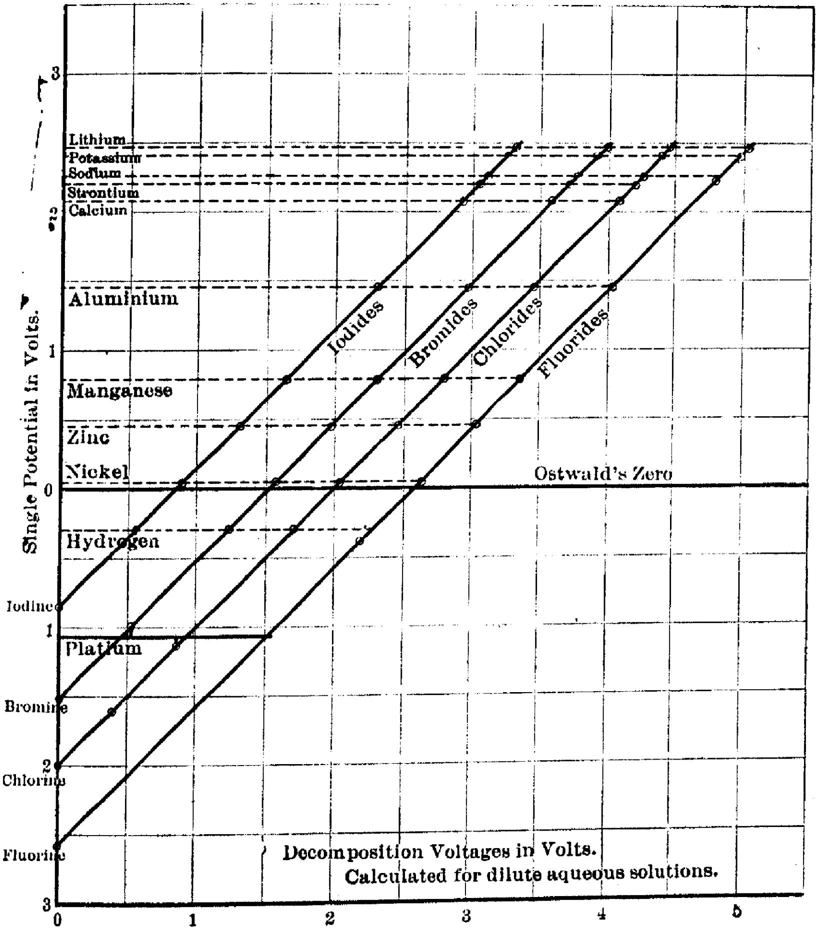

PLATE I.

A careful comparison of these values among themselves and with the experimental single potentials shows the value and the reliability of the method. Generally, the variations do not exceed one-tenth of a volt. This seems remarkable when the many sources of error in obtaining thermal data and electrode potentials are considered. Differences in the physical condition (such as mechanical strains, crystalline structure, etc.) of both the salt and of its original elements offer important sources of error. The experimental single potentials of cathions have been shown to compare favorably with calculated values. The anion single potentials will now be considered.

The experimental data was taken in the same manner and with the same apparatus as that described in several previous papers.[1]

The first halogen element, fluorine, has been given the low single potential of —1.98 volts by R. Abegg and Cl. Immerwahr[2] from decomposition voltage. This is 0.59 volt below the theoretical. In Table III, I give an experimental discharge (—2.00 volts) of the anode at a current density of about 0.030 amp. per square centimeter. This value[3] agrees with the above experimental result.

But a little consideration will show that the chemical reaction taking place is not that of the liberation of fluorine, but of oxygen and ozone. As the current density increases the products change from oxygen free from ozone[4] to oxygen containing a great deal of ozone and then to the primary product, the fluorine. These different chemical reactions appear perfectly natural when we consider that Moissan noticed a yield of 20 per cent. ozone from the reaction of gaseous fluorine upon water. From these considerations, it is obvious that to get the single potential of fluorine a much higher current density is necessary.

This I secured by taking a fine platinum wire fused in glass and broken off short. With 10 volts, .020 amp. was passed through a normal solution of potassium fluorine with this electrode as anode. This gave a current density of about 2 amp. per square centimeter. The discharge potential of the anode was —2.53 volts. This experiment was repeated with another slightly larger electrode and with a new solution. The anode discharge potential was nearly as high as the above value. The theoretical single

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[1] Patten and Mott, Trans. Amer. Electrochem. Soc., Vol. III, p. 317.
Patten and Mott. "Decomposition Curves of Lithium Chloride in Alcohols and the Electro-deposition of Lithium." Jour. of Phys. Chem., 1904.

[2] Zeit. Phy. Chem., 1900, 32, 142.

[3] The polarizations, obtained by the method of discharge potential, give low values because of the time and current required for the readings. The allowable time depends entirely on the amount and stability of the products which cause the polarization. For example, compare the discharge potentials of zinc and fluorine. The latter is given off only in small quantities and is rapidly used up by the solution. Discharge potentials given in this paper required an interval of about one-tenth of a second for their experimental determination.

[4] Gore, The Art of Electrolytic Separation, etc., p. 98.

potential of fluorine (—2.57 volts) compares favorably with this experimental value.

Another check on this value follows from a number of curves of total polarization. One of these is given in Table II, and plotted on Plate II.

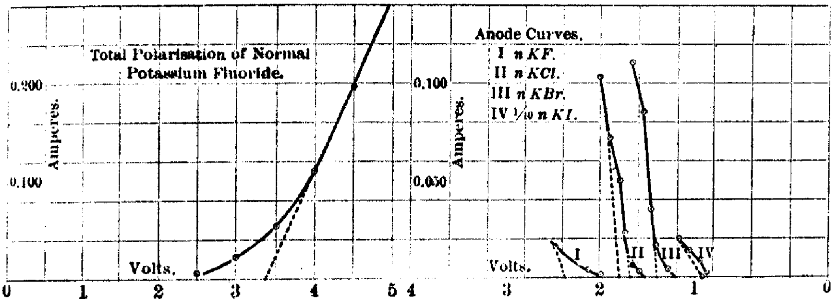

PLATE II.

TABLE II.

DECOMPOSITION—POINT CURVE FOR NORMAL POTASSIUM FLUORIDE.

Total Volts	Ampères
5.00	.300
4.50	.198
4.00	.112
3.50	.054
3.00	.022
2.50	.005

The CR line produced shows a total polarization of 3.3 volts. The cathode polarization would not exceed +.65 volt (see Table III); so the anode polarization amounts to —2.65 volts.

Other halogen salts (Table III) of potassium were electrolyzed. The anode curves are plotted on Plate III.

The anode curve of potassium fluoride shows a polarization equal to —2.4 volts (current density about 0.020 amp. per square centimeter). The CR line was obtained from the cathode curve and the total curve. The curve itself is not satisfactory because of its incompleteness, and is only reproduced for the sake of comparison.

TABLE III.

n K F.

Total Volts.	Ampères.	Anode.	Cathode.
2.00	.002	—1.97	
2.50	.004	—2.13	+.40
3.20	.016	—2.45	+.65
3.80	.100		+.93
Discharge	.100	—2.00	
n K Cl.			
2.00	.002	—1.59	+.39
2.20	.005	—1.66	+.54
2.40	.023	—1.73	+.66
2.60	.050	—1.79	+.77
2.80	.072	—1.90	+.86
3.00	.103	—2.00	+.95
Discharge	.103	—1.76	
n K Br.			
1.80	.004	—1.29	+.47
2.04	.017	—1.42	+.60
2.20	.035	—1.48	+.66
2.40	.085	—1.56	+.79
2.60	.110	—1.67	+.89
2.80	.172	—1.70	+.96
Discharge	.172	—1.34	
1-10 n K I.			
1.40	.003	— .87	+.50
1.60	.008	— .94	+.63
1.80	.014	—1.06	+.71
2.00	.020	—1.17	+.85
Discharge	.020	— .90	

The potential of chlorine has created much discussion[1] in electrochemical circles. A solution of chlorine can hardly be considered of the same nature as those of hydrogen or nitrogen in water, since the reaction of chlorine on water to form hypochlorous acid and hydrochloric acid would yield about the same heat as that found in dissolving chlorine in water. The equilibrium that might exist in the presence of water, chlorine, hydrochloric acid and hypochlorous acid has been well discussed by Müller and others.[2] So at the anode, we may expect the potential to be mainly due to these oxy-compounds of chlorine, which, of course, as they increase the conductivity[3] of the solution, therefore, tend to furnish primary products containing oxygen. So it is not surprising that the observed anode potentials are not those of chlorine, but of oxy-chlorine compounds and of oxygen.

Using the electrode, consisting of a platinum point fused in glass (the same as used in the fluorine experiment), I obtained a discharge potential of —1.81 volts. A current of 0.050 amp. (a current density of about 4 amp. per square centimeter) was passed by 11½ volts, through a twice normal solution of potassium chloride.

This calculated value of —2.00 volts applies only to dilute solution from which experiments show oxygen separates on electrolysis, and not chlorine; therefore, chlorine must have a single potential *greater* than that of oxygen in acid solution.

The anode curve (Plate III) for normal potassium bromide gives a polarization of about —1.40 volts. Bromine separates out on the electrode as can be seen from its brown color. At higher current densities, obtained with the platinum point fused in glass, the anode discharge potential was found to be —1.43 volts with a current of 0.050 amp. and a voltage of 11½ volts. This value is 0.10 of a volt below the theoretical (—1.53 volt).

Potassium iodine, with this same apparatus, gave an anode discharge potential of —.91 volts. The iodine was seen to deposit, and

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[1] Gockel,—Zeitschr. Phys. Chem., 1900. 32: 607.
Akunoff,—Zeit. Elektrochem., 1900, 7: 354.
Lorenz and Wehrlin,—Zeit. Elektrochem., 1900, 6: 339, 408, 419, 437, 445.
Müller,—Zeit. Elektrochem., 1900, 6: 573, 581. 1901, 7: 750. 1902, 8: 425.
Foerster and Müller,—Zeit. Elektrochem., 1903, 9: 171, 195.

[2] See Richardson, Jour. Chem. Soc., 1903, 83: 380.

[3] In some preliminary work on specific conductivity two years ago, I noticed that chlorine water (saturated) has a very considerable conductivity, 17.0 x 10^{-3} reciprocal ohms per cubic centimeter at 25.0° C.

this caused a rapid decrease in current flow. The pressure used was 11½ volts. This discharge potential is 0.04 volts higher than the theoretical value (—.87 volts). Bancroft[1] gives the polarization of iodine, dissolved in potassium iodide, as —0.888 volt. This is still closer to the theoretical value.

Hence the calculated single potentials of the halogen elements checks reasonably well with the experimental data, and the additive law applies to halogen salts in dilute aqueous solution. So we are able to predict the single potentials of metals,[2] the single potentials of non-metals and the heat of formation of their salts. A special application of this last case will now be considered.

LAW OF SOLUBILITY AND HEAT OF SOLUTION.—The calculated decomposition voltages for *nearly insoluble*[3] salts, for example, AgCl, CaF_2, $BaSO_4$, are much *smaller* than for the decomposition voltages as calculated from thermal data for the solid salt. This means that there is a large negative heat of solution; that is, the salt dissolves with a large absorption of heat.

In Table IV, there is a list of the voltages due to the heat of solution. Hydriodic acid has the largest heat of solution, and the voltage added to its decomposition voltage because of this heat of solution is 1.04 volt. The following points will be noted from this table: The iodides of the alkali metals dissolve with evolution of the greatest heat. They are also the most soluble of the halogen salts. The greater the atomic weight of the metal the smaller or more negative the heat of solution and the more insoluble the salt. With halogen salts of the alkali metals and alkaline earth metals, the solubility increases with the increase of the atomic weight of the halogen element. The heat of solution also follows this order.

With the uni-valent salts of Cu, Ag, Au, the solubility and heat of solution of the salt decreases both with a decrease in the atomic weight of the metal element and a decrease in the atomic weight of the halogen element. For example, silver fluoride has a positive heat of solution and is classed as a soluble salt. Silver iodide is the most insoluble of all the halogen salts of silver and has the most negative, calculated heat of solution.

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[1] Zeit. Phy. Chem., 1894. XIV: 193.

[2] Considerations set forth in this paper show that Wilsmore's (Zeit. Phy. Chem., 1900, 35, 391) calculated values for alkali and alkaline earth metals are most incorrect.

[3] Compare Nernst, Ber. d. d. chem. Ges. 1897, 30, 1557.

TABLE IV.

HEATS OF SOLUTION IN TERMS OF VOLTS.

Group	Sub-group		Flourides.	Chlorides.	Bromides.	Iodides.
Group I.	Sub-group A.	H^{I}	+0.20	+0.756	+0.94	+1.040
		Li^{I}	....	+0.365	+0.47	+0.66
		Na^{II}	—0.023	—0.046	—0.01	—0.049
		K^{I}	—0.147	—0.196	—0.23	—0.23
		Rb^{I}	....	......	.....	......
		Cs^{I}	....	......	.....	......
	Sub-group B.	Cu^{I}	....	—0.15*	.....	—0.49*
		Ag^{I}	+0.114	—0.31*	—0.55*	—0.81*
		Au^{I}	....	......	.....	......
Group II.	Sub-group A.	Be^{II}	....	......	.....	......
		Mg^{II}	+0.04*	+0.564	+0.94	+1.085
		Ca^{II}	—0.07*	+0.38	0.53	+0.603
		Sr^{II}	—0.10*	+0.24	0.35	+0.45
		Ba^{II}	—0.025	+0.04	0.11	+0.23
	Sub-group B.	Zu^{II}	....	+0.34	+0.33	+0.25
		Cd^{II}	....	+0.08	—0.01	—0.02
		Hg^{II}	....	—0.06	—0.07	—0.60* (—0.69) °*

* = calculated.

° This second value is calculated for the red mercuric iodide. Two solid phases are characteristic of the halogen salts of this sub-group.

The alkaline earth metals show relationships exactly parallel to those shown for the alkali metals. The periodic law applied to Groups I and II shows up with surprising regularity.

It would be interesting to learn how this heat of solution is distributed between the anion potential and the cathion potential.

IN CONCLUSION.—Experimental data for the single potentials of fluorine, chlorine, bromine and iodine have been obtained, showing the value of the additive law for both anions and cathions. The additive law holds much better for dilute aqueous solutions than for solid salts. Solid salts may, in different forms, possess very different amounts of energy; for example, amorphous silver iodide has a heat of formation of 8.6 large calories, while the crystalline variety has a heat of formation of 14.2 large calories.

This introduces a difference of 0.33 volts in their respective decomposition voltages.

The difference between the decomposition voltage of the solid salt and of the dissolved salt represents the heat of solution or the energy of the reaction resulting from the affinity of the salt for the solvent. Other solvents than water give very different heats of solution. Quantitative work in this field is scarce and is much to be desired.

It is shown in this paper that heats of solution of insoluble[1] salts can be calculated, and the results add force to the law that:

Solubility[2] is largely determined by the mutual affinity[3] of the solvent and solute as represented by the heat of solution.

It is my pleasure to give my hearty thanks to Dr. Patten and Professor Burgess for many favors extended me in carrying out this work.

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[1] No salt can be said to be absolutely insoluble; and if it were, the supposition of a heat of solution would be absurd.

[2] Most salts that contain water of crystalization are known to have a positive heat of solution for the anhydrous salt.

[3] The relationship of heat of solution and solubility as set forth by the author of this paper is totally different from some ideas on the relation of electroaffinity and solubility, given by Abegg and Bodländer, which have met severe criticism from Locke and others.
See Abegg and Bodländer, Zeitschr. anorg. Chem., 1899, 20, 453.
Locke, Am. Chem. J., 1902, 27, 105.
Abegg and Bodländer, Am. Chem. J., 28, 220.

9

THE PRESENT STATUS OF ELECTRIC FURNACE WORKING.

CHARLES F. BURGESS—UNIVERSITY OF WISCONSIN.

Presented before the Electrical Section February 10, 1905.

The importance of any discovery is measured ultimately by the material benefits which are derived from it. Estimated upon this basis the electric furnace may not perhaps be assigned a degree of importance comparable to that claimed by various other electrical devices. There is little exaggeration in the assertion, however, that if electric furnace development continues during the next two decades at a rate approaching the progress made in the past ten years it will have attained by that time a secure position among the most important of electrical appliances. To sum up the practical benefits, both immediate and remote, which it has already conferred would form the subject matter of an address much more pretentious than it is my purpose to undertake, yet it may be said to have only recently emerged from the experimental state.

The electrical furnace may be defined as a structure to which electrical energy is delivered for its conversion into thermal energy. Accepting this definition, the date of its invention goes back to the time when it was discovered that electricity passing through a conducting medium is converted into heat. It is therefore over a century old. Comparatively little attention was devoted to it, however, until twenty-five years ago, when Sir William Siemens devised and exhibited in operation his furnaces for the melting of platinum, iron and other metals. So important an epoch did his work mark that Siemens is with justice called the father of the electric furnace industry. The usefulness which he ascribed to the electric furnace and the possibilities which he pointed out have been more than realized. Since then results of the greatest importance have been attained. Many of nature's most closely guarded secrets have been revealed; a new chemistry of high temperatures has been evolved; new ideas as to the constitution of matter have been developed; new methods of preparing known substances have been formulated; our stores of available materials have been enriched by the discovery of new compounds. Such are the results which have been accomplished through scientific research.

Reprint from the Journal Western Society of Engineers, April, 1905.

To attempt to define the status of the electric furnace from the standpoint of all interests would require a longer dissertation than is possible at this time, and it is proposed to limit the discussion to those features which are of especial interest to the electrical engineer.

The present status of the electric furnace may be summed up in the statement that it is to-day proving a most efficient weapon in the siege which man is laying to the secrets of nature; that some of the positions won by it have been occupied with great advantage, and that many more are capable of profitable occupation. Its owes its importance, however, not so much to the wonders which it has wrought in the past as to the possibilities which it offers for the future. While it is only in process of emerging from the laboratory stage it has already reached the dignity of an agent whose services can be measured in terms of that sordid but universal unit, the dollar.

The electrical engineer is ever on the lookout for new worlds to conquer, and although aggression and conquest are his watchwords, he can well afford to stop and look back over what has been accomplished in electric furnace work. In so doing he will not only receive warning and encouragement, but he will discern many discoveries which the pure scientist has made and which he, by applying his engineering knowledge, may make of material service to man. For it is true, that even if no new scientific discoveries should be made in the future, there yet remains a broad and fertile field in the development of those discoveries which have been made but not yet utilized.

In the high temperature produced in the electric furnace it has been shown that all substances can be melted. The oft encountered statement that lime, magnesia, molybdenum, tungsten, and the like, are infusible is therefore incorrect, for not only can all known substances be melted, but they can be volatilized as well. These facts are full of significance and suggestion to the engineer. They not only show him that there are limitations upon the materials which he may use for furnace construction, introducing difficulties where the highest temperatures are to be developed, but it is possible that in the melting and fusion of materials they may undergo such transformation of their physical nature as to endow them with qualities of great value. One of the most successful industrial uses of the electric furnace is the fusion of aluminum oxide in the form of bauxite, resulting in the production of that physical form of the material designated by the trade name "alundum."

This is a duplication of nature's process for producing corundum, but the artificial product has marked advantages over the natural material in the purity, cheapness, strength and toughness, which give it greater value for abrasive purposes.

The fusion of quartz has produced a valuable material for a new kind of glassware which is indestructible by rapid or extreme variations of temperature. Various refractory materials have their refractory qualities increased by melting and subsequent cooling. Experimental investigation in this direction has only begun, but the results already obtained point to many improvements which may be made in materials for furnace construction, materials resistant to chemical corrosion, and materials possessing high heat and electrical insulating properties. The volatilization of elements and compounds at high temperatures gives new methods for the purification and separation of materials, enabling the process of fractional distillation to be applied to all substances.

It has been shown that carbon is capable of conversion into its various forms, a fact industrially utilized with great advantage by the International Acheson Graphite Company in making graphite and graphitized electrodes from the ordinray forms of coal and coke. Moissan has demonstrated the possibility of changing carbon into the diamond, and has reproduced, artificially, all the variety of diamonds which nature furnishes, alike in all respects save size. It remains for the engineer to operate this process on a large scale to produce exact equivalents and to duplicate not only the diamond but other gems.

All the oxides which had hitherto been regarded as irreducible have been reduced through the use of the electric furnace. Upon experiments which he has made, Borchers bases the claim that carbon is capable of taking the oxygen from any known compound at temperatures within the range of the electric furnace. Similarly, other reducing agents may be made effective, and the decomposition can be produced without any reducing agent whatever by utilizing the electrolytic action of the current. This has resulted in unlocking various of nature's stores, making available for man's use such materials as aluminum, magnesium, calcium, sodium, potassium, chromium, silicon, and many others which previously could be obtained only with great difficulty if at all.

The most important industrial application which has thus far been made of the reducing action is the production of aluminum, the cost of which within a comparatively few years has been reduced from $5.00 to about 30 cents per pound. The manufacture of magnesium and sodium are also industrial operations of importance.

Other processes are in the state of industrial exploitation.

The march of improvement in this direction will necessitate further development in the method of operation, and particularly a more thorough investigation into the properties and uses of the materials which can be thus produced. It has been estimated that the earth's crust holds locked up in the form of oxides and similar compounds 27.2 per cent of silicon, 7.8 per cent aluminum, 5.5 per cent iron, 3.8 per cent calcium, 2.7 per cent magnesium, and various other substances, some of which are classed among the rare elements. One of the latest triumphs in the recovery of these materials is the production of metallic silicon by Mr. F. J. Tone of Niagara Falls. This material is quoted in chemical lists at about 25 cents per gram, but by this new process it can be profitably sold at 35 cents per pound. Though thus far only a few minor uses have been found for it, it is not unreasonable to suppose that a further knowledge of its properties will point to new needs and that this most abundant element may become also a most useful one. While the metallurgy of iron has been developed without the aid of the electric current, recent work has shown that the electric furnace will be able to play an important part in the future of this metal. Calcium, which can be obtained in the form of a pure carbonate at a cost of a fraction of a dollar per ton, has not yet yielded to the attack of the industrial electrometallurgist, though most promising laboratory results have been obtained and the metal has recently been placed upon the market. When it becomes possible to obtain this metal for a few cents per pound, as will be the case beyond doubt, little effort will be required to build up a market for it since its known properties are such that it will enter the field of chemistry and metallurgy as a most powerful and advantageous reducing agent.

Magnesium, while very abundant in nature, sells for over two dollars per pound. Nearly all of this amount represents the cost of extraction, and, therefore, the possibility of a further improvement in the process is indicated. Its present cost is such as to limit its usefulness to a restricted field, but if this could be made comparable to the cost of aluminum, an analogy not impossible, it will become a metal of great service in the manufacture of alloys as well as for chemical and metallurgical purposes.

Moissan's classic researches show us that a large number of elements unite with carbon to form carbides, many of which were not known before the day of the electric furnace. Based upon this fact, though resulting from the independent discovery of the American inventor, Willson, the calcium carbide industry has been developed. This material was unknown a few years ago, but today thousands of tons are being produced annually. The reaction of this carbide with water forms that hydrocarbon, acetylene, which, although now finding its chief use as an illuminant, is capable of being transformed into other hydrocarbons. Manganese carbide reacts with water to form hydrogen and methane, thorium carbide gives ethylene, and cerium and uranium carbides yield liquid and solid hydrocarbons as well as the gaseous ones. Although the hydrocarbons other than acetylene have not been produced commercially, scientifically it is possible to produce petroleum and other like compounds. Such discoveries as these point to the great and significant fact that the whole field of organic chemistry offers itself as an incentive in the exploitation of the electric furnace.

Another class of carbides, such as those of silicon, boron, chromium, molybdenum, tungsten and titanium are stable, not only resisting the attack of water but being extremely resistant to the most active chemical agents. The first of these, silicon carbide or carborundum, has found extensive application as an abrasive, and its use has led to the development of a new industry. Its extreme hardness, approaching that of the diamond, and the refractory nature of it and similar carbides, together with properties which may yet be discovered, point to the probability as well as the possibility that other carbides will have quite as extensive industrial application.

Moissan and his contemporaries have shown that silicon, boron, nitrogen, may be made to act like carbon in producing silicides, borides, and nitrides, each new compound having its own peculiar properties, and that the field may also be extended through the manufacture of the more complex compounds, such as the silico-borides, silico-carbides, boro-carbides, etc.

A contemplation of such possibilities is most bewildering, and to quote from an address by Prof. Jos. W. Richards referring to electrometallurgical progress, "We are so overwhelmed by new things of possible use to science or industry, that we can at most investigate only a small fraction of them. It is a virgin continent of undeveloped possibilities."

ADVANTAGES OF ELECTRIC FURNACE.

The electric furnace owes its place in the scientific and industrial world to certain characteristics which it possesses and to the advantages which it offers over other means of generating heat, the principal one being the high degree of temperature which is made available. An interesting comparison might be worked out showing that civilization progresses in a rate proportional to the utilization of heat energy in its highest degree of concentration. Each additional degree of temperature which can be produced and kept under control shows itself capable of new and useful purposes, and the electric furnace has added such an extension to the range of available temperatures that it has almost doubled that previously available.

It simply requires the passage of the electric current through a conducting medium to produce heat, the intensity of which depends upon the amount of current which passes. Inasmuch as most substances retain their conductivity at high temperatures the degree of intensity, which is theoretically possible is unlimited. Practically however, limitations are placed upon it through the physical difficulties of keeping the conducting medium in place. While it retains its solid condition, the temperature is limited by the fusing point of the material; when fusion commences the difficulties of containing the melted material begin, and the temperature is limited by the point of vaporization. When volatilization begins, the gaseous materials escape from the field of action, carrying away the heat as rapidly as it is supplied to the furnace as latent heat of volatilization or as energy stored up as potential chemical energy. It is true that the temperature of volatilization might be increased by subjection to high pressure, but this involves construction of a container which can be made only of solid materials, having limitations imposed by the fusing temperatures. The electric arc maintained through a carbon vapor furnishes perhaps the highest degree of temperature attainable, the temperature of which is usually considered as being definitely fixed by the volatilization of carbon. Through limitations upon our methods of measuring these high temperatures the exact value to be assigned to the temperature of the electric arc cannot be stated, though the most satisfactory measurements give values ranging between 3,600° and 4,000° C. Whether this is the ultimate limit to be attained by electrical means is difficult to say. There is, of course, the possibility of exceeding it by maintaining the arc under a high atmospheric pressure, or by feeding electrical energy to the arc more rapidly than it can be dissipated by the volatilization of carbon, or in other words, superheating the carbon vapor. Such speculation, however, is not necessary to show that the electric furnace has unbounded possibilities, since the range of temperatures below that of the ordinary arc offers an unlimited field for usefulness.

The maximum temperature which may be obtained theoretically by the combustion of carbon in oxygen is higher than that which has been attained in the electric furnace, but practical conditions place a greater restriction upon it. At high temperatures carbon cannot be consumed to CO_2, but rather to CO, and this gaseous product escapes rapidly and carries the heat away from the furnace. Further, it is impossible under practical conditions to supply pure oxygen, and in utilizing the atmospheric supply not only must the large quantity of accompanying nitrogen be heated, but the excess of air which must always be supplied also carries away a large amount of heat. The maximum temperature which has been attainable in the combustion of fuel in the gaseous, solid or liquid form, from which volatile products of combustion are formed, probably does not exceed 2,000° C, and even this value can be obtained only at a low efficiency and under most favorable conditions for the conservation of heat.

Since the introduction of the electric furnace, other new methods have been worked out for obtaining the higher temperatures. One of these is known as the thermit method, in which aluminum is the fuel consumed, the product of combustion being aluminum oxide, which is not volatile at the high temperatures, and therefore does not carry away the heat. By this means temperatures considerably exceeding 3,000 degrees can be readily attained. Calcium, magnesium, and certain other electropositive elements may be similarly utilized for attaining high temperatures, but the electric furnace stands alone as a means of producing these temperatures economically. The great advantage of electric heating is that it is not necessarily associated with products of combustion and does not need for its production a consumption of materials. In other words it gives "pure, unadulterated heat." Therefore, for temperatures exceeding 2,000° the electric furnace, if not the only means, is the most economical one to be employed.

Another advantage which the electric furnace has over combustion furnaces is that a great amount of heat can be developed in a compact and limited space and that the same degree of temperature can be attained whether the furnace is operated on a laboratory or on an industrial scale.

From the standpoint of refractory materials the electric furnace represents a distinct gain. The temperature at which ordinary crucible or muffle furnaces can be operated is limited by the resistance which avaliable refractory materials offer to melting, and to the corrosive and fluxing action of materials to which it must be exposed. The same refractory materials may be used for higher electric furnace temperatures since the materials to be heated, as well as the source of heat, is within the refractory walls. Where the heat has to be transmitted through such walls in other forms of furnaces the material to receive the heat cannot receive so high a temperature. Further than this, the refractory walls of the electric furnace can be kept cool by artificial means such as an air blast or water circulation, and a still more advantageous property is that the material undergoing treatment may itself constitute the walls of the furnace. This advantage of interior heating is utilized in the production of phosphorous and carbon bisulphide, most of which is now produced in the electric furnace, the greater cost of electrical heating being more than compensated by the saving in crucibles and retorts, the destruction of which constituted large items under the older methods.

In the matter of control of heat, the electric furnace stands by itself, for the rapidity of heating, duration of heating, and adjustment of the temperature is under the full and exact control of the operator.

Fusions can be carried out under oxidation or reducing conditions, for the construction of the furnaces makes it very easy to operate in an atmosphere of any gas desired. Higher purity can thus be attained.

The final advantage, which is really a summary of all the others is economy of operation. The economy of the electric furnace as compared with that of other furnaces requires the balancing of electrical energy against energy obtained from the combustion of fuel; cost of installation and maintenance of the equipment, amount of labor, value of product, danger to operatives. A careful weighing of these factors in a considerable number of metallurgical and chemical operations on an industrial scale has shown the resultant advantage to lie with the electric furnace.

VARIOUS FORMS OF FURNACES.

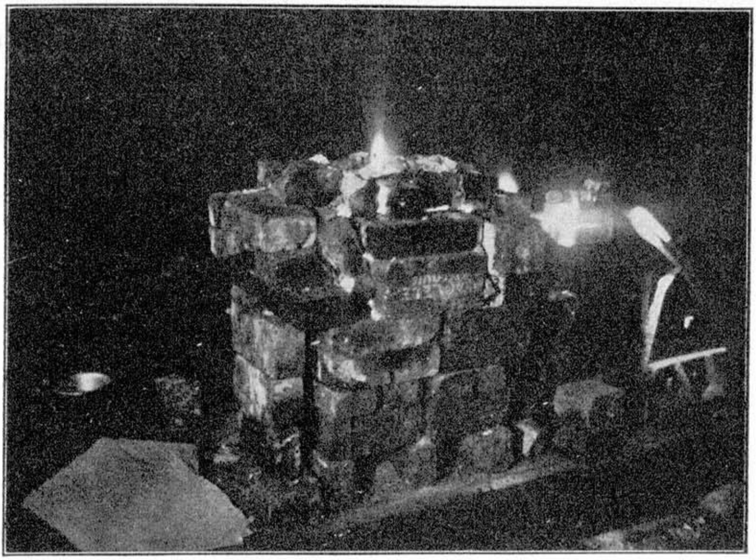
A considerable variety of expression is found in the classifications of electric furnaces by different authorities. It is common to classify them as follows:

Arc furnaces, in which the material is heated by an arc, usually established between carbon electrodes.

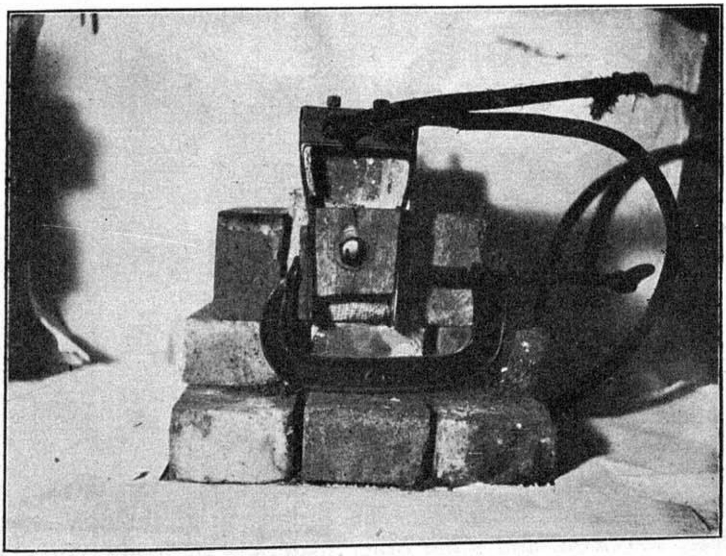
Resistance furnaces, in which the heat is developed by the passage of current through a solid conducting medium.

Electrolytic furnaces, in which heat is generated by the passage of current through a fused mass, and in which at the same time the material is decomposed by the electrolytic effect of the current.

Since in all of these classes the current flows through a conducting medium and therefore encounters a "resistance" it is not logical to employ the term resistance furnace to designate any one of them. A more satisfactory classification would be in accordance with the character of the medium which constitutes the conductor. This gives three classes:



100 H. P. Arc Furnace in Operation.



30 H. P. Resistance Tube Furnace.

1. Furnace in which the heat is developed by the passage of current through a solid conducting medium or "resistor."
    - a. The conducting medium, or core, may consist of the material which is to undergo useful transformation.
    - b. The heat is developed in a core of conducting material, and this heat is in turn communicated to surrounding material constituting the charge, either with or without the interposition of a wall separating the two materials.
2. Furnace in which the heat is developed by the passage of current through a liquid conducting medium.
    - a. Electrolytic.
    - b. Non-electrolytic.
3. Furnace in which the heat is developed by passage of current through a gaseous conducting medium.
    - a. Arc furnaces.

      Where arc plays between two or more carbon electrodes in the neighborhood of material to be heated.

      Where arc is maintained between one carbon electrode and another electrode of the material to be heated.
    - b. High tension furnaces.

      Where arc or high tension discharge plays between two electrodes in a gaseous medium for the production of chemical change in such medium.

FURNACE CONSTRUCTION.

The following are the essential features which must be considered in electric furnace design and construction:

Walls, containers, and crucibles, of refractory materials capable of resisting fusion, and the action of solid, liquid, and gaseous materials at the working temperatures.

Resistance medium, which may be solid, liquid, or gaseous.

Charge, which may be solid, liquid, or gaseous.

Electrodes, for conveying current to the resistance material.

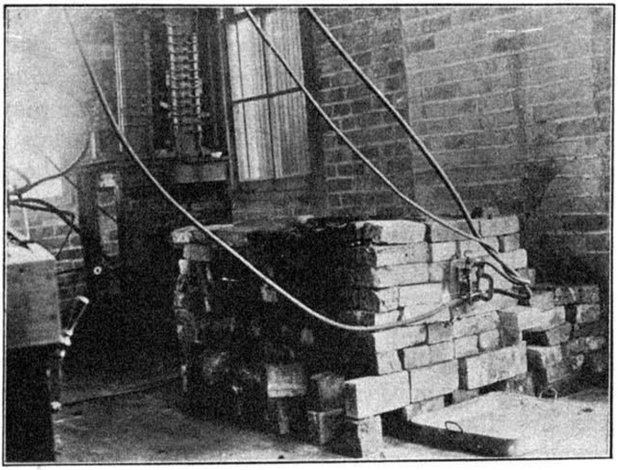
Electrode terminals.

Provisions for feeding and emptying the furnace.

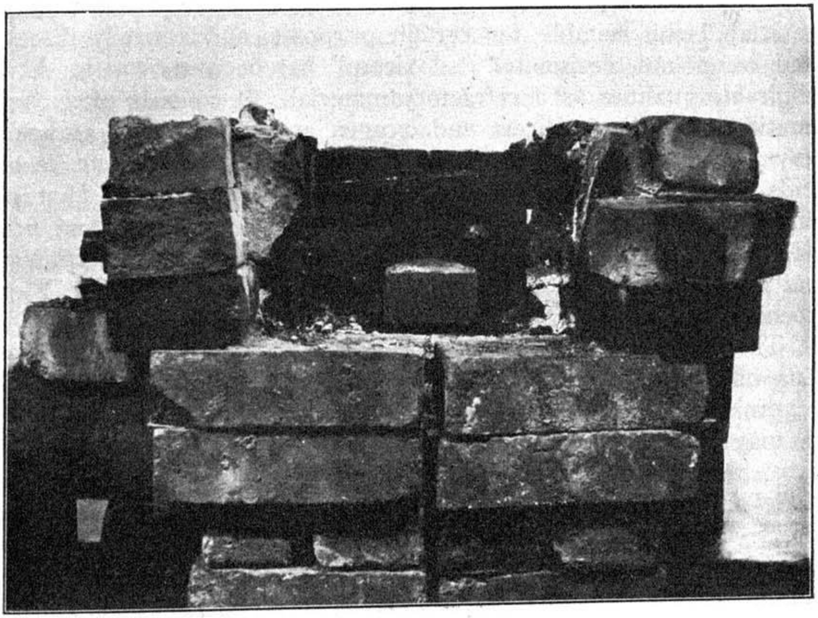
Outlets for escape of gaseous products, slags, etc.

Electrical regulating devices.

The refractory materials which are available for furnace construction are silica, magnesia, lime, chromite, alumina, carbon, graphite, siloxicon, and some other materials of minor importance. The choice of materials is governed by the temperature and the nature of the charge (whether acid or basic). For an acid lining silica is most satisfactory. This material in its highest degree of



50 K. W. Carborundum Furnace.



Section of 800 Ampere Arc Furnace.

purity resists a temperature of nearly 2,000° C. It can be obtained in the form of bricks with a sufficiently low percentage of lime or other binding material to lower its melting point only a small amount. Such bricks are rather fragile, but there is a promising possibility that bricks made of pure fused quartz may soon be available. Lime, and magnesium oxide are the materials most successfully employed by Moissan for the linings of his laboratory furnaces, and for industrial working a durable basic lining may be made of a high grade magnesite brick. Chromite and bauxite bricks are also valuable constructive materials. The most refractory substance which can be used is graphite, which can be obtained in a high degree of purity in any desired form, this being manufactured by moulding and baking carbon and subsequently subjecting it to the graphitization process. The limitations upon this material are that it must be protected from the air or other oxidizing agents to prevent its combustion, and being a good electrical conductor, the furnace must be constructed so as to avoid short-circuiting by the carbon lining.

While electrometallurgists have been casting about for suitable refractory materials, they have usefully applied the electric furnace in the production of such materials. Carborundum is a refractory material, being suitable for certain purposes, and a newly discovered compound, designated "siloxicon," has been shown to have admirable qualities as a refractory material. It consists of a combination of carbon, silicon, and oxygen and is described as being very refractory to heat, insoluble in molten iron, indifferent to all acids save hydrofluoric, and self-binding to such degree that no binder is necessary in forming crucibles, furnace-linings and fire-bricks from it. FitzGerald also calls attention to other refractory materials which can be formed in the electric furnace. (See Electrochemical Industry, Dec., 1904.)

The resistance medium or "resistor," when solid, usually consists of a core of carbon, coke, or graphite, the technical features governing the use of which are ably discussed by FitzGerald. Metals may also be used, as in the well known platinum resistance furnace. Many other substances are available especially when we include those compounds which at ordinary temperatures are insulators, but which become conductors upon heating. Where such materials are used provisions are necessary for starting, somewhat similar to that used for starting the Nernst lamp, which, indeed, is a miniature electric furnace whose principles of construction may well be applied to furnaces of larger size.

Examples of liquid resistance materials are the aluminum furnace, and certain types of electric furnaces which have been applied for the melting of iron, steel, and other metals. Gaseous resistance mediums are utilized in the various arc furnaces and in the processes used for the production of nitric acid from the air.

The electrode problem is one that presents difficulties to the furnace designer. Baked carbon and graphite are by far the most important electrode materials. An ideal electrode material should possess high electrical conductivity, have little deterioration, not react chemically with the heated material with which it makes contact or introduce impurities into the charge. Carbon and graphite while fulfilling these requirements better than any other available materials are still very deficient as shown by the fact that electrode consumption constitutes a large proportion of the cost of various industrial operations and, in fact, is the real barrier to the commercial success of various promising processes. The electrode which usually projects a certain distance outside the furnace will burn away unless protected from the air. Various methods have been adopted for doing this, such as encasing in a thin iron covering, or keeping it cool by a continual stream of water. In some of our experiments at the University of Wisconsin it has been found that certain fused substances could be formed on the surface making a layer of glass completely excluding the air, and protective even at a white heat.

Iron and certain other metals may in some cases be used as electrodes where carbon is prohibited, and to ensure their durability they are kept cool by a continual stream of water. This protection is afforded by a decrease of efficiency, due to the carrying away of considerable quantities of heat.

Another problem, which is by no means insignificant, is the matter of electrode connection. It is difficult to ensure good conductivity between a metal in contact with carbon or graphite, and poor contact results in excessive development of heat at that locality. The brittle and fragile nature of the electrode materials preclude tight clamping. One of the leading electrometallurgical companies using graphite electrodes in a process in which that material suffers little or no corrosion, nevertheless was a large consumer of graphite, as the unequal expansion of that material and the metal terminals to which contact was made caused much breakage.

An ingenious form of furnace which avoids electrode difficulties by eliminating the electrodes altogether has been developed. This is accomplished by causing the resistance material to constitute the secondary of a transformer. This induction type of furnace can be used only to heat materials having a good conductivity such as a melted metal, since it is not possible to set up a high pressure in the secondary of a transformer, when the secondary consists of a single turn. A furnace of this type is reported to be in successful use for the melting of iron and the production of steels. While it is true that electrode difficulties are thus eliminated, additional complications arise as the heating trough must be long and narrow, conducing to excessive radiation and low efficiency; the core of the transformer and the primary windings must be kept cool, to do which still further lowers the percentage of useful heat; and the construction of the transformer is necessarily such as to give it a low efficiency and low power factor.

The provisions for feeding and emptying the furnace have much to do with its successful operation and many laboratory processes fail commercially on this ground. The laboratory furnace is necessarily an intermittent one, as it is usually necessary to cool down and take the furnace apart to recover the charge. To a certain extent the intermittent furnace has been successful industrially, the carborundum furnace being an example. Calcium carbide was made exclusively by the intermittent process until commercial conditions demanded continuous operation and a complete reconstruction of the forms of furnaces to attain it. The ultimate success of the industrial application of the electrical furnace demands that it be so constructed that material can be fed to it continually and the finished material likewise extracted, for its efficiency is thus greatly enhanced, the load on the generators is maintained constant, uniformity of product is ensured, and equipment can be used with greatest efficiency. Continuous operation also calls for the escape of gaseous products, or any slags or other by-products which are formed.

It was previously pointed out that the degree of temperature, control of speed of operation, and speed of gradation from one temperature to another are subject to the will of the operator. This is true, however, only when he has suitable regulating devices and apparatus, the design and construction of which lies wholly within the province of the electrical engineer. Where the furnace furnishes an absolutely constant load the problem becomes simple, but is almost too ideal to be considered. Even where operation is continuous, any change in the rate of feeding or the withdrawing of the material, inequality of the material, outside temperature, etc., introduce variations, allowance for which must be made by the operator. For constant current working, regulating devices similar in principle to those of the arc lamp may be provided, and in fact some of the furnace patents have simply been arc lamp patents slightly modified. The regulation must be effected in such manner that short-circuiting or sudden change in the resistance in the furnace shall not harm the generating system, or interfere with the operation of other furnaces receiving power from the same generators. In intermittent working, the regulating apparatus must permit adjustment from no load to full load, either gradual or rapid as the case may demand. The alternating current has naturally lent itself more satisfactorily than the direct and consequently is used almost exclusively. Multiphase currents are in many cases superior to the single phase on account of the more even distribution of heat, and the use of such currents introduces additional electrical problems.

COMPARATIVE EFFICIENCY OF THE ELECTRIC FURNACE.

It has been pointed out that the electric furnace has won an industrial position, not as a competitor of the combustion furnace, but rather in the field of high temperature working where the latter cannot enter. To a small extent, however, it has become a rival to fuel furnaces owing to certain advantages it possesses, such as safety to workmen and purity of product. As an example of this, take the manufacture of carbon bisulphide and phosphorus, most of which is now produced electrically. Only a few years ago it was generally predicted that there was little possibility of the electric furnace being so developed as to compete with ordinary metallurgical furnaces in the production and treatment of metals such as iron, steel, copper, lead and zinc. While it was admitted that perhaps the electric furnace might ensure lower labor and depreciation charges, less waste of material, higher quality of product and other advantages, it was stated that the cost of electric energy was so much greater than an equivalent amount of heat energy, derived directly from combustion, that no possibility of equal economy could exist. Calculation, as well as recent developments, shows this view to be erroneous.

Assuming that coal at $2.50 per ton has a calorific value of 14,000 B. T. U. the quantity of heat energy obtainable for one dollar is 11,200,000 B. T. U. One electrical horse-power-year has for its heat equivalent 22,400,000 heat units. If electrical horse-power-year generated by means of steam be assigned a value of $50, one dollar will produce about 450,000 B. T. U. Assuming equal efficiency in the utilization of the heat derived from the two sources the ratio of the cost of energy is as one to twenty-five. This discrepancy shows the handicap which steam-generated electricity has for electric furnace operation. The development of enormous water power has resulted in great reduction in the cost of generating electrical energy in certain localities. There has been much discussion of late as to how cheaply hydraulically generated electrical power can be produced. In the report of the Commission appointed by the Canadian Government to investigate electrometallurgical process a value of $10.00 per horse-power-year was given as a reasonable estimate. At this figure, the heat units per dollar becomes 2,250,000, which is about one-fifth that obtainable from one dollar's worth of coal.

The question of efficiency of heat utilization comes in to even up matters still more. It is a well known fact that the efficiency of the combustion furnace is less than 100 per cent by an amount dependent upon the heat which is radiated or conducted away from the furnace, that which goes up the chimney with the products of combustion, and various other minor losses. The percentage loss increases with elevation of temperature, and at a rapidly increasing ratio as the temperature rises.

The efficiency of the ordinary furnace for steam generation is not far from 60 per cent, this high value being attained by the low temperature, about 250° C., to which the steam is heated. The metallurgical furnace having the highest efficiency is the blast furnace for the production of pig iron, which has a thermal efficiency of from 50 to 80 per cent. This exceptional economy is due to the fact that the fuel is in direct contact with the material to be heated, producing a direct transference of heat. However, for this purpose, the cheaper grades of fuel cannot be used, a hard pure coke or charcoal being required at a cost several times greater than that for the cheaper kinds of fuel.

In the reverberatory furnace, in which the products of combustion pass directly over the charge to be heated, the efficiency is much lower, and a still lower value is obtained in those furnaces in which the heat must pass through refractory walls. In such crucible, muffle, and retort furnaces the efficiency varies from 2 to 10 per cent.

Table I gives results of efficiency calculations on several types of furnaces, as compiled from various authorities:

TABLE I.

Product	Type	Thermal Efficiency
Steam		50-60%
Cast Iron	Blast	52-66%
Steel	Acid Process	11.9
Steel	Basic Process	10.0
Pig iron	Reverberatory	8.5
Wrought iron	Reverberatory	5
Steel	Siemens Crucible	4
Steel	Greenwood Crucible	2
Zinc	Retort	2 to 3

The values of efficiency given for steel and wrought iron are based upon comparisons of the heat theoretically required to raise the metal to the molten state, with that furnished by the amounts of coal used in the practical operation of the various processes and assuming a calorific value for the fuel of 14,000 B. T. U.

Captain Stassano (Report of Canadian Commission, p. 180) says that "the utilization of the potential heat of the fuel in the ordinary furnaces is maintained to a very limited and low degree, varying, in fact, from 2 per cent to 3 per cent and even less, in the ordinary fires of a forge, rising to 10 per cent in the common reverberatory furnace, and reaching the maximum of 18 per cent to 20 per cent in those modern gas furnaces with regenerators (Martin-Siemens' Type)."

ELECTRIC FURNACE EFFICIENCY.

The simplest and most easily effected of the energy transformations with which we have to deal is the change of electrical into heat energy, such transformation being easily effected at an efficiency of 100 per cent. This cannot, however, be taken as the value for electric furnace efficiency, for we can consider only that heat which is usefully applied. The heat usefully applied may be that required for melting or volatilizing a substance, or for producing other desired physical or chemical changes in it, and it is this amount of heat as compared with the total heat equivalent delivered to the furnace that determines its efficiency. Prof. Jos. Richards (Trans. Am. Elec. Chem. Soc., Vol. 2, 1902) discusses electric furnace efficiencies at length, and from his calculations Table II is compiled:

TABLE II.

Type.	Product,	H. P.	Temperature.	Efficiency
Acheson	Graphite	1,000	3300° C	75%
Jacobs	Fused Al_2O_3	200		74%
Acheson	Carborundum	1,000	3000°	76.5%

The conclusion is drawn that a commercial efficiency of 75 per cent is readily obtainable in electric furnaces ranging in size from 200 to 1,000 H. P., and this value can undoubtedly be raised by increasing the size and bettering the construction as regards heat insulation.

The estimates of efficiency at high temperatures can be only approximations, for ignorance regarding specific heats of material at such temperatures is a bar to exact calculations.

From previous calculations it can be seen that the industrial electric furnace operates at an efficiency over five times as great as that of the industrial combustion furnace, and consequently electrical energy at $10.00 per year can compete on an even basis with coal at $2.50 per ton.

The electric furnace efficiencies, as calculated by Richards, are obtainable while working at temperatures of 3,000° and above, which is far in excess of that attainable in combustion furnaces. A comparison even more favorable to electrical heating may be obtained where the electric furnace is applied to lower temperature working, such as in the metallurgical treatment of iron and steel. Sir William Siemens found an efficiency of 50 per cent in utilizing 2-horse-power for melting iron, and with such efficiency attainable in a small laboratory furnace, the larger industrial furnaces ought to be nearer 100 per cent than 50 per cent. Captain Stassano, from calculation and experience, says that the electrical steel and iron furnace can be safely assumed to have an efficiency of 80 per cent.

Of such great promise is the use of electrical energy in the metallurgy of iron and steel that the Canadian Government appointed a Commission to thoroughly investigate the state of the art. The report, which has recently been distributed, is a most important addition to our electrometallurgical literature and will undoubtedly do much toward establishing confidence in electric furnace methods. Table III gives extracts from this report, the figures being obtained by tests which the Commission made upon various processes in operation in Europe:

TABLE III.

Process	Product	Mean H. P.	H. P.—year per ton of product	Power Factor	Frequency
Heroult	Pig Iron	248	.47	75 (about)	80
Keller	Pig Iron	834	.475	73.7	50
Keller	Pig Iron	308	.229	56.4	37
Kjellin	Steel	195	.116	67.2	15
Kjellin	Steel	203	.145	64.9	15
Heroult	Soft Steel	480	.153		33
Heroult	Tool Steel	462	.153		33
Heroult	Structural Steel	465	.10		33
Keller	Steel	240	.112	85 (about)	40

"Coke used in crucible melting in Sheffield to-day probably varies from 2 to 3½ tons per ton of steel produced, and even in the large gas fired furnaces employed in America and Germany probably one ton of slack, costing not less than $2.50, is necessary."

The .15 H. P.-year necessary to produce one ton of steel by the electrical processes has for its heat equivalent 3,360,000 B. T. U. and one ton of coal at 14,000 B. T. U. per pound has a value of 28,000,000 units. If the gas firing process be assumed to have 10 per cent efficiency, the efficiency of the electrical process figures out about 80 per cent, thus confirming previous estimates.

To quote from the "Conclusions" of the Report, we have the following significant statements:

1. "Steel, equal in all respects to the best Sheffield crucible

steel, can be produced by the Kjellin, or Heroult, or Keller process at a cost considerable less than the cost of producing a high class crucible steel.

8. "Pig iron can be produced on a commercial scale at a price to compete with the blast furnace only when electrical energy is very cheap and fuel very dear. On the basis taken in this report, with electrical energy at $10.00 per E. H. P.-year, and coke at $7.00 per ton, the cost of production is approximately the same as cost of producing pig iron in the modern blast furnace."

The report of the Canadian Commission demonstrates the possibility of employing electric heating for low temperature furnace working by showing that it has an opportunity in the metallurgy of iron and steel. This was deemed only a most remote possibility a few years ago. Now if the metallurgy of iron can find a place for the electric furnace, how much greater opportunity there is for it in the successful treatment of some of the other metals. The present methods of extracting zinc are notoriously inefficient. Not only is the 80 per cent efficiency of the electric furnace as compared with the 3 or 4 per cent efficiency of the ordinary zinc furnaces capable of resulting in an economy, but various other advantages may be attained as well. The cost of zinc production under present conditions involves incomplete extraction from the ore, absorption of zinc by the walls of the retorts, rapid destruction of retorts, and losses in the condensation of zinc. Electric furnace methods present opportunities for materially remedying these defects. In laboratory trials made at the University of Wisconsin it has been found possible to completely extract the zinc, so that none of it remains in the charge or is retained in the walls of the furnace. No practical form of furnace for this purpose has been evolved, however, the principal difficulty being in effecting continuous operation, a requirement which is almost imperative.

It is of importance that our metallurgists should continue their researches in the practical application of the electric furnace to the smelting of copper and other ores, not only those which are now successfully treated by other methods, but more especially that large class of ores which has proved refractory to all economical processes so far as known.

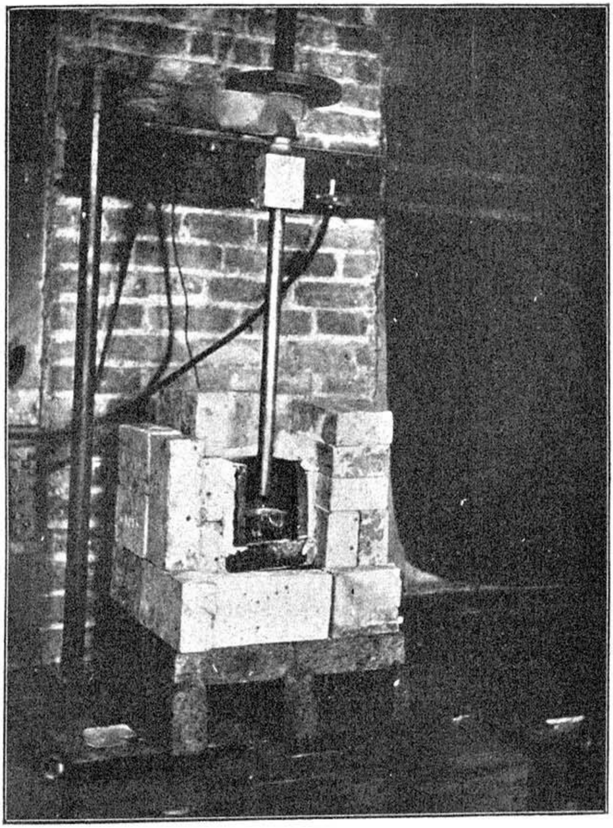
Various miscellaneous applications of minor importance might be cited. The electric welder is essentially an electrical furnace which has been most successful industrially. We have been working in our laboratory on an electric furnace for the tempering of high melting tool steel with considerable success, the process consisting in maintaining a fused bath at a high temperature and immersing the steel to be treated in it.

The electric furnace seems to point the way to a limitless outlet for all the electrical energy which can be developed. The pessimist who points to the calcium carbide industry to support his claim that the electric furnace has been over-developed takes an extremely narrow view. It is true that the enthusiasm with which investors went into the carbide industry resulted in overproduction and a consequent failure of some of the plants, but instead of being a setback for the electric furnace it has been an advantage. The strenuous efforts to find uses for the furnace equipment in other directions has resulted in a successful production of iron and its various alloys. Recent experimental work seems to indicate that calcium carbide will work out its own salvation. It has been discovered that if calcium carbide be heated in the presence of nitrogen, which may be obtained from the air, a calcium cyanamide is formed which, when treated with steam, forms ammonia, and when treated with water and fused with sodium carbonate gives sodium cyanide and ammonia. In other ords, it constitutes a process for fixing the nitrogen of the air.

In this connection may be noted a new and interesting apparatus which might properly be classed as an electric furnace and which is used for making nitrogen compounds from the air by means of electrical discharges. A paper presented at the meeting of the International Electrical Congress a few months ago in St. Louis, giving the results of tests on a new method by Prof. C. Birkeland and Mr. Eyde of Christiana, shows that it is possible to produce 1,490 lbs. of nitric acid per horse-power year, from which can be made calcium nitrate and other nitrates of unlimited usefulness to agricultural interests. The world is facing the possible calamity of an exhaustion of the nitrate beds of Chili, which according to estimates cannot continue to supply the demand for sodium nitrate for more than forty or fifty years. This sodium nitrate, selling at 2 cents per pound, and used chiefly as a fertilizer has its chief value in its content of nitrogen, and the cost of nitrogen per pound from this source is about 12 cents. According to Prof. Birkeland's statement one pound of nitrogen in the form of nitric acid can be produced electrically for an expenditure of power of about 3 cents. The energy consumption is not, therefore, an effectual barrier to the economic production of nitrogen compounds from materials which are most abundant and inexhaustible, and a process worked out along such lines will probably be ready for adoption on a large scale before nature's store of valuable nitrates becomes exhausted.

DISCUSSION.

Mr. A. Bement—M. W. S. E. (by letter)—I observe that it is stated that Siloxicon is self-binding to such a degree that no special binder is necessary in forming crucibles, etc., and would ask how such crucibles are fired. It is my understanding that Siloxicon requires a binder, at least if it is to be fired with combustion of carbon or hydrogen. It may be, however, that if the electric furnace was used, that it could be fused without a binder, and this is the point upon which I seek information.



Section of Vertical Laboratory Electric Furnace.

I observe a repetition of an old statement that CO instead of CO_2 is produced at high temperatures. I would like very much to have this matter explained. It is unreasonable to have a high temperaure accompanied by the production of CO, because then heat is liberated only to a small extent, and high temperature cannot be had without large heat development. It is not altogether clear to me whether Prof. Burgess means that this is the condition which prevails with combustion in air or oxygen. Personally, I know that maximum or theoretical CO_2 may be secured in the combustion of carbon and hydrogen with coal. I should appreciate it very much if Prof. Burgess will explain this matter.

I would ask whether the temperatures are all given in Centigrade degrees.

The efficiency of 60 per cent. secured in steam generated as given in this connection is too low, because an efficiency of 80 per cent. is attainable and I suppose the efficiencies for the electric furnace are given on the same basis, therefore the efficiency of steam production is greater than here intimated; in fact, the efficiencies of these various methods do not differ much.

Prof. Burgess—The statement that siloxicon has self-binding properties is based upon information received from an engineer who has thoroughly investigated the material. If the siloxicon is finely powdered, molded, and then fired in an oxidizing atmosphere, the free carbon is oxidized and there is also a surface oxidization of the silicon carbon compound, the resulting silica giving a bond which has a certain degree of mechanical strength.

In reply to the question concerning the production of carbon monoxide instead of carbon dioxide I would say that it is a well-known fact that carbon dioxide begins to dissociate to a marked degree at temperatures of about 1,800 deg. C. and the dissociation increases as the temperature is elevated. Until such point is reached that complete dissociation of the carbon dioxide occurs, giving carbon monoxide and oxygen. The mere fact that carbon dioxide cannot exist at the highest temperatures shows that we cannot utilize all of the heat units stored up in carbon when the highest degree of temperatures are required.

The statement that a steam generating furnace can operate at an efficiency higher than 60 per cent. cannot be denied. I took 60 per cent. as being perhaps the average of steam generating furnaces as they are ordinarily operated and not as they can be operated when the highest degree of refinement is observed. In a like manner I have not assumed 80 per cent. as the highest electric furnace efficiency. It is quite possible that the electric furnace can be operated at an efficiency considerably above 80 per cent. if the heat in the material drawn from the furnace can be made to pass into the material as it is introduced into the furnace.

Prof. D. C. Jackson—M. W. S. E.—I know little about the electric furnace, except, perhaps, in regard to the cost of developing and maintaining laboratories relating to applied electrochemistry.

I have great confidence in the future of the electric furnace as a revolution producer. It has already revolutionized some of the ideas of those most deeply versed in chemistry, and it will certainly revolutionize many more and after having done that, it will revolutionize some of the processes of manufacture which we now know well, and consequently may change the value of things in such a way as to revolutionize some of our modes of life.

The electric furnace is really not known today as it will be in a very few years. Prof. Burgess' prophecy, I am sure he himself thinks, is a very conservative one.

Mr. Lubberger— M. W. S. E.—I am very much interested in the problem of the electric furnace from another point of view. I am looking up all the literature I can get hold of on the subject of radium.

It seems to me that an electric furnace does not work by its heat alone, but by direct action. In the experiments at Niagara Falls, as far as I know, the nitric acid was made by electric sparks; on the other hand, nitric acid is also made in arcs of large current capacity and high temperature.

As you probably know, radium is supposed to consist of electrons, which are quickly moving particles. If such a particle runs against another particle, there is simply a mechanical collision, and in an electric furnace the moving electrons cause really a series of mechanical, and by this, also, chemical changes. I would like very much to know if anything in the line of electronal action has been investigated, or if this direct mechanical motion is responsible for these chemical changes in the electric furnace.

Prof. Burgess—The exact part which the electric arc plays in the production of nitric acid is perhaps not well understood. It is generally assumed that a discharge of electricity through a mixture of nitrogen and oxygen will cause a union of the two gases, but whether it is by the heating effect alone or by a sort of catalytic effect of the discharge is perhaps difficult to determine. I believe that Mr. Lubberger is entirely correct in assuming that something else beside great heating is active in producing the chemical changes which are brought about in the electric furnace.

Mr. Warder—I would ask the Professor if he cannot tell us something about the fused quartz as a glass for astronomical purposes. It is being claimed that it possesses certain very great values for certain special astronomical research.

Prof. Burgess—Fused quartz or melted silica constitutes a remarkable physical material, although to what extent it has been successful as a substitute for glass in astronomical apparatus I cannot say. Vessels made from fused quartz have been available only during the past few years and it was not very long ago that the price of a small silica crucible was ten dollars. Such a crucible, looking like glass, will stand a temperature about 800 degrees higher than ordinary glass and it is not affected by the greatest fluctuations in temperature no matter how suddenly applied Fused quartz is not hygroscopic, is insoluble in water and unaffected by most chemical reagents, and is therefore a most valuable material for most scientific purposes.

The earlier methods of building up these crucibles was by utilizing the hydrogen flame, melting a grain of silica and fusing it to the main body until a structure of the desired size and shape was attained. Considerable improvement has been made and the electric furnace has become of considerable use in the manufacture of fused quartz apparatus. One of the principle difficulties in making the transparent quartz is the elimination of the bubbles of gas. There does not seem to be much difference between the softening and boiling points of silica, and consequently it is almost impossible to get it perfectly fluid so that the contained gases can readily rise to the surface.

For many purposes, however, transparency is not essential and quartz tubes can be made which resemble porcelain in appearance by drawing an arc in a bed of pure quartz sand.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 25, 1905. President Carhart in the chair.

NOTES ON ECONOMIC TEMPERATURES OF COPPER-REFINING SOLUTIONS.

BY CHARLES F. BURGESS.

The temperature co-efficient of metallic conductivity is an important factor which enters into the calculations of the electrical engineer in his design of electrical conductors and apparatus. The temperature co-efficient of electrolytic conductivity, on account of its much greater magnitude, is a factor of correspondingly greater importance to the electrochemist. Unfortunately, however, the constants in the latter case are much more uncertain, and have not been worked out to the degree of accuracy as have metallic conductors.

That the electrochemist is dependent more upon experimental trial than upon well-known data in the determination of his constants is demonstrated in the admirable paper presented by Dr. Bancroft before this Society on "Electrolytic Copper Refining." (Vol. IV, Transactions). This paper contains various suggestions relative to the economical refining of copper, an important one of which is that greater economy can be effected if the solutions are run at a higher temperature than has been commonly adopted by the refineries.

The pressure between the two electrodes of a copper-refining tank is the sum of two quantities, the polarization pressure and the drop caused by the current flowing through the electrolyte. The former is small and may be considered as practically constant for a given solution, being influenced very slightly by the temperature. The IR drop through the electrolyte varies, however, in a marked degree with change of temperature, and it is this variation which causes the falling off in applied pressure necessary to pass a given current through the cell as the temperature rises.

Abstracts from the data given in the paper above referred to show that with copper electrodes one centimeter apart, in a solution containing 16 per cent. copper sulphate crystals and 9 per cent. free acid, and with a current of 3.5 ampères per square decimeter, the pressure at the electrode terminals is, for various temperatures, as given in Table I.

TABLE I.

Temp.	Voltage at Electrode Terminals	In Terms of Voltage at 20°
20°	.354	100
30	.298	84.2
40	.248	70
56	.217	61.3
60	.188	53
70	.165	46.6
80	.142	40
90	.129	36.4

From these figures it appears that the pressure at 70 degrees is less than half that required at 20 degrees for the same current, and consequently that the cost for power is less than one-half. It is stated that "by expressing voltage in terms of the voltage at 20 degrees," as is done in column 3, "the effect of the distance between the plates is eliminated," and that "the percentage variations hold for any set of plates in the same solution."

This assumption, which served as a basis upon which various conclusions were drawn, would undoubtedly be correct if we are concerned only with the specific resistance of the electrolyte itself, but since it is the virtual resistance between the electrodes that is involved, the assumption is not justified.

The resistance of the cell includes the resistance between the electrode surfaces and the electrolyte, and the resistance of the electrolyte itself. The former is of considerable magnitude in comparison with the latter when the electrodes are close together, and of much less relative magnitude when a considerable column of electrolyte intervenes. The temperature co-efficient at the electrode surface resistance is much greater than the temperature co-efficient of the electrolyte, and unless these separate resistances and their corresponding temperature co-efficients be known, it is impossible to calculate the temperature co-efficient of the complete cell with electrodes five centimeters apart from measurements on electrodes one centimeter apart.

The following experiments bearing on this point were performed: A solution consisting of 160 g. $CuSO_4 \cdot 5H_2O$ and 90 g. H_2SO_4 per liter was employed. Two copper plate electrodes, 2 inches wide, completely occupied the cross-section of a rectangular glass vessel, 2 inches x 5 inches x 5 inches deep. Electrodes were first placed 4½ inches apart, with the electrolyte 2¼ inches deep, and a current of about one ampère applied. The glass trough was heated by means of a water bath and, with constant stirring, the temperature was gradually raised. A similar run was made with the electrodes placed about ⅜ inch apart. The observations are given in the following tables. Measurements of current and pressure were made with Weston portable instruments recently calibrated.

TABLE II.

With electrodes 4½ inches apart.

Temp.	Voltage at Electrodes.	In Terms of Voltage at 20°
20°	1.57	100
23.5	1.5	95.5
31	1.35	86
41	1.22	77.7
49	1.17	74.5
60	1.1	70
67	1.07	68

TABLE III.

With electrodes ⅜ inch apart.

Temp.	Voltage at Electrode Terminals.	In Terms of Voltage at 20°
20°	.36	100
24	.32	89
30	.27	75
38	.22	58
46	.18	50
52	.16	44.5
60	.14	38.9
67	.13	36

The counter e.m.f. taken upon interrupting the current was constant at about .025 volt.

The tables II and III, and corresponding curves, Fig. 1, show clearly that the lowering of voltage is not proportional to the increase of temperature regardless of the distance between the plates, but that on the other hand the temperature effect is far more marked when the electrodes are close together than when they are far apart. In other words, the apparent temperature co-efficient is dependent upon the distance between electrodes, being greatest when the electrodes are close together.

We are not, therefore, warranted in saying that the most economical temperature in a cell with the plates one centimeter apart is the most economical for a cell with the plates ½ inch or 1½ inches apart, as in the series and multiple refining systems respectively.

An explanation for this marked variation in temperature co-efficient with various distances between electrodes is afforded in that phenomenon which Gore chose to call "transfer resistance." "Transfer resistance," as defined by him *(Phil. Mag.* V. 21, 1886, p. 130), is "a species of electric resistance distinct from that of polarization and ordinary conductive resistance, varying greatly in amount in different cases, which exists at the surfaces of mutual contact of metals and liquids in electrolytic and voltaic cells," and "this resistance varies largely in amount with different metals in the same solution, and with the same metal in different solutions." Gore measured the effect of this "transfer resistance"

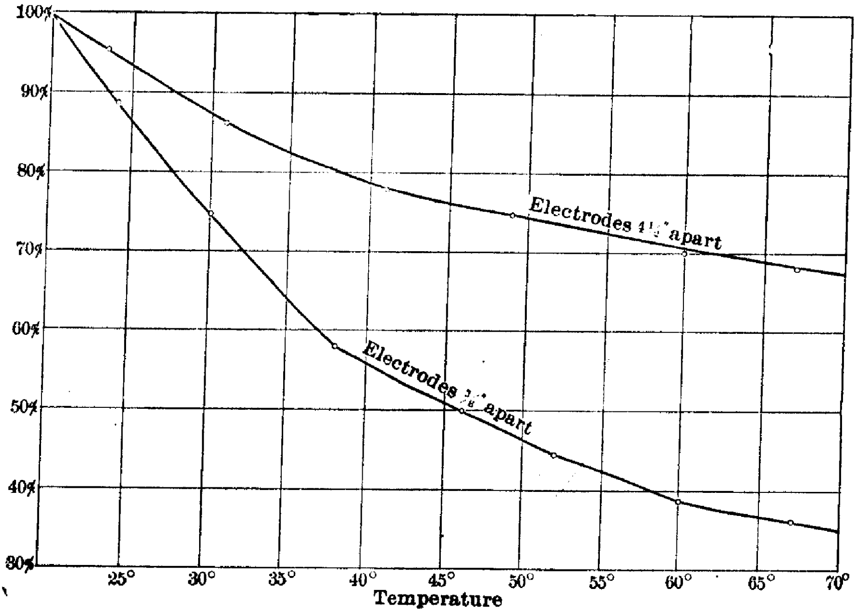


Fig. 1

by means of the heating effect on the air inclosed in a thin platinum electrode, as well as by other means described in later papers published in the same volume of the *Philosophical Magazine*.

A distinction is made between the term "transfer resistance" and "surface resistance," the latter including the changes in the electrolyte produced by electrolysis. It was found that in general this resistance is greater at the cathode than at the anode, and that by increase of temperature the transfer resistance is usually and considerably reduced. In a short-circuited cell, using a platinum cathode and zinc anode, he states that raising the temperature from 14 degrees to 95 degrees increased the e.m.f. by 8.38 per cent., while the amount of current flowing was 220 per cent. greater, this being due largely to the decrease of the "surface resistance."

If there exists, therefore, a resistance at the electrode surface apart from the resistance of the electrolyte itself, of such nature that it has a great temperature co-efficient, we have an explanation of the dependence of the apparent temperature co-efficient of an electrolyte upon the distance between the electrodes, the reduction of the "transfer resistance" producing a greater proportion of the total change when the electrodes are close together than when farther separated.

To obtain additional and more accurate data upon this phenomenon, a rectangular slate tank, of the dimensions 2½ inches x 6 inches x 6 inches deep, was fitted with copper electrodes, one set being accurately spaced at ⅜ of an inch apart, and another set at 1½ inches. The electrodes fitted so closely in the cell that only one side of each plate was active as an electrode surface. The solution used was a 16 per cent. $CuSO_4$ $5H_2O$ and 9 per cent. H_2SO_4. The tank was heated over a sand bath, the electrolyte being stirred to maintain uniformity and avoid concentration effects.

In Table IV are given data showing the effect of increase of temperature on the resistance. The columns marked "apparent specific resistance" give the resistance per cubic inch as calculated from the current and applied pressure; those marked "corrected specific resistance" give the values obtained by deducting the polarization pressure, which was determined by the voltmeter immediately after interrupting the current. The electrolyte was not heated beyond 56° C, on account of the failure of the cement of the tank to stand a higher temperature. The current of one ampère had a density of 20.8 ampères per square foot.

TABLE IV.

Electrodes ⅜″ apart.			Electrodes 1⅝″ apart.	
Apparent Sp. Res.	Corrected Sp. Res.	Temp.	Apparent Sp. Res.	Corrected Sp. Res.
3.95 ohms	3.74 ohms	29° C	2.16 ohms	2.105 ohms
3.12 "	2.91 "	40 C	1.85 "	1.79 "
2.70 "	2.50 "	50 C	1.64 "	1.59 "
2.50 "	2.29 "	56 C	1.56 "	1.51 "

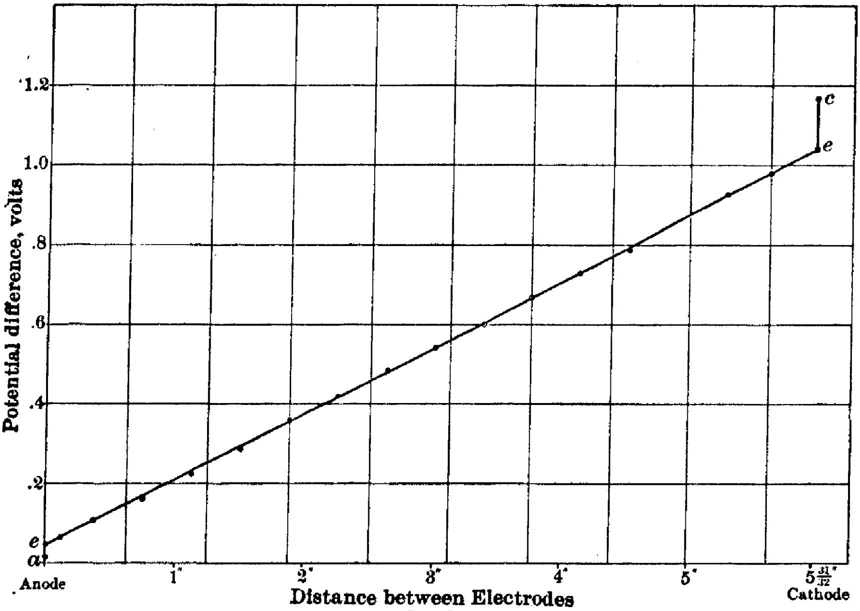


Fig. 2

It is to be noted that while the specific resistance with the plates close together decreased 36.7 per cent. for an increase of temperature of 27 degrees, the specific resistance with the plates farther apart decreased only 27.7 per cent.

To determine what influence the free acid might have on this variation of specific resistance, a run similar to the preceding was made, using a neutral solution of 16 per cent. copper sulphate crystals. Table V gives the results of this run.

TABLE V.

Electrodes ⅜" apart.			Electrodes 1½" apart.	
Apparent Sp. Res.	Corrected Sp. Res.	Temp.	Apparent Sp. Res.	Corrected Sp. Res.
11.85 ohms	11.73 ohms	32° C	11.00 ohms	10.97 ohms
11.45 "	11.30 "	37 C	9.97 "	9.95 "
10.82 "	10.67 "	40 C	9.60 "	9.57 "
9.96 "	9.86 "	46 C	9.20 "	9.17 "
9.55 "	9.48 "	50 C	8.73 "	8.72 "
9.35 "	9.30 "	52 C	8.63 "	8.60 "

The specific resistance is seen to decrease 21 per cent. with electrodes ⅜ inch apart, and 21.5 per cent. with the electrodes spaced 1½ inches. From this it may be concluded that the change of resistance with temperature is due almost entirely to temperature co-efficient of the electrolyte itself, and not partially to electrode effects, as is the case when the solution is acidulated.

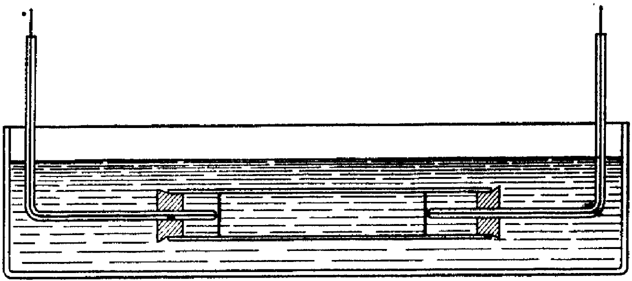


Fig. 3

A further analysis of the electrode effect was made by tracing the fall of potential from the anode to the cathode. This was done by means of the normal "calomel" electrode, the liquid terminal of which consisted of a glass rod drawn to a fine point and bent in such a way that it could be placed in contact with the electrode, and then moved step by step measured distances toward the other electrode. The potential differences between the normal electrode and the copper electrode were measured by the well-known potentiometer method.

The data relating to this test are given in Table VI, and the results plotted in Fig. 3.

TABLE VI.

Current p 1 amp. = 18.9 amp. per sq. ft.
Distance between electrodes = 5-31/32".
Solution: 160g. cuSO$_4$ 5H$_2$O and 90g. H$_2$SO$_4$ per liter.

Temperature = 22° C.
Measurement of fall of potential made by means of glass rod terminal of calomel electrode drawn to a fine point and placed at various distances from the electrodes.

Distance of normal electrodes terminal from anode.	Volts.	
0	.0106	=anode polarization.
0	.0424	=potential between electrode and solution.
⅛"	.0635	
⅜	.106	
¾	.163	
1-⅛	.222	
1-½	.286	
1-⅞	.354	
2-¼	.413	
2-⅝	.477	
3	.536	
3-⅜	.600	
3-¾	.664	
4-⅛	.725	
4½	.787	
4⅞	.850	
5¼	.916	
5⅝	.980	
5-31/32	1.037	
5-31/32	1.176	= potential between anode and cathode.

Total polarization as measured by voltmeter = 0.2 volt.
Cathode polarization = .0106. Anode polarization = .0094.
Specific resistance, eliminating electrode effect = 1.26 ohms per cubic inch.
Specific resistance, as calculated from current and applied pressure = 1.5 ohms.
Specific resistance, as calculated from current and applied pressure, with electrodes 1-½" apart = 2.12 ohms.
Specific resistance, with electrodes ⅜" apart = 4.67 ohms.
Specific resistance, with electrodes ⅛" apart = 11.46 ohms.

It is to be noted that the fall of potential through the electrolyte is represented by a straight line, which is to be expected if a solution of constant composition be maintained by suitable stirring. The polarization, as measured by the voltmeter upon interruption of the current, was .02 volt, apportioned nearly equally to the two electrodes. There is a resistance effect at the surface of the copper electrodes, causing a fall of potential much more marked than the polarization effect. This surface resistance appears to be considerably greater at the cathode than at the anode, as shown graphically by the vertical lines *ec* and *ae*, respectively.

It might be urged that this marked drop of potential at the electrode surfaces is due only to polarization, and that the method of measuring polarization by opening the circuit gives only a portion of the total value. This is hardly possible, however, since a polarization of about .2 volt would have to be assumed, which is apparently out of the question.

Neither does it appear to be due to changes of composition of the solution as a result of electrolysis, since in this case the effect would be materially decreased by agitation of the electrolyte. In making the measurement it was noted that the agitation of the solution had very little influence on this surface resistance.

The question arises as to whether this surface resistance is an inherent mutual property of the metal and the solution, or whether it is produced as a result of the flow of current. It is apparent that the flow of current has some influence on the amount of the resistance, as shown by the fact that it is different at the two electrodes when a direct current flows. Mr. O. P. Watts has given me permission to quote from his laboratory notes some data bearing upon this point.

A glass tube, as shown in Fig. 3, was filled with a copper sulphate solution containing 100 grammes of the crystals and 100 grammes of sulphuric acid to the liter. Copper disc electrodes closely fitting in the tube were adjusted by means of a glass tube passing through the rubber stopper at either end of the tube. The specific resistance of the electrolyte maintained at 23° C, by immersion in a constant temperature bath, was determined first by means of an ampèremeter and a voltmeter, using a current density of 4.2 ampères per square decimeter, and then by the Wheatstone bridge method, using an induction coil as the source of current and the telephone receiver as the detector. In Table III, column 2, is given the apparent resistance per cubic centimeter by means of the fall of potential method, and in column 3 similar values by the bridge method.

TABLE VII.

Distance between Electrodes.	Ohms per c. c. By Ammeter and Voltmeter.	Ohms per c. c. By Wheatstone Bridge.
20	2.02	1.84
18	1.95	1.79
16	2.04	1.81
14	2.01	1.82
12	2.08	1.83
10	2.09	1.88
8	2.26	1.81
6	2.38	1.95
4	2.74	2.03
3	3.17	2.19
2	3.81	2.43
1	6.19	3.24

The apparent specific resistance with the electrodes one centimeter apart is about three times as great as the true specific resistance when the direct current is flowing, and when the very small alternating current, the distance is not so great, though it is still quite marked. This shows, therefore, that the electrode effect is not a result of electrolytic products, since it also accompanies the flow of alternating current of such small value as to make the accumulation of electrolyte products impossible.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

PRESIDENT CARHART: Mr. Burgess' paper is open for discussion. I am sorry Professor Burgess is not here to discuss it.

PROF. W. S. FRANKLINS I am surprised to hear the author set aside, as being out of the question, the existence of as much as 0.2 volt of polarization in the neighborhood of a copper electrode. The results of Mr. Freudenberger and myself, as found with copper electrodes, show the existence of polarizations running up to 0.1 volt with current densities which, I take it, were much smaller than those which Professor Burgess used. The table given by Professor Burgess on page 58 is a table of observed electromotive forces which can be separated into two distinct parts, one of which is proportional to the distance between the electrodes, namely, the *ri* part, and the other is constant in value. It is upon a set of observations exactly like this that Mr. Freudenberger and I separated the reversible and the irreversible polarization.

F. A. LIDBURY: Did you find the polarization in the case of copper to exist in the cathode or in the anode?

PROF. FRANKLIN: We made no attempt to separate the polarization into cathode or anode parts. Our first object was to show the existence of both a reversible and an irreversible polarization without regard to its seat at one electrode or the other.

MR. LIDBURY: According to Professor Burgess' paper, on page 56, the resistance is at the cathode.

MR. CARL HERING: Quite a number of years ago I made some tests with a standard Daniell's cell, and found that the electromotive force was quite appreciably influenced by differences of pressures on the two liquids. On the test described on page 58, it seems to me that such pressures might cause quite appreciable differences in the results, because, as I understand the experiment, the tube was sealed with two corks, and a slight amount of gas liberated in the tube would create a different pressure, and that might affect the result quite appreciably.

DR. M. DE K. THOMPSON: On page 53 Professor Burgess gives the measurement of the counter-electromotive force in this cell, and finds it to be only .025 volt; and I suppose it is from that observation he states that the .2 volt is out of the question. I suppose he had a concentrated solution of copper sulphate in the experiment on page 58. No gas would be liberated in that case, and there would be no change in the pressure.

MR. HERING: I am well aware of the fact that there *ought* not to be gasing; but I am also aware of the fact that there very often is gasing, and when the tube is sealed there will be a pressure produced. As soon as the copper sulphate has been exhausted even from only a molecularly thin layer next to the cathode, there will be sulphuric acid next to the cathode, and there will be gases formed, even though invisible in amount.

PROF. FRANKLIN: The electromotive forces he says were .025 volt, according to the statement, on interrupting the current; the reversible polarization, however, exists only while the current is flowing, and it vanishes when the current ceases to flow.

PRESIDENT CARHART: Irreversible or reversible?

PROF. FRANKLIN: The irreversible polarization exists while the current is flowing; it is this that I had in mind in connection with the 0.1 volt.

DISCUSSION.

(Communicated by Lawrence Addicks previous to the meeting.)

Prof. Burgess presents a series of data very interesting to me, but I am sorry he does not attempt to answer the conundrum. There can be no question that a transfer resistance of considerable magnitude exists in copper refining work, and that it is ohmic in its nature. Polarization effects can easily be separated by measuring the voltage at different current densities with a constant temperature. The voltage for zero current density can then be found by extrapolation. A common figure for polarization in an actual copper refining cell is 0.02 volt.

For some time I have been inclined to think the explanation of transfer resistance is connected with the presence of gases near the electrodes. The specific resistance to be dealt with must be very high, as the effect is entirely within a layer of exceedingly small thickness, but free gas, at least, would have practically no conductivity. The cathode effect is greater than the anode, but the hydrogen naturally at the cathode has half the valence and therefore twice the volume of the oxygen near the anode. On the one hand, the temperature co-efficient of this layer is enormous, and on the other, both the solubility of gases in liquids and the volume of free gas are greatly affected by temperature. The effect becomes small at high temperatures, and in a boiling solution there could be no gas effects. The parallel seems to me at least suggestive.

The amount of transfer resistance also seems to be closely connected with the acidity of the electrolyte, as the results in the paper indicate. Laboratory results on the specific resistance of electrolytes indicate that there would be money in carrying the free acid in the electrolyte to over 20 per cent., but in practice about 13 or 14 per cent. is found to be the economic limit, even with unlimited circulation to overcome the polarization tendency of the higher acid electrolyte. While I have never directly determined the cause of this apparent discrepancy, it is doubtless due to increased transfer resistance.

A paper read at the Seventh General Meeting of the American Electrochemical Society, held at Boston, Mass., April 27, 1905. President Carhart in the chair.

AN OPTICAL METHOD FOR OBSERVING THE DIFFUSION IN ELECTROLYTES.

BY CARL HAMBUECHEN.

A great deal of investigation has been directed within recent years to the study of the relationship existing between the composition of the electrolyte and the character of the deposition which may be obtained from it. It is known that the quality of deposit depends upon the chemical compositions of the solution, current density, temperature, nature of the anode material, viscosity, and the diffusion of the solution surrounding the anode and cathode.

The study of diffusion in an electrolytic cell has not received the attention which it should, and certain erroneous conceptions are held in regard to it. One of these is that we have a gradual change of density from the anode to the cathode produced by the migration of the ions. Whatever differences of density there may be, however, at the immediate surfaces of the electrodes, there is almost no variation in density on a horizontal line extending across the cell. In all active electrolytic cells there is a continual systematic movement of the electrolyte aside from that caused by gases which may be liberated, and it is for the purpose of observing this movement of the electrolyte that the method of investigation described in this paper was adopted.

If a narrow glass vessel, containing a light liquid, superposed upon a heavier one, be placed in the path of light from a projection lantern, the image on the screen will show a distinct line between the two solutions, even though the eye cannot detect it within the cell. This line is produced on the screen through differences in the refraction of the light as it passes through the solution of non-uniform density.

A glass vessel of dimensions shown in Fig. 1 was filled with a solution of iron sulphate, and two iron electrodes, A and C, were suspended therein. The cell was made of such size that it could be placed as a slide in a stereopticon lantern, and, upon focusing, a good image of the cell was thrown upon the screen. Before the passage of current, no disturbance or non-uniformity of electrolyte was noted, but upon passing three-tenths of an ampère for a few minutes, definite horizontal lines appeared, extending from the anode to the cathode, indicating that the solution had become stratified by layers of different concentration, the lighter layers being at the top of the cell and the heavier ones at the bottom. In this experiment the lines were first seen to form at the bottom of the cell and gradually rise to the top. A stream of heavy anode solution could be observed flowing to the bottom of the cell, and the lighter cathode solution flowing in a steady stream to the top.

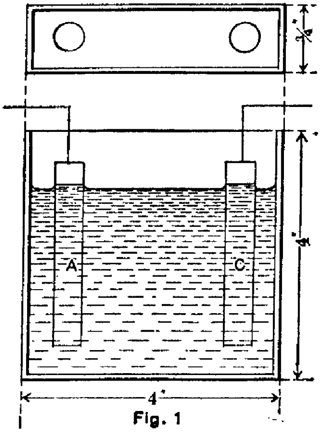


Fig. 1

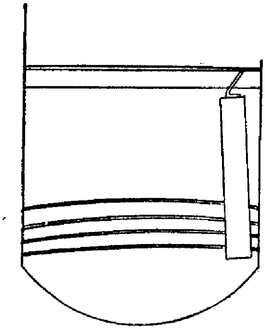


Fig. 2

Fig. 2 is a photograph showing the stratification of such solution, in which the horizontal lines caused by the difference in the refraction of the light, and also the heavy anode solution streaming to the bottom, can be noted.

By studying the stratification of an electrolyte produced in this manner a number of the difficulties encountered in the electrodeposition of metals can be explained. The rapid rising of the cathode solution explains the corrugated appearance which metallic deposits sometimes assume, and the non-uniformity in the density of the electrolyte explains the differences in the appearance of the deposit at different parts of the cathode.

By tracing out in a cell of this sort the paths taken by the solution, methods can be easily devised for altering such paths so as to meet practical requirements by means of suitable baffle plates or by an arrangement of electrodes.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

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AN INVESTIGATION OF THE BORIDES AND THE SILICIDES

BY

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PREFACE.

During the last two decades, notable contributions have been made to the field of chemistry through the use of the electric furnace. The high temperatures, made available by the conversion of electrical into thermal energy, have resulted in the discovery of a host of new compounds, and the duplication by art of various of nature's processes.

Among the compounds which play a prominent part in this "new chemistry of high temperatures," are the borides and the silicides; and it is the purpose of this paper to present the results of an experimental investigation of some of these compounds, together with a brief, yet comprehensive, account of these two series of chemical compounds, which have become of scientific and commercial importance through the advent of the electric furnace.

The methods most generally used heretofore for the preparation of the borides and the silicides have been synthesis from the elements, and reduction of a metallic oxide by excess of boron or silicon. Either of these methods requires as a preliminary the preparation of the non-metal, a long and difficult task, particularly in the case of boron, the purification of which by the method of Moissan[1] took from ten to fifteen days at a minimum. It therefore seemed to the writer that an experimental investigation of the possibility of the preparation of the borides and the silicides from their commercially available oxygen compounds by a single reaction in the electric furnace would be of value. This is one of the problems of this

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[1] C. R., 114 : 392-7 (1892). Ann. de Chim., 6 : 296-320 (1895).

investigation. A second problem was the production by means of the electric furnace of a new series of definite chemical compounds, the silico-borides.

For this investigation all the resources of the electrochemical department of the University of Wisconsin were put at the writer's disposal by Professor C. F. Burgess, who by this, and by his personal interest and encouragement, has placed the writer under lasting obligations, which are here gratefully acknowledged.

O. P. W.

Laboratory of Applied Electrochemistry,
University of Wisconsin,
May, 1905.

AN INVESTIGATION OF THE BORIDES AND THE SILICIDES.

I.

HISTORICAL OUTLINE.

The history of the borides may be said to begin with the discovery by Descostils in 1808[2] that platinum could be fused by heating it with borax and lamp-black. This gave a product that was hard, brittle, and crystalline, which, dissolved in acids, left a residue of boric acid. It was a full half century from this first recorded instance of the combining of platinum and boron, before a boride of platinum of definite composition was isolated.

Similarly in regard to the silicides, the first discovery was the mere fact of the combination of silicon with the metals, followed after many years by the isolation of definite chemical compounds. In 1810, Davy[3] discovered that the earths, silica, alumina, and glucina, when heated with iron and potassium, yielded a brittle ingot of a crystalline texture, harder and whiter than iron. In 1812, Berzelius[4] announced that a mixture of silica and carbon, heated in the presence of iron filings, gave a white metal which, attacked by acids, yielded silica. Boussingault[5] found that steel could be made with silicon in

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[2] Ann. de Chim., 67 : 68 (1808).

[3] Ann. de Chim., I, 75 : 152.

[4] Ann. de Chim., I, 81. 178.

[5] Ann. de Chim., II, 16 : 10-16.

place of carbon; and that platinum, heated with carbon, took up silicon from the crucible, becoming brittle, harder, and less dense. The number of such alloys with boron and silicon increased, and finally crystalline compounds of definite composition were separated from them.

With the use of the electric furnace for scientific research, the isolation of new borides and silicides received a tremendous impetus. It was not the promise of great commercial value which caused this sudden and remarkable extension of these series, nor the fact that new borides and silicides were likely to have strange and marvellous properties; quite the contrary, —their family resemblance is so strong that nothing short of a chemical analysis serves to distinguish between certain members of both series. It was the fascination of exploring this new realm of high temperature chemistry that led to experimentation, and since, in addition to carbon, boron and silicon are the chief elements whose compounds with the metals are stable at electric furnace temperatures, the inevitable result was a great increase in the list of borides and silicides. The phosphides, arsenides, and sulphides are other series of compounds stable at electric furnace temperature, which are as yet only incompletely investigated.

The bulk of the original literature concerning the borides and silicides is contained in the German and French chemical periodicals, and is available in English only through brief abstracts scattered in various chemical journals, and in the two English translations of Moissan's "Le Four Electrique."

It has been the purpose of the writer to collect from the original sources and to set forth in the appended tables the most important physical and chemical properties of the borides and silicides in such form that the data may be useful to all experimenters in this field.

TABLE I.—*Action of the metals upon silicon.*[6]

Metals which do not form silicides.	Metals in which silicon dissolves at high temperatures, but separates again as crystals on cooling.
Aluminum. Antimony. Bismuth. Cadmium. Gold. Lead. Potassium. Silver. Sodium. Tin. Zinc.	Aluminum.[7] Silver. Antimony. Bismuth. Tin.[8] Zinc.[8] Lead. Gold.[9]

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[6] Vigouroux, Ann. de Chim., 12 : 5 (1897).

[7] Announced by Deville and Wöhler, Ann. de Chim., III, 49 : 73 (1857).

[8] Announced by Deville and Caron, Ann. de Chim., III, 67 : 435 (1863).

[9] Metals in second column, with the exception of gold, are arranged in order of their solvent power for silicon. Moissan and F. Siemens, C. R., 138 : 1299 (1904). Bull. Soc. Chim., 31–32 : 1015 (1904).

TABLE II.—*Physical Properties of the Borides and Silicides.*

	Literature and Discovery.	How Made.	Description.	Hardness.	Specific Gravity.
Al_2B_4	Wöhler & Deville, Ann. de Chim. 52:63–91 (1858).	$K_2BF_6+KCl+Al$	thin coppery, hexagonal crystals.		
Al_2B_{24}	Wöhler & Deville, " " " " (Supposed to be Boron.)	$K_2BF_6+KCl+Al$	black, thin leaves.	9+	2.53 at 17°
$Al_3B_{48}C_2$	Wöhler & Deville, " " " " (Supposed to be Boron.) Composition and formulae of last two due to Hampe, Ann., 183:90 (1876).	B_2O_3+Al	yellow crystals.	9+	2.61
BaB_6	Moissan & P. Williams, C. R., 125:629–34 (1897); Bull. Soc. Chim., 17:1015–20 (1897).	$B_2O_3+BaO+Al+C$	small regular cryst.	9+	4.36 at 15°
$Be_6B_6C_4$	Lebeau, C. R., 126:1347-9 (1898)	BeO+B in carbon crucible.	brilliant metallic cryst.	....	2.4
CaB_6	Moissan & Williams, C. R., 125:629–34 (1897); Bull. Soc. Chim., 17:1015–20 (1897).	$B_2O_3+CaO+Al+C$	transparent cubic or rectangular cryst.	9+	2.33 at 15°
CB	O. Mulhauser, Z. anorg. Chem., 5:92 (1894).	B_2O_3+C	bluish black, greasy feeling, malleable.	....	
CB_6	Moissan C. R., 118:556 (1894); Ann. de Chim., 9:280-6 (1896). A. Joly, C. R., 97:456 (1883).	B+C Fe+B+C Cu+B+C	black, brilliant cryst.	9.8	2.51
CoB	Moissan, C. R., 122:424 (1896); Ann. de Chim., 9:273–85 (1896).	Co+B	brilliant prisms several mms. long.	7+	7.25 at 18°
CrB	Moody & Tucker, J. Chem. Soc. Trans., (1902) p. 14–17.	Cr+B	gray, metallic.	8	5
FeB	Moissan, C. R., 120:173 (1895); Ann. de Chim., 9:273-85 (1896).	Fe+B	metallic crystals.	....	

MnB	B. du Jassonneix, C. R., 139:1209 (1904).	Mn_3O_4+B and treated by chlorine.	brillant metallic powder.	....	6.2 at 15°
MnB_2	Troost & Hautefeuille, C. R , 81:1263-6 (1875); Ann. de Chim., 9:65 (1876).	$B_2O_3+Mn_3C$	violet gray crystals.		
Mo_3B_4	H. R. Moody & S. A. Tucker, J. Ch. Soc. Trans. (1902) 14–17.	$Mo+B$	pale brass color, brittle.	9	7.1
NiB	Moissan, C. R., 122: 424 (1896); Ann. de Chim. 9: 273–85 (1896).	$Ni+B$	brilliant prisms several mms. long.	7+	7.39 at 18°
Pt_2B	Martius, Annalen 109: 79 (1859); Descostils, Ann. de Chim. 67:88 (1808).				
SiB_3	Moissan & Stock, C. R., 131: 139-43 (1900); Ann. de Chim. 20: 433 (1900).	$Si+B$	brilliant black rhombic crystals, yellow if thin	9+	2.52
SiB_6	Moissan & Stock. C. R , 131: 139-43 (1900 ; Ann. de Chim. 20: 433 (1900).	$Si+B$	thick, black cryst.......	9+	2.47
SrB_6	Moissan & Williams, C. R., 125: 629-34 (1897); Bull. Soc. Chim., 17: 1015 (1897)	$B_2O_3+SrO+Al+C$	black crystalline powder.	9+	3.28 at 15°
ThB_4	B. du Jassonneix, C. R., 141: 191–3 (1905	ThO_2+B	yellowish metallic powd'r	....	7.5 at 15°
ThB_6	B. du Jassonneix, C. R., 141: 191–3 (1905)	ThO_2+B	reddish violet powder	....	6.4 at 15°
WB_2	Moody & Tucker, (see CrB)	$W+B$	silvery, metallic.		
Zr_3B_4	Moody & Tucker E. Wedekind, Ber., 35: 3929-32(1902).	$Zr+B$			
$BaSi_2$	Disc. by C. B. Jacobs, July, 1899. Chem. News, 82: 149 (1900).				
$CaSi_2$	Disc. by Wöhler, Ann. de Chim. 69: 224 (1863); Ann., 127: 255 (1863).	$Si+CaCl_2+Na$			
	G de Chalmot, Amer. Chem. J., 18: 319 (1896).	$CaO+SiO_2+C$			
	C. B. Jacobs, British Assoc. (1900) p. 699.	$CaCO_3+SiO_2+C$			
	*Moissan & Dilthey, C. R., 134: 503-7 (1902); Ann de Chim., 26: 289 (1902); Bull.Soc Chim., 27: 1199 (1902).	$Si+CaO$	gray, brilliant cryst.	6.8	2.5
CSi	Schutzenberger, C. R., 114: 1089–93 (1892).				
	Discov. E. G. Acheson, 1890. Moissan, Ann. de Chim.,9: 296-300 (1896).	SiO_2+C $Si+C$ Fe_2Si+C $Fe+SiO_2+C$	colorless hexagonal crystals.	9+	3.12

TABLE II—Continued.

	Literature and Discovery.	How Made.	Description.	Hardness.	Specific Gravity.
Ce_2Si_3	Ullik, Chem. Central., 1865 p. 1045	Electrolysis of $3KF.2CeF_4$			
$CeSi_2$	*J. Sterba, C. R., 135:170 (1902); Ann. de Chim., 2:229–32 (1904).	CeO_2+Si	lamellar steel gray cryst. brittle.	....	5.67 at 17°
Cr_3Si	Zettel, C. R., 126:833-5 (1898).	$Cu+Al+Cr_2O_3$ in silicate crucible	gray arborescent cryst. powder.	6+	6.52 at 18°
Cr_2Si	Moissan, C. R., 121:621-6 (1895); Ann. de Chim., 9:289 (1896)	$Cr+Si$ $Cr_2O_3+SiO_2+C$	metallic cryst.	9+	
Cr_3Si_2	*Lebeau and J. Figueras, C. R, 136: 1329-31 (1903).	$Cu+Cr+Si$	brilliant prisms.	6+	5.6 at 0°
$CrSi_2$	G. de Chalmot, Amer. Chem. J., 19:69 (1897).	$Cr_2O_3+SiO_2+C$	gray metallic needles.	....	4.39
Cr_2AlSi_3	W. Manchot & A. Kieser, Ann., 337:353-61 (1904).	$Cr+K_2SiF_6+Al$	....	5	4.7
Cr_2AlSi_4	W. Manchot & A. Kieser, Ann., 337:353-61 (1904).	$K_2Cr_2O_7+K_2SiF_6+Al$	....	5+	4.8
Co_2Si	Vigouroux, C. R., 121:686-8 (1897); Ann. de Chim., 12:175 (1897).	$Co+Si$	steel gray cryst.	....	7.1 at 17°
$CoSi$	Lebeau, C. R., 132:556 (1901); C. R., 135: 475-7 (1902); Ann. de Chim., 27:271-7 (1902).	Cu_2Si+Co	brilliant prisms and octahedra.	....	6.3 at 20°
$CoSi_2$	*Lebeau, Ann. de Chim. 27:271-7 (1902)	$Cu_2Si+Co+Si$	dark bluish cryst.	4.5	5 3 at 0°
Cu_2Si	Vigouroux, Ann. de Chim., 12:184 (1895); C. R., 122;318–19 (1896). G. de Chalmot, Am. Chem. J., 19:118 (1897).	$Cu+Si$	steel gray, brittle crystals: reddens in air.	very hard	6.9 at 18°
Cu_4Si	E. Vigouroux, C. R., 142:87-8 (1906).	$Cu+Si$	silver white: reddens in air.	hard	7.48 at 0°
Fe_2Si	Disc. by Hahn, Ann, 129:57-76 (1864).	$Si+Na+NaCl+FeCl_2+CaF_2$	feebly magnetic	....	6.61 at 23°

	Moissan, C. R, 121:621-6 (1895); Ann. de Chim., 9:289 (1896).	$Fe+Si$ Fe_2O_3+Si	small metallic magnetic prisms.	....	7.0 at 22°
	*Lebeau, Ann. de Chim., 26:5-31 (1902).	$Fe+Si$	brilliant gray octahedra.	6+	6.85 at 20°
Fe_3Si_2	G. de Chalmot, J Amer. Chem. Soc., 17:923 (1895).	$Fe+SiO_2+C$	brittle white cryst. feebly magnetic.	very hard	6.36
$FeSi$	Encyclopaedie Fremy, Vol. 20: p. 93.	$SiCl_4+Fe$			
	Lebeau, C. R., 128:933 6 (1899); Ann. de Chim., 26:5-31 (1902).	$Fe+Cu_2Si$	metallic tetrahedric cryst	7+	6.17 at 15°
$FeSi_2$	Disc by Hahn, Ann., 129:57-76 (1864); G. de Chalmot, Am. Chem J., 19:122 (1897).	Fe_2Si+HF Fe_2Si+HF			
	*Lebeau, Ann. de Chim., 26:5-31 (1902).	$Fe+Si$	brilliant cryst	4+	5.40 at 15°
Li_6Si_2	Moissan, C. R., 134:1083-7 (1902); Bull. Soc. Chim., 27:1203-7 (1902).	$Li+Si$	brilliant indigo blue cr'st very hygroscopic.	....	1.12
Mg_2Si and Mg_4Si_3	Wöhler, Ann., 107:119 (1858): Wöhler, Ann. de Chim., 54:218 25 (1858); Geuther, J. f. pract. Chem., 95:424; Phipson, Proc. Roy. Soc, 13:217 (1864).				
Mn_2Si	Brunner, Pogg. Ann., 101:264 (1857); Wöhler, Ann, 106. (1858).				
	Vigouroux, C.R., 121:771-3 (1895).	$\left\{\begin{array}{l} Mn+Si \\ Mn_3O_4+SiO_2+C \\ Mn_3O_4+Si+H_2 \end{array}\right.$	gray metallic crystals, brittle.	....	6.6 at 15°
	*Lebeau, C. R 136:89-92; 231-6 (1903).	$Mn+Cu+Si$	brilliant prisms.	....	6.2 at 15°
$MnSi$	Carnot & Goutal, Ann. des. Mines, 18:27 (1900); H. N. Warren, Chem. News, 78:319 (1898);				
	*Lebeau, C.R, 136:89-92 (1903).	$Mn+Cu+Si$	brilliant tetrahedric crystals.	8-9	5.9 at 15°
$MnSi_2$	G. de Chalmot, Am. Chem. J., 18:536 (1895).	$Mn_3O_4+SiO_2+CaO+C$			
	*Lebeau, C. R., 136:231-3 (1903).	$Mn+Cu+Si$	small dark gray octahedra.	....	5.24 at 13°
Mo_2Si_3	H. N. Warren, Chem. News, 78:318 (1898);				
	*Viguoroux, C. R, 129:1238-9 (1899).	MoO_2+Si	silver white prisms.		
Ni_2Si	Viguoroux, C. R., 121:686-8 (1895).	$Ni+Si$	steel gray crystals.	....	7.2 at 17°
Pt_2Si	Disc. by Guyard, Bull. Soc. Chim. 25:510 (1876); *Viguoroux, C. R., 123:1 7 (1896): Ann. de Chim., 12:188 (1897).	$Pt+Si$ $Pt+Si$	....	....	13.8 at 15°

TABLE II.—Continued.

	Literature and Discovery.	How Made.	Description.	Hardness.	Specific Gravity.
RuSi	Moissan and Manchot, C. R., 137:229-32 (1903); Ann. de Chim., 2:285 (1904) Bull. Soc. Chim., p. 559 (1904).	Ru+Si	metallic white prisms	very hard.	5.40 at 4°
$SrSi_2$	See $BaSi_2$...........................	$SrCO_3+SiO_2+C$	bluish white	hard.	
Ti_2Si	L. Levy, C. R., 110:1368 (1890; 121:1148 (1895).	$TiCl_3+Si$			
W_2Si_3	Viguoroux, C. R., 127:393 (1898); Moissan C. R., 123:13 (1896); Warren, Chem. News, 78:318 (1898).	WO_3+Si	steel gray metallic crystals.	....	10.9
V_2Si	Moissan & Holt, C. R., 135:493-7 (1902); Ann. de Chim., 27:277-88 (1902).	VC+Si $V_2O_3+Cu+Si$	silver white prisms	....	5.48 at 17°
VSi_2	Moissan & Holt, C. R., 135:493-7 (1902); Ann. de Chim., 27:277-88 (1902).	V_2O_3+Si	brilliant metallic prisms	....	4.42
Zr Si_x	E. Wedekind, Ber., 35:39:29 (1902).	ZrO_2+Si	dark crystals.		

The numbers denoting hardness in the above table are according to Mohr's scale; 6, orthoclase; 7, quartz; 8, topaz; 9, corundum; 10, diamond.

* In case of several articles upon the same compound, that marked by the asterisk is the more comprehensive.

Additional references are as follows:

A summary concerning silicon and silicides to the year 1897, Vigouroux, Ann. de Chim., 12 : 5–71 ; 153–197.

The preparation and properties of amorphous silicon, Vigouroux, C. R., 120 : pp. 94, 367, 554, 1161, 1393 (1895).

New properties of amorphous silicon, Moissan, Bull. Soc. Chim., 27 : 1198 (1902).

Silicon by electrolysis, Gore, 1884, Chem. News, 50 : 113–4 ; Hampe, 1889, Chem. Zeitung, 12 : 841 ; Minet, 1891, C. R., 112 : 1215–18.

Controversy concerning the existence of a silicide of silver, H. N. Warren, Chem. News, 67 :303–4 (1893) ; Moissan, C. R., 121 :621–6 (1895) ; G. de Chalmot, Am. Chem. J., 18 :95 (1896) ; Moissan, Ann. de Chim., 9 : 294 (1896).

The preparation of amorphous boron, Mossian, C. R., 114 : 392–7 (1892) ; Ann. de Chim., 6 : 296–320 (1895).

Mulhauser (Chem. Zeitung, 26 :807) claims the discovery of silicon carbide for E. H. and A. H. Cowles, in 1884.

Unless there is other experimental evidence than that adduced in the original publication, it seems to the writer that the formulae given by H. R. Moody and S. A. Tucker for the "borides" of chromium, molybdenum, tungsten and zirconium, should be accepted by the chemical world with more than the proverbial "grain of salt." The only experimental evidence given for these formulae is as follows:

CrB. "10 g. chromium and 2.1 g. boron were heated in the electric furnace for six minutes by a current of 175 amperes at 60 volts. The product contained 82% chromium, hence it is a definite chromium boride of the formula CrB." It should be noted that the charge contained originally 82.6% chromium.

Mo_3B_4. "6 g. molybdenum and 1 g. boron were heated twenty minutes by 230 amperes at 70 volts. Analysis showed 86% molybdenum, hence the formula." This charge contained 85.7% molybdenum.

WB_2. "4 g. tungsten and 0.2 g. boron, after five minutes heating by 175 amperes at 65 volts showed 89% tungsten, therefore the formula is WB_2." The charge contained 88.9% tungsten.

Zr_3B_4. "15 g. zirconium and 2.2 g. boron were heated by 200 amperes at 65 volts for five minutes. Analysis showed 86% zirconium." The charge contained 87.2% zirconium.

It is probable that these four metals are capable of forming compounds with boron in definite proportions. It is possible that the formulae assigned are the correct ones for such compounds,—but these experiments *prove* nothing of the sort. From the energy and time of heating, the temperatures were very moderate, even low, for the electric furnace. Under these conditions all the elements concerned are only slightly, if at all, vaporized, so that the experiments consisted, in each case, in heating together two non-volatile elements in pre-determined proportions, and finding them in the same proportions in a homogeneous ingot after cooling. The only deduction from this is, that the two elements concerned are capable of alloying in the proportions originally taken. This is an excellent field for further investigation. E. Wedekind[10] has obtained compounds of zirconium with boron, and with both boron and carbon by reduction of zirconium oxide by boron, but has not as yet been able to purify them or to assign a formula to either. It is the opinion of the writer that definite borides and silicides of iridium, osmium, uranium, and many of the metals of the rare earths, can be isolated, although these are as yet unknown.

In the following table (Table III), compiled from the original literature, the vigor of chemical action of reagents upon the borides and the silicides is indicated as follows:

N = no action.
S = slight action.
SS = very slight action.
R = acts readily.
V = acts vigorously.
VV = acts violently.
VVV = acts with incandescence.

Numerals indicate the approximate temperature in degrees centigrade.

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[10] Ber., 35: 3929–32 (1903).

TABLE III.—*Chemical Properties of the Borides and Silicides.*

Reagents	H_2SO_4	HNO_3	HCl	HF	HCl+HNO_3	KOHsol.	Fused KOH	Fused K_2CO_3	Fused Na_2CO_3+KNO_3	Oxygen	Chlorine	HCl gas	Fluorine	H_2O
Al_2B_4....	....	R	SS	......	......	SS	......	......	....	....	VV at 800°	......	......	....
Al_2B_{24}...	SS	R	N	......	......	......	VVV	......	....	....	....	......	......	....
$Al_3B_{48}C_2$	SS	V	SS	......	......	N	......	......	....	....	....	......	......	....
BaB_6 ..	N-dil. S-conc.	VV	N	......	......	......	......	......	....	....	V-800°	......	VVV 20°	N 250
$Be_6B_6C_4$.	R	R	R	R	......	......	......	......	....	N-20 SS-800	VVV 450	......	......	....
CaB_6...	N-dil. S-conc.	VV	N	......	......	......	......	......	....	....	V-800	......	VVV-20	N 250
CB.......	N	N	N	N	N	N	R	R	....	....	....	......	......	N
CB_6......	N	N	N	N	N	N	V	V	....	N-500 V-1000	....	......	......	N
CoB ...	N-dil. S-conc.	V	SSS	......	VV	......	VVV	VVV	V	VVV 800	VVV 800	......	......	S
CrB	S	S	S	......	S	......	......	......	....	....	....	......	......	N
FeB....	N-cold S-hot	V	SS	N	V	......	V	V	....	VVV 800	V 800	......	......	S
MnB	V	V	R	V	......	S	VV	VV	....	R 700	V 800	......	VVV-20	S
MnB_2....	R	R	R	R	R	R	...	......	....	....	....	......	......	N
Mo_3B_4 ...	S	S	S	......	V	......	......	......	....	....	....	......	......	N
NiB....	N-dil S-hot	V	SSS	......	VV	......	VVV	VVV	V	VVV 800	VVV 800	......	VVV 20	S
Pt_2B...	....	....	....	......	......	......	......	......	....	....	....	......	......	....
SiB_3	S-hot	S	N	N	......	......	R	V	V	....	VVV 800	......	VVV 100?	....

TABLE III.—Continued.

	H_2SO_4	HNO_3	HCl	HF	HCl+HNO_3	KOH-sol.	Fused KOH	Fused K_2CO_3	Fused NA_2CO_3+KNO_3	Oxygen	Chlorine	HCl gas	Fluorine	H_2O
SiB_6	S-hot	R	N	N	......	......	S	V	V	......	VVV 800	......	VVV 100	....
SrB_6 ...	N dil. S conc.	VV	N	......	......	......	......	......	......	......	V 800	......	N 20 VV hot	....
ThB_4.....	N-cold	V	V-hot	......	......	N	VVV	......	......	S 800	V 500	R 500	VVV warm	....
ThB_6.....	N	R	N	N	......	N	VVV	......	......	S-800	V 500	R 500	VVV warm	....
WB_2.....	S	S	S	......	V	......	......	......	......	......	......	......	......	N
Zr_3B_4....	S	S	S	......	S	......	......	......	......	......	......	......	......	N
$BaSi_2$....	......	R	R	R	R	......	......	......	......	S	......	......	......	R
$CaSi_2$....	......	SS	R	VV	......	R	......	......	......	SS 900	VVV 800	......	VVV 20	SSS
$CeSi_2$..	R dil. V-conc.	R	S 20 R 100	V	......	N-dil. R-conc.	VVV	......	......	SS	N 20 VVV 800	......	V 20	SSS
Cr_3Si....	N	N	N	R	N	......	S	......	V	......	VVV 800	......	......	....
Cr_2Si....	N	N	......	S-20	......	......	S	......	R	......	R 700	......	......	....
Cr_3Si_2.	N	N	S-conc. 100	V	......	......	......	V	....	SS 1100	R 400	R	......	N
$CrSi_2$....	......	....	N-20	R	N-20	......	......	......	R	......	......	......	......	....
Cr_2AlSi_3.	N	N	N	R	N	N	R	......	......	......	R 800	......	......	....
Co_2Si....	SS	SS	SSS	R	......	N	......	R	V	S 800	VVV 800	R 800	VVV 20	....
$CoSi$.....	N	N	R	......	S	SS	VV	R	....	SS 1200	V 300	R 700	VVV-warm	....
$CoSi_2$....	N	N	SS	V	......	S	VV	......	......	SSS 1200	V 300	......	VVV-warm	....
Cu_2Si..	R	V	R	S	......	......	......	R	R	N cold S 800	......	......	......	....
Cu_4Si....	S	V	S	SS	S	S	......	......	......	......	......	......	......	....
Fe_2Si....	N	N	V	R	R	S	......	......	R	......	......	......	......	..

$FeSi$	N	N	SS	V	SSS	...	V	V	V	...	...	...	...	...
$FeSi_2$	N	N	N	R	N	S-100	VV	...	...	SS 1200	VVV 650	R 700	VVV 20	...
Li_6Si_2	VV	VV	V	...	...	...	...	...	...	...	VVV-warm	...	VVV-warm	V
Mg_2Si	...	VV	R	R	...	N	...	...	...	...	...	...	...	...
Mg_4Si_3	...	V	...	...	...	N	...	...	...	...	...	...	...	...
Mn_2Si	...	SS	R	V	V	S	VV	VV	VV	R 800	VVV 500	VVV600	VVV-hot	...
$MnSi$	N	N	SS	...	...	...	...	...	...	SS 1000	...	...	...	...
$MnSi_2$	N	N	...	R	...	R	...	...	...	...	...	...	...	...
Mo_2Si_3	...	N	N	N	N	SS	...	VV	...	...	VVV 300	...	...	...
Ni_2Si	SS	SS	SSS	R	...	N	...	R	V	S 800	VVV 800	S 800	VVV 20	...
Pt_2Si	N	N	N	N	R	SS	...	SS	...	...	R 20	R	R	...
$RuSi$	N	N	N	...	...	...	S	S	S	burns	S	...	R	...
$SrSi_2$	...	R	R	R	R	...	...	...	...	S	...	...	...	S
Ti_2Si	...	...	...	...	...	...	...	...	...	...	...	...	...	...
W_2Si_3	...	N	N	N	N	SS	...	VV	...	...	VVV 250	N 1000	...	...
V_2Si	N	N	N	V 20	N	N	V	...	R	...	R 800	R 800	R-warm	N
VSi_2	N	N	N	V	N	N	V	...	...	N 800	R 800	R 800	V-hot	...
CSi	N	N	N	N	N	...	S	...	...	N 1000	{ SS 600 R 1200	...	...	...

In general, the borides and the silicides are brittle, metallic, harder than the corresponding carbides, and very resistant to chemical reagents. As seen from Table II, the usual method of preparing these compounds has been that of direct synthesis from the elements; occasionally the metallic oxide has been reduced by boron or silicon, and still more rarely, the oxygen compounds of both the metal and the non-metal have been simultaneously reduced by carbon or magnesium.

II.

REDUCING AGENTS.

This investigation requires a survey of the field of possible reducing agents, their properties, advantages, and limitations.

CARBON.

Carbon constitutes the most important reducing agent in technical metallurgy, and it has certain advantages over other substances for reduction in the electric furnace. It is cheap, it is a powerful reducing agent at high temperatures, so slightly volatile that it remains in the furnace, while the product of its action is a gas, and hence escapes as soon as formed. This last is an important advantage of carbon over most other reducing agents, which usually leave in the furnace slags that are hard to break up and difficult to get rid of by chemical means.

The great disadvantage of carbon is its tendency to form carbides with nearly all metals which are produced in the electric furnace, and also in the presence of silica or borax, to form the carbides of silicon and boron, extremely resistant to chemical reagents and difficult to remove from the product desired. In the reduction of the metallic oxides, the amount of carbon in the product may be made very small, and even negligible in some cases, by using an excess of metallic oxide in the charge. In the preparation of borides and silicides from their oxygen compounds, however, this method of removal of carbon from the product is not available. If carbon, boric anhydride, and any metallic oxide are mixed in the proportions necessary for complete reduction, and then an excess of the metallic oxide be added for the purpose of removing carbon from the alloy or chemical compound which is desired, after reaction has occurred the unreduced substance will be, not the excess of metallic oxide, but its equivalent, as regards oxygen, of boric anhydride. Unlike the metallic oxide, this will have little, if any, effect in removing from the product any carbon which may have been taken up during the reduction.

Hence it will be seen that carbon is not a suitable reducing agent for use in the preparation of borides and silicides by the method proposed in this investigation.

SODIUM AND POTASSIUM.

Sodium and potassium, so often employed by chemists for difficult reductions, cannot be used at the high temperature of the arc furnace because of their violent action and volatility.

ALUMINUM.

The use of aluminum as a reducing agent began about the middle of the last century, but has assumed practical importance only within the last six years. The usefulness of carbon as a reducing agent is limited to the reduction of oxides, except that it removes the oxygen from ternary compounds such as the sulphates. Aluminum, however, is an effective reducing agent for sulphides and chlorides, as well as oxides.

The following outline shows in part the development of its use as a reducing agent.

1858. Deville and Wöhler[11] reduced boron trioxide by aluminum.

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[11] Ann. de Chim., 52:63 (1858).

1858. Wöhler[12] formed a chromium-aluminum alloy from chromic chloride.

1859. Beketoff[13] produced a 33% barium-aluminum alloy from barium chloride and barium oxide.

1860. Michel[14] made aluminum alloys with manganese, iron, nickel, and titanium from their chlorides, also of tungsten and molybdenum from a mixture of chloride and oxide.

1861. Tissier[15] introduced silver sulphide into fused aluminum and reduced it, but failed to reduce the sulphides of zinc, iron and copper!

1888. Beketoff[16] obtained potassium and rubidium from their hydroxides by aluminum, but found that sodium and potassium separated aluminum from its chloride:

1888. L. Levy[17] made an alloy of titanium and aluminum.

1893. Greene and Wahl* produced manganese on a commercial scale by heating a mixture of manganese oxide and granlated aluminum.

1895. Vigouroux[18] reduced silica by powered aluminum.

1896. Moissan[19] by introducing a mixture of metallic oxide and aluminum filings into a bath of fused aluminum, made alloys of aluminum with molybdenum, nickel, titanium, tungsten and uranium. He made a chromium-copper alloy by adding a chromium-aluminum alloy to copper, and then removed the aluminum by copper oxide.

1896. Combes[20] substituted a metallic sulphide or chloride for the oxide of Moissan's method in order to secure a better separation of the alloy from the slag.

1898. Goldschmidt[21] heated in a crucible, mixtures of granulated aluminum with metallic oxides, chlorides and sulphides,

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[12] Ann., 106 : 118.

[13] Ann., 110 : 374.

[14] Ann., 113 : 248 ; 115 : 102.

[15] C. R., 52 : 931.

[16] Ber., 21 : 424.

[17] C. R. 106 : 66.

* J. Frank. Inst. 135 : 218–23.

[18] C. R., 120 : 1161–4.

[19] C. R., 122 : 1302–3.

[20] C. R. 122 : 1482–4.

[21] Ann., 301 : 19–28, J. Soc. Ch. Ind., 17 : 543–5.

producing a metal free from carbon and aluminum. In this way he reduced the sulphides of cobalt, lead, molybdenum, nickel and zinc, and stated that all sulphides could be reducd by aluminum except those of barium, calcium, lithium, magnesium, potassium, sodium and strontium (cf. Tissier above). He next turned his attention to the reduction of the oxides, from which he separated either in the pure state, or as alloys of aluminum, the elements boron, calcium, cerium, chromium, cobalt, copper, iron, lead, manganese, molybdenum, niobium, potassium, sodium, tantalum, thorium, tin, titanium, tungsten, vanadium and zirconium, but found that aluminum would not reduce magnesia. He then developed his now well-known method of igniting the charge from the top by means of a cartridge of barium peroxide and aluminum, fired by magnesium ribbon.

1898. Franck[22] reduced phosphates, with the formation of aluminum phosphide (Al_5P_3) and the liberation of phosphorus, and reduced the carbonates of barium, calcium, lithium, potassium, sodium, and strontium by heating with pulverized aluminum. The metal liberated alloyed with excess of the reducing agent. He remarked that the oxides of copper, lead and silver were reduced explosively, and that the presence of calcium sulphate in calcium phosphate caused explosive reduction. Goldschmidt had called attention to explosions caused by sulphates, in reducing ferric oxide and molybdenum oxide.

1901. Duboin[23] reduced the alkaline earths by ignition with powdered aluminum or magnesium in hydrogen.

1903. Rossi[24] reduced ores of titanium and tungsten in ton lots, by melting aluminum in the electric furnace, and then feeding in the ore. The product contained only traces of aluminum and carbon.

1904. Goldschmidt[25] gave an account of his production of

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[22] Chem. Zeitung, 22:236–45, J. Soc. Ch. Ind., 17:612.

[23] C. R., 132: 826–8.

[24] Electrochem. Ind., 1: 523.

[25] Electrochem. Ind., 2: 145–7.

carbon-free metals and alloys. In 1902, Dr. Goldschmidt had succeeded in obtaining, by his process of firing a charge of the oxide and pulverized aluminum, only the following metals in a solid, coherent mass: chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, niobium, tantalum, and tin. Later the niobium was found by Muthmann to contain aluminum. Silica and vanadic acid were not reduced, while barium, beryllium, boron, cerium, thorium, titanium, tungsten, and uranium were scattered throughout the slag. Alloys of these metals have been produced, however, by adding to the charge some easily reducible oxide like that of iron, to supply heat enough to secure fusion and a complete reduction.

1905. W. Huppertz[26] in attempts to reduce titanium oxide by the Goldschmidt process, in order to bring about complete reaction, combined electric heating with the alumino-thermic method. With certain precautions, he believes that it will be possible in this way to produce pure titanium in large masses from rutile.

As indicated above, aluminum as a reducing agent has received much attention from scientific investigators, and has proved very efficient. Aside from its high price, it has two disadvantages; one will be mentioned under slags; the other is its remarkable tendency to form alloys. In respect to the number of metals with which it will unite, it equals, if it does not exceed, carbon. When it is used in ingots for the reduction of metallic oxides, an alloy of aluminum is usually produced. Goldschmidt has overcome this difficulty by using aluminum in the form of powder or grains. There are, however, as mentioned, certain oxides from which only alloys can be obtained by this method.

Early in the course of this investigation, entirely independently of the work of Huppertz, the writer developed a method of firing in the electric furnace a charge consisting of powdered aluminum and any other powdered substance or substances that he desired to reduce, and obtained a product free both from

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[26] Abstract in Electrochem. Ind., 3: 35, of articles in Nos. 17-22 Metallurgie.

carbon and aluminum. Besides applying the method to rutile, as was done by Huppertz, titanic, boric and tungstic "acids" were similarly reduced, and by the addition of a retarder, to check the vigor of reaction, ordinary Goldschmidt charges were fired in the electric furnace without accident. The first such experiment was made in December, 1904, from which time the method was regularly used. In all about fifty reductions were made by powdered aluminum in the electric furnace.

CALCIUM CARBIDE.

Like aluminum, calcium carbide is a convenient medium for the storage in concentrated form of energy derived from steam or water power, so that it can be conveniently transported and applied in a small space.

H. N. Warren[27] appears to have first suggested the use of calcium carbide as a reducing agent, stating that the oxides of chromium, cobalt, copper, iron, lead, manganese, molybdenum, nickel, tin, and tungsten yield calcium alloys when heated with calcium carbide.

Moissan [28] reduced metallic oxides by calcium carbide in the electric furnace, and obtained the carbides Al_4C_3, Cr_3C_2, Mn_3C, Mo_2C, SiC, TiC, and W_2C. With the easily reducible oxides of copper and lead, he found reaction to occur before the charge was heated to fusion. The equation of reaction for lead oxide is

$$CaC_2 + 5PbO = 2CO_2 + CaO + 5Pb.$$

The reduced metal contained no calcium, contrary to the results of Warren's experiments. Reduced bismuth and copper were also free from calcium. In the course of Moissan's article, he said that he had previously[29] indicated that calcium carbide is a strong reducing agent. This statement, however, is not borne out by the article referred to, in which no mention

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[27] Chem. News, 75 : 2, Jan. 1st (1897).

[28] C. R., 125 : 839-44 (1897) ; Bull. Soc. Chim., III, 19 : 870 (1897).

[29] C. R., 118 : 501 (1894).

is made of calcium carbide as a reducing agent. The only experiments which might be construed to bear upon its reducing properties, are heating it with some powerful oxidizing agents. With fused "chromic acid," calcium carbide became incandescent. Potassium chlorate and nitrate at their melting points had no sensible action upon it, but at a red heat, they produced incandescence. Lead peroxide with calcium carbide became incandescent at a dull red heat. These experiments were described, but with no deductions as to the reducing character of calcium carbide.

Tarugi[30] confirmed Warren's formation of calcium alloys by the reduction of the oxides of copper and lead, and stated that all salts of antimony, bismuth, cadmium, cobalt, gold, nickel, platinum, silver, tin, and zinc, when heated with calcium carbide, yielded alloys (cf. Warren) readily decomposable by water. He reduced the oxide, phosphate, chloride, sulphate, carbonate, and borate of copper.

B. Neumann[31] reduced metallic oxides, chlorides, carbonates, and mixtures of these, with calcium carbide by heating the charges in clay crucibles in a furnace. He found that chlorides are most easily reduced, and gave the following equations:

$$M_2\,O+2\,MCl+CaC_2=6\,M+CaCl_2+2\,CO.$$

With sodium chloride as flux, copper, lead and nickel are obtained in mass while some metals are scattered in globules, and others vaporize.

$$M_2SO_4+2\,M_2O+CaC_2=6\,M+CaSO_4+2\,CO.$$
$$M_2CO_3+2\,M_2O+CaC_2=6\,M+CaCO_3+2\,CO.$$

In a brief article[32] Fr. von Kügelgen stated that carbon dioxide is formed in these reactions instead of carbon monoxide, and supported this contention in a long article.[33] He gave as the equation of reaction:

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[30] Gazetta chim. ital., 29, i, 509–512; Abstract in Chem. Zeit., 23: 292 (1899); Abstract in Zeit. f. Electroch., 7: 542 (1899).

[31] Chem. Zeitung, 24: 1013–4.

[32] Chem. Zeit., 24: 1060 (1900).

[33] Zeit fur Electrochem., 7: 441–50; 557: 573 (1901).

$$MCl_2+4\ MO+CaC_2=5\ M+CaCl_2+2\ CO_2.$$

In addition to a long series of metallic oxides, chlorides, and mixtures of these (among them sodium chloride and magnesium chloride), he reduced sodium and potassium hydroxides by calcium carbide. Magnesium oxide is not reduced, but alumina is partially reduced. Mixtures of carbide with the following may be kindled by a match: zinc chloride, copper chloride, copper oxide, silver chloride, tin chloride, bismuth chloride, chromium chloride.

This difference of opinion in regard to the formation of carbon monoxide or carbon dioxide in the reduction resulted in a lengthy controversy between Neumann[34] and Kügelgen.[35] The facts appear to be that with easily reducible compounds, the product is mainly, and in some cases entirely, carbon dioxide; at the higher initial temperatures required by compounds which are reduced with greater difficulty, increasing amounts of carbon monoxide appear as a product.

Geelmuyden[36] used calcium carbide as a reducing agent in the electric furnace. He reduced boric anhydride with the production of calcium boride, and also reduced the sulphides of antimony, iron, lead and magnesium. The metals vaporized with the exception of iron; this was contaminated by carbon. Aluminum sulphide was not reduced by calcium carbide.

Calcium carbide, then, reduces the same classes of compounds as are reduced by aluminum and is especially advantageous to use for mixtures of an oxide with a choride or a sulphide. It seems to be settled that calcium alloys are produced in certain reductions, but the exact conditions which cause their formation are not yet established. The products are contaminated by carbon under the same conditions, and possibly to the same extent, as if free carbon were used for reduction.

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[34] Chem. Zeitung. 24: 1013–14; 26; 176, 1108 (1902); 27: 1026–8 (1903).

[34] Chem. Zeitung, 24. 1013–14; 26: 176, 1108 (1902); 27: 1026–8 (1903). Zeit. f. Electrochem., 8: 772–5; 795; 939 (1902); 9: 699–701 (1903).

[35] Chem. Zeitung, 24: 1060 (1900); 27: 743 (1903). Zeit. f. Electrochem., 7: 541, 557, 573 (1901); 8: 781 (1902).

[36] C. R., 130: 1026–9 (1900).

ALUMINUM CARBIDE.

Aluminum carbide would seem especially advantageous for scientific purposes in the reduction of mixtures of oxide with chloride or sulphide.

SILICON CARBIDE.

B. Neumann[37] states that by using sodium carbonate as a flux, carborundum reduces metallic oxides. Carborundum has been tested by the writer in the preparation of silicides, for which use it has the advantage of serving at once as reducing agent and source of silicon. Similarly, boron carbide might be used to advantage for making borides, but so far as the writer knows, this has not yet been tried.

CALCIUM.[38]

If we may rely upon the claims of several experimenters, the problem of the production of calcium has been solved, and we may soon expect to find it on the market at a price that will make it available for use on a large scale. Current prices are as follows:

London, April, 1905:	
One pound bars	$3 92
Five pound tins, per pound	$2 32
New York, May, 1905:	
One hundred grams	$3 00
One pound	$10 00

As a reducing agent, it may be regarded, like aluminum and calcium carbide, as merely a convenient medium for the

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[37] Zeit. f. Electrochem., 8: 772 (1902).

[38] K. Arndt, Zeit. f. Electrochem., 8: 861 (1902). Borchers and Stockem, Zeit. f. Electrochem., 8: 751–8; 938 (1902). Borchers and Stockem (translation), Elect. World and Engin., 40: 1002. J. H. Goodwin, J. Amer. Chem. Soc., 25: 873–6 (1903). J. H. Goodwin, Proc. Amer. Philosoph. Soc., Vol. 43: No. 178; Abstracted Electrochem. Ind., Feb. 1905: p. 80–81.

storage, transportation, and application of the energy of water power or that derived from coal. Where purity of the product of reduction is of importance, calcium would seem as a general reducing agent superior to any other. In the electric furnace it should reduce most, if not all, of the oxides, chlorides, and sulphides which we are now able to reduce by other agents. It contains no carbon to be introduced as an impurity into the product. In the reduction of oxides alone, the slag formed, lime, is easily fluxed by certain substances, and even if it should remain as calcium oxide in the furnace, its density, tenacity, hardness, and resistance to acids are all less than for alumina, and render it in these respects a much less objection able substance to have in the furnace than the latter.

The metal in granular or powdered form, can undoubtedly be used as aluminum now is in the Goldschmidt method of reduction. For this use it will be superior to aluminum for difficult reductions. For one equivalent of oxygen, its heat of oxidation is ten per cent. greater than that of aluminum—a sufficient increase to insure the completion of certain reductions that by aluminum are only partial. Mixtures of oxides with calcium will undoubtly have a considerably lower kindling point than those with aluminum, a quality which will be a convenience, and will tend to cause more rapid and complete reaction.

A disadvantage of calcium as compared with aluminum is its oxidation at ordinary temperatures. Another, and possibly serious objection to calcium as a reducing agent in the electric furnace, is to be seen in the strong oxidizing action of fused lime upon silicon, boron, chromium, cobalt, iron, manganese, nickel, and titanium in the experiments of Moissan.[39]

In spite of these objections to the use of calcium as a reducing agent in the electric furnace, the writer regards it as the most promising of any agent yet suggested for difficult reductions.

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[39] C. R., 134 : 280 (1902).

"MISCHMETALL."[40]

The latest reducing agent for oxides is the "mischmetall" produced from the cerite minerals, and consisting of cerium forty-five per cent., lanthanum twenty per cent., didymium fifteen per cent., and the remainder of samarium, erbium, gadolinium, and yttrium. The advantages claimed for this over the other metallic reducing agents, are its low kindling point, 150°, and the ready fusibility of the oxides formed by its action, as compared with magnesia and alumina. Its low kindling point causes an exceedingly rapid reaction, and the fusible slag produced permits the reduced metal to collect to a regulus. By its use the following metals were obtained from their oxides in a state of the highest purity: cobalt, chromium, iron, manganese, molybdenum, niobium, tantalum, and vanadium. The oxides of lead, tin, titanium, and zirconium yielded only alloys. With silica the reaction is feeble. Tungstic acid is reduced but gives only a dark brown mass. The authors believe that by working with kilogram lots, a regulus of tungsten might be obtained.

III

SLAGS.

A matter of nearly as great importance as the reducing agent, is the nature of the slag formed by its action. Some of the effects of slags have already been mentioned. The following classification of the action of slags, while based on their action in an electric furnace of the arc type, will apply more or less to all high temperature work.

1. A fluid slag conduces to complete reaction; with a solid slag, reaction will be incomplete. This points to the selection of different reducing agents according to the maximum tem-

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[40] L. Weiss and O. Aichel, Ann., 337 · 370–89 (1904). Abstract J. Chem. Soc., 1905, p. 164.

perature attained—or at least permits the use at high temperatures of reducing agents which could not be used at lower temperatures. The success of the Goldschmidt method of reduction depends upon the attainment of a temperature at which the slag, alumina, is perfectly fluid. The substitution of a sulphide for part of the metallic oxide in the charge should help in the more difficult reductions by the Goldschmidt method on the core of a more fluid slag, since aluminum sulphide is more fusible than aluminum oxide.

2. The slag protects the metal or metallic compound which is dense enough to sink through it from the direct radiation of the arc, and yet if fluid, the slag conveys heat very rapidly to this metallic charge or product.

3. A considerable quantity of slag fixes at its own boiling point the maximum temperature to which the product is subjected.

4. The slag may exert a purifying or an injurious effect upon the product, according to its chemical nature.

5. By adding calculated amounts of metallic oxide to the slag, used as a protection, metals may be melted below the arc without contamination by the carbon which falls from the electrodes. This method of fusing carbon-free metals has been developed in the course of this investigation.

IV

ELECTRICAL EQUIPMENT.

SOURCE AND CONTROL OF THE CURRENT.

The dynamo which supplied current for most of the experiments was a direct current 110 volt machine, rated at 825 amperes. Alternating current with variable voltage was also available up to twenty kilo-watts, and was occasionally used.

The direct current most frequently used was controlled by an iron water-pipe rheostat of ten equal sections in series, having a total resistance of 0.5 ohm. With all but one section of the rheostat short-circuited, 600 amperes was delivered at a pressure of 80 volts at the furnace terminals. Of the total energy transformed by the generator, the per cent. delivered to the furnace was as follows:

Average for an entire experiment	68 per cent.
During maximum load (600 amp. x 80 volts)	73 per cent.
Highest per cent for ten consecutive minutes in any experiment	80 per cent.
Highest per cent ever attained, for two minutes, by running the furnace directly from the dynamo	94 per cent.

The furnace was started with the entire rheostat in the circuit, which explains the low average. In experimental work, the convenience of this method of control more than compensates for the waste of energy. This waste of energy might be considerably diminished by having some sections of the rheostat of one-half and one-third the resistance of the others, with a generator voltage of eighty or ninety instead of one hundred and ten.

It is stated by Mrs. Ayrton[41] "without some external resistance, it is impossible to maintain a silent arc between solid carbons." From the behavior of the arc when the resistance of the rheostat was reduced to only 0.05 ohm, the writer believed that even this resistance might be dispensed with, and yet the arc would run steadily. This was verified by an experiment. The furnace was heated, as usual, with the line voltage at 110. The voltage regulator was then cut out, the voltage lowered to 70, and the last section of the rheostat short-circuited. The only resistance external to the arc was that of the cables and armature,—between 0.012 and 0.018 ohm. The arc ran satisfactorily, although not so steadily as with one section of the rheostat in the circuit. The voltage of the generator was then raised to 80 with the result that the widest variations of current for an arc 1⅞ inches in length was from 310 to 450 amperes. It is probable that most of this variation

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[41] The Electric Arc, p. 250

was due to the defective form of the anode, developed during the preliminary heating. The average resistance of the arc was twelve times that of the remainder of the circuit, and consequently the per cent. of energy delivered to the furnace was 92 +.

In this experiment, it was observed that when the arc became silent after it had been "shrieking," the voltage across the terminals diminished and the current increased. This is contrary to Mrs. Ayrton's observation upon the open arc.[42]

These differences between the action of the arc lamp and the arc furnace would undoubtedly yield interesting results if thoroughly investigated.

ELECTRIC FURNACES.

For the production of metallic borides and silicides by the direct reduction of oxygen compounds, the horizontal arc furnace was decided upon as most easily managed and best suited to the purpose.

Several different materials of construction were tried and rejected. Finally magnesite brick was decided upon as being by far the most resistant material available for the furnace. Other materials tried were limestone, ordinary fire brick, chromite, and silica brick. The only limestone obtainable was very easily broken, and as a furnace material cracked badly, even when protected from the arc by a graphite lining. It is quite possible that a harder, stronger limestone, and particularly a dolomite, might prove a satisfactory material for furnace construction. Ordinary fire brick cannot be used for the inner zone of an arc furnace because of its fusibility. Silica and chromite brick, while less fusible than fire brick, are still far from satisfactory. The former fuses and disintegrates by the heat of the arc, and the latter cracks badly before its fusing point is reached. Both are distinctly more fusible than magnesite brick, and are more readily attacked by slags.

In point of infusibility, magnesite bricks are very satisfac-

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[42] The Electric Arc, p. 279.

tory, being melted to a depth of less than ¼ inch by ten minutes exposure to an arc of 600 amperes at 80 volts only an inch below the brick. They do, however, crack under the influence of heat, and must be handled very carefully. These brick were obtained from the Harbieson-Walker Refactories Co.

In form, the furnaces consisted of a box built of magnesite brick without cement, surrounded by a second layer of fire brick. The dimensions of the horizontal arc furnace were: outside—20 inches square, 26 inches high; and inside—8¾ inches long, 7 inches wide, 7 inches deep—429 cubic inches. The outside dimensions included the ventilated base of fire brick. Although the table on which the furnaces stood had a thick cement top, it was found necessary to have air circulation between the body of the furnace and the table top. The furnace is shown in Figure I.

The cover consisted of two magnesite bricks, and the electrodes entered through holes drilled in the bricks which formed the ends. Later, the ends were simply built up around the electrodes, and the cracks stuffed with asbestos paper. This type of furnace, with two modifications, was used in about one hundred and thirty experiments.

Much trouble was experienced from the contamination of the products by iron. Even after all materials that entered into the composition of the charges were rendered iron free, the iron was still found, and its source was finally discovered to be the magnesite brick. A fused metal resting upon these in the presence of a strongly reducing slag, will be contaminated by iron. To remedy this, a bed of powdered magnesia, free from iron, was spread an inch deep in the bottom of the cavity. This prevented any contamination from the bottom of the furnace, but there was still occasional contamination from the side walls. For a part of the work, the entire inside, except for the bottom and the upper half of each end, was lined with inch-thick sheet graphite. Although this introduced carbon, it effectually prevented contamination by iron, and greatly prolonged the life of the magnesite brick. With the graphite lining, the inside dimensions were 8¾ inches by five inches by six inches—262 cubic inches.

It would have been an advantage if the bottom of the furnace had been laid in cement, or strapped with iron to prevent the bricks from separating with the alternate expansion and contraction.

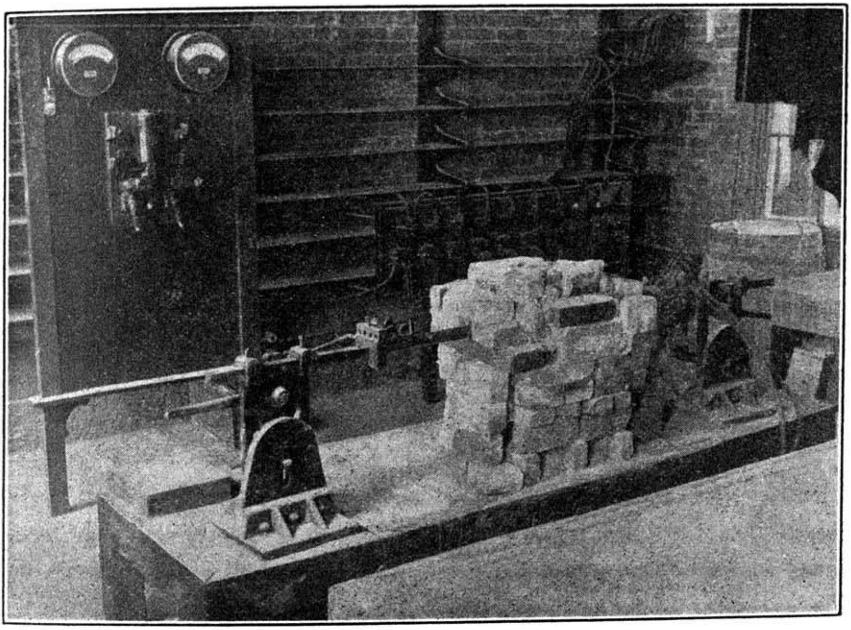

FIGURE 1.—The Electric Furnace.

For the short duration of the heating, fifteen to twenty minutes, with a powerful current for less than half this time, the heat insulation was found to be ample. The outside layers of brick could be removed by the bare hands, if done as soon as the current was shut off, although an hour later, they might become red-hot. The nearer air-tight the furnace is, without actually being so, the better.

The electrodes used were of Acheson graphite. The maximum current permissible on account of oxidation of the electrodes outside of the furnace has been determined in the course of this work to be as given in the following table for twenty minutes heating:

Table IV.

Diameter.	Amperes.
1 inch.	400+.
1¼ inch.	650+.
1½ inch.	900.
2 inch.	1600.

The capacity of the first two sizes is from direct measurement; that of the last two is calculated from the areas of their sections, since the maximum current used, 700 amperes, never heated them to redness. If the heating is prolonged to an hour or more the current allowable is about fifteen per cent. less than in Table IV.

Although 600 amperes has been used for a short time with one inch electrodes, these become red their entire length, and undergo oxidation. It was found that this oxidation could be prevented by painting them with a paste of water glass and carborundum dust.

Moissan ("Le Four Electrique") has given the size of carbon electrodes suitable for furnaces of different horse-power. As he ordinarily used fifty or sixty volts, the latter value has been used in calculating the following table, except in one case where he specified seventy-five volts. The results as calculated from Moissan are given in Table V.

Table V.

Diameter.		Amperes.
m. m	Inches.	
16–18	$\frac{11}{16}$	120
27	1	450
40	1½	1,250 (100 H. P.)
50	2	3,700 (300 H. P.)

In this table the current densities per unit area increase greatly with increase of diameter, although from the fact that the radiating surface increases less rapidly than the cross section, the reverse would be expected. Either the capacity of the smaller electrodes is greatly underrated, or that of the larger ones much overrated. The only carbon electrode tried by the writer was of one inch diameter, and this became red-hot outside the furnace at 150 amperes, although Moissan stated that he was able to use 450 amperes. It would be of interest to the worker with the electric furnace to know whether the relative conductivities of carbon and of graphite for heat are in the same ratio as their electrical conductivities, as is the case for the metals. If this is so, there will be no advantage of either over the other in regard to the amount of heat wasted by conduction from the furnace.

On account of their being such good conductors of heat, the graphite electrodes used should be the smallest that will carry the desired current. They should be slightly pointed before use, and set exactly in line in the furnace. The sôurce of any irregularity in the operation of the arc is usually found in the anode, which corrodes irregularly, while the cathode keeps in good order without attention. One advantage of alternating over direct current for the arc furnace is that both electrodes tend to keep in good form.

V.

EXPERIMENTS.

After this detailed consideration of the subject of reducing agents, the general action of slags, and the construction and operation of the furnaces employed, attention may be directed to the problems proposed, viz., the production of borides and silicides from their oxygen compounds by a single reaction in the electric furnace, and the production, if possible, of certain silico-borides by the same means.

The experimental work, results of which are here given, covered a period extending from December, 1903, to May, 1905, and included 160 electric furnace runs, with associated analytical work. Each run involved the preparation of the materials, the weighing and mixing of the charge, the partial or complete construction of the electric furnace before, and the dismantling after, a run, and required from one to seven hours, varying with the time needed to prepare the materials of the charge, and to construct the furnace.

In addition to this, there was the disintegration of the product by acids, always requiring a day or more, and in some cases involving the trial of a number of organic in addition to the mineral acids. When a crystalline residue remained, this was tested qualitatively, and if promising, was subjected to a quantitative analysis.

Several runs of the furnace were for the purpose of preparing materials needed, such as borax glass, and boric anhydride; others, although not described in detail, contributed to the results obtained; while there were many experiments which were of use only in showing what arrangement of furnace or what materials were to be avoided.

A most serious limitation upon the work was the difficulty of carrying on the analytical processes. The resulting products required the working out and application of new methods of analysis. Boron, especially, presented much difficulty in its determination, and the available methods for its determination, especially when combined with various metals, are at best only partially satisfactory approximations. In several of these analyses the writer is indebted to Mr. William Hoskins of Chicago for valuable assistance.

PRELIMINARY EXPERIMENTS.

Beginning in December, 1903, a series of experiments were undertaken in the preparation of silicon in the electric furnace. Silica, glass, and calcium and sodium silicates were used as the source of silicon, and the reducing agents were carbon, aluminum, and carborundum.

The following difficulties were noted in the reduction by carbon:

a. The melting point, 1430° C.,[43] and the boiling point of silicon are evidently near together, and as the reduction temperature is high, much silicon was often vaporized.

b. The specific gravity of silicon (2.34) is about the same as that of most of the silicate charges used (S. G. quartz 2.5), hence the silicon remained diffused in the slag in small spheres instead of settling to the bottom in a single mass.

c. Because of its brittleness, the masses of silicon that were occasionally obtained were broken in removing them from the slag.

The best results were secured with a charge containing much sodium silicate, thus lowering the density of the fluid bath and permitting the silicon to sink in it. By this means, a bar of silicon six inches long, 1¼ inches wide, and ¾ inch thick was formed in the furnace, but was broken into three pieces in removing it from the slag.

Reduction by aluminum was easily accomplished by adding the metal in lumps, to any melted silicate of the alkali or alkali-earth metals, containing cryolite or fluor spar as a flux for the alumina formed. When the action was brief, the resulting lumps of metal on treatment by hydrochloric acid, left the silicon as a crystalline powder. By prolonged action, the product appeared to be massive silicon, but still contained a trace of aluminum.

Nineteen experiments were tried, mainly with some type of resistance furnace. A method frequently used was to cover the electrodes with fragments of the silicate, start the arc, and as soon as a fluid bath was formed to draw the electrodes apart and allow the melted silicate to serve as the resistor.

By these various methods, a few pounds of silicon were produced in globules and fragments. This afterward served as a source of silicon in some of the experiments which follow.

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[43] F. J. Tone, in Electrochem. Ind., 3: 183 (1905).

SILICIDES.

The first effort in this field was an attempt to prepare a new silicide, that of phosphorus. Phosphorus unites with many metals to form compounds akin to the borides, carbides and silicides. Since compounds of silicon with both boron and carbon have been obtained, it seemed probable that phosphorus would also unite with silicon. Further encouragement was found in the existence of the following compounds: SiS_2, $SiSe_2$, BP, and B_5P_3.

The first experiment consisted of the reduction by carbon of a mixture of phosphoric acid and silica. The charge was made according to the molecular proportions ($2HPO_3 + SiO_2 + 7C$) by dissolving glacial phosphoric acid in water, and stirring in finely pulverized silica and carbon. The mixture was dried, ignited, and then heated in an open graphite crucible in the electric furnace for four minutes at 500 amperes and 50 volts. A greenish-yellow flame was seen at first, but it quickly died out. The product looked like the original mixture, and gave no indication either of phosphorus or of a phosphide when treated with acids.

With the idea that fused copper or copper silicide would make a good solvent for the interaction of silicon and phosphorus, the following charge was prepared:

Glacial phosphoric acid	40 grams.
Carborundum	20 grams.
Silica	5 grams.
Copper	30 grams.
Aluminum	20 grams.

This mixture was heated in a covered graphite crucible for 13 minutes at 200 amperes and 60 volts. When the metallic product was treated with hydrochloric acid, a gas was evolved which burned with a greenish-yellow flame when kindled. The product appeared to be metallic phosphides only.

Slight variations of this experiment were tried, but with no better results.

Direct union of the two elements was next tried, with tin as a solvent. Red phosphorus was dissolved in melted tin, and a phosphor-tin produced, containing 7 per cent. phosphorus. This was heated with pulverized silicon by the blast lamp, but without effect upon the silicon. Then the electric furnace was used. All silicon had vanished, and the crystalline metal had a strong odor of phosphorus. Hydrochloric acid acted upon it readily, and the gas evolved, burned, when kindled, with a yellow flame and the formation of a white smoke. If any silicide of phosphorus had formed, it was destroyed in dissolving the tin.

As the results of these experiments were not encouraging, the attempt to prepare a silicide of phosphorus in the electric furnace was abandoned.

Production of Silicides from Sulphide Ores.

The possibility of forming silicides by the simultaneous reduction of silica and a metallic sulphide was next investigated. The experiments were confined to such material as was immediately available and were directed to the formation of silicon-metals, not to the isolation of silicides of definite formulae.

Silicon-Copper from Chalcocite (Cu_2S.)

A charge was prepared consisting of 63.2 grams chalcocite, 24 grams ground quartz, and 35 grams calcium carbide, the proportions having been determined from the equation,

$$Cu_2S+SiO_2+CaC_2=Cu_2Si+CaS+2\ CO.$$

The calcium carbide was estimated as 80 per cent. pure.

The source of heat was a resistor of granular graphite upon which was placed the crucible containing the charge. This crucible was cut from a block of Acheson graphite, as it had been found by previous experiment that the ordinary "graphite crucibles" used for metallurgical operations, were destroyed in an electric furnace of this or the arc type. The heat record was:

Time.	Amperes.	Volts.	Resistence.	Per cent. of resistance at outset.
5:55	160	100	0.62 ohms	100
....	200	98	.49 ohms	79+
5:59	340	92	.23 ohms	37+
6:00	500	83	.17 ohms	27+
6:01	550	80	.14 ohms	22.5

Although the charge had been intensely heated, no metal was found. It was reheated in a similar way for 17 minutes without effect. Lime as a flux and fresh materials were added, giving it the composition,

Sand	360 grams.
Chalcocite	379 grams.
Lime	324 grams.
Calcium carbide	35 grams.
Anthracite coal	120 grams.

This was heated half an hour at 300 amperes and 70 volts in a vertical furnace consisting of a box built of sheet graphite, 5 inches square and 6 inches deep. The charge served as one electrode. The result was an ingot of brittle white metal weighing 250 grams. By analysis, the composition was:

Copper	81.6 per cent.			
Iron	7.7 per cent.		Cu_2Si	24.75 per cent.
Silicon	6.4 per cent.	*or*	Fe_2Si	9.62 per cent.
Carbon	1.0 per cent.		Copper	61.35 per cent.
Undetermined	3.3 per cent.			
	100.0 per cent.			

As no sulphur was present, it is evident that the ratio of lime to sulphur used in this case, 4.2:1, was sufficient for its removal. The product contained 16 grams of silicon, or 10 per cent. of the total silicon in the charge. The yield was 53 per cent. of the combined weight of metal and silicon in the charge.

Ferro-silicon from ferrous sulphide.

$$FeS+2\,SiO_2+CaO+4\,C=FeSi_2+CaS+4\,CO.$$

In the first experiment, 560 grams of ferrous sulphide, 448 grams of lime, and an excess of glass were reduced by anthracite coal in the vertical furnace. The time of heating was 40 minutes by a current of 200 amperes at 50 volts. The product, a low grade of ferro-silicon, contained a small amount of sulphur. The ratio of lime to sulphur in this charge was 2.2:1, yet this is far above the theoretical ratio, 1.75:1. An explanation offered for the failure of the considerable excess of lime to remove all sulphur is that the lime entered into combination with the large excess of glass present, so that the usual stage of equilibrium between these weights of ferrous sulphide and lime was not attained.

In a second experiment, ferrous sulphide was reduced in the horizontal arc furnace at a higher temperature. The charge was in accord with the equation,

$$FeS+SiO_2+CaC_2=FeSi+CaS+2\,CO,$$

with the addition of sodium chloride and cryolite as a flux. The heating was for 16 minutes at 450 amperes and 87 volts. The yield was 80 per cent. of the weight of metal and silicon only 53.3 per cent. of the combined weight of metal and silicon in the charge. Had the charge contained an amount of lime equivalent to the carbide, the ratio of lime to sulphur would have been 2.0:1; yet the product was free from sulphur. This tends to confirm the view that the glass was responsible for the presence of sulphur in the previous experiment.

Silicon-nickel from Millerite.

The charge of 107 grams NiS, 110 grams SiO_2, and 54 grams of powdered aluminum was heated in the horizontal arc furnace. Only a few globules of brittle, white metal, silicon-nickel, resulted. A fire brick had melted and flooded the interior of the furnace with slag. The experiment was not repeated.

Silicon-molybdenum from molybdenite.

$$MoS_2+2\ SiO_2+2\ CaC_2=MoSi_2+2\ CaS+4\ CO.$$

The charge consisted of 48 grams molybdenite, 86 grams ground quartz, and 300 grams calcium carbide. The large excess of carbide was used in the hope that much of it would remain unchanged and yield a slag that could be decomposed by water. This charge was heated in the vertical furnace for 25 minutes by a current of 400 amperes and 70 volts. The result was an ingot of metallic lustre, white, brittle, and harder than quartz. Its weight was 32 grams. There was in the charge 28 grams of metal, 40 grams of silicon, and an excess of carbide over that required theoretically for complete reduction, so that the yield was only 47 per cent. of the theoretical amount. Water had but a very slight action on the slag, showing that the carbide was practically all destroyed. As expected, the slag evolved much hydrogen sulphide when treated with hydrochloric acid.

Other experiments were tried upon molybdenite using aluminum powder as a reducing agent, with similar results in regard to the nature of the product and the per cent. of yield.

Conclusions.

1. Metallic sulphides and silicates can be simultaneously reduced by calcium carbide or aluminum, with the production of a silicon alloy.
2. The total yield based on both the metal and non-metal in the charge is little above 50 per cent.
3. The use of carbon or a carbide as reducing agent introduces carbon into the metallic silicides of those metals capable of uniting with carbon.
4. The product can be obtained entirely free from sulphur by the use of lime or aluminum.

A NEW SILICIDE OF MOLYBDENUM.

The only silicide of molybdenum heretofore known is that discovered by Vigouroux in 1899, having the formula Mo_2Si_3. In one of the attempts to prepare a silico-boride of molybdenum, the writer believes he has demonstrated the existence of a higher silicide.

The charge consisted of 70 grams molybdic acid, 30 grams silica, 50 grams boric anhydride, 106 grams copper, and 120 grams aluminum, one-half in the form of powder, with cryolite as a flux and lime as a retarder to the reaction. This charge was heated 16 minutes in the horizontal arc furnace by a current of 350 amperes at 70 volts. The resulting ingot of metal was pulverized in an iron mortar, and treated for several days with hot nitric acid diluted by its own volume of water. After washing, the residue was treated by dilute hydrofluoric acid, and washed by water, alcohol, and ether. It was then dried as much as possible by the filter-pump, and heated for several hours in a drying oven. The residue consisted of aggregations of flat, dark crystals with a metallic lustre. Analysis showed the composition to be:

Molybdenum	63.4 per cent
Silicon	31.2 per cent.
Iron	1.1 per cent.
Boron	2.1 per cent.
	99.8 per cent.

Hot hydrofluoric acid dissolved some silicon and all the iron present. The residue from this treatment was unaffected by boiling aqua regia, but was completely soluble in a mixture of hydrofluoric and nitric acids. Table II shows that hydrofluoric acid is without action upon the boride of iron, therefore all the iron must be present as silicide; hence the boron is present as molybdenum boride. Iron boride was undoubtedly present in the original ingot, but was destroyed by the treatment with nitric acid. Since crystallization occurred in a large amount of copper, there can be no free silicon present. After deducting the silicon required by the amount of iron present as $FeSi_2$, and the molybdenum required by the boron, the residual molybdenum and silicon are far from the proportions required by the formula Mo_2Si_3, but correspond closely with that required by the formula $MoSi_2$. There is a slight excess of silicon even over the amount required by this formula.

The action of several reagents upon this substance is as follows:

Boiling nitric acid.	No action.
Boiling aqua regia.	No action.
Boiling hydrofluoric acid.	No action.
Fused sodium carbonate.	Action with incandescence.
Fused sodium nitrate.	Slow, but complete decomposition.

Its specific gravity is 6.31 at 20.5° C.

An earlier experiment in which a mixture of molybdenite and silica was reduced by calcium carbide, gave a similar result in the ratio of silicon to molybdenum.

While no pure silicide of molybdenum has been isolated in this experiment, the only way that the writer can explain the content in silicon is by the presence of a silicide of molybdenum richer in silicon than Mo_2Si_3, and probably having the formula $MoSi_2$.

BORIDES.

The preparation of silicides by the method proposed having been successfully accomplished, it seemed reasonable to suppose that the borides might be readily prepared by the same treatment, and a series of experiments was conducted with that end in view.

Molybdenum Boride.

$$3\,MoS_2+3B_2O_3+9\,Al=2\,Al_2S_3+3\,Al_2O_3+3\,MoB_2+Al.$$

A charge of 94 grams molybdenite, 41 grams boric anhydride, and 47 grams aluminum powder was heated in the arc furnace for ten minutes with a current of 450 amperes at 60 volts. The result was 39.5 grams of somewhat brittle, white metal that scratched quartz. It was attacked by hot nitric acid and was completely dissolved by hot aqua regia. A qualitative test indicated that it contained boron in some quantity. Analysis proved its composition to be:

Molybdenum	85.3 per cent.
Iron	8.8 per cent.
Silicon	1.2 per cent.
Boron (by difference)	4.3 per cent.

The product, then, contained only 1.7 grams boron out of a total of 12.8 grams in the charge, and consisted of molybdenum boride dissolved in a large excess of molybdenum.

Chromium Boride.

A mixture of 300 grams potassium dichromate, 200 grams of borax, 800 grams of calcium carbide, 100 grams of aluminum, and 20 grams of fluor spar was heated 55 minutes with a current that averaged 360 amperes at 75 volts. The resulting slag was not acted on by water. The metallic product, weighing 66 grams, was of a dull white color, and cut quartz readily. On standing in air several days, it cracked in many places. Nitric acid had no visible effect upon it, but in hot hydrochloric acid there was a slow evolution of a gas of very disagreeable odor. This gas was probably hydrogen with traces of acetylene and boron hydride. Chromium and boron were found in the solution, which, after several days, was complete. Cold hydrofluoric acid had no visible effect even when nitric acid was added to it. Analysis indicated 7.0 per cent. iron, 0.9 per cent silicon, 1 per cent. carbon, 4 per cent. boron, 78.9 per cent. chromium, and aluminum which was not determined.

As it was thought that the bad odor of the gas evolved was due to the presence of a trace of an aluminum boride, which by treatment with acids yielded boron hydride, the experiment was repeated, with the aluminum omitted and 30 grams of carbon added in its place. The result was 130 grams of a very brittle, crystalline metal that failed to scratch quartz. Nitric acid did not act on it, and hydrochloric acid acted only slowly when hot. The gas evolved had no noticeable odor. Hydrofluoric acid at 60°, either alone or with the addition of nitric acid, had but a very slight action upon it. Analysis gave iron 9.0 per cent., chromium 78.9 per cent., silicon 0.2 per cent., carbon 5.0 per cent., boron 1.8 per cent.

The first of these products was a ferro-chromium-boron alloy, and the second, a ferro-chromium-carbon alloy. The iron in each case came from the "carbide," in which 0.6 per cent. would be sufficient to account for the iron found in the products.

Manganese Boride.

A Goldschmidt charge consisting of manganese dioxide, boric anhydride, and powdered aluminum in theoretical proportions was placed within a Hessian crucible, and this was placed inside a strong steel cylinder,[44] packed with powdered quartz. The cover was tightly bolted on, and the charge ignited by the electric current. The result was an ingot of metal weighing 25 grams, a yield of 72.2 per cent. of the total manganese and boron in the charge. Analysis proved its composition to be:

Manganese	71.7	per cent.
Silicon	1.0	per cent.
Iron	4.0	per cent.
Boron (by difference)	23.3	per cent,

The iron came from the fuse wire by means of which the charge was fired. The metal was finely crystalline, and *strongly magnetic.*

The product was, then, a mixture of the two borides of man-

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[44] This apparatus was devised by Prof. C. F. Burgess for firing Goldschmidt charges under great pressures, and was placed by him at the disposal of the writer.

ganese, MnB and MnB_2, with the boride of iron. The boride of iron is probably magnetic, although no statement in regard to this is made by Moissan. It is, however, remarkable that so small an amount (4.5 per cent.) should render the whole mass magnetic. It should be noted that manganese appears to be the essential ingredient in the magnetic alloys formed from non-magnetic metals.[45]

Other experiments by this method, yielded similar results.

BORIDES AND SILICIDES BY ELECTROLYSIS.

Several experiments were tried to test the possibilities of employing an electrolytic method of preparing these compounds.

The first electrolysis attempted was that of borax with the addition of cryolite, carried out in the vertical furnace. The container was a section of 4-inch iron steam-pipe, five inches high, resting upon a magnesite brick in the center of which was the iron cathode. The charge was melted by striking an arc from a graphite anode, which was changed for a bar of wrought iron 1¼ inches in diameter as soon as the charge was fluid. The electrolysis was conducted with a current of 300 amperes. Metallic globules rose to the surface and burned brightly. The iron anode was rapidly consumed, and in 25 minutes, about 5 inches of it had melted away.

The resulting metal could be broken by severe pounding with a hammer. The fracture was quite different from that of either wrought iron or cast iron. Analysis gave 94.6 per cent. iron, 1.5 per cent. silicon, 1.5 per cent. carbon, 2.5 per cent. boron. Moissan has shown that iron containing 10 per cent. of boron is more fusible than cast iron. In this experiment, the iron evidently melted as soon as sufficient boron, carbon, and silicon had united with it to lower its fusing point to the temperature of the bath.

The experiment was repeated with a weighed iron anode which in 22 minutes lost 533 grams for 73.7 ampere hours.

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[45] R. A. Hadfield, Chem. News, 90: 180 (1904). Dr. Hensler, Electrotechnische Zeitschr., March 2, 1905.

This is seven times the amount of iron dissolved by the same current by electrolysis in solutions. This current is the equivalent of 10 grams of boron, so that the product probably contained 1.8 per cent. boron. Similar results were obtained by the electrolysis of glass with an iron anode.

Wishing to learn whether the position of the electrodes had any influence upon the electrolysis or not, an experiment was conducted with horizontal iron electrodes a foot apart. The anode lost 121 grams, and the cathode 118.5 grams for 194 ampere hours, a loss per ampere hour of only 8 per cent. of that when the anode was directly above the cathode.

In these experiments, then, the reduction of the borax or the silica seems to be due to a secondary reaction of the metal liberated at the cathode, and not to a direct liberation of the non-metal at either the anode or the cathode. With an iron anode, the resulting alloy contains between one and three per cent. of boron. Metals whose borides and silicides are more infusible than those of iron ought to yield richer alloys.

SILICOBORIDES.

After three years of experimental research with the electric furnace, Moissan said:[46] "At high temperatures we have a simple chemistry, and we obtain only a single combination, always of a simple formula." It is seen from Table II that this statement is true of the majority of the borides and the silicides even down to the present.

On the other hand, there is evidence to show that ternary compounds can exist even at the temperatures of the electric furnace. In "siloxicon" (Si_2C_2O), discovered by Acheson, and the double carbide of tungsten and chromium ($W_2C.3Cr_3C_2$),[47] we have what appear to be definite chemical compounds of three elements. The production of any ternary compound in the electric furnace renders it at least possible that there shall ultimately be obtained several series of such substances, just as there are now known several series of binary compounds.

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[46] Ann. de Chim., 9: 277 (1896).

[47] Moissan, C. R., 137: 292 (1903).

The names silicoboride and borosilicide were applied as early as 1893 to complex products of the electric furnace containing among other elements boron and silicon, but no definite chemical compounds had been isolated. Several facts seemed to the writer to point to silicon and boron as promising elements with which to form a ternary metallic compound. They each unite readily with many metals, to produce substances of remarkable stability, and they also unite with each other. The attempt was accordingly made to isolate a definite compound containing a metal, boron, and silicon.

Iron, chromium, nickel, and cobalt were selected as the most promising and convenient metals with which to experiment.

Ferric oxide was prepared from electrolytic iron. With 100 grams of this was mixed 60 grams of pulverized borax glass prepared from pure borax, 72 grams silica, 114 grams powdered aluminum, 60 grams ingot aluminum, 70 grams copper as crystallizing medium, and 100 grams of cryolite. This mixture was heated 14 minutes in the electric furnace at an average of 26.7 kilowatts. The result was 135 grams of hard crystalline metal that could be broken only with much difficulty. As nitric acid acted on it only very slowly, it was heated with 115 grams more of copper, and 175 grams of aluminum. The product from this was crushed in an iron mortar, heated for six days in 50 per cent. nitric acid, repulverized, and the treatment with nitric acid continued two days more. As a qualitative test indicated the presence of copper, the substance was again ground in the iron mortar, and the treatment with nitric acid continued. By the microscope it was found that the resulting powder did not consist of definite crystals, but of irregular metallic fragments. It was strongly magnetic and contained boron. Analysis showed its composition to be:

Iron	72.3 per cent.		Cu_2Si	1.22 per cent.
Silicon	17.2 per cent.		Cr B	4.36 per cent.
Copper	1.0 per cent.		Fe B	35.3 per cent.
Chromium	3.6 per cent.	*or*	Fe_2 Si	26.48 per cent.
Boron (by diff'ce).	5.9 per cent.		Fe Si	31.82 per cent.
	100.0 per cent.			99.2

The absence of any free silicon was assured by the large amount of copper in which it was crystallized. The presence of chromium was explained by the softening of part of a chromite brick in the furnace.

A formula for an iron silicoboride can be computed from this analysis as follows:

			Per cent divided by atomic weight.		
Iron........	72.3 per ct	76.5 per ct.	1.366	x 6 =	8.1
Silicon.....	17.2 per ct.	18.0 per ct.	.643		3.85 or $Fe_8Si_4B_8$
Boron......	5.14 per ct.	5 5 per ct.	500		3.00
	94.64 per ct.	100.5 per ct.			

Another portion of the original ingot was treated for a week with hot aqua regia, being reground during this treatment. The residue was still magnetic, and contained boron as well as a trace of copper. The microscope showed that the substance was homogeneous. It would seem to be either an iron silico-boride, or a solidified solution of $Fe_2Si.3FeSi.3FeB$. Its magnetic and chemical behavior support this view. Fe_2Si is magnetic and is readily attacked by aqua regia. FeB is probably also magnetic, and is dissolved by either nitric acid or aqua regia. FeSi is non-magnetic and insoluble in both acids. From the magnetic properties of the substance, from its appearance under the microscope, and the treatment by acids to which it was subjected, it would seem impossible that these three compounds should exist separately in the residue.

Eight other experiments were tried, mainly with electrolytic iron as the source of that element. The results varied greatly. In several cases the product was completely soluble in nitric acid. In others, the residue obtained oxidized so readily while drying that it could not be obtained pure, even by washing with much alcohol and ether. Further experiments, for which time is at present lacking, are needed to establish beyond doubt the existence of a silicoboride of iron.

Nickel oxide, by a similar process, yielded a metallic residue containing 21.0 per cent. silicon and 11.45 per cent. iron. The source of the iron was found to be an impure nickel oxide.

Five experiments with pure nickel oxide were unsatisfactory, as the product was completely dissolved by nitric acid.

Tungstic acid, silica and boric anhydride were reduced in the presence of copper, but the product was entirely dissolved by nitric acid. This is a surprising result, as the silicide of tungsten is completely insoluble, and the boride only slightly attacked by this acid.

Similar experiments were tried with molybdic acid, but with unsatisfactory results.

More encouraging results were obtained from potassium dichromate, but further investigation is needed upon this.

Although these experiments have failed to yield a series of silicoborides, the writer does not yet regard such a series of compounds as impossible. The failure may be due to the method used, which is not suited to the production of compounds of the metals with boron. It is the writer's intention to take up this investigation again at the earliest opportunity, using the method of synthesis from the elements.

VI.

ELECTRICAL AND OTHER DATA CONCERNING THE ARC FURNACE.

In this series of experiments many observations were made upon the length of arc, its variation in resistance, electrode consumption, etc. Some of these observations are included here as of interest, and perhaps of value to other experimenters.

The longest arcs obtained were 15.5 and 14.4 cm. (6 1/2 and 5 11/16 inches) at 104 volts, the former at 800 amperes. At the usual voltage of 80 on the furnace terminals, the length of arc for 600 amperes varied from 6 to 7.5 cm. (2⅜ to 3 inches) as a rule.

Resistance of the arc depends upon:

a. Length.

b. Current strength. (See Table VI.)

Increase of current increases the cross section of the arc.

c. Temperature of the furnace.

During the rise in temperature at the beginning of an experiment the arc must be gradually lengthened if the current is to be maintained constant. When a cold charge is fed into a hot furnace the current is diminished.

TABLE VI.—*Effect of varying currents upon the resistance of the arc*

No. of Experiment.	Amperes.	Volts.	Resistance.	R_1:R
98	600	75	.118	1
	360	75	.202	1.71
	210	79	.369	3.12
	190	82	.425	3.60
	150	81	.533	4.51
	140	83	.586	4.96
	120	79	.651	5.51
	120	81	.668	5.66
	100	81	.803	6.80
	70	80	1.136	9.62
	55	85	1.538	13.03
	40	92	2.293	19.43
111	580	78	.127	1
	400	72	.173	1.36
	330	77	.226	1.78
	280	77	.266	2.09
	200	81	.398	3.14
	160	81	.499	3.93
	200	76	.373	2.94
	180	66	.359	2.83
	150	77	.568	3.18
	120	75	.618	4.87
	130	75	.569	4.48
	120	70	.576	4.53
	120	70	.576	4.53
	110	71	.638	5.02
	75	83	1.099	8.66
	70	80	1.136	8.95
	80	89	1.105	10.97

d. Quantity and nature of vapors within the furnace. An increase in the amount of vapors of sodium and of silicon lowers the resistance. Possibly there are vapors which are capable of increasing the resistance. (See Table VII.)

The data of Table VI were taken at the close of experiments when the furnace was very hot. Maintaining the length of arc unchanged, the current was cut down by increasing the external resistance. The pairs of bracketed readings were made about ten seconds apart with the same resistance in the circuit. An entire set of readings occupied about three minutes, so that the temperature within the furnace was practically constant. The column $R_1 : R$, shows the increase in resistance of the arc as the current is diminished and the external resistance is increased. Curves from Table VI are shown in Figure 2.

From the above and other similar data, the writer draws the conclusion that *the arc tends to maintain a constant ratio between its own resistance and that of the remainder of the circuit, or an arc of fixed length tends to maintain a constant voltage.*

In experiment 111, the external resistance was varied about 900 per cent., the maximum varation in voltage of the arc was 14.1 per cent., and the average, only 1.8 per cent. The rise in voltage seen in the last readings, occurred but a few seconds before the arc died out. One readily pictures the shrinking of the arc to a mere pencil of carbon vapor as the current is diminished.

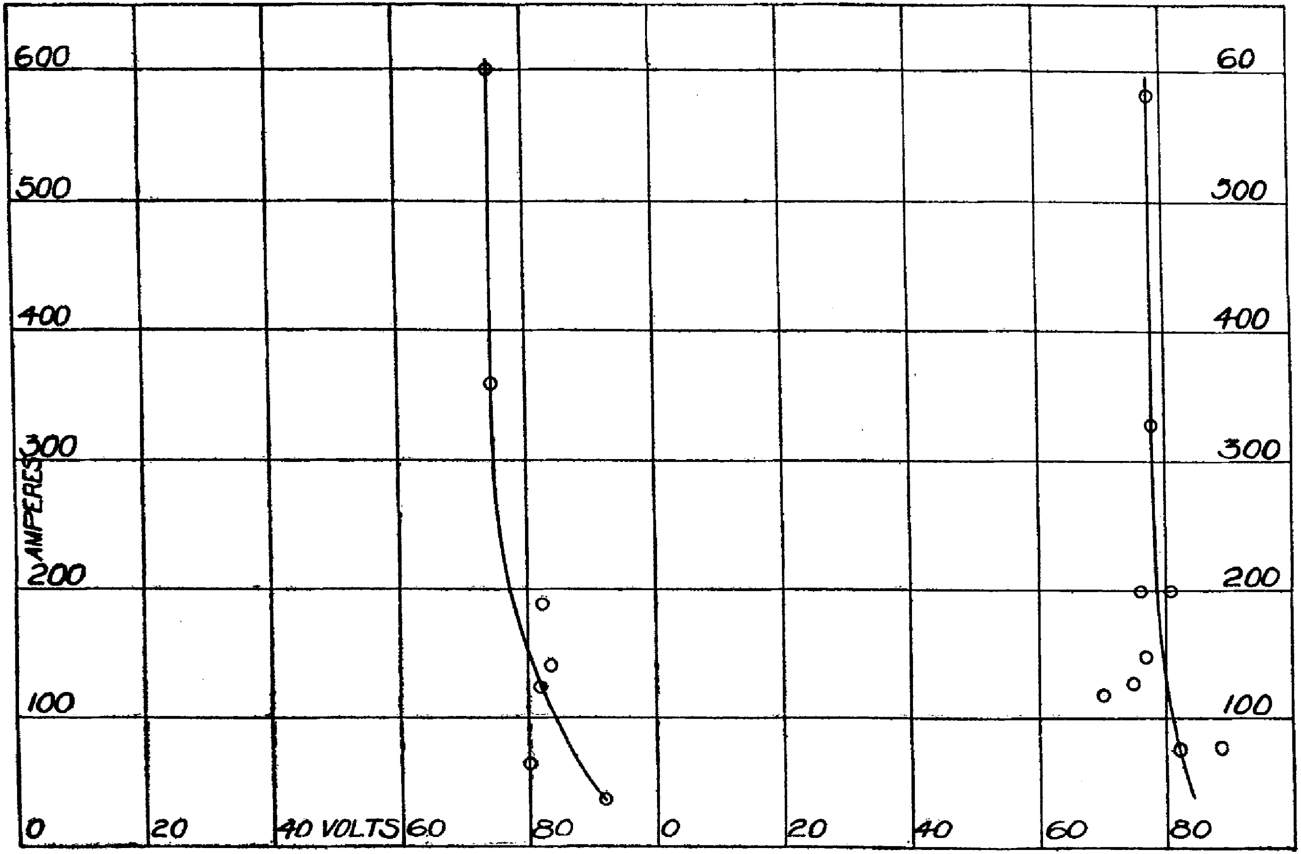

FIGURE 2.—Curves of Resistance, from Table VI.

TABLE VII.—*The effect of vapors upon the resistance of an arc of constant length.*

No. of experiment.	Amperes.	Volts.	Resistance.	Change in resistance. Per cent.	
20	350	75	.214	....	
	400	68	.170	—20	Silicon vapor suddenly formed.
118	160	82	.512	....	
	300	65	.216	—59	Yellow flame suddenly appeared.
	230	75	.239	—53	
126	250	82	.328	....	Little flame.
	300	75	.250	—24	Much flame.
	230	80	.348	+ 9	No flame.
132	640	72	.113	....	Much flame from furnace
	600	74	.123	+ 9	Flame continued.
	500	81	.162	+42	Flame instantly ceased.
	560	77	.138	+22	Flame started again.
	570	77	.135	+19	Flame continued.

The above records were made after the vigor of the chemical reaction was over, for at the height of the reaction, the fluctuations of the instruments were usually too rapid to be read.

Comment upon these figures is scarcely necessary. It will be readily seen that the effect of vapors may in some cases demand reckoning upon.

FIGURE 3.—Curious Electrical Phenomenon.

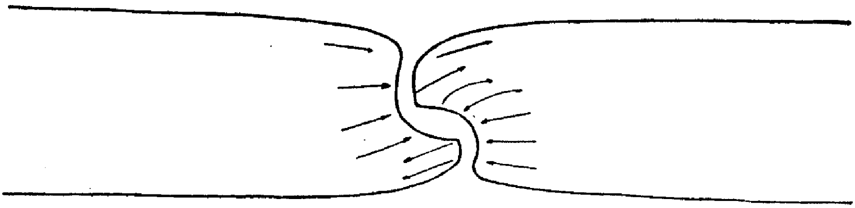

TABLE VIII.—*General Data Concerning the Arc Furnace.*

Exp. No.	Diam. of Electrodes.	Average K. W.	Time in Min.	K. W. x Min.	Volts.	Amp.	Length of Arc.		Resistance.		
							Inches.	C. M.	Total.	Per inch.	Per cm.
129	$1\frac{1}{2}$	28.0	36	1008	104	800	$6\frac{1}{8}$	15.5	.123	.020	.0079
61	$1\frac{1}{4}$	30.5	12	366	80	600	$3\frac{3}{4}$	9.5	.126	.034	.0132
121	$1\frac{1}{2}$	28.6	30	859	81	550	$3\frac{13}{16}$	9.6	.141	.037	.0147
123	$1\frac{1}{2}$	28.6	61	1521	78	570	3	7.7	.130	.043	.0169
88	$1\frac{1}{4}$	24.2	28	696	78	560	$2\frac{3}{4}$	7.0	.133	.048	.0190
150	2	21.8	45	980	68	650	2	5.05	.098	.049	.0194
86	$1\frac{1}{4}$	33.3	15	500	75	600	$2\frac{1}{4}$	5.7	.118	.055	.0207
89	$1\frac{1}{4}$	18.1	38	687	70	400	$2\frac{7}{8}$	7.3	.168	.058	.0230
99	$1\frac{1}{4}$	28.7	14	402	76	600	2	5.05	.120	.060	.0238
09	$1\frac{1}{4}$	26.0	25	670	80	550	$2\frac{1}{8}$	5.4	.138	.065	.0255
04	$1\frac{1}{4}$	31.1	8	249	79	550	$1\frac{3}{4}$	4.4	.118	.068	.0268
94	$1\frac{1}{4}$	24.7	10	247	82	500	$2\frac{3}{16}$	5.6	.157	.072	.0280
100	$1\frac{1}{4}$	26.1	14	414	78	600	$1\frac{11}{16}$	4.3	.123	.073	.0286
107	$1\frac{1}{4}$	29.9	23	482	80	300	$2\frac{7}{8}$	7.3	.259	.090	.0350
127*	$1\frac{1}{2}$	28.1	45	1264	103	150	$5\frac{11}{16}$	14.4	.679	.119	.0470

* The current was cut down from 400 amperes to 150 by drawing out the arc instead of increasing the external resistance as usual. This is responsible for the abnormal resistance found.

The effect of an increase of current in lowering the resistance of the arc has already been pointed out; the other factor appears to be the temperature, estimating this from both the average, and the total energy delivered to the furnace.

As has been already stated, the source of trouble when the arc is unsteady is to be found at the anode, and seems to the writer to be due to insufficient heat to maintain there a layer of carbon vapor. A very interesting phenomenon was twice observed with an alternating arc; namely, that the electrodes interlocked, as shown in full size drawing, Figure 3.

There is a deposition upon as well as a vaporization of each electrode. The points of each are coated with smooth, lustrous graphite of extremely fine grain. There are two separate arcs. Each half of the current wave has its own exclusive territory on the electrodes. Each arc dies out with reversal of current; yet sufficient carbon vapor remains in its crater so that when this electrode is once more anode, the path of least resistance is from the crater rather than from any other part of the electrode. This phenomenon occurred only with a low voltage and large electrodes, and would seem to be possible only when the crater of the anode during each phase is small in comparison with the area of the end of the electrode.

Observations were made upon the loss in weight of graphite electrodes during several experiments. The results are given in Table IX.

TABLE IX.—*Loss in weight of electrodes.*

	Exp. No.	Diameter of electrode	Time.	Average K. W.	K. W. x time.	Loss in Grams.								
						Total.		Ratio.	Per minute.		Per average K. W.		Per K. W. minute.	
						Anode.	Cathode.	An.Cath.	Anode.	Cathode.	Anode.	Cathode.	Anode.	Cathode.
		Ins.												
A. C.......	150A	1	37	6.9	229	17	14.3	1.19	.46	.40	2.40	2.35	.074	.062
A. C	151B	1	60	11.6	695	28.8	19.6	1.47	.48	.32	2.48	1.69	.041	.028
D. C.......	151A	1	9	13.4	120	11.3	2.02	5.13	1.24	.23	.84	.16	.094	.019
	139	1½	22	23.7	632	16.3	20	.81	.71	.87	.59	.72	.026	.031
	136	1½	58	25.1	1,457	59.3	32	1.87	1.02	.55	2.33	1.23	.040	.022
	138	1½	39	32.2	1,266	54.2	17	3.19	1.39	.44	1.68	.52	.043	.013
	137	1½	55	28.4	1,561	82.2	43	1.93	1.51	.78	2.91	1.51	.053	.028
	140	1½	22	23 7	523	49.0	15	3.27	2.23	.68	2.07	.63	.095	.029
Average.	......	......	......	......	.....	52.3	25	......	1.37	.66	1.92	.92	.051	.025
	152	2	57	20.8	1,186	103.8	37.6	2.72	1.82	.66	4.98	1.81	.105	.038
	148	2	27	31.3	845	166.2	70.2	2.37	6.20	2.96	5.31	2.24	.197	.083
Average.	......	.....	.....	......	.....	135	53.9	.....	4.01	1.81	5.15	2.03	.151	.061
Furnace filled with illuminating gas.	141	1½	38	31.4	1,142	23.5	10.4	2.26	.62	.27	.76	.33	.021	.009
	150	2	45	21.8	980	42.8	15.9	2.69	.95	.35	2.00	.73	.043	.016
	155	2	64	26.5	1,894	82	73	1.12	1.34	1.14	3.09	2.75	.043	.038
	151	2	46	14.2	656	56.1	9.3	6.03	1.22	.20	3.95	.65	.085	.014
	147	2	22	19.5	430	40.8	32	1.27	1.85	1.45	2.04	1.60	.095	.074
Average.	......	......	......	......	....	55.4	32.5	......	1.34	.78	2.77	1.43	.066	.035

Direct current was used in all except the first two experiments. These are marked A. C. and to them the terms anode and cathode do not apply. In these the electrode losing the more in weight extended into the furnace much farther than the other.

Electrode losses seem to be due to three causes:

1. Volatilization from the crater, confined to the anode.
2. Oxidation.
3. Disintegration—particles fall from the electrodes.

(1) is independent of, (2) and (3) dependent upon, the length of electrode within the furnace. The total loss is diminished about 50 per cent. by filling the furnace with illuminating gas; this can diminish only (2) and (3). The losses with 2-inch electrodes were double those with 1½ inch diameter. This points again to the use of the smallest possible electrodes. It should be stated, however, that only a single pair of two inch electrodes were tested.

VII.

CONCLUSION.

The results obtained by this series of experiments are the following:

1. The proposed method of preparing the borides and the silicides of the metals by the simultaneous reduction of the oxygen compounds of both elements is not suited to the preparation of the borides, but can be used successfully for the silicides.

2. The existence of a new silicide of molybdenum has been indicated.

3. An investigation of the possibility of a new series of electric furnace products, the silicoborides, has been made Although the experiments indicate the existence of such a com-

pound of iron, they must still be regarded as merely preliminary. The results with chromium and molybdenum were encouraging, but by no means conclusive.

4. Data concerning the arc furnace heretofore unpublished, have been obtained.

In addition to these experimental results, it is believed that Tables II and III, which have been found most convenient for reference during these researches, may prove a useful contribution to the literature of the borides and the silicides, and that the method of firing "Goldschmidt charges" in the electric furnace, discovered during these experiments, will prove very valuable in special cases.

APPENDIX.

In the interval between the completion of this thesis and its publication, two new borides, ThB_4 and ThB_6,[48] and a new silicide of copper, Cu_4Si,[49] have been prepared, and the data concerning them have been incorporated in Table II. Two articles have also been published which touch upon the principal problem of this thesis, namely the preparation of metallic borides and silicides from their oxygen compounds, thus avoiding the difficulties attending the isolation of boron and silicon. The method used in both cases was that of reduction by powdered aluminum, but without the use of the electric furnace.

In the first case[50] a mixture of the metallic oxide, the non-metal, and aluminum was ignited by a magnesium cartridge. By this method two phosphides Fe_2P and Mn_3P_2 were prepared. In attempting the more difficult reductions of silica and boric anhydride, the oxide of copper or of tin with an equivalent amount of aluminum was added to the charge to supply the heat required to produce a good fusion. By this means an ingot of silicon-copper containing 10 per cent. silicon was obtained, and also the silicide of iron, FeSi. From the oxides of iron and boron an ingot was obtained which contained boron, concerning which the author remarks, "It is difficult to isolate a definite boride." All these products contained traces at least of aluminum. The idea of adding an extra quantity of aluminum and an equivalent amount of some harmless oxidizing material, here published for the first time, so far as the writer has observed, is a valuable advance in the applica-

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[48] B. du Jassonneix, C. R., 141: 191–193 (1905).

[49] E. Vigouroux, C. R., 142: 87–88 (1906).

[50] A. Colani, C. R., 141: 33–35 (1905).

tion of aluminothermy to chemistry. The writer has independently applied the same idea to the reduction of tungsten oxide, using the alkaline-earth peroxides as the source of oxygen.

C. Matignon and R. Trannoy[51] confirm the experiments of Colani in regard to the production of binary compounds by the alumino-thermic method, and, in addition to a number of phosphides and arsenides, produced the silicides of manganese, chromium, copper, cobalt, nickel, and iron by inducing reaction in a strongly heated mixture of metallic oxide, silica, and aluminum. Borides of manganese and iron were similarly produced. In this case the high temperature necessary to the separation of the metallic product from the alumina. was secured by starting the reaction in a mass already heated to a high temperature.

These two series of experiments confirm the writer's conclusion that silicides may be readily prepared directly from silica by reduction with aluminum, and they further show that this can be done without the aid of the electric furnace. Since the production of silicon on a commerical scale by F. J. Tone of Niagara Falls this has become of minor importance. The production of the borides of manganese and iron by this method does not confute the writer's conclusion, that, as a general method, the simultaneous reduction of a metallic oxide and boron anhydride by aluminum is not suited to the production of metallic borides. It can be used successfully in the case of the easily reducible metallic oxides, but not for those of titanium, tungsten, and many others. The problem of obtaining the extra heat needed above that supplied by the reaction in such difficult reductions is a very interesting one, and is being approached from different points of view by many investigators in various parts of the world.

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[51] C. R., 141 : 190.

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A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

THE ELECTRIC SMELTING OF ZINC.

BY OLIVER W. BROWN AND WILLIAM F. OESTERLE.

Much attention has been given to the reduction of zinc ores, by electrical and other means, during the last few years. This is not surprising when one realizes that the ordinary zinc smelting process is the most wasteful metallurgical operation used industrially at the present time. The fuel consumption, the cost of repairs and the loss of zinc are very large. The average life of the retorts used in many works is only forty to fifty days; while the loss of zinc is seldom less than 10 per cent., and sometimes more than 25 per cent. of the zinc in the ore.

Another great drawback to the process is that the retorts will hold only about 65 pounds of ore. The zinc retorts most commonly used are fire-clay tubes about four feet two inches long, eight inches in diameter and 1¼ inches thick. They are made closed at one end, and into the mouth of each retort is fitted a fire-clay condenser. They are supported at each end by projections from the walls of the furnace; and are placed in horizontal rows in the furnace in such a manner that the flames entirely surround them while they are being heated.

The most important zinc ore is the sulphide, and this ore, before distilling in the retorts, must be roasted for about forty-eight hours in a separate roasting furnace to convert it into an impure oxide. One to two per cent. of the zinc in the ore is generally lost by volatilization during the roasting process; and the roasted ore still contains one to two per cent. of sulphur, which keeps back an equivalent amount of zinc in the retorts.

The roasted zinc ore is mixed with coal and coke, and charged into the previously heated retorts. The retorts and contents are then heated for about twenty hours, up to a white heat. The zinc oxide is reduced to metal by the white-hot carbon, or carbon monoxide, and distills down into the fire-clay condensers, where it condenses, in part as a fine powder and partly as fused metal. The reduction temperature of zinc oxide, as shown by the work[1] of W. McA. Johnson, is about 1,033° C.; however, all of the zinc will not be expelled from the retort below a white heat. The molten metal is generally drawn from the condensers into a ladle three times during the distillation. Some of the zinc vapor passes through the pores and cracks of the retorts and is lost, while the fire-clay retorts themselves often absorb as high as 15 per cent. of their own weight of metallic zinc. A part of the metal remains in the charge after distillation, because the retorts can not be heated to the temperature required to expell all of the zinc without cracking or melting them. The charge from which the zinc has been distilled generally contains at least 2½ per cent. of metallic zinc, and often much more than this amount. Only pure ores can be used, as the iron and calcium in low-grade ores form a very corrosive fusible slag, which corrodes through the retorts at a comparatively low temperature. The retorts can not be made much longer or wider than those used at present and still hold up their own weight and that of the charge, when heated to a white heat.

As crude and wasteful as this method is, it is employed to produce nearly all of the zinc used at the present time. The enormous amount of heat wasted during the smelting of zinc ores, the loss of zinc, and the cost of operating this process, has caused the problem of the extraction of zinc from its ores to be a favorite field of research with many investigators.

Electrochemists have attacked this problem along three different lines, namely, the conversion of the zinc in the ore into a salt soluble in water and the subsequent electrolytic precipitation of the metal from an aqueous solution; conversion of the zinc to chloride and the electrolytic separation of the metal from the anhydrous fused salt; and the electric smelting of zinc ores.

A special endeavor has been made to develop electrical processes by which zinc can be economically extracted from complex and low-grade ores, which can not be smelted in the ordinary manner.

Of all the processes which have been suggested, involving the electrolytic precipitation of zinc from aqueous solution, that

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[1] Trans. Amer. Electrochem. Soc., 5, 211 (1904).

developed by Hoepfner is the only one that appears to have approached a commercial success. Brunner, Mond & Co. have during the last few years turned out a very pure electrolytic zinc from their works at Wilmington, near Chester, England. Little is known concerning the details of their process except that it is based on the Hoepfner patents.

The Hoepfner process was also used in a works located at Fuhrfort, Germany, from 1895 to 1897, but it has been discontinued. In this works metallic zinc and chlorine were produced by the electrolysis of a solution of zinc chloride. The chlorine was converted into bleaching powder. A description of this process has been published by Guenther.[2] It seems that its success was not great. The large amount of power required to precipitate zinc from aqueous solutions will always be one of the greatest hindrances to any process of this kind.

Many electrochemists have believed that the treatment of low-grade zinc ores could be successfully accomplished by a process in which the zinc is separated by the electrolysis of some anhydrous fused salt of zinc, like the chloride. Richard Lorenz, Borchers, Swinburne, Ashcroft and others have endeavored to develop processes for zinc extraction depending on the electrolysis of fused salts. In this field the Swinburne-Ashcroft process[3] seems to be the best and to have a very bright future.

Few trials in the electric smelting of zinc ores were made until within the last few years, although the Cowles Bros., of Cleveland, carried out experiments on the smelting of roasted zinc ores by electrical heating as early as 1882. These early experiments did not lead to a commercial process.

C. Casorette and F. Berboni,[4] of Milan, Italy, have invented a furnace for smelting zinc ores which contains two muffles, the second being heated by electrical means.

An electric arc furnace for smelting zinc ores has recently been invented[5] by Dr. C. F. T. de Laval. In his furnace the pulverized zinc ore, mixed with the proper reducing and fluxing

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[2] Eng. and Mining Journal, May 16, 1903.

[3] Chlorine Smelting with Electrolysis, James Swinburne, Electrochemist and Metallurgist, *3*, 68 (1903).

[4] Zinc Smelting, C. Casorette and F. Berboni, Milan, Italy; British Patent No. 472, May 19, 1900. Eng. and Min. Jour., *76*, 163 (1903).

[5] French Patent No. 325,895, Oct. 21, 1902. U. S. Patent granted to Dr. de Laval, August 29, 1903.

materials, is fed into the top of an electric furnace in such a manner that in descending it presents an inclined surface to the heat radiated from an arc. The zinc vapors are conducted to a condenser, while the gangue as it descends into the lower part of the furnace is fused and is drawn from the furnace in the molten condition. It is claimed that in smelting 40 per cent. zinc ore in a 100 kw. furnace, nearly five kgs. of metallic zinc are produced per kw. day.

The Cowles Bros., Casorette and Berboni, and de Laval have tried to design electric furnaces in which roasted zinc ores could be smelted in the ordinary manner, except that the heat be generated by electrical means.

A. Dorsemagen,[6] of Wesel, Germany, has worked out a process in which he smelts a zinc ore in an electric furnace with the simultaneous production of a valuable by-product. His process is designed for the treatment of zinc silicate ores. He mixes a zinc silicate ore with carbon in proportions indicated by the reaction $Zn_2SiO_4+5C=2Zn+SiC+4CO$, and heats the charge in an electric furnace. The zinc distills out and is condensed in the usual manner, while the silicon of the ore combines with carbon, forming carborundum. The inventor claims the advantages of supplying the heat required for the reduction of the zinc ore and the formation of silicon carbide at the same time, thus reducing the loss of heat due to radiation and the amount of heat required to previously heat the reacting materials.

If a process were devised to electrically smelt unroasted zinc sulphide ore, the advantages of electrically heating the charge could be realized, while at the same time all the cost of roasting the ore could be saved. After experimenting for about two years on the extraction of zinc from its ores by electrolysis of fused salts and of aqueous solutions, the writers attempted to find such a process. We have obtained interesting results from a process[7] based on the electrical smelting of charges of unroasted zinc blende, lime and carbon, mixed in proportions corresponding to the following equations:

$$(a)\quad 2ZnS + 2CaO + 7C = 2Zn + 2CaC_2 + CS_2 + 2CO,$$

$$(b)\quad 2ZnS + CaO + 4C = 2Zn + CaC_2 + CS_2 + CO.$$

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[6] U. S. Patent No. 716,008, Dec. 16, 1902.

[7] U. S. Patent No. 742,830, Nov. 3, 1903. All of the experiments carried out jointly by Oesterle and Brown were performed in the electrochemical laboratory of Indiana University.

Before giving any of the results of our work we wish to refer to the process patented[8] by Paul Dankwart, of Deadwood, S. D. The process described by Dankwart is similar in some respects to that employed by us. Dankwart smelts mixed sulphide ores containing zinc, with lime, coke and sodium sulphate. He mixes the different materials in such proportions that the sulphur of the ore is converted into alkaline and alkaline earth sulphides, while the zinc is liberated as vapor and is condensed in the usual manner. Dankwart's process is very similar to that of Kirkpatrick-Picard,[9] of London, except that Dankwart adds sodium sulphate to the charge of sulphide ore, lime and carbon, used by Kirkpatrick-Picard, and also carries out his process in an electric furnace.

Kirkpatrick-Picard's process is represented by the following reactions:

$$\begin{aligned} &ZnS + CaO + C = Zn + CaS + CO \\ &PbS + CaO + C = Pb + CaS + CO \\ &4ZnS + 2Fe_2O_3 + 6C = 4Zn + 4FeS + 6CO \\ &4PbS + 2Fe_2O_3 + 6C = 4Pb + 4FeS + 6CO. \end{aligned}$$

He forms the mixture into briquets before the distillation.

The writers first tried the reduction of a charge containing equal molecular weights of zinc blende (59.6 per cent. zinc in ore) lime and carbon (coke) in an enclosed electric resistance furnace lined with firebrick. This is the same charge as that used by Kirkpatrick-Picard. When this charge was heated in the electric furnace the ore was readily reduced, the metallic zinc distilled out and a portion of it condensed in an iron tube which served as condenser. The material remaining in the furnace after the distillation, consisting of impure fused calcium sulphide, contained only 0.13 per cent. of metallic zinc.

We next made a study of the electric reduction of charges of zinc blende, lime and carbon (coal or coke), mixed in proportions corresponding to the equations (*a*) and (*b*) given above.

When a charge containing 194 grams of zinc blende (59.6 per cent. zinc), 112 grams of lime and 84 grams of coke was heated in an enclosed firebrick lined electric resistance furnace, with a current of 50 ampères at 30 volts for two hours, zinc distilled and

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[8] Process of Recovering Zinc from Sulphide Ores, P. Dankwart, U. S. Patent No. 746,798, Dec. 15, 1903.

[9] U. S. Patent No. 692,148, Jan. 28, 1902.

condensed, and the impure carbide remaining in the furnace contained only 0.036 per cent. of metallic zinc and 2.89 per cent. of sulphur. The other impurities in the carbide naturally depend on the purity of the ore treated.

When working with the very small furnace required to smelt charges containing only 194 grams of ore, it was not deemed desirable to endeavor to condense the largest possible proportion of the distilled zinc in a solid metallic form. As experience has shown, the difficulties in condensing the zinc as liquid metal, instead of zinc dust, disappear as the size of the furnace is increased.

The analyses of gases coming from the furnace during the operation, of the materials in the furnace after smelting, etc., show that the changes which take place in the smelting are probably best represented by equations (*a*) and (*b*).

Some additional experiments which were carried out during 1903 and 1904 by one of the writers[10] on the reduction of zinc blende, furnished the following results:

When the following charge: 3.98 kg. zinc blende (containing 58.0 per cent. of zinc), 2.24 kg. lime (containing 38.2 per cent. of magnesia), 0.84 kg. of carbon (equal weights of coal and coke), was smelted in an enclosed electric resistance furnace, the material remaining in the furnace after the distillation contained only 0.10 per cent. of metallic zinc. This experiment shows that even when a lime very high in magnesia is used, practically all of the zinc is reduced and distills out of the furnace. However, it is hardly necessary to remark that good calcium carbide can not be made when a lime containing 38 per cent. of magnesia is used.

The internal dimensions of the furnace in this experiment were: length, 12.5 inches; depth, 8.5 inches, and width, 4.5 inches. The inner walls and bottom of the furnace were of magnesia brick. A layer of dry lime was placed on the outside of the magnesia brick, then a layer of firebrick, followed by another layer of lime, and finally the whole was encased in a sheet-iron jacket. A round Acheson graphite electrode, two inches in diameter, entered the furnace at each end. These electrodes were fastened firmly into plates of Acheson graphite 0.5 inch thick, which were placed vertically at each end of the furnace, and reached from the bottom

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[10] **Brown, Laboratory of Applied Electrochemistry, University of Wisconsin.**

to within 1.5 inches of the top. In order that the furnace should be gas tight, the portions of the graphite electrodes which passed through the walls of the furnace were packed in powdered magnesia brick.

The materials comprising the charge were passed through a 20-mesh sieve and thoroughly mixed, before placing in the furnace.

Connection between the two end electrodes was made by two cores of broken carbons (broken to pieces about 0.5 to 1 inch), which were imbedded in the charge. The lower core of granular carbon was placed 2 inches from the bottom of the furnace, while the second core was about 4 inches above the lower core.

The charge was filled into the furnace to within 1.5 inches of the roof, and was covered with a layer of broken pieces of coke. A carbon tube, 0.5 inches internal diameter and 12 inches long, penetrated the side wall of the furnace, about 2 inches from one end and 2 inches from the top. The tube passed nearly horizontally through the walls of the furnace, the outer end being about 0.5 inch lower than the inner. On the outer end of this carbon tube was fastened a short piece of 1.5 inch iron pipe, which was surrounded with asbestos, and served as condenser for the zinc. The outer end of the pipe was nearly closed with fire-clay. At intervals during the distillation of the zinc the fire-clay plug was removed and the melted zinc, which had condensed, was allowed to flow out.

The furnace was closed at the top by an Acheson graphite plate, 0.5 inch thick. A layer of lime was placed over the graphite plate, and on this were placed three layers of fire-brick. When the furnace was sealed with dry powdered lime in this manner it was quite tight, and very little gas escaped except through the condenser.

A current of about 172 ampères and 68 volts was passed through the furnace for six hours and forty minutes. Zinc vapors had stopped coming from the furnace when the current was broken.

After the furnace was allowed to cool and the cover removed, it was found that the charge was a loose porous mass, which could nearly all be removed with the hands. The temperature had not been sufficient to fuse the charge, although all but 0.1 per cent. of the zinc was expelled from the furnace.

In order to gain some idea of the temperature required to reduce and distill the zinc from various charges, and also the relative value of various charges, four different mixtures were made up and heated in a hot coke fire in a wind furnace.

The materials in each charge were pulverized to pass a 20-mesh sieve and well mixed. The blende used contained 58.6 per cent. of metallic zinc. The charges were as follows:

No. 1 contained zinc blende, 97; lime 28, and coke, 24 grams, and corresponds to the equation,

$$2ZnS + CaO + 4C = 2Zn + CaC_2 + CS_2 + CO.$$

No. 2 contained zinc blende, 97; lime 56, and coke, 42 grams, and corresponds to the equation,

$$2ZnS + CaO + 7C = 2Zn + 2CaC_2 + CS_2 + 2CO.$$

No. 3 contained zinc blende, 97; lime 56, and coke, 12 grams, and corresponds to the equation,

$$ZnS + CaO + C = Zn + CaS + CO.$$

No. 4 contained zinc blende, 97; silica 120, and coke, 24 grams, and corresponds to the equation,

$$2ZnS + SiO_2 + 4C = 2Zn + SiC + 2CO + CS_2.$$

The four charges were placed in separate assay crucibles, loosely covered, and placed in a hot coke fire. Charges 1, 2 and 3 were heated two and three-fourth hours, while charge No. 4 was heated two and one-sixth hours. A zinc flame burned from the mouths of crucibles 1, 2 and 3 while they were being heated, but no zinc flame was given off from crucible containing charge No. 4, indicating that no reduction took place in No. 4.

An analysis of charges 1, 2 and 3 after heating showed that about 55 per cent. of the zinc had been reduced and volatilized in each case. A practically complete reduction and volatilization of the zinc takes place when either charge 1, 2 or 3 is heated in an enclosed electric furnace, with a current of 50 ampères and 30 volts for two hours or less.

Only 5 per cent. of the zinc in charge No. 4 was lost during the heating. This loss was probably due to mechanical loss in removing the ignited charge from the crucible after firing.

A charge made up in the same proportions as in No. 4, but containing zinc blende, 194; silica 260, and coke, 48 grams, was heated in an enclosed electric resistance furnace for one hour, with a current of 120 ampères and 50 volts. Only a very small amount of metallic zinc (about one gram) was found in the condenser, and an analysis of the powder which collected in the condenser showed that it contained only about 4 per cent. more metallic zinc than the charge which was placed in the furnace. The material remaining in the furnace after heating contained 3.98 per cent. of metallic zinc.

These data show that zinc sulphide is not reduced to metal when mixed with silica and carbon and heated to a very high temperature. The temperature attained in this experiment was high enough to volatilize most of the charge out of the furnace, yet the zinc ore was not reduced to metal.

Attention has often been called to the fact that processes requiring widely different conditions can not be successfully carried on together. This is probably very true of the production of zinc and calcium carbide. The conditions required for the reduction of zinc and the production of calcium carbide are so different that there is little chance for their simultaneous economic production. Even if many of the drawbacks could be overcome, the production of a sulphur free carbide from a charge of zinc sulphide, lime and coke, is most probably impossible. Also, if calcium carbide is to be made as a by-product, only the purest zinc sulphide could be smelted, as all of the impurities in the ore would contaminate the carbide. However, a method of smelting high-grade zinc ores is not needed so much as a process which will economically obtain the zinc from ores high in iron, etc.

Another disadvantage in the production of zinc and carbide in the same operation is that the sulphur can not be recovered in a suitable condition, as the greater portion of any carbon disulphide which may be formed in the reduction is burned to sulphur dioxide, which escapes from the furnace in a highly diluted form.

Two very promising lines of investigation are open to those who wish to find an economical electric method of smelting zinc ores. Roasted zinc ores may be smelted in the electric furnace, with coal or coke, and just enough other material to form with the impurities an easily fusible slag which may be continuously tapped from the furnace. Electric smelting under these conditions has the advantage over the ordinary method in that it may be made entirely continuous; that the walls of an electric furnace can be easily constructed of materials which are impervious to zinc vapors and which will not be corroded by the slag, thus enabling the temperature to be raised to a point at which all of the zinc will be expelled from the ore; and that the heat is applied internally, thus preventing the large waste of thermal energy occurring in the ordinary smelting process. Ores high in iron and other impurities could be easily smelted, as the walls of an electric furnace can be made of materials which will withstand the corrosive action of the slags.

It seems possible that zinc sulphide might be economically smelted in the electric furnace, without a preliminary roasting, if ore, lime and carbon be mixed in proportions required for producing metallic zinc, calcium sulphide and carbon monoxide. The fused calcium sulphide could then be tapped from the furnace and the sulphur subsequently recovered. All but traces of the zinc can be distilled from such a charge, as is shown by one of the experiments given above, in which the residue remaining in the furnace contained only 0.13 per cent. of zinc.

It is a question of only a few years until someone will devise an electric furnace process by which zinc ores, high in iron, etc., and which can not be treated by the old method can be economically smelted and by which practically all of the zinc in the ore will be saved.

The writers wish to thank Prof. C. F. Burgess for his helpful suggestions, and for placing at their disposal most excellent facilities for electric furnace experiments.

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DISCUSSION.

PROF. BURGESS: The original idea of Mr. Brown when he undertook work on zinc reduction was that he could make calcium carbide and distil zinc simultaneously; this can undoubtedly be done, but the criticism of that plan from the practical standpoint would be similar to a criticism which might be offered in reference to the Gin electric furnace process for producing steel, which was presented to us yesterday. To design a furnace to carry on two operations requiring different temperatures at the same time is next to impossible where economy and simplicity are considered. It violates a well-established principle in construction that a machine or furnace constructed to carry on one operation efficiently cannot attain other results essentially different at the same time, and maintain the efficiency.

Dr. Richards: I think it would have been much better if on page 177 there had been given more definite information than the mere statement that it simply took so much more current—so many more amperes—to do the work in one case than in the other. Mr. Johnson, in doing similar work, has given us the temperatures at which the reactions take place. In the reactions "A" and "B" the formation of carbon bisulphide is interesting, as it is a strongly endothermic compound and absorbs heat in its formation instead of giving out heat. The thermochemical equations furnish interesting discussion if analyzed.

In equation (a) for instance, there must be supplied:

To decompose 2 ZnS	86,000	calories
To decompose 2 CaO	263,000	"
To help form 2 CaC_2		
To help form CS_2		
Total absorbed	386,900	"
Furnished by 2 CO	58,320	"
Net heat absorbed	328,580	"

In addition to this immense amount of heat absorbed chemically, the hot products, if assumed to be at 1,300°, would contain approximately 150,000 calories of sensible heat, so that a total heat supply of over 475,000 calories must be supplied to the charge to distill off 2 Zn = 130 grammes of zinc, or over 475,000 large Calories per 130 kilograms of zinc.

Such a charge, in grammes, was worked off in an experimental laboratory furnace by a current of 50 amperes at 30 volts, for two hours. The heating value of this current is 2,500,000 gramme calories, showing a net efficiency of about 20 per cent.

On a large scale, 60 per cent. efficiency should be possible, at which rate 2 horse-power would produce 390 grammes of zinc in two hours, or at the rate of 5 horse-power hours per kilogramme of zinc, or 2.25 horse-power hours per pound. At 0.25 cent. per horse-power hour, the cost of power would be 0.56 cent. per pound of zinc produced.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

NOTES ON THE USE OF ALUMINUM AS A REDUCING AGENT.

By Oliver P. Watts.

The use of aluminum as a reducing agent is now of such importance that any extension of its field of usefulness seems worthy of record, and accordingly the writer presents a new way of using it, which yields results heretofore unattained by other methods.

The early method of adding the substance to be reduced to a bath of fused aluminum gave, in the hands of Moissan and others, only alloys. Dr. Goldschmidt, by using the aluminum as grains or powder in his now well-known method, successfully overcame the tendency of the aluminum to alloy with the reduced metal, and thus produced a long series of carbon-free metals.

There remained, however, certain metals, *e. g.*, titanium and tungsten, which could not be obtained in a pure state even by this process. Success depends upon the attainment, as a result of the chemical reaction, of a temperature so high that reaction takes place completely, and that the products are perfectly fluid. The reaction of aluminum with the oxides of titanium and tungsten fails to yield this required temperature, hence these metals cannot be obtained by the Goldschmidt process. Yet their alloys with some metal whose compounds are more easily reduced by aluminum may be thus obtained. The addition to the charge of the oxide of iron, for example, supplies the heat necessary for a complete reduction and for the agglomeration of the resulting iron alloy. In this way Dr. Goldschmidt produces ferro-titanium and ferro-tungsten.

By a modification in the method of using the fused bath of aluminum, A. J: Rossi (*Electrochem. Ind.,* 1903, Vol. I, 523) succeeded in obtaining ferro-titanium and ferro-tungsten in large quantity and free from aluminum. His method consists in melting the aluminum in an electric furnace, feeding in the mixed oxides to be reduced, and after reaction has occurred, adding an excess of the oxides to remove the last traces of aluminum from the alloy produced.

In the absence of any statement to the contrary, the writer deems it improbable that this process, so successful in producing the ferro-metals, would yield titanium or tungsten free from aluminum. To remove all aluminum from an alloy, even at electric furnace temperatures, requires that the oxidizing agent used shall not be extremely difficult of reduction. In experiments by the writer on the reduction of fused silica and silicates in the electric furnace by adding ingot aluminum, some of the latter always remained in the silicon reduced. The large excess of fused silicate with which the product was in contact failed to remove the last traces of aluminum. It is reasonable to suppose that titanium oxide would act no more energetically than silica as an oxidizing agent.

There seems, then, to be lacking a method by which aluminum as a reducing agent may be made to yield the pure metals, titanium, tungsten, uranium and some others.

In the course of a long series of experiments, begun in 1904, on the production of metallic borides and silicides, the writer discovered that Goldschmidt charges could, by a slight change, be fired with safety in an electric furnace of the arc type. Powdered fluorspar or cryolite was added to the charge to reduce the velocity of reaction. Other inert powders could no doubt be substituted for these. The charge was placed in the cavity of a furnace with a magnesite lining, the cover put on, and an arc started just above the charge. The usual heating was for five minutes at 300 ampères and 70 volts, followed by five minutes more at 600 ampères and 80 volts. About fifty reductions were made by this method. The reaction was occasionally vigorous, but never explosive, although 350 grams of powdered aluminum were used in some cases. The metallic oxides used were those of iron, nickel, cobalt, chromium, manganese, molybdenum, titanium and tungsten. The amount of retarder was diminished in the case of the less readily reducible oxides. In a few cases reaction could have been brought about by the usual method of an igniter, but owing to the presence of silica, boric anhydride, or both, most of the charges required the heat supplied by the electric arc to complete the reaction.

Having once established that the electric arc may safely be used to start and to carry to completion reactions in which finely divided aluminum is used, the application of the method is obvious. The heat of the electric furnace may be substituted for that formerly obtained by the addition to the charge of some easily reducible oxide, thus yielding pure metals instead of only alloys of titanium, tungsten, etc. A condensed account of such a combination of electric heating with the alumino-thermic method as applied by W. Huppertz to the production of titanium from rutile may be found in *Electrochemical Industry*, 1905, Vol. III, 35.

Laboratory of Applied Electrochemistry,

DISCUSSION.

Dr. Richards: This method of reducing oxides by means of aluminium as a strong reducing agent was first tried by Tissier; and the first time he tried it he blew his furnaces to pieces and very nearly lost his life.

The easily-reducible oxides are reduced with the evolution of such a large amount of energy that the local temperature is extremely high. The temperature probably reaches between 3000° and 4000° C., when an easily reducible oxide is reduced by aluminium. With iron, it reaches in the neighborhood of 2500° to 2700° C.

The more difficultly reducible oxides—those which, when reduced by aluminium, give a less excess of heat—are difficult to operate upon because there is not enough excess of heat in the formation of the alumina to melt the resulting alumina and reduced metal, and the reaction tends to stop itself.

The device which is used by Mr. Watts is that of furnishing sensible heat in the material which is to react, and therefore putting the reduction of these strong oxides on the same basis as the automatic reduction of the more-easily reducible ones. The mixture being heated up to bright redness, you have the amount of sensible heat which is in the mixture added to the excess of heat which is in the formation of alumina over that of the oxide reduced, and the resulting temperature is sufficient to melt the oxide formed and the metal. A necessary condition for the reduction of these oxides is that the oxide formed, which is largely alumina, shall be melted as well as the metal.

In speaking of Mr. Rossi's experiments, there is a factor which has not been sufficiently taken into account. When the metal is reduced by aluminium the bath first of all contains a lot of the aluminium itself, and as the bath contains less and less of the aluminium to react, the energy with which it reacts upon the metallic oxide becomes less and less, being diminished by the energy with which the aluminium is alloyed with the metal; and, therefore, we have the difficulty of getting a pure product of these metals. The affinity with which the last of the aluminium is held in the alloy, puts a limit to the purity of the metal which can be obtained by Mr. Rossi's method.

PRESIDENT BANCROFT: When working with an aluminum and iron oxide mixture on a small scale—for instance, in the lecture room—we have had great difficulty in getting really satisfactory results; and we have only obtained them by adding magnesium. I have been told that Goldschmidt also adds magnesium and that some of his chromium, when analyzed, contains traces of magnesium. I should like to ask whether any body knows anything about that as a fact. I merely state it as a rumor.

MR. BURGESS: It is true that you can start the reaction very much more readily that way; but if you want to go to a little more trouble you can eliminate the magnesium by using an iron fuse wire to start the reaction.

DR. RICHARDS: Perhaps your remark is caused by the fact that a little magnesium is used as an igniter or fuse. I do not think that any magnesium is put into the mixture, as an essential constituent. A little magnesium ribbon stuck into the charge is often used in the laboratory process and perhaps on a large scale used as a fuse for starting the reaction.

PRESIDENT BANCROFT: In working with a small crucible, radiation is, of course, very high. We started the mixture with barium peroxide, but did not get satisfactory results without the addition of metallic magnesium. Of course, that would not mean that you would not get very good results if you were working with five kilogramme lots and a correspondingly lower radiation.

A paper read at the Eighth General Meeting of the American Electrochemical Society, held at Bethlehem, Pa., Sept. 19, 1905, President Bancroft in the Chair.

SOME OBSERVATIONS ON THE INFLUENCE OF ARSENIC IN PICKLING SOLUTIONS.

BY CHARLES F. BURGESS.

A sulphuric acid pickle which exerts a vigorous dissolving action upon an iron or steel surface may be rendered almost completely inert by the addition of a small amount of arsenic. Over a half century ago this fact was pointed out by E. Millon,[1] who, however, did not attempt to explain why a trace of arsenic has the property of exerting this remarkable protective action.

This phenomenon is of considerable significance to the chemist and the electrochemist, for it indicates that arsenic is a disadvantageous impurity where free and rapid action of sulphuric acid upon iron is desired; that its presence may be advantageous when the rapidity of the action of the acid is to be diminished. Millon claims that arsenic in acids other than sulphuric reduces their activity in corroding various metals, and assuming this to be true, may it not be expected that arsenic when present as an impurity in the metals themselves may render them less susceptible to corroding influences in general?

The writer has been unable to find that the attention has been given to the study of this subject to which its suggestiveness and usefulness entitles it. In what manner does arsenic render an iron surface passive is possibly a question for the electrochemist to answer, and any suggestions or information bearing upon this point will be welcomed by the author.

Some preliminary experiments upon the effect of arsenic in sulphuric acid solutions have been done in the Applied Electrochemistry Laboratories of the University of Wisconsin, some of the results of which are here given.

A five normal solution of sulphuric acid was used in the various tests, and to a portion of this solution was added a small quantity

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[1] Comptes Rendus, 1845 *22*, 37.

of arsenic in the form of As_2O_3. Although the exact quantity was not determined, it was present only as a small part of 1 per cent. To determine quantitatively the influence of the pure solution and that containing arsenic, strips of spring steel were subjected to their action, and the dissolving and the weakening of the steel measured. The steel ribbon used consisted of a high grade of untempered spring steel, carrying a thin film of black scale, and having a cross section of 5-16 x .16 inch. From this, pieces about one foot in length were cut, and these were immersed for a depth of six inches in the respective solutions.

Table I gives results on the dissolving effect of the acids upon strips which had been freed of scale by rubbing with fine emery.

Table I.

Dissolving effect of acids with and without arsenic.

Time	Pure Acid Solution		Loss	Solution Containing Arsenic		
	Wt. Before	Wt. After		Wt. Before	Wt. After	Loss
20 min.	5.1628 g.	5.1156 g.	.0472 g.	5.0342 g.	5.0290 g.	.0052 g.
40 min.	5.1156 g.	4.9096 g.	.2060 g.	5.0290 g.	5.0268 g.	.0022 g.
60 min.			.2532 g.			.0074 g.

The facts to be noted from this table are that in one hour's time the amount of iron dissolved by the arsenic free solution is about 34 times that dissolved by the impure solution; also that during the first twenty minutes the ratio between the action of the two solutions was 9.1 to 1, and during the last forty minutes the ratio increased to 94 to 1, showing that the protective action of the arsenic increases with the time. In the pure solution the rate of corrosion increases, as shown by the fact that over four times as much iron was dissolved during the last forty minutes as during the first twenty; while with the solution containing arsenic the rate of solution materially decreased. It was also noted that the steel when first immersed in the impure solution liberated hydrogen, but this evolution quickly diminished, and at the end of one hour the evolution of hydrogen had ceased, while in the pure acid the evolution of this gas was vigorous and undiminished.

It is well known that acid solutions exert a harmful influence on steel, aside from that occasioned by the removal of some of the metal. This is supposed to be due to the liberation of hydrogen and the absorption of it by the metal, rendering it weak and brittle. So marked is this effect that certain classes of steel articles, such as steel piano wire, clock springs, measuring tapes and the like cannot be pickled, and it is claimed by some that they cannot be nickel plated without damage.

To determine whether arsenic exerts an influence harmful or otherwise upon this weakening property of acids, a small testing machine was devised by means of which the brittleness of a strip of steel could be approximately determined.

The steel strip to be tested rests on fixed edges, spaced one-half inch apart. The movable edge is advanced slowly and steadily by means of a micrometer screw until the strip snaps in two, and the deflection thus measured is taken as an approximate indication of the flexibility.

Inasmuch as the steel strip showed variations in its flexibility on samples taken from various places in the coil, measurements were made on the pickled and unpickled portions of each sample tested. The results of observations are given in Table II, the column marked "Per cent. weakening" being derived by dividing the decrease in deflection after pickling by the deflection of the unpickled part.

TABLE II.

Solution	Time	Deflection		Per cent. Weakening
		Pickled	Unpickled	
Pure	5 minutes	.100″	.152″	
		.094	.156	
		.088		
	Ave. . .	.094	.154	39.
With Arsenic	5 minutes	.156	.156	
		.152	.156	
		.154		
		.154		
		.158		
	Ave. . .	.155	.156	0.64
Pure	10 minutes	.080	.170	
		.070	.160	
		.066	.158	
		.078		
	Ave. . .	.074	.163	54.5
With Arsenic	10 minutes	.150	.170	
		.152	.166	
		.158	.170	
		.154		
	Ave. .	.154	.169	8.9
Pure	15 minutes	.062	.158	
		.054	.158	
		.066		
	Ave. . .	.061	.158	61.4
With Arsenic	15 minutes	.142	.150	
		.150	.160	
		.152		
		.154		
	Ave. . .	.149	.155	3 87
Pure	60 minutes	.060	.160	
		.056	.140	
		.050	.160	
	Ave. . .	.056	.153	63 5
With Arsenic	60 minutes	.158	.178	
		.160	.174	
		.154	.172	
		.160		
		.160		
	Ave. . .	.158	.175	9.7

It will be noted that arsenic exerts a marked influence in diminishing the rotting effect of the sulphuric acid solution. A solution of hydrochloric acid having a corresponding strength was also tested, and it was found that while the presence of arsenic in it exerts an influence similar to that exerted in sulphuric acid, its influence is not as pronounced.

It is generally recognized that the nickel-plating process, as usually operated, has a decided weakening effect on thin steel springs and the like, and the supposition is justified that it is the pickling part of the process that is largely responsible for the trouble. To determine whether a steel spring pickled in an arsenic containing pickle and subsequently nickel-plated would be stronger than when pickled in pure acid before plating was the purpose of measurements, the results of which are given in Table III.

TABLE III.

	Deflection.		Per cent. weakening
	Before pickling	After plating	
Pickled in pure acid and nickel plated.	.172″ .172	.140″ .154 .140 .144 .148	
Average . . .	.172	.145	15.6
Pickled in acid containing arsenic and nickel plated.	.160 .168 .172	.158 .158 .154 .146 .158 .154	
Average . . .	.167	.155	7.2

All the above experiments show that the effects of arsenic are sufficiently pronounced to warrant a further experimental study, especially in determining quantitatively the influence of varying percentages of arsenic in various strengths of acid solutions. Such information will undoubtedly be of direct practical value to the electro-plater and others who have to do with pickling solutions.

That arsenic exerts an influence to be reckoned with has been recognized for some time by users of sulphuric acid solutions. By some it is held to exert a deleterious influence; that its presence in a pickle gives rise to dark and irregular colorations on the surface of iron articles subjected to its influence, thus adding to the many difficulties inherent in the process of preparing surfaces for receiving electro-deposits. Another disadvantage attributed to arsenic is that it makes the useful action of the solution exceedingly slow. On the other hand, it is claimed by Meurice[1] that the presence of arsenic may be decidedly advantageous to an acid pickle, since when present in suitable proportion it reduces the consumption of acid while increasing the effectiveness of its work.

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University of Wisconsin.

DISCUSSION.

MR. HERING: It occurred to me that there might be several explanations of this action. What we generally term iron, is not iron at all, but is a mixture of three things: iron, carbon and carbide of iron; and one reason why it dissolves in sulphuric acid is because those ingredients form electrolytic couples, causing local currents. If that is the case, any arsenic in the solution will probably be plated onto the carbon; hence the local electrochemical action which dissolves the iron, will be weakened by this change of one electrode from carbon to arsenic. This might be one explanation. Whether arsenic will deposit on iron the way copper does from copper solutions, I do not know, but if it does, this might be another explanation, as we know that if iron is placed in sulphuric acid containing copper sulphate, it will at once be covered with copper and will then be less rapidly attacked than if not covered with copper.

The paper furthermore suggests to me that possibly this action might be made use of advantageously in coatings for protecting iron, that is, to protect iron against being attacked by rust or by liquids; it might be quite possible that the use of arsenic in such protecting compounds would be effective.

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[1] Bull. de l'Assoc. Belge. Chimistes, 9, 343, abstracted in "The Metal Industry," Aug., 1903.

A paper to be read at the Ninth General Meeting of the American Electrochemical Society, to be held at Ithaca, N. Y. May 1, 2 and 3, 1906.

[ADVANCE SHEETS.]

OBSERVATIONS ON THE CORROSION OF IRON BY ACIDS.

BY C. F. BURGESS AND S. G. ENGLE.

It is well known that the rate at which iron corrodes or combines chemically with its surrounding medium depends upon various factors, including temperature, pressure, nature of corroding agent as to chemical composition and purity, speed with which the resulting compound is removed from the corroding surface, and the physical and chemical state of the iron itself.

Many features of scientific and technical interest have been pointed out by investigators of this subject, and there has been produced a large mass of scattered and fragmentary information, ranging from the solvent action of various acids on the individual metallographic constituents of iron alloys to the observations of the pickler that the acid which he obtains from one manufacturer is satisfactory while that which he obtains under the same name from another manufacturer is worthless.

It is the purpose to record here the results of a few observations made in connection with a more extensive study of electrolytic iron under a grant from the Carnegie Institution of Washington. These observations deal mainly with the rapidity of solution of several grades of iron in dilute acids.

The corroding mediums employed were normal solutions of sulphuric and hydrochloric acids, distilled water and chemically pure acids being used. The solutions were kept at room temperature (about 22° C.) and during corrosion, additions of acid were made to keep the solutions at a nearly constant content of free acid.

The several grades of iron which were compared included electrolytic iron which had been deposited from a mixed sulphate and chloride solution, the same iron which had been heated to about 1,000° C. and allowed to cool slowly, soft sheet iron, low in carbon, such as is used in the manufacture of transformer plates, and which are herein designated as transformer iron, a temper steel, such as is used in the manufacture of knife blades, and an ordinary grade of cast iron. Sample plates were prepared from these materials, each having about 5 square inches of surface area. The surfaces, prior to immersion in the acids, were ground smooth on an emery wheel to give uniformity and freedom from scale and impurity. The samples were weighed and immersed for measured periods in the acid solutions, removed therefrom and dipped into dilute sodium hydrate, rinsed in hot water, dried and weighed.

The specimens were suspended in the solutions by means of a grooved stirrup of hard rubber, and arranged in such manner that the separate plates did not make contact with each other.

TABLE I.

Loss in grams per square inch per hour. Solution-normal H_2SO_4

Hour	1st.	2d.	3d.	4th.	5th.*	6th.
Electrolytic	.0319	.2933	.4029	.4098	.5137	.4805
Electro, heated	.0053	.0162	.0088	.0112	.0063	.0078
Cast iron	.0758	.0947	.0737	.0373	.0335	.0525
Steel	.0163	.0085	.0703	.1181	.1135	.0974
Transformer iron	.0090	.0136	.0028	.0074	.0084	.0081

Hour	7th.	8th.	9th.†	10th.	11th.	Average
Electrolytic	.4284	.4221	. .	. .	. .	.3728
Electro, heated	.0071	.0067	.0084	.0120	.0105	.0091
Cast iron	.0638	.0581	.0668	.0677	.0842	.0643
Steel	.1182	.1371	.1344	.1153	.1396	.0971
Transformer iron	.0097	.0104	.0107	.0112	.0119	.0093

* Added 3.1g. H_2SO_4 per liter to replace that consumed by iron.
† " 4.6 " " " " " " " "

Table I shows the relative rates of corrosion of the five samples of iron for successive hours during the progress of the test. The striking facts which are brought out numerically in this table, and graphically in the curves plotted on Plate 1 are that electrolytic iron in the condition which it possessed just as it was taken from the tanks, corroded at a far greater rate than did the other samples, about six times as rapidly as the cast-iron, four times as rapidly as the steel, and nearly forty times as rapidly as the transformer iron. It is also shown that the heat treatment to which the electrolytic iron was subjected, conferred upon it the property of resisting corrosion to a great degree, the heated electrolytic iron dissolving at a hardly appreciable rate as compared with the samples which had been unheated.

As indicated in the table, the specimen of unheated electrolytic iron was removed from the test at the end of the eighth hour, this having been done on account of its having been practically consumed. That this sample was acted upon far more vigorously than were the others was shown by the rapid evolution of hydrogen which proceeded from it.

In removing the test specimens from the solution at the end of each hour, a certain amount of loosened material became detached, except in the case of the electrolytic samples, which remained smooth and bright; and to avoid any irregularities in the weight determinations which might result from this, duplicate samples were again placed in normal solutions of the acids and left for seventeen hours without disturbing. As regards rates of corrosion in this test, the various grades of iron held the same relations as they did in the first run, while in the hydrochloric acid, the steel showed the least tendency to dissolve. The results of this run are given in Table II. In this table are given also the rates at which zinc of the grades known as "chemically pure" and "commercial" were dissolved in sulphuric acid.

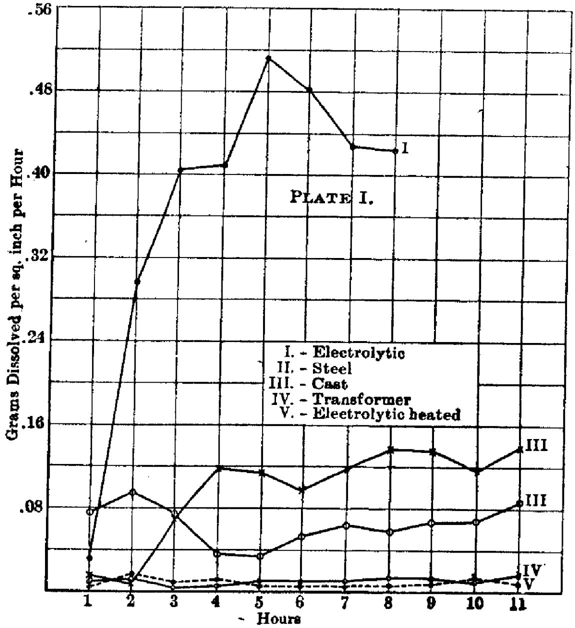

TABLE II.

Loss in grams per square inch per hour on a 17 hour run.

	In normal H_2SO_4.	In normal HCl.
Electrolytic	.4575 g.	.2146 g.
Electro, heated	.0209 "	.0083 "
Steel	.0946 "	.0026 "
Cast iron	.0796 "	.1058 "
Transformer iron	.0279 "	.0095 "
Zinc, c. p.	.1410 "	
Zinc, commercial	.2607 "	

It is a well-known fact that pure zinc dissolves in acids much more reluctantly than does the less pure metal, this phenomenon commonly being attributed to the influence of the more numerous galvanic couples which are produced by the larger number of particles of impurity in the latter grade of zinc. Reasoning from this analogy, it would be natural to expect that electrolytic iron, having a high degree of purity, as compared with the other samples, would dissolve at a much slower rate. The striking evidence that this is not the case is shown by the above data and curves, and the remarkable chemical activity of the electrolytic iron calls for explanation. From the fact that electrolytic iron contains considerable quantities of hydrogen, in an occluded or combined condition, it might be suggested that we should look to the influence of this element as the cause of this phenomenon. This view has for its support the observation that upon heating the iron to a red heat, and thus driving off most of the hydrogen, the corrodibility is decreased in a remarkable degree.

It is the belief of the writers, however, that if hydrogen produces an influence, it does so only indirectly, and that the crystalline structure should be taken into account. Electrolytic iron, as deposited from its electrolyte, assumes a marked crystalline structure, as shown plainly not only by the microscope but also to the unaided eye. The nature of this structure, as shown on fracture, varies from needle-and-fern-like forms to a more dense and compact condition, depending upon current density, composition of solution, and other factors. These structures disappear upon heating to a bright yellow heat such as was used to drive off the hydrogen, and an examination by the microscope shows the iron to assume the form which is characteristic of that of a pure wrought iron, typical ferrite grains being plainly apparent. Incidentally, it might be noted that this change in structure is accompanied by marked alteration in the physical properties, the iron changing from a hard and extremely brittle condition to a soft, tough state.

To determine whether the crystalline structure of electrolytic iron has an influence on the rate of dissolving in acid solution, two samples were chosen, one of which was coarsely crystalline, deposited from a ferrous ammonium sulphate solution with a small amount of ferrous chloride, and the other deposited from a solution containing a larger percentage of chloride and which gave a much more dense and fibrous deposit. The results are given in Table III.

TABLE III.

Loss in grams per square inch per hour on a 17 hour run. Normal H_2SO_4.

Electrolytic iron, coarsely crystalline	.4805 g.
Same iron heated	.0685 "
Electrolytic iron, more dense	.3291 "
Same iron heated	.0225 "

At the Bethlehem meeting of the American Electrochemical Society, a paper was presented, dealing with the presence of arsenic in sulphuric acid as influencing the activity of the acid on iron. The various samples herein described were subjected to a normal sulphuric acid solution which contained a small amount of arsenic, and after twenty-two hours, the amount of iron dissolved from all of the specimens was so small as to be undetected, the electrolytic, as well as the other forms of iron, becoming practically passive in the arsenical solution. The explanation which has been offered for this phenomenon is that the iron receives, by contact with the solution, an extremely thin coat of arsenic which resists the action of the acid and protects the underlying metal. While such coating was not detected by the eye, the presence of arsenic was shown by the following test: A strip of pure iron which had become passive by the action of arsenic in sulphuric acid, was removed from the solution and washed in running water for several hours. It was then put into a Marsh's Apparatus and acted upon by a strong solution of arsenic-free sulphuric acid. The gases which were evolved were delivered through a solution of silver nitrate, soon producing the characteristic black metallic silver precipitate, caused by the presence of the arsenicuretted hydrogen gas. A similar sample of iron which had not been subjected to the arsenical solution produced no black precipitate.

From the fact that an extremely small amount of arsenic in the presence of iron can enable that iron to resist a corroding influence as strong as that exerted by sulphuric acid, it is natural to infer that this element might be employed in protecting iron from atmospheric and other corroding influences.

In studying the influence of arsenic on steel, Mr. J. E. Stead found[1] that arsenic, instead of being the enemy of the steel maker, as had been commonly assumed, might, in fact, under certain conditions, be his friend, in imparting desirable properties to low carbon steels. Among other observations, he noted that in iron wires containing from .11 per cent. to .21 per cent. of arsenic and carbon from .10 per cent. to .4 per cent., the corrosion by sea water was materially lower than in wires of similar composition, but with lower amounts of arsenic. He says: "Oxidation is retarded by the presence of small quantities of arsenic."

We have not found references to additional work along this line, and in view of the great importance of continued study on the corrosion of iron, and the possibility of using arsenic as a means of imparting greater durability, a further study of the influence of this element seems warranted.

To determine whether electric potentials of iron, with its corroding electrolyte, has any relation to its tendency to corrode, the contact potentials of the various specimens used in this investigation were measured by the use of the normal calomel electrode, the value of which is assumed as —.56-volt. The results of these observations are given in Table IV. The electrolytic iron is placed at the head of the list according to these measurements, as it is also at the head of the list arranged according to the rate of solution. On the other hand, the arrangement of the other samples is not similar, and, consequently, we cannot assume that the single potential is anything more than a rough guide in suggesting tendency to corrode. It is interesting perhaps to note that all the specimens assumed a more electronegative potential in the arsenical solutions than in the others.

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[1] Journal of the Iron and Steel Institute *I*, p. 96. (1895),

TABLE IV.

Single potentials of metals. (Calomel electrode = —.56) at 24° C.

	n. H_2SO_4	n. $FeSO_4$ (neutral)	n. H_2SO_4 (with arsenic)
Electrolytic iron	.0476 volt.	.1164 volt.	—.073 volt.
Electrolytic iron heated	.0270 "	.1056 "	—.146 "
Transformer iron . . .	—.0183 "	.1028 "	—.156 "
Cast iron	—.045 "	.0518 "	—.115 "
Steel	—.062 "	.0303 "	—.136 "

CONCLUSIONS.

That the rate at which an acid dissolves iron depends largely upon the elements with which the iron is associated does not need the confirmatory data here given to establish its truth. It is well known that the various metallographic constituents of iron and its alloys resist in differing degrees the attack of acids, and, consequently, different grades of iron show differences of durability.

That the percentage of purity is not the controlling factor is here shown by the observations that the heated and unheated specimens of electrolytic iron, essentially the same as far as chemical composition is concerned, exhibit the widest possible variations in rate of solution.

The crystalline or granular structure of iron seems to influence rates of corrosion in a marked degree.

The rapidity with which unheated electrolytic iron liberates hydrogen in a dilute acid solution suggests a useful application of this material in the production of pure hydrogen by replacing zinc, which is now commonly used. From Table I, it is observed that from equal surfaces of exposed metal, electrolytic iron liberates hydrogen about four times as rapidly as does pure zinc, and twice as rapidly as the commercial grade.

Another advantage in the use of electrolytic iron in hydrogen generation lies in its higher purity and the consequent increased purity of the resulting gas, as compared with that which is obtained from zinc. One pound of iron produces 16 per cent. more hydrogen than does one pound of zinc, and if a sufficient demand for iron for this purpose should arise, it could be supplied at a cost materially less than that of zinc.

Traces of arsenic are shown to exert such a marked influence in protecting iron from the corroding action of acids that the employment of this element for protection against ordinary corrosion appears worthy of further investigation.

While the measurement of electric potentials of iron against corroding agents seems to afford some indication as to the rapidity with which it will become attacked, it does not seem possible to establish definite relations between electric potentials and corrodibility.

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A paper presented at the 23d Annual Convention of the American Institute of Electrical Engineers. Milwaukee, Wis., May 28-31, 1906.

(*Subject to final revision for the Transactions.*)

MAGNETIC PROPERTIES OF ELECTROLYTIC IRON.*

BY C. F. BURGESS AND A. HOYT TAYLOR.

Iron which has been deposited electrolytically from an aqueous solution is not necessarily a definite product, but varies in chemical composition and physical constitution, depending upon the adjustment of the various factors which govern the deposition. High purity is a property frequently ascribed to electrolytic iron, and it is probably a fact that by no other means can iron be purified to as high a degree as is possible by the electrolytic method. It is safe to say that absolutely pure iron has never been produced either electrolytically or by any other method.

The incentive which has led to a large amount of work on the electrolytic refining of iron is the need of a material of a high degree of purity to serve as a basis for the study of iron and its alloys. Until comparatively recently electrolytic iron has, however, been something of a curiosity due to the difficulty of depositing it in anything but thin layers. Several years ago an investigation was undertaken in the applied electrochemistry laboratory of the University of Wisconsin looking to the production of electrolytic iron in large quantities, and as a result it has been demonstrated that iron may be refined at a rate and a cost comparable to that existing in electrolytic copper refining. A further investigation of the production and properties of electrolytic iron and of various alloys made from it, has been made possible by a grant from the Carnegie Institution of Washington and while working under this grant, nearly one ton of electrolytic iron has been produced, and plates one inch in thickness and weighing 75 lb. have been made. In following the question of a large scale production, particular

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*[Owing to the late date at which the manuscript of this paper was received, it has been put in type for use of members at this meeting without thorough review.—*The Editing Committee.*]

attention was not given to the matter of purity, and as a result the iron which was produced did not equal the best grades of iron obtained on the market. Marked improvement has been made recently, the following analyses for which acknowledgement is made to Mr. Andrew A. Blair, showing something of the degree of purity obtainable.

	No. 1.	No. 2.
Sulphur	None.	0.001%
Silicon	0.013%	0.003%
Phosphorus	0.004%	0.020%
Manganese	None.	None.
Carbon	0.012%	0.033%
Hydrogen	0.072%	0.083%

It may be noted that hydrogen is present in an amount greatly exceeding all the other impurities combined, and it is to the presence of this element that the characteristic properties of electrolytic iron are usually ascribed. It is well known that electrolytic iron as taken from the depositing solution is usually hard and brittle, and to such a degree that it may be crushed to a powder. Upon heating to a temperature of about 1000° cent. and upward, it becomes soft and malleable.

The exact cause of this remarkable change of physical properties is not clearly apparent, though since some hydrogen has been observed to be given off during the heating operation, a relationship has been held to exist between the hardness of the iron and the hydrogen content. Some doubt is cast upon the existence of such relationship through the fact that similar amounts of hydrogen have been found in soft electrolytic iron which had been fused and in hard brittle iron before fusion, and the question is one calling for further investigation.

It is well known that the magnetic properties of electrolytic iron are altered to a great degree by heat treatment, and it is the purpose of an investigation now under way to establish the relationship between coercive force, permeability, hysteresis constants, etc., and the temperature at which the iron is heated. This paper is intended only as a short preliminary report on work which has been under way for some time, but which owing to difficulties encountered in depositing and machining of the samples to be tested, has made but slow progress.

To prepare the test specimens necessary for the Rowland ring method of magnetic measurement, plates of electrolytic iron about one inch in thickness were deposited from a ferrous sulphate solution slightly acidified, containing also a small amount of ammonium sulphate. This deposition required about eight weeks. The resultant plate was ground smooth, and the ring was made from it by drilling and grinding, care being taken to prevent the metal from becoming heated. The first ring had to be rejected on account of a crack which developed in it. The first one upon which the measurements here described were made, had an average radius of 4.34 cm. and a rectangular cross section 1.158 cm. by 1.278 cm.

The primary winding of No. 18 wire was chosen to give a field strength of 20 dynes per ampere of primary current, and the secondary winding had 350 turns of No. 26 wire.

A Rowland D'Arsonval galvanometer whose calibration curve was accurately known, was used ballistically in obtaining the first hysteresis curves by the step by step method. The calibration curve of such a galvanometer is generally not a straight line, and this fact, combined with the change of the logarithmic decrement with various external resistances renders the computations somewhat laborious, since the factor of reduction depends on the size of the deflections and on the total secondary circuit resistance. It has the advantage of having a definite control, not depending on the earth's magnetic field, and for this reason has tempted many to use it in connection with ballistic methods for magnetic induction. Unfortunately in many cases the instrument is assumed to have a *constant*; that is the factor to change from deflections to inductions is taken the same for all deflections. This is certainly not the case in many instruments of this type.

Later on in this work the Rowland galvanometer was discarded and a Nalder instrument of the suspended astatic needle type was used. This was provided with a thick laminated iron shield to exclude external magnetic disturbances, and proved to be very satisfactory. The logarithmic decrement, or damping factor, was so small, even on closed circuit, that it could be neglected, and it was therefore not necessary to calibrate it with a standard solenoid, but rather with an Elliot condenser and standard cell.

One of the principal difficulties encountered was the elimination of errors due to *magnetic viscosity*. This is the slow but very appreciable change of magnetic induction which takes place some time after the change in field has been made, and hence is not taken account of in the galvanometer deflection. Thus an additive error is introduced in the step-by-step method, depending on the number of steps made. We very early discovered that the maximum induction as determined by this method did not agree with that obtained by the method of reversals, and much time was spent in running down the discrepancy, which is by no means peculiar to electrolytic iron. In fact this part of the work is the subject of a separate report by one of us, to be published a few months later. Suffice to say here, that the additive errors due to viscosity may be eliminated by the following modification of the step-by-step method.

The primary P of the test ring (Fig. 1) is connected through the reversing switch C_2 and the single pole switch S_2 with the storage battery and ammeter A. The storage battery is connected with a sliding contact wire rheostat, r, through the two switches S_3 and S_4, which have flexible leads with clips which can be attached to the rheostat at any desired point, The secondary of the test ring is connected through the resistance R_1, the switch S_1, the reversing switch C_1 and the control coil K with the galvanometer G. This is the same scheme of connections used in the ordinary step-by-step method. The modification lies in the method of procedure, which for that part of the hysterises curve between saturation point and retentivity point is as follows:

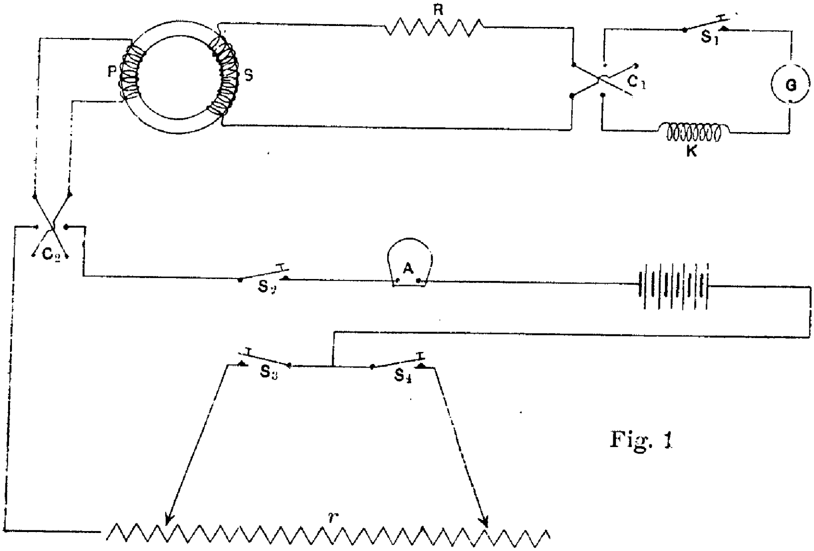

FIG. 1.

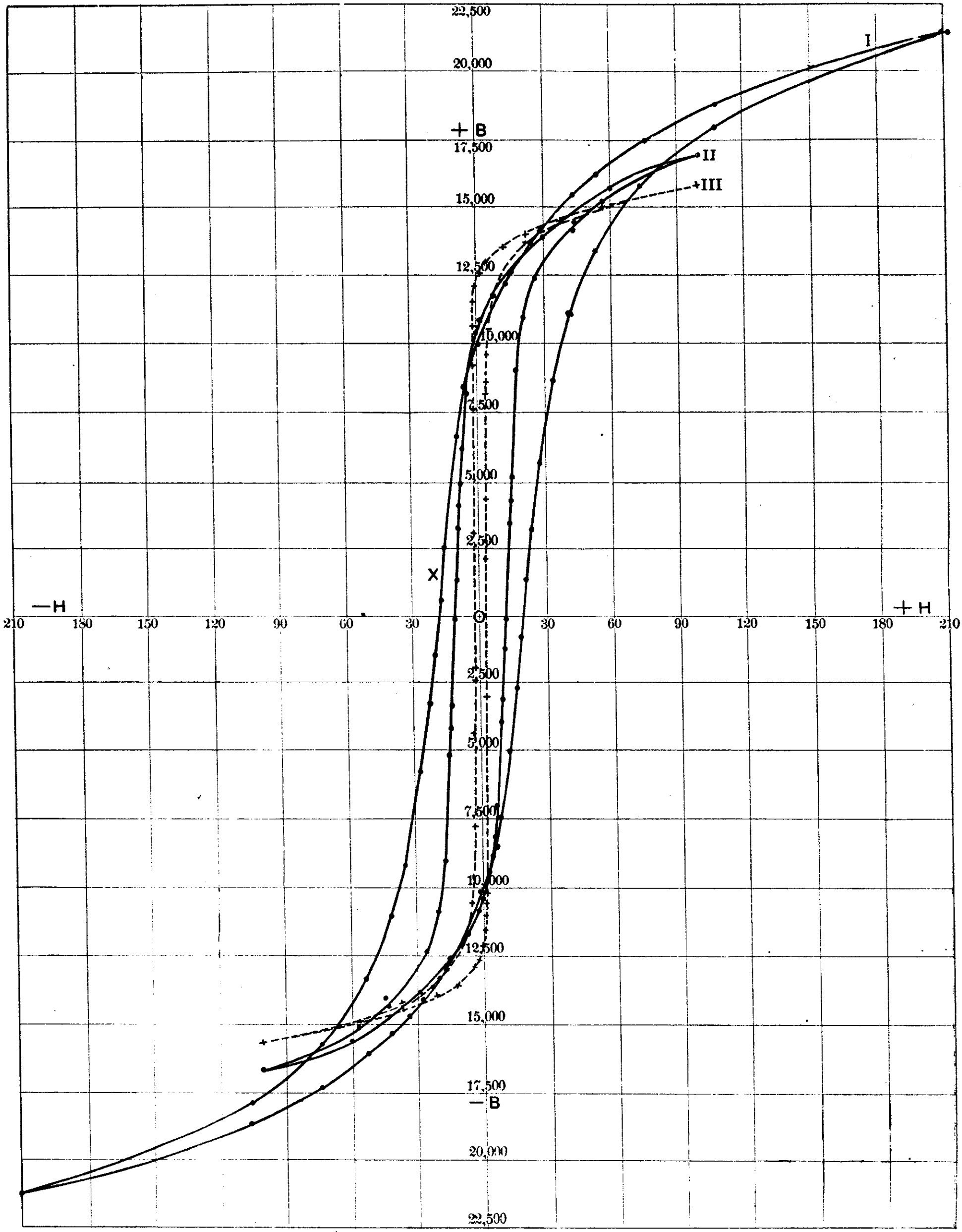

Fig. 2.

[Burgess]

S_3 is connected to the rheostat in such a position that the primary current is sufficient to produce a saturation field. S_4 is then connected at such a point on the rheostat that if S_3 were open a primary current would flow corresponding to any desired field less than the saturation field. At the end of any observation the switches will be in these positions: S_1 closed, S_2 closed, S_3 open, S_4 closed. For the next observation, the procedure is as follows:

Open S_1. Set S_4 for the next primary current desired, corresponding to a field less than for the previous observation. Close S_3, bringing the iron to saturation point. Close S_1 and bring the galvanometer to rest with the control coil K. Then finally, open S_3, observing the galvanometer throw. This gives the change in induction from saturation point to any desired lower field, and the method is the same for all points between saturation point and retentivity point.

For the points between retentivity and negative saturation the induction changes are reckoned from the retentivity point, and the switches at the end of an observation will be in the same positions as for the first case. For the next observation the procedure is as follows: Open S_1. Set S_4 for the next primary current desired. The induction will have some value such as at X on the largest curve, Fig. 2. Reverse C_2, and close S_3, bringing the iron back to saturation point. Open S_2, bringing the iron to retentivity point. Reverse C_2 again. Close S_1 and bring the galvanometer to rest. Close S_2, and observe the deflection of the galvanometer. This gives the change in induction from retentivity point to any point such as X. The method is the same for all points as far as negative saturation. The other branch of the curve is done in the same way. It takes nearly twice as long to run a curve by this method as by the step-by-step method, but the errors due to magnetic viscosity are practically eliminated.

Curve 1, Fig. 2, was not obtained by this method, as we were not at first aware that the magnetic viscosity existed to any serious extent in the electrolytic iron. The values of B are probably several per cent. too low, but the curve shows several rather remarkable properties. The iron is evidently very hard, as indeed, its other physical properties show. The coercive force is 18 dynes, and the retentivity 10 000. This would have come a little higher had the viscosity error been eliminated. It seems that the field of 210 dynes does not saturate the iron, although it carries the induction to the high value of 21 250. At the same time there is relatively little area added to the hysteresis loop by running the field so high.

It is known that heating causes the liberation of hydrogen from electrolytic iron, the evolution beginning at comparatively low temperatures and increasing as the temperature is raised. The test ring was heated for several hours at a temperature of 200° cent., and magnetic tests again made. These gave a curve almost identical with the first, and showed either that it is not the hydrogen in itself which contributes to the magnetic properties of electrolytic iron or that the amount of hydrogen liberated was not sufficiently great to materially alter the magnetic measurements.

The ring was then unwound, embedded in magnesium oxide, and heated for eight hours at about 1 200° cent. In this process a small portion was corroded on one side, necessitating the turning down of the ring, and hence a different choice of windings. The ring was found to be much softer than at first, and on being tested with the step-by-step method, gave values for the magnetic induction 17% lower than those obtained by the method of reversals. As explained earlier in this paper, this was traced to magnetic viscosity, and a modified ballistic method was devised to eliminate the error. The dotted curve we obtained by this method, and comparison with the large curve shows that a tremendous change had taken place with the heating at 1 200° cent. The iron is now in the condition of a rather soft steel, with a coercive force of about 2.5 dynes, a retentivity of 12 500 and a large amount of magnetic viscosity in the steep parts of the curve. A second heating of the ring to over 1 200° cent. produced no appreciable change in the magnetic properties.

Another ring was prepared of electrolytic iron deposited from a solution maintained more nearly neutral than in the former case, the deposit being somewhat less hard and brittle and the fracture showing a finer crystalline structure. The mean radius of this ring was 4.175 cm.; the width of face 0.97 cm.; and the thickness 0.768 cm.

The primary turns were 418, and the secondary 350. The curve II was obtained from this ring by the modified ballistic method, and is evidently like curve I except that the peculiarities are not so marked. A field of 100 dynes gives a maximum induction of 15 750, and a retentivity of 10 300. The coercive force is 11 dynes. The iron is still very hard but its other physical properties also indicate that it is not so hard as the first sample.

After some further tests have been made on this ring it will be heated to various temperatures and tested, with a view of determining at just what temperature the area of the hysteresis loop begins to change rapidly.

Magnetic viscosity is usually found in rather soft steels, of low coercive force, or even in many samples of soft iron. It was therefore a matter of surprise to find that the step-by-step method gave values of the maximum induction for ring II 6% lower than those obtained by the method of reversals, and by the modified ballistic method. This indicates a considerable amount of magnetic viscosity. We hope to have some laminated annealed rings in the near future, and to continue this investigation with these and with some rod samples, as well as with the rings already on hand.

A paper read at the Ninth General Meeting of the American Electrochemical Society, Ithaca, N. Y., May 2, 1906. President Bancroft in the Chair.

STRUCTURE OF ELECTRO-DEPOSITS.

BY CHARLES F. BURGESS AND OLIVER P. WATTS.

It is a well-known fact that electro-deposits may be made to exhibit a great variety of physical structures; in fact, it has been suggested that all forms of vegetation may be imitated in metal, deposited electrolytically. It is not the reproduction of the various forms of vegetation, but rather the prevention of their formation that measures the success of deposition for technical purposes.

The factors which influence the structure are, current density, temperature, circulation of solution, composition of electrolyte, gases, or other impurities dissolved in the electrolyte, and the thickness of the deposit.

It is not the purpose of this paper to discuss in detail the influence produced by a variation of each of these factors, but rather to point out some peculiarities of the physical structure of electrolytic iron. These observations are incidental to an investigation of the production and properties of electrolytic iron now in progress under a grant from the Carnegie Institution of Washington.

With suitable adjustment of the factors above named, it has been found that the deposition of iron in thick layers may be carried on with almost the same ease and rapidity as is the case with copper and some other metals.

One of the difficulties which may be encountered in the deposition of iron or other similar metals is vertical grooving, as illustrated in Fig. 1. This appears to be due to the upward flow of the electrolyte at the cathode surface, the dilute solution flowing upward through channels which conform to and start from protuberances near the bottom of the cathode. Among the methods of preventing this grooving are agitation of the solution and the proper choice of solution density and composition. The addition of an inert salt will diminish the changes of specific gravity of the electrolyte in the neighborhood of the cathode, due to depletion of electrolyte by deposition of the metal.

Another troublesome feature is that caused by gas bubbles adhering to the deposited metal. These bubbles insulate the portions of the plate beneath them, thus producing pitting, and the metal may even pile up around the bubbles so completely as entirely to enclose them. Fig. 2 illustrates a surface in which the influence of gas bubbles is apparent, the light portions representing the ridges between bubbles. It is commonly assumed that these gas bubbles are due to the liberation of hydrogen, but it is the belief of the authors that air may be equally responsible with, or more so than, hydrogen in giving rise to this trouble. In the deposition of iron, it has been found that the gas pitting is more pronounced with a solution freshly prepared than it is after the current has been flowing for some time. Also that after allowing the solution to stand idle for some time, the gas bubbles will be copiously liberated when the cell is again started. Agitation of the electrolyte by blowing air through it, is not practicable, through the increased liberation of the gas

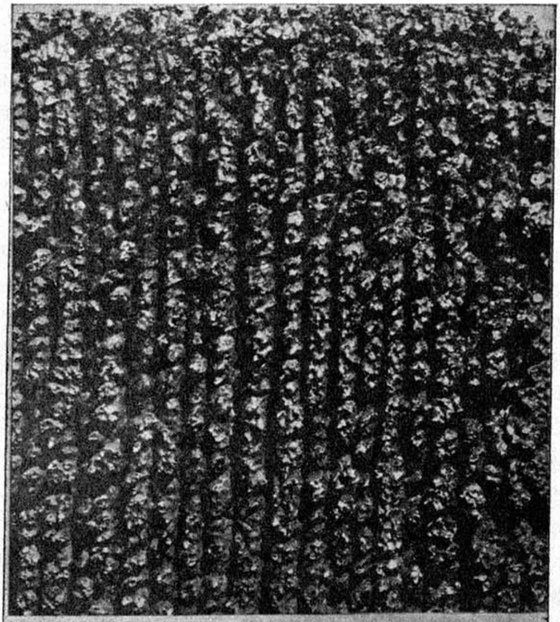

Fig. 1. Vertical Grooving.

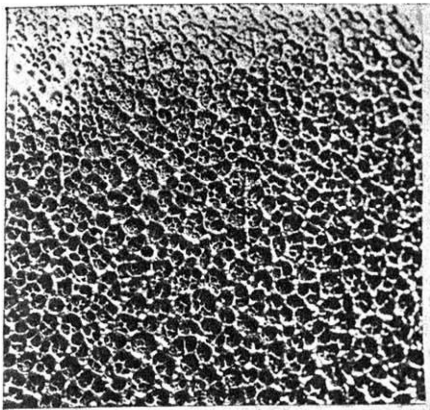

Fig. 2. Pitting Produced by Gas Bubbles.

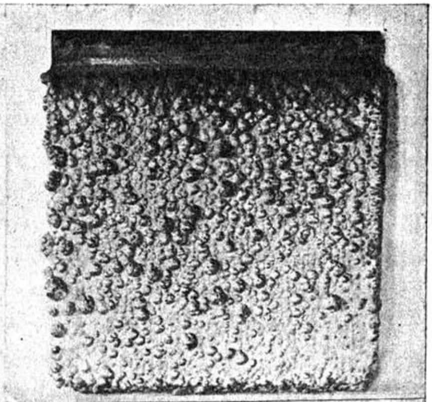

Fig. 3. Iron Cathode, two months growth.

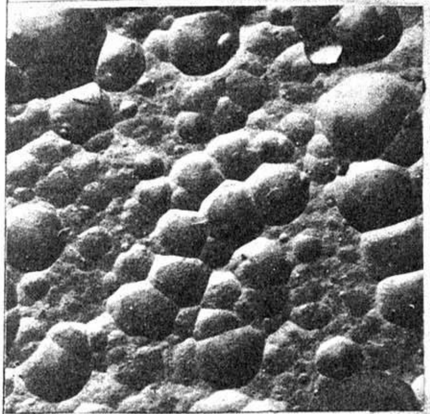

Fig. 4. Cathode Nodules.

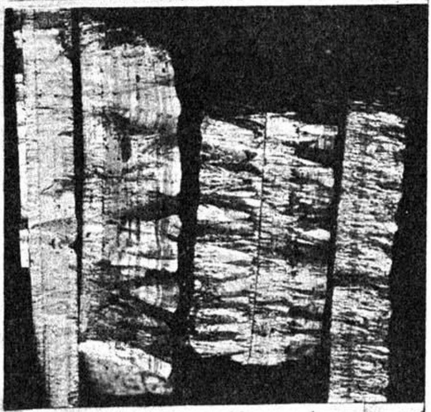

Fig. 5. Surfaces of Fracture.

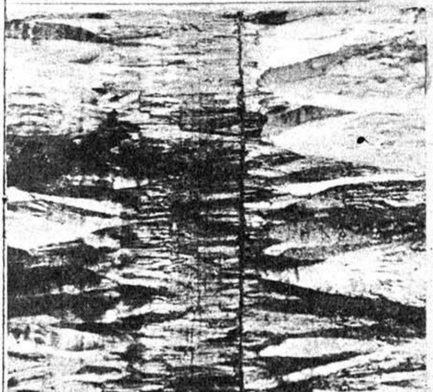

Fig. 6. Fractured Surface Magnified about 4 diameters showing starting sheet.

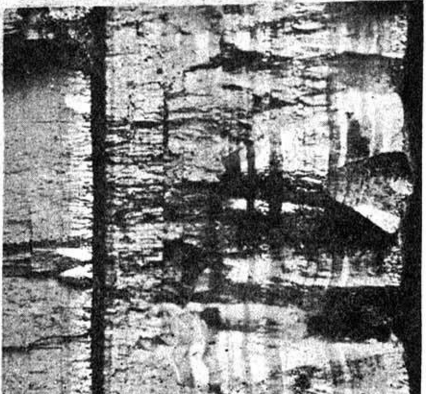

Fig. 7. Fracture showing conical growths.

caused by it; and, in fact, the deposition proceeds most satisfactorily if air is kept, as far as possible, away from the solution. It is well known that air is soluble to a certain extent in various solutions, and it appears that the flow of the electric current has the effect of driving this air out of the electrolyte onto the cathode. A remedy which may be used for overcoming this defect, at least in the case of iron, is to boil the solution, driving out the air as far as possible.

Employing a current density of about ten amperes per square foot, temperatures between 20° and 30° C., a solution of ferrous sulphate and ammonium chloride, with a centrifugal pump for circulating the electrolyte through the series of tanks, and, observing precautions for the exclusion of dissolved gases, it has been found possible to deposit iron to a thickness of at least 1 inch. The thickness is usually limited by the degree of roughness on the surface. The iron made during the first few days of deposition appears smooth; later, small irregularities may become apparent, and these increase in number and size as the process is continued.

Fig. 3 illustrates a cathode of iron in which the deposition has proceeded for two months.

Fig. 4 illustrates more in detail the appearance of the surfaces, showing nodules in various stages of development. The convex hummocks vary in size from those which require a microscope to detect them to those which measure ½ inch or more across. The natural form of these growths is of a circular cross section, the diameter increasing steadily with the thickness of deposit. Where two of these growths interfere, deformation takes place, producing a honey-comb appearance, as shown in the group near Fig. 4.

Just what produces these characteristic growths is perhaps, a matter of speculation. The ideal deposit is one which is dense, homogeneous, and smooth on the surface. It is possible that the roughness of the iron deposit just referred to, may be due to minute particles of impurity suspended in the electrolyte, which attach themselves to the surface receiving the deposit. The current tends to cover up such particles, and the hump thereby produced, steadily increases in magnitude. This is commonly offered as the explanation, though we have been unable to find such particles with a microscope.

Fig. 5 illustrates the fracture of four different iron cathodes, the lower one being a dense and rather smooth deposit and the one above showing how such dense deposit may assume that peculiar structure which makes itself apparent on the surface in Fig. 4. The third section in Fig. 5 shows a deposit in which the cones grow in both directions from the starting sheet. The difference in thickness on the two sides of the starting sheet, is due to the variation in the current density on the respective sides. The top section shows an electrolytic deposit which is of a fibrous nature.

Fig. 6 shows a larger magnification of the fracture, and the growths which appear to take root near the surface of the starting sheet and extend onward, are quite apparent.

Fig. 7 shows two fractured cathodes, the larger illustrating the characteristic tooth-like growth, and the other demonstrating that by acidifying the solution, the conical growths may be suppressed until the plate has attained a considerable thickness. If the nodular deposits are struck a sharp blow with a hammer, some of the conical-shaped growths will become separated from the main body of the metal, leaving cavities sometimes ½ inch or more in depth. A group of these teeth which were collected in breaking up an iron cathode is illustrated in Fig. 8. It will be noted that some of them are almost perfect cones, while the sides of others show interferences produced by adjacent growths.

Another characteristic which is prominent in most of the figures referred to, is shown by the lines parallel to the starting sheet, which indicate surfaces of cleavage along which the metal is liable to separate when mechanically disintegrated. These surfaces of cleavage seem to be produced when any marked change in or interruption of the depositing process occurs. If the current is interrupted for a time, or if the cathodes are removed from the tank and exposed to the air, a cleavage surface may be produced. It is also believed that a sudden change in the current density may have the same effect. The differences in structure produced by variations in the current density are illustrated in Fig. 9, which is a fracture at right angles to the surface of deposition, which had been polished, etched, and magnified to seventy-one diams. The strata which are shown and which average 2 mm. in thickness, indicate the thickness of iron deposited each day of twenty-four hours. Striations are the

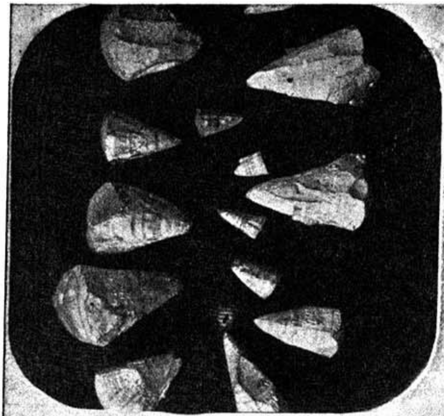

Fig. 8. Conical growths within deposit.

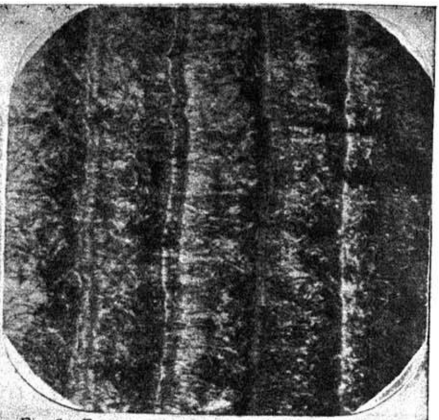

Fig. 9. Fracture of Iron Cathode, magnified showing layers deposited each day.

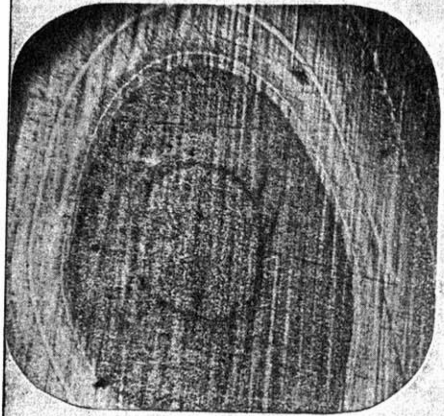

Fig. 10. Polished Section of Nodule.

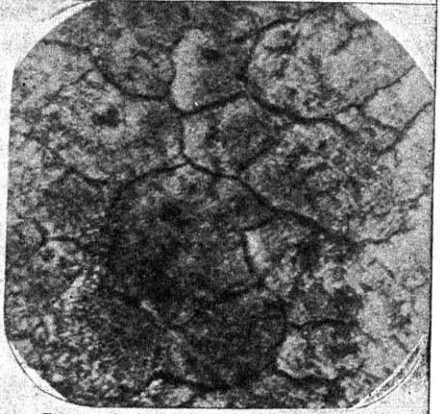

Fig. 11. Section of Electrolytic Iron magnified 250 diameters.

Fig. 12. Electrolytic Iron heated.

Fig. 13. Swedish Iron.

result of varying the current density, due to the method of operating the plant, which consisted in charging storage batteries in series with the iron cells for eight hours, and discharging at a lower current density for the remainder of the twenty-four hours.

Fig. 10 shows a polished and etched section of one of the nodules, such as are illustrated in Fig. 8. This reveals the laminated structure of the nodule, the magnification being twenty diams. and not sufficient to show the granular elements of the mass, as in Fig. 11, which is a magnification of the previous section to 225 diams. This reveals the fact that the mass of the iron is made up of grains bearing a striking similarity to ferrite, but differing from the normal ferrite structure in the absence of visible orientation of crystals composing the grains. The characteristic ferrite structure may be developed, however, by heating electrolytic iron; Fig. 12 shows such structure produced by heating electrolytic iron to about 1,000° C., polishing and etching the section, and magnifying to 132 diams. The light and dark patches are due to the different orientation of the crystals which go to make up the separate grains of ferrite. The unrefined iron, when subjected to the same treatment and magnification, is illustrated in Fig. 13, in which we have the typical ferrite grains. The black spots distributed throughout and between these grains are attributed to slag fibres which are contained in the Swedish iron, and which are entirely absent from the electrolytic iron.

That the characteristic nodular structure of electrolytic deposits is not peculiarly an electrolytic phenomenon is shown by the striking similarity of these deposits to those which are produced in nature. Figures 14 and 15 show two surface photographs taken from electrolytic iron and hematite. Fig. 16 is a similar photograph of the surface of a mass of manganite. Several other minerals that have resulted from deposition from a solution show a similar appearance.

This striking similarity of structure between certain minerals deposited by natural processes and some of the products of electrolytic deposition are not confined to the surface, but extend throughout the materials, as is seen in Figures 17, 18, and 19, which are photographs of fractured specimens of hematite, of limonite, and of electrolytic iron, respectively.

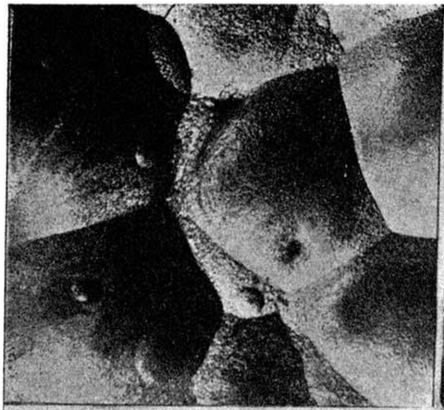

Fig. 14. Electrolytic Iron Nodules.

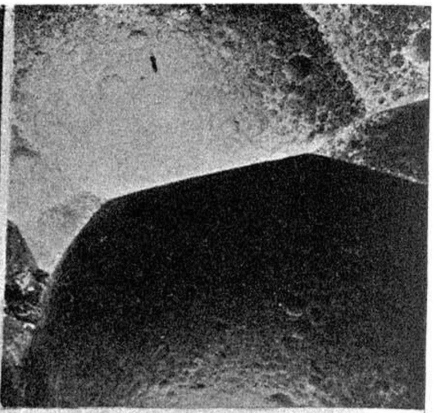

Fig. 15. Hematite.

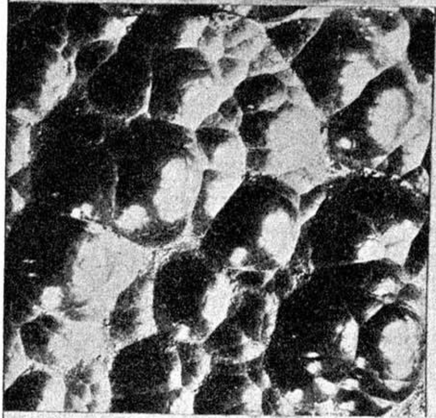

Fig. 16. Manganite.

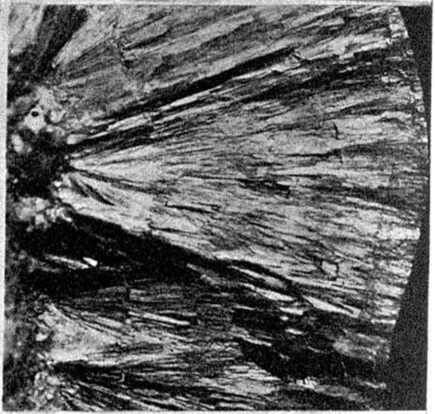

Fig. 17. Fracture of Hematite.

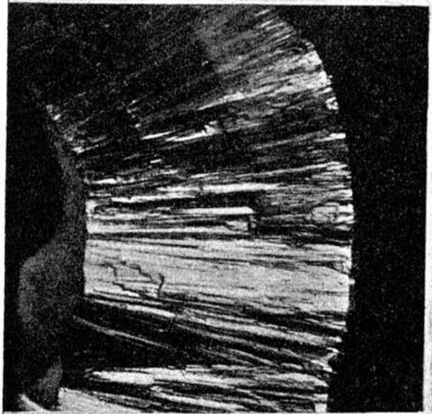

Fig. 18. Fracture of Limonite.

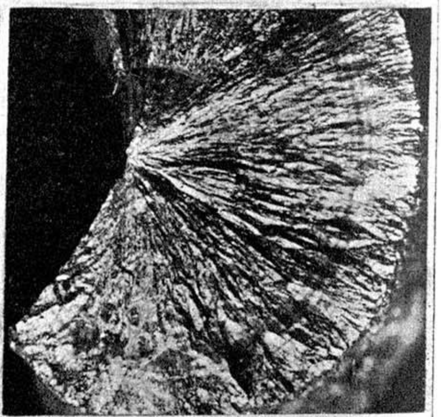

Fig. 19. Fracture of Electrotytic Iron.

Manganite has a similar fracture. In view of these facts, the time may yet come when the geologist, seeking better understanding of the natural deposition of minerals from solution, will experiment in the laboratory, and with the aid of the electric current, be able to observe during their growth and obtain, in a few weeks, forms which in nature required years for their production. It is well, too, that the electrochemist should keep in mind that the process of deposition, as carried out by means of the electric current in the laboratory, although an artificial process, is yet closely related to such examples of natural depositing as have already been cited, and, in so far as the two processes are alike, must be subject to the same laws.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

Mr. S. S. Sadtler: I would like to ask what differences in the structure are noticed by increasing the rapidity of deposition of the iron,—whether you succeeded in getting much smoother deposits.

Prof. C. F. Burgess: That was one of the problems we had to meet—to find the current density that would give us the best deposit; and we found that that range was rather small, lying between 5 and 15 amperes per square foot. Of course, the current density had to be adjusted in conjunction with the other variable factors; and the influence on the physical structure which a change in the current density would make, depends upon what your adjustments of temperature, circulation and other factors are. It is hard to state what the effect of current density is on the physical structure.

Mr. Sadtler: The range is not quite as great as in copper or silver depositing, is it?

Prof. Burgess: Well, I think it is. The trouble comes in getting thick plates. We can use a great range of current density for iron if we want to get only a film of it; but when we come to get thick plates the trouble develops.

PRESIDENT BANCROFT: Is your commercial scale so colossal that you could not afford to stir your solutions vigorously?

PROF. BURGESS: We stir by circulating it. By putting a stirrer in each tank we would agitate the solution so much that it breaks up the film that forms on the surface, thereby letting in too much air.

A paper read at the Ninth General Meeting of the American Electrochemical Society, held at Ithaca, N. Y., May 1, 1906, President Bancroft in the Chair.

A NEW SILICIDE OF MOLYBDENUM.

BY OLIVER P. WATTS.

During the last fifty years the preparation of the metallic silicides has been a fruitful field for experimental investigation. In the year 1893 only eleven compounds of silicon, with seven different metals, were known. The application of the electric furnace to this line of research resulted in a great extension of the list of metallic silicides, now thirty-two in number. And the end is not yet.

The existence of a silicide of molybdenum seems to have been first pointed out by H. N. Warren[1], but it was first isolated by Vigouroux[2] in 1899. Its constitution is expressed by the formula Mo_2Si_3. It consists of silver-white prisms of metallic appearance, and is not acted on by any single acid or by aqua regia. The substance was prepared by the reduction of a mixture of the oxides MoO_2 and MoO_3 by 40 per cent. by weight of silicon in a carbon crucible in the electric furnace. The excess of molybdenum in which the silicide was contained was then removed by using the ingot as anode in hydrochloric acid. The crystalline residue resulting from this treatment was further purified by the successive action of aqua regia, caustic potash solution, and hydrofluoric acid, but still contained as impurity a small amount of iron silicide which could not be removed.

In 1904-5 the writer attempted to prepare a series of compounds of the metals with both silicon and boron, *i. e.*, silico-borides. Among other metals employed was molybdenum, and, although the method used, that of the simultaneous reduction in the electric furnace of the oxides of the three elements, proved unsatisfactory for the production of silico-borides, one of these experiments seemed to indicate the possibility of the existence of a higher silicide of molybdenum than that prepared by Vigouroux. This ex-

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[1] Chem. News, *78*, 313 (1898).
[2] Comptes rend. *129*, 1238-9.

periment consisted in heating in the horizontal arc furnace a charge composed of 70 grams "molybdic acid," 30 grams silica, 50 grams boric anhydride, 106 grams copper, and 120 grams aluminum, one-half in the form of powder, with cryolite as a flux and lime as a retarder to prevent too violent a reaction. The charge was placed on a bed of magnesia and heated for 16 minutes by a current of 350 amperes at 70 volts. The resulting ingot was pulverized in an iron mortar, and treated for several days by frequently renewed quantities of nitric acid diluted with an equal volume of water. The residue was then treated by dilute hydrofluoric acid to remove silica, washed by water, alcohol and ether, and dried. The product consisted of aggregations of flat, dark crystals with a metallic lustre. Analysis showed their composition to be,

	Per cent.
Molybdenum	62.4
Silicon	34.2
Iron	1.1
Boron	2.3

Treatment by hot hydrofluoric acid removed some silicon and all the iron present. The residue was unaffected by boiling aqua regia, but was completely soluble in a mixture of hydrofluoric and nitric acids.

Now hydrofluoric acid really dissolves all the silicides of iron, but is without action upon the boride of iron, therefore all the iron was present as silicide; hence the boron is present as molybdenum boride. Iron boride was undoubtedly present in the original ingot, but was destroyed by the treatment by nitric acid. Since crystallization occurred in a large amount of copper there can be no free silicon present. After deducting the silicon required for the iron present as $FeSi_2$, and the molybdenum required by the boron, the residual molybdenum and silicon are far from the proportions required by the formula Mo_2Si_3, but correspond closely with the formula $MoSi_2$.

The action of several reagents upon this substance is as follows:

Boiling nitric acid—no action.

Boiling aqua regia—no action.

Boiling hydrofluoric acid—no action.

Fused sodium carbonate—action with incandescence.

Fused sodium nitrate—slow, but complete decomposition.

Its specific gravity is 6.31 at 20.5° C.

An earlier experiment, in which a mixture of molybdenite and silica was reduced by calcium carbide, gave a similar result in the ratio of silicon to molybdenum.

While no pure silicide of molybdenum has been isolated in these experiments, the only explanation the writer can offer for the high content in silicon is by the presence of a silicide of molybdenum richer in silicon than Mo_2Si_3, and probably having the formula $MoSi_2$.

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IRON AND CALCIUM.

By Oliver P. Watts.

Received July 13, 1906.

Now that calcium has become available for experimental purposes, and could no doubt be produced cheaply enough for commercial use, provided there were a large demand for it, any new experiments with this metal, although they have yielded results of no constructive value, may yet contribute something to our all too scanty knowledge of the properties and uses of this interesting element. It is with this in mind that an account of the experiments which follow is presented. One of the most promising fields for the use of calcium would seem to be in metallurgy, particularly in the metallurgy of iron, where it might prove an efficient substitute for the deoxidizing agents—silicon, manganese, and aluminum. In addition to its action as a deoxidizing agent, calcium might be expected to be of value in removing sulphur and phosphorus from iron. A proposal to use calcium for these purposes raises the question of the extent to which any excess of calcium will alloy with the iron, and its effects upon the latter metal. These are the questions concerning which some preliminary experiments have been made.

Four attempts were made to form alloys of calcium with iron by fusing together the two metals. In order to prevent oxidation of the calcium before the iron reached its melting-point, the calcium was hammered into a cavity drilled in a cylinder of pure iron, and an iron cap either screwed or hammered tightly into the opening, so that it would have required an internal pressure of several hundred pounds per square inch to force out the cap. The cylinder was placed in a crucible of Acheson graphite lined with magnesia, tightly covered with the same materials, and heated in an electric furnace of the resistance type until the iron melted. Owing to the low density of calcium, the weight of this metal used in each case was small.

	I.	II.	III.	IV.
Weight of calcium taken..............	1.6	4.5	6.0	14.3
Per cent. of calcium taken...........	0.23	1.4	0.77	3.78

The results as to the alloying of the two metals were uniform—no calcium was found in the melted iron. Two changes in composition were, however, made by the calcium. In IV the content both of silicon and of carbon was increased to 0.32 per cent. silicon and 0.218 per cent. carbon. The same iron melted under like conditions, but, without the calcium, contains 0.01 to 0.09 per cent. silicon and 0.03 to 0.04 per cent. carbon, so that the actual increase was 0.83 gram silicon and 0.65 gram carbon. The first thought would naturally be that this increase of silicon and carbon was due to impurities in the calcium used, but this would require that metal to contain 5.8 per cent. silicon and 4.5 per cent. carbon. The gas evolved by the action of this calcium on water had only the faintest odor, and burned with a non-luminous flame, indicating the absence of any considerable amount of calcium carbide. The calcium came from Germany and was not analyzed by the writer, but analysis of similar metal by B. Larsen[1] gave 0.11 per cent. CaC_2. The only tenable inference seems to be that the silicon and carbon are reduction products of the action of the calcium upon silica present as impurity in the magnesia lining, and upon carbon monoxide in the atmosphere within the crucible. In previous attempts to produce alloys of iron high in aluminum, by melting together the two metals in a similar crucible buried in a carbon resistor, the reducing action upon the carbon monoxide was so great as to form large amounts of aluminum carbide. It was therefore expected that calcium would act similarly, and it is only surprising that the extent of this action was not greater. In this connection the action of calcium upon carbon dioxide was tested by kindling a thin piece of the metal in the air, which was difficult to do with the highest heat of a Bunsen burner, and plunging it into a jar of the gas. It burned brilliantly, much more so than in air, leaving as solid products, lime, calcium carbide and carbon. A further attempt at alloying iron and calcium was made by heating 2 grams of calcium within a cylinder of pure iron for seventeen hours at 850–880°. The calcium melted, but no trace of alloying was found. C. Quasebart, of Aachen,[2] also obtained negative results in several attempts to alloy calcium with iron.

As a last resort in the endeavor to alloy iron with calcium, iron oxide was reduced by calcium filings in the presence of excess of calcium. The charge, consisting of 42 grams calcium filings, 60 grams pulverized Fe_3O_4, and 20 grams of calcium in lumps,

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[1] Chem. Centr. 2, 1466 (1905).

[2] Electrochem. Met. Ind. May, 1906, p. 190.

was put into a magnesia crucible. This was enclosed in a strong steel cylinder, devised by Professor C. F. Burgess for firing thermite and similar charges under great pressure, and kindly placed at the disposal of the author. The charge was fired electrically by means of an iron fuse-wire. The reaction was very vigorous and resulted in a metallic ingot and several small pellets. In cold water gas was slowly evolved from the metal at a few points on the surface and calcium hydroxide was formed. For analysis a small piece was heated for three hours in water until all evolution of gas had ceased. It was then washed, dissolved in hydrochloric acid, and found to contain 0.3 per cent. of calcium. Although this amount of calcium came from the interior of the mass of metal, in view of the failure of all other attempts to make an alloy it seems probable that the calcium was imprisoned by the sudden cooling after reaction occurred and held mechanically, not alloyed with the iron.

The diffusion of phosphide of iron through solid iron at high temperatures has been pointed out by J. O. Arnold.[1] Experiments were tried to see if calcium, when heated in contact with iron containing phosphorus and sulphur, would diminish the amounts of these elements sufficiently for the change to be detected by the microscope. To prepare metal for this treatment, coarsely pulverized electrolytic iron was mixed with sulphur and placed in a magnesia-lined crucible, while red phosphorus was enclosed in a cylinder of pure iron and placed in another crucible; both were melted in the electric furnace.

	For sulphur.	For phosphorus.
Weight of iron in charge	372.4 grams.	438.62 grams.
Weight of non-metal in charge	7.6 "	13.5 "
Percentage of non-metal in charge	2	2.76
Percentage of non-metal found	0.3	1.96
Weight of non-metal combined with iron	1.13 grams.	8.62 grams.

Holes were drilled in the ingots; into these were put 5.0 grams and 7.3 grams of calcium respectively, and the openings were closed by caps of pure iron. The ingots were packed in powdered magnesia in a crucible, and heated five hours, at 1200–1300° in a gas furnace. They were badly oxidized, particularly at the tops. All calcium had vanished and the ingot had become perfectly homogeneous, except that the boundaries of the cavity which had contained the calcium could still be distinguished.

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[1] J. Iron Steel Inst. 1894, I, p. 107.

Each ingot was of the same structure throughout, the caps of pure iron having the same appearance under the microscope as the rest of the ingot. Dark areas, probably of phosphide eutectic, were distributed quite uniformly throughout the ingots. The calcium in this experiment was probably oxidized partially, and perhaps wholly, by oxide of iron.

In the same way calcium was melted with iron containing phosphorus and sulphur. Eight grams of calcium removed all of the 0.37 gram of sulphur present in one ingot, and 11 grams of calcium removed 0.61 gram out of a total of 6.04 grams of phosphorus present in the other ingot, thus reducing the percentage of the latter element from 1.96 to 1.56.

These experiments show:

1. That iron and calcium do not form alloys.

2. That by the reduction of the oxides of carbon the latter element may be introduced into fused metals to which calcium is added.

3. That any commercial application of calcium to the removal or phosphorus from iron is impracticable.

The above observations were made incidental to an investigation of iron alloys, now in progress under a grant from the Carnegie Institution.

LABORATORY OF APPLIED ELECTROCHEMISTRY,
UNIVERSITY OF WISCONSIN.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 4, 1907; President Carl Hering in the chair.

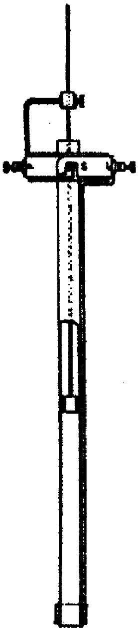
RAPID MEASUREMENT OF ELECTROLYTIC RESISTANCE.

BY CHARLES F. BURGESS.

The specific resistance of an electrolyte varies in a marked degree with variations in concentration, temperature, and purity. Notwitstanding this fact, comparatively little use of resistance seems to be made in the handling of solutions in technical operations. An increase in the amount of various acids and salts in aqueous solutions from 5 parts to 10 parts per hundred produces a decrease of approximately 50 per cent. in the specific resistance, while the corresponding variation in the specific gravity is in the neighborhood of 3 per cent. The sensitiveness, therefore, of a resistance measurement as a means of determining the strength of a solution is materially greater than that of a density determination. The degree with which water approaches purity may be more readily judged by a resistance measurement than by a measurement of its specific gravity.

In technical works, where solutions are handled, the control is usually effected by the use of the hydrometer and by chemical analysis. Devices for the determination of specific resistance are scarcely known outside of the laboratory, though the sensitiveness and range of its measurements are greater than those obtained by the hydrometer. Resistance measurements, correctly interpreted, may, in many cases, enable chemical analyses to be dispensed with, Even in electrochemical work, where the specific resistance has a practical significance, other than in throwing light upon the composition of solution, little use is made of this measurement. The electro-plater makes daily use of his hydrometer, but knows the "resistometer," if it may be so called, only as a laboratory instrument.

The lack of a more extensive practical use of specific resistance measurements may perhaps be found in the fact that the methods of measurement are not sufficiently simple and accurate. While the hydrometer measurement requires only the immersion of a graduated glass tube into the electrolyte, the measurement of resistance usually requires that a sample of the solution be transferred to a calibrated glass vessel and measurements made with instruments of a cost which may be objectionable. Unless troublesome precautions are taken, the temperature of the electrolyte in the testing cell may differ from that of the main body of the electrolyte, and temperature corrections must therefore be made.



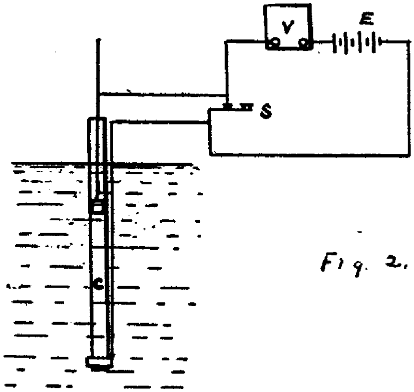


Fig. 2,

A description is here given of a simple method of resistance measurement, which has been in successful use in the Applied Electrochemistry laboratories of the University of Wisconsin for several years, and by which the time and trouble required for taking a reading is little greater than that needed for determining the temperature by means of a thermometer, or the specific gravity by a hydrometer. Aside from features of simplicity and convenience, the method has been found to give results sufficiently accurate for many technical purposes, and the possibility also exists, where suitable precautions are taken, of attaining a considerable degree of precision, as required in research work.

No new principles are involved in this method, which is based upon the fact that a resistance placed in series with a voltmeter and a source of electrical pressure decreases the voltmeter reading. The apparatus required consists of a glass tube with suitable electrodes, as shown in Fig. 1, a voltmeter of the ordinary type, and a source of constant electrical pressure, such as may be cheaply and conveniently furnished by a few dry cells connected in series. The electrode tube, as illustrated in Fig. 1, consists of a glass tube, with its upper end passing through a square ebonite block. Upon this block are mounted the two binding posts, one of which makes connection to an adjustable electrode placed inside of the tube, and the other to a fixed electrode placed outside of the tube near the bottom. The two terminals are kept normally short-circuited by means of the spring, *s*, and this contact may be broken by pressure of the fingers applied at the points *a* and *b*. The operation of the measurement consists in connecting the tube terminals through a voltmeter to a source of constant pressure, as shown diagrammatically in Fig. 2. The tube is dipped into the electrolyte so that both electrodes are immersed. The electrodes being normally short-circuited by the switch, *s*, the column of electrolyte, *c*, is placed in series with the voltmeter and, consequently, decreases the voltmeter reading. The resistance of the column of electrolyte, *c*, is represented by the expression.

$$R = R' \frac{E - E'}{E'}$$

Where R′ is the resistance of the voltmeter, E is the total pressure measured with the switch closed, and E′ is the reading of the voltmeter with the switch open. The specific resistance may be derived from this value by knowing the dimensions of the column of electrolyte or by calibrating the instrument with a standard solution.

With the electrodes fixed at a certain distance apart, and with an unvarying source of pressure, a voltmeter may be calibrated so as to indicate directly the specific resistance.

There is an advantage in the fact that the column of electrolyte is at the same temperature as the main body of the liquid; and the instantaneous flow of current, which is necessary in taking the voltmeter reading, cannot heat the electrolyte to an amount sufficient to cause appreciable variation of temperature.

This method is simply a modification of the fall of potential method of resistance determination, in which the voltmeter is made to serve the purpose of both voltmeter and amperemeter. It is necessary that the resistance of the voltmeter be accurately known, and this instrument should preferably be of the high resistance type. The voltmeter made by the American Electrical Instrument Company, having a resistance of exactly 100 ohms per volt of scale division is especially convenient for this purpose.

It is evident that for the highest degree of sensitiveness, the dimensions of the column of electrolyte should be adjusted so as to be somewhere near equal to the resistance of the voltmeter. For a tube from 0.5 to 1 centimeter in diameter and about 20 centimeters long, a voltmeter reading from 6 to 10 volts should be suitable when measuring electrolytes of high conductivity. A higher voltage may be used to advantage when high resistance solutions are being studied.

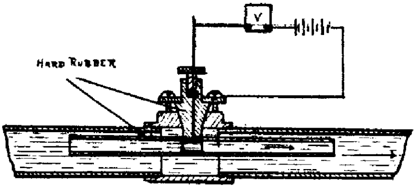


Fig. 3.

A source of error, which must be recognized, is the polarization which may exist between the two electrodes when connected in series with the voltmeter. This may be eliminated by taking readings with the inner electrode set successively in two different positions, but in practice it is preferable to choose the electrodes of such materials that the polarization may be negligible. For example, in measurement of copper solutions, copper electrodes should be employed. It is evident that the higher the voltage employed the less is the percentage of error possible by polarization, and this constitutes an advantage in the use of higher pressures.

Various modifications of this method naturally suggest themselves. The tube, instead of being straight, may be bent in such form as may be most convenient.

Where a record is desired on a solution flowing through a pipe, it may be obtained in the manner illustrated in Fig 3, where a hard rubber tube within the metal pipe carrying the liquid has a branch which projects through the walls of the pipe, and which carries the wire leading to the electrode. The pipe thus serves as one of the electrodes, the columns of electrolyte, on both sides of the inner electrode being in parallel. An example of the application of this device is its use in the discharge pipe of a filter press, the voltmeter indicating the completeness of the washing of a filter cake.

It is evident that this method of measurement lends itself readily to the use of a recording voltmeter.

Laboratory of Applied Electrochemistry,
University of Wisconsin.

DISCUSSION.

Mr. J. L. Wills: I would like to ask Prof. Burgess if the polarization is negligible, or if it enters into consideration?

Prof. C. F. Burgess: The polarization has to be taken care of. Platinum electrodes in sulphuric acid solution will give a polarization of over a volt. With 6 volts applied pressure, this polarization may introduce an error of 15 per cent. The instrument, with electrodes at fixed distance, may be calibrated so as to take that into account, or electrodes may be chosen to reduce polarization to a minimum; for example, if using a copper sulphate solution, copper electrodes would be used. Another method of reducing or eliminating polarization errors is to employ a high pressure, say 100 volts, which is possible when using a glass tube of small bore. The polarization would then come down to a pretty small percentage of error. This is intended as a convenient technical instrument, rather than a highly accurate scientific one.

President Hering: I think Prof. Burgess should have emphasized the fact more strongly that the polarization must be recognized; if the polarization be neglected, it may in some cases lead to very large errors. I calculated two cases as illustrations; in one of them the resistances were selected as is recommended; the error was 35 per cent.; another, in which a resistance of the solution was one-tenth that of the voltmeter, and the error was 194 per cent.; that is nearly three times the true resistance, which shows that the method is not applicable at all if the polarization is neglected, unless it is eliminated. In other words, the counter e. m. f., when reduced to its equivalent as resistance, may become a very large quantity. Prof. Burgess says that the electrodes should always be chosen so that the polarization may be neglected. This often cannot be done; hence, the second method he suggests may very often have to be used, and I would suggest that it might be well if he would add the formula for that second method, in which two measurements are made to determine the resistance.

In reading over the paper, another method suggests itself to me which eliminates some of the difficulties. It is simply a substitution method, using the same tube that he describes, but connecting it in series with an adjustable known resistance and a voltmeter. A plug resistance is preferable. Plug this resistance to zero, set the electrode up to the highest point in the tube, and take the reading of the voltmeter. Then move the electrode down a certain known distance, and adjust the resistance until the voltmeter reads the same. Then the reading of this resistance is the resistance of that column of liquid. You merely substitute a known resistance for the unknown one, and in that way the polarization is absolutely eliminated, because it occurs in both measurements; the polarization is, moreover, the same in both, because the current is the same; the current is the same because the voltmeter reads the same. In the second method which is described, he also makes two readings, so that my method involves no more work than his second method. Furthermore, you do not have to know the resistance of the voltmeter. The polarization is not eliminated approximately, but absolutely. In Prof. Burgess' second method it is only approximately eliminated, because the currents in the two different readings are different. Moreover, you do not have to know the resistance of your voltmeter, and it does not have to read correctly in volts; a mere indicator or galvanometer would answer, and there are no calculations involved; the reading is direct.

Prof. C. F. Burgess: I would say that the purpose of this arrangement is to simplify the method just described. Mr.

Hering proposes using a voltmeter and a calibrated resistance, and says that it isn't necessary to know the resistance of the voltmeter, but a voltmeter always has fixed resistance; and why not make use of it if possible? By using the voltmeter resistance we can do away with the calibrated resistance. The polarization error can be almost completely eliminated by moving the internal electrode, the tube being graduated as a burette, first having the inner electrode at a certain position, and taking the voltmeter reading, and then moving it a given distance while observing the change in voltmeter reading. It is a very simple calculation to see how much resistance it takes to produce the observed change of voltmeter reading.

PRESIDENT HERING: This is what I referred to as the second method you described. Of course, if it is an objection to have a second calibrated resistance, the method you describe is better than the one I mention.

MR. GROWER: Temperature has a big effect on specific resistance. The errors from temperature in ordinary hydrometer measurements are never more than a few per cent., whereas the specific resistance will vary 20 or 30 per cent., due to ordinary variations of temperature. Where the temperature is approximately known, I think the method is pretty good.

A paper read at the Eleventh General Meeting of the American Electrochemical Society, in Philadelphia, Pa., May 3, 1907; President Carl Hering in the chair.

THE ACTION OF CARBON ON MAGNESIA AT HIGH TEMPERATURES.

BY OLIVER P. WATTS.

The advent of the electric furnace has caused a demand for refractory materials of a higher order than those formerly employed. Carbon, carborundum, siloxicon, magnesia, and alumina are proposed, or already in use, for electric furnace construction. Of these, carbon is easily the first, in point of resistance to extreme heat, but its oxidation, its high conductivity for heat and electricity, and the avidity with which it combines with most of the metals, unite to prevent its exclusive use for such purposes. Carborundum is next to carbon in resistance to heat, is a poorer conductor, and oxidizes much less readily than carbon, but, like it, combines with metals at very high temperatures. Siloxicon promises to be a valuable refractory material as soon as it can be obtained in the form of bricks, or of sheets of sufficient strength for use.

Of carbon-free refractory materials, magnesia is the most important. It is more refractory than alumina, chromite, or lime, is not so readily attacked by fused oxides, and is not changed to carbide when heated to high temperatures in contact with carbon. Concerning the latter point, Moissan said (Traité de Chimie Minerale, Vol. 3, p. 955; Electric Furnace, p. 240, Trans. by V. Lenher):

"This explains why it is possible to fuse magnesia and bring it into a liquid state in a carbon crucible without reduction of the oxide. At the melting point of magnesia, magnesium carbide cannot exist."

In August, 1905, when the writer was employed in the preparation of iron alloys, under a grant from the Carnegie Institution to Prof. C. F. Burgess, a curious phenomenon was observed. It has only recently been investigated, and forms the subject of this paper.

One of the many varieties of electric furnace experimented with for the purpose of melting iron and forming the alloys consisted of a granular carbon resistor in walls of magnesia brick, with crucibles standing on a graphite shelf just above the resistor. Although the iron was melted by this arrangement, an unexpected difficulty was encountered in the apparent vaporization of the resistor. In an hour and a half after starting the furnace, more than half the resistor had disappeared, and the interior walls of the furnace were coated with a black, soot-like crust to the depth of ½ inch. This was thought at first to be due to impurities in the material of the resistor, so Acheson graphite was substituted for the granular carbon, but with the same result. Crushed coke and arc-light carbons were also tried, but without improvement. The resistance increased as the resistor became more and more attenuated, until the maximum pressure available—100 volts—failed to maintain sufficient energy in the furnace to heat it properly. In one case, the resistance increased in twenty minutes from a minimum of 0.19 ohms to 2.10 ohms. The rate of formation of the black deposit in the furnace increased with the temperature.

At a cursory glance, this phenomenon appeared to be a distillation of carbon, and a consideration of the energy density supported this view. The dimensions of the resistor were 13 x 2½ x 2 inches. The maximum energy used was 66 K.W., or 1,035 watts per cubic inch of resistor. A carborundum furnace, with a resistor 14 feet long and 21 inches in diameter, using 1,000 horse-power, would have an energy density of only 3.2 watts per cubic inch, provided no current passed outside of the core. As this furnace had proved useless for the preparation of iron alloys, it was abandoned for other types, the wasting away of resistor and the formation of the soot-like deposit being ascribed to distillation of the carbon by the extremely high energy densities used.

Since that time, the same phenomenon has been noted by others. H. M. Goodwin and R. D. Mailey (Tr. Amer. Electrochem. Soc., 1906, Vol. 9, p. 90), when endeavoring to prepare fused magnesia in a carbon tube, observed that a black product condensed in the cooler part of the tube. It was found that this was not a carbide, but its chemical composition was not ascertained.

What is the nature of this curious action? That this is not a case of the simple distillation of carbon is indicated from its occurring only in the presence of magnesia. Is the magnesia a catalytic agent for the distillation of carbon? The writer has observed that not only is a block of carbon corroded by contact with a fragment of magnesia, but a smooth surface of the latter is deeply pitted by contact with a bit of hot carbon. There is, then, some reaction between carbon and magnesia. The visible black product would seem to exclude the idea that the reaction is a simple reduction of the magnesia by carbon, and the failure to find a carbide, together with Moissan's experiments in decomposing an impure magnesium carbide by heating it in the electric furnace, would seem to show that a carbide of magnesium has not been formed at any stage of this reaction.

FIG. 1.

A sheet of graphite corroded to the depth of ⅛ inch by contact with a tube of magnesia.

Recently, experiments were undertaken by the writer to clear up, to his own satisfaction at least, this puzzling behavior of carbon and magnesia in the electric furnace. The first question was to find the relative weights which act upon each other. For this purpose, a weighed amount of electrically-shrunk magnesia was placed in a weighed and covered crucible of

Acheson graphite; this was placed inside a larger, covered crucible, and buried in a resistor of granular carbon, where it was heated two and a half hours, with an average of 37 kilowatts. The experiment was afterward repeated.

	Time Min.	Average Energy K. W.	MgO taken	Loss grams	MgO %	Loss grams	Graphite %
1	145	37	106 g.	34.8	76.9	13.4	23.1
2	55	32.2	25.117	6.294	75.6	2.18	24.7

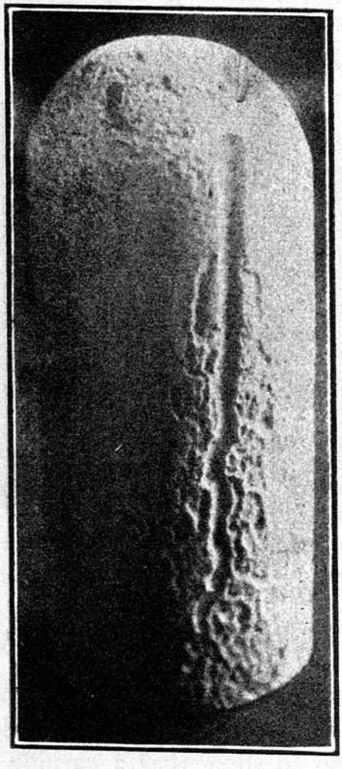


FIG. 2.

A magnesia lining corroded by the iron which distilled out of it and absorbed carbon.

The molecular weight of magnesia is 40.36. In Experiment 1, each 12 grams of carbon carried away with it 40.14 grams of magnesia; in Experiment 2, 35.54 grams. Losses due to oxidation of the carbon by the air originally inclosed in the crucible would lower the observed ratio below that in which the substances really react. This accounts for the low ratio of loss of magnesia in the second experiment, for this loss by oxidation would be nearly the same in both cases, but because of the small weights employed in Experiment 2 the percentage of error is largely increased.

The next problem was to determine the composition and cause of formation of the black product. For this purpose, a mixture of graphite and electrically-shrunk magnesia was packed around a carbon rod 5 inches long and ¼ inch in diameter, and heated for two minutes by 25 K.W. The product condensed on a water-cooled copper tube as a firm black coating, 2 mm. thick. Water proved to be without action upon this. In hot dilute hydrochloric acid it kept its original form, but became a deeper black, and much magnesium chloride was found to be in solution. When free from iron, this action occurred without evolution of gas, Ignited on platinum over a blast lamp, it lost in weight and turned white. Quantitative results are as follows:

	Loss on ignition in air	MgO	Fe_2O_3
1	20.9%	77.3%	1.4
2	21.3%	74.6%	—

Treating by hydrochloric acid, collecting the insoluble black residue and igniting this, the results are:

	Loss	MgO	Fe_2O_3
3	23.2%	—	—
4	22.93%	75 82	1.71

Whether ignition occurs before or after treatment by hydrochloric acid, the loss of weight is approximately the same. Analysis of the product indicated carbon and magnesia in the proportion in which they were found to react with each other.

The next question was whether this black substance is a compound or a mixture. It is uniform in appearance, even under the microscope, and is of considerable tenacity. No physical means have been found of separating it into magnesia and carbon. Its heat of combustion from two determinations in a Mahler bomb-calorimeter was 8,265 and 8,267 calories per gram of carbon burned. Combustion was not quite complete in either case, and in view of the uncertainty introduced by the corrections made for incomplete combustion, the value obtained is fairly close to the heat of combustion of a gram of amorphous carbon, 8,080 calories. An exact agreement would lead to the conclusion that it is a mere mixture of magnesia and carbon.

If it is a compound, it must have the composition indicated by the formula MgCO, or some multiple of this. The heat of combustion for a gram molecule of this is deduced from experiment as follows: Weight of substance taken, 1.6206 grams; residue, 1.2791 grams; loss, .3415 gram. Calories, 2,823; calories per gram of carbon burned, 8,267. Further loss on igniting the residue in air, .0155 gram; total loss, .3570 gram. Hence the weight of the original substance burned in the bomb is 1.5483, the calories per gram of original substance is 1,823, and the calories for 52.36 grams is 95,466. The equation for its combustion as the compound MgCO would be:

$$MgCO + O_2 = MgO + CO_2 + 95{,}740 \text{ calories.}$$

Since the heats of formation of magnesia and carbon dioxide are 145,500 and 97,000, respectively, this would require for the substance, if a compound, a heat of formation of about 147,000 calories. So high a heat value for the product does not, in the writer's opinion, agree with the nature of the reaction between magnesia and carbon. Reaction begins at a high temperature, is very moderate at the outset, and becomes more rapid only by increase in the temperature of the furnace, which would seem to indicate that heat is absorbed, not evolved, by the reaction. This requires that the product or products possess a less, instead of a greater, heat of formation than magnesia.

By grinding in a ball-mill 23 parts of graphite and 77 parts of magnesia, a mixture results which, in physical and chemical properties, is like the product of the electric furnace.

Several later preparations have shown considerable variation in composition:

	Carbon	Magnesia
A	34.36 34.82	65.74 64.66
B	46.09	53.88
C	38.34	—

These had the same properties as the earlier products, and were made in the same way, except that the graphite used was passed through a 100-mesh sieve. The higher carbon content is probably due to graphite carried over mechanically by the more vigorous reaction, resulting from the use of finely-divided graphite.

What is the *modus operandi* of the evaporation and condensation of this carbon and magnesia? Alone, neither vaporizes, except to a trifling extent, at the temperatures attained in the furnaces. The writer offers the following explanation: The reaction $MgO + C = Mg + CO$ is a reversible one under the different temperatures existing in the hottest and the coolest portions of the electric furnaces used. At the higher temperature, the reaction is endothermic, proceeding from left to right of the equation, and producing a mixture of magnesium vapor and carbon monoxide, while at some lower temperature, probably slightly above the upper limits of temperature attainable by combustion processes, the reverse exothermic reaction occurs, and magnesium burns at the expense of the oxygen of the carbon monoxide, producing a mixture of magnesia and carbon. When a furnace is extremely hot, this reverse reaction cannot occur inside the furnace, and the mixture of magnesium vapor and carbon monoxide burns in the air, producing the dazzling light frequently observed. The solid product collecting on the bricks of the furnace is pure white, provided the magnesia is free from iron.

Whether the black substance be a compound or a mixture, the writer has shown that it is chemical action, not a low melting or boiling point, that prevents the use of magnesia in contact with carbon at extremely high temperatures. In ignorance of this important fact, the writer once gave much time and experimentation to the attempt to melt tungsten without introducing carbon, while using magnesia linings in graphite crucibles. The linings failed at the temperature at which the tungsten became plastic, but before it was fully melted. As parts of the linings were missing and that which remained had not been liquefied, the writer came to the incorrect conclusion that magnesia sublimes at high temperatures.

Thinking that a current of hydrogen might so separate the carbon monoxide and magnesium vapor that their reaction with each other would be partially prevented, and that metallic magnesium might be obtained, a mixture of magnesia and carbon was heated in hydrogen, in a carbon tube furnace. No magnesium was found. The product was an extremely fine powder of a uniform light slate color. It had a distinct odor, like acetylene, and decomposed water with evolution of a gas and formation of a white solid. It appeared to be a carbide of magnesium, but sufficient amounts of it for analysis and a study of its properties have not as yet been prepared.

In making iron alloys in the electric furnace, the crucibles used were lined with magnesia, to prevent contamination of the alloys by carbon. These linings were always baked in the crucible before putting in the charge, and as a result of this baking a curious corrosion of the outside of the lining was often produced. It was usually confined to one side, and is well shown in the accompanying photograph, Fig. 2. It is evident that some liquid, very corrosive toward magnesia, had trickled down between the lining and the wall of the crucible. In such cases of corrosion, the lower part of the crucible always contained highly-carbonized iron, either sticking to the walls in solidified drops, or collected in the bottom. The source of this iron was the magnesia used to form the lining, for this contained about 7 per cent. of oxide of iron, and was therefore brown in color. When baked to a very high temperature, the linings became white, and contained but a trace of iron. Heated to lower temperatures, the color of the resulting linings was darker, and they were slightly, if at all, corroded on the outside. When linings were made from magnesia that originally contained no iron, or that which had been once baked in the electric furnace until white, there was no corrosion, and the crucible was free from carbonized iron. The action then appears to be as follows: When the temperature is high enough, iron oxide vaporizes, and coming in contact with the walls of the crucible, is reduced, collecting as microscopic spheres of iron. These grow in size until large enough to flow downward under the influence of gravity, when the flowing drop grows by absorption of those with which it collides. As the iron flows downward, it takes up graphite from the crucible until saturated, and vigorously reduces the magnesia wherever it touches it.

To test more fully this corrosion of magnesia by a carbonized metal, holes 11/16 inch in diameter were bored in a block of graphite; weighed amounts of copper, tin, nickel, chromium, and iron were put into different holes, electrically-shrunk cylinders of magnesia were placed on top of the metals, and one magnesia cylinder put in a hole containing no metal. The block was covered by a sheet of graphite, buried in a granular resistor, and heated. The results of several experiments were as follows:

		Cu	Ni	Cr	Fe	C	Sn	Time min.	Average energy
1	Metal	6 g	6 g	6 g	6 g		6 g	50	26 K.W.
	Magnesia	15	15	15	15		15	—	—
	Loss	2.3	3.7	10.7	3.3		7	—	—
2	Metal	10.54	10.50	10.50	10.53	—	10.50	40	25
	Magnesia	6.79	6.72	7.7	7.25	7.01	6.06	—	—
	Loss	0.10	1.84	0.72	.35	.01	.06?	—	—
3	2 continued		—	—	—	—		110	34
	Losses		4.88*	6.69*	6.90*	1.64		—	—

		Cu	Siloxicon	SiC	Fe	C		
4	Magnesia	6.2332	8.0445	8.0709	7.9642	6.1430	80	23
	Loss	1.1501	8.0445*	6.0000	7.9642*	1.4150	—	—

The losses marked thus "*" indicate that all magnesia had disappeared. The interior dimensions of the resistor furnace used were 18 x 5½ x 7½ inches. These results show that several carbides reduce magnesia far more rapidly than pure carbon does. As was anticipated, copper and tin had but slight, if any, action as carriers of carbon to the magnesia. For vigor of action, the order of the substances tried is as follows: Siloxicon, chromium, iron, nickel, carborundum, carbon, copper, tin. The magnesia adhered firmly to the copper and tin, but to none of the other materials.

The results of these experiments are briefly stated in the following summary:

1. At extremely high temperatures, magnesia and carbon react rapidly, and in a closed vessel a solid black product results.

2. Reaction occurs according to the equation $MgO + C = Mg + CO$.

3. This reaction is reversible, and at a lower temperature reforms the magnesia and carbon as an intimate mixture.

4. Magnesia containing iron oxide in large amount may be freed from this impurity by heating strongly in an electric furnace of the resistance type.

5. Magnesia is reduced more rapidly by certain carbides than by pure carbon. The carbides of iron, nickel, and chromium are

particularly active in this respect, as are also siloxicon and carborundum.

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DISCUSSION.

Dr. J. W. Richards: I think the explanation given by Mr. Watts is correct, because the compound MgCO in such case would be analogous to magnesium carbonyl and would probably, as such, be a gas at temperatures above a low red heat, and liquid below that, and therefore it is an improbability that this could possibly be a compound of the formula MgCO.

Secondly, we all know that silicon, aluminum and magnesium can reduce CO at the temperature of molten steel; therefore, the reverse reaction, the reduction of CO by magnesium itself at the temperature of the furnace, is very probable, and the reduction of magnesia more actively by carbon dissolved in the iron than by carbon itself, is quite in line with what is observed in the blast furnace, where large quantities of silicon are reduced, not by the carbon, but by the carbon dissolved in the iron, which is the only rational explanation of the presence of such large amounts of silicon as are found in the pig iron. The observation of Mr. Watts is quite in line with this well-known phenomenon of blast-furnace practice.

Mr. Reed: It seems to me that we could explain that in this way: That magnesium carbonyl is formed at a certain temperature, and that in a gaseous state is conveyed to another portion of the tube, and there the carbon reduces. The carbon is set free, and the oxygen is taken by the magnesium. That would also explain the fact that the substance has a calorific power equal to that of carbon.

Dr. W. D. Bancroft: I supposed that the formula for nickel carbonyl was $Ni(CO)_4$, so I really don't see why this should be classed as magnesium carbonyl.

Dr. H. E. Patten: I have done this in a vacuum furnace and with temperatures high enough, and if there is sufficient space for the magnesium to get away, it deposits as magnesium, and you will get this black body right where the magnesium deposits. As carbon monoxide is stable at high and not stable at low temperatures, it seems reasonable to suppose that the reaction goes one way at high temperatures, and on cooling down the reaction reverses.

PROF. C. F. BURGESS: Dr. Watts has credited to various other people the discovery of this point. He does not claim that he discovered this as a new phenomenon.

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A paper read in abstract by Dr. Jos. W. Richards at the Twelfth General Meeting of the American Electrochemical Society at New York City, October 18, 1907; President C. F. Burgess in the chair.

THE METALS IN ORDER OF THEIR BOILING POINTS, AS ARRANGED FROM MOISSAN'S EXPERIMENTS IN THE DISTILLATION OF METALS AND ALLOYS.

By Oliver P. Watts.

The widespread introduction of the pyrometer into both scientific and technical metallurgy has resulted in an increase in the accuracy and extent of our knowledge of the melting points of the metals. Their boiling points, however, are still an almost unknown quantity. A knowledge of the latter is of importance to the experimenter with the electric furnace, for in the production of metals from their ores, the boiling point of the metal fixes the maximum temperature of the furnace, consistent with a good yield.

Although it would be most satisfactory to have the boiling points of the metals expressed in degrees centigrade (or Fahrenheit), it is not necessary that they be so stated in order to be of service in electric furnace work. An arrangement in order of their boiling points, with some indication of the magnitude of the intervals between successive members of the series, would be of practical use.

Before the advent of the electric furnace the boiling of metals was an unusual phenomenon, except in the case of the more volatile ones, such as mercury, sodium, potassium, and zinc. In 1893, Moissan[1] established that aluminum, copper, gold, iron, manganese, platinum, silicon, silver, tin and uranium can be distilled in the electric furnace. Twelve years later he returned to this subject, and in a series of quantitative experiments determined the weights of various metals boiled away under the same conditions, and also the changes in composition produced in several alloys by heating them in the electric furnace.

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[1] Comptes Rendus, 116, 1429.

The first experiments consisted of the distillation of alloys of copper with zinc, with cadmium, with lead, and with tin, and of an alloy of lead with tin.[2]

The tube furnace[3] used consisted of a carbon tube passing transversely through the walls and cavity of a furnace consisting of two hollow blocks of lime. The tube was heated by an arc beneath it, and the alloy was contained in a carbon boat inside the tube. The arc furnace also used was made from two blocks of lime, and the alloy was held in a carbon crucible below the arc. The time was reckoned from the melting of the alloy.

I. "Charges of 40 grams of alloy containing 60 per cent. copper and 40 per cent. zinc were heated in the tube furnace by a current of 450 amperes at 110 volts, for periods of 1, 2½, 5 and 8 minutes. In each case the residue was free from zinc."

II. "Seventy-five grams of copper and 25 grams of cadmium were heated in the arc furnace by 400 amperes at 110 volts. Samples of 8 grams, removed at the end of three minutes, and 45 grams, removed after six minutes, contained but a trace of cadmium."

III. Copper and lead.

"*a.* Eighty grams of copper and 20 grams of lead were heated in the arc furnace by 500 amperes at 110 volts. A sample of 20 grams removed after two minutes contained 14.7 per cent. lead, a sample of 30 grams at the end of five minutes contained 5.2 per cent., and 8 grams, after eight minutes, contained only 0.8 per cent. lead."

"*b.* Seventy-five grams of copper and 75 grams of lead, after three minutes' heating by 600 amperes at 110 volts, contained no lead."

"*c.* Ninety-seven grams of copper and 60 grams of lead, heated in the arc furnace for six minutes, left a residue of 45 grams, containing no lead."

"*d.* Charges of 60 grams copper and 40 grams lead were heated in different crucibles, with the following results:

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[2] Moissan and O'Farrelley. Sur la distillation d'un mélange de deux metaux. Comptes Rendus, 138, 1659-1664 (1904).

[3] Comptes Rendus, 117, 679 (1893).

No.	Total time	Time of distillation	Residue	Per cent. lead
1	4 min.	¾ min.	78 grams	26.6
2	3½ "	1½ "	67.5 "	13.1
3	3 "	1 "	64.5 "	13.9
4	——	2 "	60.5 "	9.1
5	——	2 "	14 "	0.0

"The alloy used in No. 4 was the residue of No. 3, and that used in No. 5 was the residue of No. 4."

IV. Copper and tin.

"*a.* Forty grams of an alloy containing 48 per cent. tin was boiled for one minute in a tube furnace. The residue contained 52.8 per cent. tin, 47 per cent. copper."

"*b.* Charges of 30 grams of an alloy containing 25 per cent. tin were heated in a tube furnace—

No. 1. Two trials, heating 20 minutes, left a residue containing 46.7 per cent. tin.

No. 2. After treating five minutes at 600 amperes, the residue contained 30.5 per cent. tin.

No. 3. Heating ten minutes at 600 amperes left a residue containing 30 per cent. tin."

"*c.* One hundred and forty grams of copper and 60 grams of tin were heated in the arc furnace at 500 amperes. Samples removed at the end of three, six and nine minutes had the following composition:

After 3 minutes, 29.9 per cent. tin.
After 6 minutes, 29.7 per cent. tin.
After 9 minutes, 33.7 per cent. tin."

"c_2. Thirty grams of copper and 70 grams of tin were heated by 500 amperes at 110 volts in a small carbon crucible in a large arc furnace, in order to moderate the action of the arc. The residue contained, after three minutes, 69.4 per cent. tin; after six minutes, 69.5; after nine minutes, 65.5; and after twelve minutes, 62.3 per cent. tin."

"*d.* Thirty-one grams of copper and 40 grams of tin were heated in a small arc furnace by 500 amperes at 110 volts. After boiling for three minutes, a sample of 16 grams was removed and found to contain 60.1 per cent. tin. After six minutes, a sample of 20 grams contained 59.7 per cent. tin, and after nine minutes, a sample of 9 grams contained 60.4 per cent. tin. This sample of alloy distils in the same proportion as its components."

"c_1. Sixty grams of copper and 40 grams of tin were heated in a covered crucible by 400 amperes at 70 volts. Samples were withdrawn from time to time and analyzed."

	Time heated	Time distilled	Residue	Per cent. tin
1st Exp.	4 min.	2 min.	96.5 grams	40.4
	5 "	2½ "	95 "	——
	5 "	2½ "	85.4 "	41.8
2d Exp.	5 "	2½ "	89 "	40.4
	5½ "	3 "	71.5 "	43.2
	4½ "	2½ "	44 "	46.1
	5 "	— "	31.5 "	50.6

"e_2. Twenty grams of copper and 40 grams of tin were heated by 400 amperes at 70 volts as above, with the following results:

Time heated	Time distilled	Residue	Per cent. tin
4 min.	2 min.	92 grams	79.9
7½ "	5 "	82 "	78.2
6½ "	3 "	62.5 "	77.7
4½ "	– "	51.5 "	76.3

"e_3. Thirty grams of copper and 70 grams of tin, after three minutes' boiling by the same energy as above, left a residue of 65 grams, which contained 65.3 per cent. tin."

V. Tin and lead.

"a_1. Fifty grams of tin and 50 grams of lead were heated in the arc furnace by 400 amperes at 110 volts. A sample of 8 grams removed after two minutes contained 4.8 per cent. lead, and a sample of 20 grams removed after five minutes contained 1.5 per cent. lead."

"a_2. Fifty-five grams of tin and 5 grams of lead, similarly heated, contained after one minute of boiling 5.8 per cent., and after five minutes, 0.28 per cent. lead."

"*b.* Sixty grams of tin and 40 grams of lead heated in the arc furnace by 450 amperes gave the following results:

Time heated	Time distilled	Residue	Per cent. tin
1½ min.	½ min.	61.5 grams	83.1
2 "	¾ "	59.5 "	87.8
3 "	1½ "	50 "	96 6
2½ "	1¼ "	41 "	99 7

"In the copper-tin mixtures, with excess of copper the tin increases in the residue, but with excess of tin in the original, the tin diminishes in the residue, in each case approaching the composition indicated by the formula CuSn for the residue."

Initial per cent. tin	Time heated	Per cent. tin in residue
25	20 min.	47
40	10 "	50.6
55	5 "	56.8
80	.10 "	76.3
70	12 "	62.3
60.2	9 "	60.4

"These experiments show that the boiling point of tin is above that of copper. Since the melting point of tin is 226° C., and that of copper 1056° C., tin shows a very extended range of temperature for the liquid state.

The distillation of metals shows examples of three types of the distillation of liquids:

Copper-lead acts like partially miscible liquids, such as ether and water.

Tin-lead acts like completely miscible liquids, such as alcohol and water.

Copper-tin acts like water and formic acid, having a certain temperature at which their vapor pressures are equal."

The writer would call attention to the fact that the formula CuSn requires 65.1 per cent. tin, instead of 60.4 as obtained by Moissan as a residue of distillation. This divergence may perhaps be due to the carbon with which the alloy quickly becomes saturated. Recent experiments by the writer seem to indicate that tin dissolves less carbon than copper when heated to very high temperatures. A greater affinity of carbon for copper than for tin would tend to prevent the evaporation of copper, and so might produce the divergence noted above.

Alloys of gold with copper and with tin were next investigated.[4]

VI. Gold and copper.

"Alloys of gold and copper were made containing 10 and 50 per cent. of gold. These were heated with the following results:

Per cent. gold	Wt. taken	Amp.	Volts	Time	Furnace	Residue			Gr. distilled	
						Wt.	Per cent. Cu.	Per cent. Au.	Cu.	Au.
10	100 gr.	500	70	4 m.	arc	77	89.02	11.33	21.45	1 28
10	39 "			5 "	tube		89.09	10.72		
50	46 "				arc	44	49.00	52.22	1.44	0 90
50	28 "			7 "	tube	23	42.8	57.02	4.15	0.89

VII. Gold and tin.

Per cent. gold	Wt. taken	Amp.	Volts	Time	Furnace	Residue			Gr. distilled	
						Wt.	Per cent Sn.	Per cent. Au.	Sn.	Au.
40	200	500	70	3	arc	185	59.7	41.8	9.55	2.67
40	200	500	70	4	arc	149	53.88	45.9	39.72	11.61

"In the distillation of the alloys of gold and tin the furnace contained a copper tube cooled by a stream of water, and a bell glass was placed over a hole in the top of the furnace. The purple of Cassius condensed in the bell glass, having the composition 49.15 per cent. SnO_2, 36.93 per cent. CaO, 9.90 per cent. gold. The lime was removed by treatment with dilute hydrochloric acid to obtain the pure purple. Other oxides act similarly when vaporized with gold. Alumina yields a pale rose color, magnesia a violet, zirconia a rose or violet, and silica a fine purple color."

The last alloys to be tried were those of silver.[5]

"These experiments were carried out in a graphite boat in the tube furnace described in Comptes Rendus, *138*, 1659 (1904). The metals were especially prepared for this research. The

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[4] **Moissan.** Sur la distillation de l'or, des alliages d'or et de cuivre, d'or et d'etain, et sur une nouvelle préparation du pourpre de cassius. Comptes Rendus, **141**, 977-983 (1905).

[5] **Moissan** and **T. Watawabe.** Sur la distillation des alliages d'argent et de cuivre, d'argent et d'etain, d'argent et de plomb. Comptes Rendus, **144**, 16-19 (1907).

alloys were made and analyzed, the residue was analyzed after each distillation, and the distillate was found by loss. Time was reckoned from the moment the alloy became liquid. The current was kept as constant as possible at 500 amperes and the voltage at 110. Vaporization began in 35 seconds, and after three minutes a certain amount of graphite had been dissolved by the alloy."

VIII. Silver and copper.

Time. Minutes.	Weight Taken.	Residue.	Loss.	Loss per cent.	Composition of alloy.				Grams distil'd.	
					Initial.		Final.			
					Silver.	Copper	Silver.	Copper	Silver.	Copper
1	39.1434	38.2113	0.9321	3.	48.85	51.04	49 86	50.64	0.070	0.630
2	39.7698	38.9113	0.8585	2.16	"	"	49.29	50.89	0.248	0.496
3	40.5854	36.1218	4.4636	11.	"	"	45.11	54.63	3.531	0.982
4	40.0604	35.6215	4.4389	11.08	49.12	51.18	47.42	52.02	2.782	1.973
5	40.5914	22.0588	18.5356	36.28	"	"	20.91	78.64	15.322	1.30
6	40.3194	20.8413	19.4781	48.31	"	"	17.98	81.34	16.052	3.630
7	36.1314	21.6544	15.4770	42.84	"	"	18.54	81.27	13.729	0 893
9	38.9549	26.4700	12.4849	30.60	49 55	49.65	18 33	80 70		
13	39.5539	13.6100	25.9439	65.59	"	"	4 77	94.43	18.404	6.786
15	39.3404	6.7740	32 5664	82.77	"	"	3.62	95.22	19.249	13.111

"During the first three minutes there is little change in the amount of silver in the boat, and the amount of vapor may be regarded as nearly constant to the sixth (fifth?) minute. Then the amount of silver in the alloy suddenly diminishes. It is possible that up to the beginning of the fourth minute there was a definite alloy, but this would be stable only in the liquid state, for a metallographic and physical study of the alloys of copper and silver does not indicate the existence of any definite compound of these two metals. The longer the distillation, the richer the alloy in copper. The boiling point of copper is then higher than that of silver."

The weights of each metal distilled were not given in Moissan's tables, but have been computed and added by the writer. There is some error in the data given for the distillation of nine minutes duration, for, according to the composition stated, the original alloy contained 19.302 grams of silver and 19.341 grams of copper, and the residue contained 4.850 grams of silver and 21.361 grams of copper, so that the amount of silver distilled would be about 2 grams more than the total loss in weight, while the copper shows a gain in weight of nearly the same amount as a result of the distillation.

IX. Silver and tin.

"Moissan and O'Farrelley have established that the boiling point of tin is higher than that of copper. It was of interest to see if there was a decided difference between the boiling points of tin and silver. The alloy was heated under the same conditions as for the alloys of silver and copper, and vaporization began ten seconds after fusion. Silver, like copper, has a lower boiling point than tin."

Time Minutes.	Weight of Alloy.	Weight of Residue.	Loss Grams.	Loss Per Cent.	Composition of Alloy.				Grams Distilled.	
					Initial.		Final.			
					Silver.	Tin.	Silver.	Tin.	Silver.	Tin.
2	40 7328	39.6966	1.0362	2.55	36.98	64.04	33.72	65.53	1.678	0.0655
6	40 7481	17.8956	22.8525	56.08	"	"	10.14	88.87	13.2544	10.1910
10	39.0705	9.4836	29.5869	75.73	"	"	2.83	93.65	14.1798	16.1367

X. Silver and lead.

Time Minutes.	Weight of Alloy.	Weight of Residue.	Loss Grams.	Loss Per Cent.	Composition of Alloy.				Grams Distilled.	
					Initial		Final.			
					Silver.	Lead.	Silver.	Lead.	Silver.	
1	40.9330	28 6775	12.2955	30.04	46.24	52.95	60.75		1.5045	
2	38 7852	3.1460	25.6392	66.10	"	"	83.06		7.0110	
2½	42 8045	4.3244	38.4801	89.89	"	"	96.81		15.6078	

Experiments in the distillation of copper[6] and of the metals of the platinum[7] and iron[8] groups, and of titanium[9], were carried out in the arc furnace with a tube of copper of 15 mm. bore placed just above the crucible and 2 cm. from the arc, to serve as a condenser. The tube was cooled by a stream of water forced through it by a pressure of 10 atmospheres. A tall bell glass was set over the hole in the top of the furnace to serve as an additional condenser. These experiments are summarized in the following table:

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[6] Moissan. Sur la distillation du cuivre. Comptes Rendus, **141**, 853 (1905).

[7] Moissan. Sur l'ebullition de l'osmium, du ruthenium, du platine, du palladium, de l'iridium, et du rhodium. Comptes Rendus, **142**, 189-195 (1906).

[8] Moissan. Sur l'ebullition du nickel, du fer, du manganèse, du chrome, du molybdène, du tungstène, et de l'uranium. *Ibid.*, pp. 425-430.

[9] Sur la distillation du titane et sur la temperature du soleil. Moissan. *Ibid.*, pp. 673-677. A single article covering all of these experiments may be found in Annales de chimie et de physique, 8, 145-181 (1906).

Metal	Grams taken	Furnace	Min. heated	Energy Amp.	Volts	Grams distil'd	Remarks
Copper	300	arc	5	300 x	110	50	Filaments of copper condensed on the cold tube. The residue is covered by a coating of graphite.
"	"	"	6	"	"	160	
"	"	"	8	"	"	233	
Gold	150	"	5½	500	110	10	Residue is covered by a film of graphite, and is 99.98% gold. Cavities in its outer surface indicate the absorption of gas.
"	"	"	6½	"	"	20	
"	"	tube	4	"	"	17	
Osmium	100	arc	4	500	110		Vapors condensed on cold tube. Meta not melted.
"	"	"	5	600	110	16.5	Only partially fused.
"	150	"	5	700	"	29	Entirely melted. Residue contains 3.9% graphite.
Ruthenium	150	"	3	700	"	16.5	Fused and boiled. Residue = 4.8% graphite.
"	"	"	5	500	"	10	Boiling point lies between those of Pt and Os.
Platinum	150	"	5	500	"	12	Ingots contain blow holes, proving the evolution of gas, and also contain graphite.
"	"	"	6½	"	"	19	
Palladium	23		2	500	"	3.2	Boiled. Residue saturated by carbon.
"	150	arc	5	"	"	9.63	Metal boils quietly and "wets" walls of crucible.
Iridium	150	"	5	500	"	9.0	Metal boils quietly and "wets" walls of crucible.
Rhodium	5	tube	1½	500	"	—	Melted in 30 sec. Vapors condensed.
"	150	arc	4	"	"	4	Melted and boiled.
"	"	"	"	"	"	6.1	Residue = 2.19% carbon.
"	"	"	5	"	"	10.2	Drops and crystals of metal condensed on cold tube.
Nickel	150	"	5	500	"	56	Distillation began in 1 minute. Cold tube is coated by microscopic crystals.
"	200	"	9	"	"	200	
Iron	150	"	5	500	"	14	Distillation of iron is difficult because of violent evolution of gas just below the boiling point.
"	825	"	20	1000	"	400	
Manganese	150	"	5	500	"	80	Metal used contained 2% carbon.
Chromium	150	"	5	"	"	33	Residue is chromium carbide.
Molybdenum	150	"	5	500	"	0	Not melted.
"	"	"	5	700	"	0	Well fused. Evolves gas like iron.
"	"	"	20	"	"	56	Metallic cubes and octahedra on cold tube.
Tungsten	150	"	5	500	"	0	Not melted.
"	"	"	20	800	"	25	Boils at higher temperature than any other member of the iron family.
Uranium	150	"	5	500	"	0	Fused.
"	"	"	5	700	"	15	Residue is a carbide.
"	200	"	9	900	"	200	Abundant vapors in 4 minutes.
Titanium	500	"	5	500	"	9	Only the surface was melted.
"	150	"	5	"	"	11	The titanium used contained 3.2% carbon.
"	150	"	6	"	"	17	
"	300	"	7	1000 x	55	110	All fragments were melted but the surface was not horizontal.

All of these metals take up carbon when melted. The metals of the platinum group are quickly melted and brought to the boiling point. With 150 grams of metal, fusion occurs in one to two minutes, and boiling in four minutes. The following details concerning the distillation of a few metals, may prove of interest:

Palladium.—"One hundred and fifty grams of metal, at 500 amperes and 110 volts, melts quickly, 'wets' the walls of the crucible, dissolves carbon, and finally boils quietly. Vapors condense on the cold tube and escape around the electrodes. The melted lime, which extends a certain distance from the crucible, is colored black. If 150 grams of palladium, saturated with carbon, be withdrawn from the furnace and allowed to cool, graphite comes to the surface and covers it with lamellar, superimposed crystals. When a solid crust is formed, one hears sharp cracklings, the surface of the metal cracks, and here and there brilliant drops and crystalline mushrooms of melted metal appear. The surface of the metal is of a bluish color, with rainbow reflections, and shows dendrites at right angles and confused crystals. On the cold tube there is a coating of very small crystals mixed with metallic spheres."

Iron—"The distillation of iron presents a new difficulty. As soon as it takes up carbon and is melted, it absorbs a large amount of gas, as many experimenters have proved. A little below its boiling point these gases escape rapidly and throw out drops of metal. This can be proved by placing 50 grams of iron in a boat in the middle of a carbon tube which passes through the electric furnace. On heating the under side of the tube for several minutes, the metal is seen to melt rapidly, preserving a perfectly horizontal surface. After several seconds, the temperature continuing to rise, bubbles of gas begin to break the surface, then there is an abundant shower of drops, and by the end of the third minute, the remaining liquid boils quietly. In stating the weight of iron distilled, allowance was made for this spattering of the iron. After the distillation, a felting of small, brilliant, clear gray crystals is recovered from the cold tube, but these agglomerate if the heating is prolonged. The distilled metal takes the form of the tube. Sometimes one finds in the midst of the distilled product clusters of interlacing scales, apparently welded at the base, and spindle-shaped. There have been found, too, square shapes, and an octahedron, which seemed to be formed of piled up crystals; but usually these forms are very vague, for the condensation of the vapor is much too rapid to admit of regular crystallization. If the experiment is a little prolonged, the lime distills at the same time the iron is depositing on the tube, then melts and acts on the metal. When the lime which forms the furnace contains sulphates, the distilled metal includes a small quantity of sulphide of iron.

"The crystalline dust obtained in all of these experiments by condensation of the metallic vapor on the cold tube has the same chemical properties as the metal when ground fine."

From the extensive data quoted, obtained by Moissan and his co-workers, the writer has attempted to arrange the entire series of metals treated, in the order of their boiling points. This is a difficult task to accomplish satisfactorily, and probably an impossible one to carry out with complete accuracy. In several cases the difference between the weights of two metals distilled is within the limit of experimental error. The specific heats and unknown latent heats of vaporization may also cause errors in the tabulation, as the writer could not make allowance for these factors. The only known points in the series are the boiling points of zinc, 940° C., and of copper, 2100°., C., as determined by Féry.[10] The boiling point of tungsten was then assumed to be 3700° C.; and the other metals were arranged between these limits. The number standing opposite each metal is not claimed to be its boiling point, but only as an indication of its relative position in the series which begins with zinc at 940° C., and ends with tungsten at some unknown temperature above the melting point (3200° C.).

Zinc	940°C	Titanium	2700°C
Cadmium	1025	Rhodium	2750
Lead	1250	Ruthenium	2780
Silver	1850	Gold	2800
Copper	2100	Palladium	2820
Tin	2170	Iridium	2850
Manganese	2200	Osmium	2950
Nickel	2450	Uranium	3100
Chromium	2500	Molybdenum	3350
Iron	2600	Tungsten	3700
Platinum	2650		

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[10] Annales de chimie et de physique [7], 18, 428 (1903).

The order for the first six metals with reference to each other is correct, since it was obtained from the distillation of alloys. The position of manganese with reference to tin and copper is doubtful. Gold is surprisingly high in the series, and if correctly placed, is second only to tin in the wide range of temperature of its liquid state. Further and more conclusive experiments may lower the position of gold. Moissan's experiments show that there is considerable vaporization of titanium before it melts, but even so, the low position here necessarily assigned for its boiling point must be a surprise to anyone who has tried to fuse this extremely refractory metal. The writer thinks that further experiments, particularly in the absence of air, may greatly change the place of titanium.

With the greatly regretted death of Moissan, this series of experiments has been brought to an untimely close. Now that he has established that the most refractory metals can be distilled with ease and regularity in the electric furnace, it remains for others, with the aid of the optical pyrometer, to ascertain the exact boiling points of the metals, and so fill a wide gap in our knowledge of the constants of Nature.

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DISCUSSION.

Prof. Jos. W. Richards: This is a discussion of Moissan's experiments in the distillation of metals and alloys in the electric furnace. The alloys taken are copper and zinc, copper and cadmium, copper and lead, copper and tin, tin and lead, gold and copper, gold and tin, silver and copper, silver and tin, and silver and lead, and then some experiments on the metals themselves, copper, gold, osmium, ruthenium, platinum, iridium, rhodium, nickel, iron, manganese, chromium, molybdenum, tungsten, uranium and titanium, to determine the ease with which they volatilized in the electric furnace.

Having gathered that information together from a great many different publications of Moissan, Dr. Watts has drawn some conclusions, or tried to, as to the relative volatility of these different metals, and on page 151 he has drawn up a statement in which he shows the boiling point of zinc at 940°C.; the boiling point of copper, as determined by Fery, is 2,100°C., and that of tungsten was assumed to be 3,700°C., and the other metals are arranged in that schedule in their relative order as derived from these experiments, and given a provisional temperature, it being clearly stated that the temperature given is only provisional and not absolute, but that the relative position of those is probably correct.

In the way of discussion, I think Dr. Watts has done a useful thing in getting the data together. We must bear in mind, however, that many of these data are determined from alloys, and not by accurate tests on the pure metals, such as zinc, cadmium, lead, silver, copper, tin, manganese, etc., and I think that a radical mistake has been made in drawing conclusions as to the relative volatility of the metals from their relative volatility from alloys, because the volatilizing of a metal from an alloy is like boiling one substance from another in solution. You cannot draw an exact inference as to the relative volatility or the boiling point from different solutions. As an example of that, I notice by the table that the boiling point of zinc is taken as 940, and that of cadmium is estimated as 1,025. It appears from these experiments that from some alloys cadmium volatilizes more difficultly than zinc. This estimated boiling point, however, is contrary to the facts as to the volatility of cadmium and zinc, since we know that the boiling point of cadmium is 775°, and of zinc 930°.

The evident cause of that discrepancy is that the alloys of cadmium and copper, let us say, are stronger than the alloys of zinc and copper, and in consequence the cadmium is held tighter by the copper and comes off at a relatively higher temperature than the zinc. That source of error permeates all these experiments made on the alloys, and the inferences drawn from them.

MR. WATTS *(Communicated):* I thank Prof. Richards for correcting my error in placing the boiling point of cadmium above that of zinc, and for his very clear explanation of its cause. This source of error applies, however, only to the relative order of cadmium, zinc and lead, not to all the experiments with alloys, as stated by Prof. Richards. The order of the boiling points of lead, silver, copper and tin may be accepted as settled by the experiments described since an alloy or a mixture of each metal with that next in order was boiled, and the weight of each metal distilled was determined. With alloys of silver and copper, experiment VIII, the weight of silver distilled exceeded that of copper, hence silver has the lower boiling point. Similarly for the alloy of silver and lead, lead proved to be the more volatile, and of copper and tin, copper was slightly more volatile.

An address delivered at the Thirteenth General Meeting of the American Electrochemical Society, held at Albany, N. Y., April 30, 1908; Past-President H. S. Carhart, LL. D., in the Chair.

[PRESIDENTIAL ADDRESS.]

THE CORROSION OF IRON FROM THE ELECTROCHEMICAL STANDPOINT.

BY C. F. BURGESS.

Depreciation is a subject which is to-day occupying the attention of financiers, economists and accountants. It is one which presents various phases, none of which is more important than those of obsolescence and physical decay. For one of these the engineer may be held responsible; the other he should work to prevent. Obsolescence comes as a direct result of new discoveries in science and their adaptation to man's use. Physical decay apparently follows the working out of nature's processes, yet it has been proved possible for the scientist and engineer largely to reduce the rapidity with which such decay progresses.

In the use of iron as the most important structural material, attention has been given hitherto more to design and erection than to preservation, but as the amount of erected iron increases, the importance of preserving it likewise increases. The older our existing iron structures become, the greater is the need of retarding their decay.

The phenomenon physical decay of iron and its alloys has long been known, but is little understood. To control it, a deeper knowledge of the underlying causes is necessary. When we recognize the fact that iron structures depreciate annually in value through physical decay at a rate varying from perhaps one per cent. to twenty or more per cent., we have a means of stating the importance of this in money units. When viewed from the standpoint of safety to life, as well as that of preservation of property, the matter takes on a far greater significance.

The importance of this subject from economic, socialistic, governmental and humanitarian standpoints should be sufficient to enlist interest in the work, quite aside from the fascination which it exerts in itself. As Sir Roberts Austen has said: "The study of metals possessess an irresistible charm for us quite apart from its vast national importance. Metals have been sadly misunderstood; in the belief that animate beings are more interesting experimenters have neglected metals, while no form of matter in which life can be recognized is thought to be too humble to receive encouragement. Bacteria with repulsive attributes and criminal instincts are petted and watched with solicitude and comprehensive schemes are worked out for their development and culture."

It is not difficult to show that methods which have proved so fruitful in results when applied to the study of living things are singularly applicable to metals and alloys, which really present close analogies to living organisms. Their anatomy, the structure and framework, are being studied under the microscope, their biology and pathology by means of the pyrometer and various other devices. Thus do we study power of endurance, effect of stress, and recovery from fatigue when allowed to rest.

Corrosion of iron may be considered as the generic term covering a number of diseases peculiar to iron and iron alloys. So little is understood as to the causes of even the most common of these diseases that to prescribe for them requires considerable assurance on the part of the experimenter. There is an insistent demand at the present time for further experimental study of corrosion and for the gathering of accurate records on corrosion phenomena.

Some of our leading authorities hold that primarily iron corrosion is an electrolytic phenomenon. Such a view was advanced by W. R. Whitney (Journal Am. Chemical Society, 1903, p. 394), and this was corroborated and notably extended by W. H. Walker (Journal Am. Chem. Soc., 1906, p. 1251). A. S. Cushman, through some interesting experiments described to our society last year, also sought to ascribe corrosion to electrolytic action.

The acceptance of such a belief would place upon the electrochemist the first responsibility of making a thorough study of iron corrosion, and it is certainly true that such research would offer him a most attractive field for work.

In viewing corrosion of iron as an electrochemical action, it may be desirable to divide into classes various kinds of corrosion encountered in practice. The first class to be considered is:

Corrosion of Underground Structures.

It is well known that under normal conditions iron pipes buried in the earth for distribution of gas and water will corrode so slowly that the life may well exceed a century. The owners of such pipes were greatly disturbed not many years ago to find that a disease had been contracted by their pipes, presumably through association with electric railways. They attempted, and are still attempting, to demonstrate to the courts that the railway companies are responsible for damage caused to their pipes by the leakage of currents from the railway returns.

It has been shown beyond doubt that current flowing from iron to earth subjects the iron to electrolytic corrosion, but beyond discovering methods for mitigating the destruction, the electrochemist has not succeeded in freeing from electrolytic trouble pipes located near a single-trolley railway.

This phenomenon has attracted such attention that to many people the term "electrolysis" is synonymous with destruction of underground pipes. In spite of extensive study which has been given to this matter it is interesting to note various curious beliefs which are held even by some of these experts. Thus we have the disputed point as to whether current flowing from iron to earth will cause a quantitative corrosion as required by Faraday's laws; some hold that the earth conducts to a certain degree metallically and therefore a small current density may not cause any corrosion whatever; while others assert, and probably more correctly, that Faraday's laws hold exactly for large and small currents alike. Testimony has been given to the effect that the flow of current through the earth results in the deposition of a coat of iron upon pebbles in the earth, a phenomenon certainly of interest to those who have experienced the difficulty of depositing iron under most favorable conditions upon a conducting cathode. The statement is repeatedly made that current flowing from the rails to the pipes does not produce electrolysis, but that current flowing in the reverse direction is dangerous. This, of course, is only another case of "whose bull is gored."

In the study of this type of corrosion the electrochemist is called upon to clear up erroneous beliefs by quantitative measurements. So far remedies applied have been qualitative rather than quantitative, and before accurate work can be done in treating this trouble a large amount of data must be made available; such as the specific electrolytic conductivity of various earths—clays, gravels, etc. The minimum electromotive force for flow of current must be more carefully studied to determine whether an electromotive force, no matter how small, will cause electrolysis, or whether polarization is to be counted upon.

Some authorities assert that if the direction of the flow of current can be reversed occasionally the electrolytic corrosion of both electrodes may be prevented, the argument being that current flowing from the iron will carry iron in a solution and that some iron will be redeposited when the direction of the current is reversed. This remedy has been attempted in the operation of certain electric railways by reversal of the polarity of the generators once a day, or every hour, or even more frequently, and the observations made during such practice led to the conclusion that the more frequently the reversals are made the less is the danger from electrolysis. In fact, when we carry this practice to its extreme limit and have a reversal several times a second we arrive at alternating current transmission, the advent of which is generally assumed will be an absolute cure of electrolytic troubles, although some experts assert that an alternating current system of distribution will not remedy present difficulties. The writer's experience in depositing iron from a solution even under the most favorable laboratory conditions has led him to believe that the chance conditions to be met with in the earth are not unlikely to make it possible to deposit iron from the earth on to the metallic electrode. Consequently relief from an occasional reversal of the current does not appear practical of attainment. This statement may not apply, perhaps, when the frequency of reversals is so rapid as to make the current come under the classification of alternating current.

Galvanic Action.

Iron in contact with a metallically conductive material electronegative to itself, and both making contact with an electrolyte, constitute an active electrochemical system in which the iron is subject to corrosion. The rate of corrosion depends upon the electromotive force, upon the conductivity of the electrolytic and metallic conductors, and upon the polarization. If the electrolyte is such that the hydrogen is liberated on the electronegative surface it may produce polarization sufficient to stop the flow of current. If a depolarizing material be present the polarization will be decreased and the increased current thereby produced results in increased rate of corrosion. (Walker, et al; Journal Am. Chemical Society, 1906, p. 1251).

As examples of an electrochemical system of this type, the following well known case may be named: An iron ship in a harbor with a copper sheathed ship are considered undesirable companions, since if metallic contact be made between the two, the iron suffers by being made the anode of a huge electrochemical system of which the copper ship is the cathode and the sea water the electrolyte. It is not good practice to attach a bronze propeller on a steel shaft of sea-going ships, for unless suitable protective steps are taken the neighboring steel will be damaged. The more electronegative the material the more marked is the electrolytic action, and some forms of conductive carbon have properties such as to make the electrolytic action particularly pronounced. Various investigators have pointed out that carbon cinder imbedded in an iron surface, or carbon making contact with iron in any way engenders corrosion by galvanic action. This action takes place whether the piece of iron is of large or small size and the kind of action produced by particles of microscopic size is identical with that produced by the large particles. The uncombined carbon which chemical analysis shows to exist in certain kinds of iron may therefore increase the corrodibility of such iron. The measurement of the single potential of iron sulphide shows this to be electronegative to iron and its presence in iron will give rise to active couples. It can hardly be doubted that such surface exposing spots of iron sulphide is one upon which electrolytic action will take place if an electrolyte be present.

Almost any microphotograph of iron and its alloys shows non-uniformity of composition of surface exposed to corrosion, and we are justified in the belief that the micrographic constituents should be studied in dealing with iron corrosion from the electrochemical standpoint. We do not know in what electrochemical order the ferrite, pearlite, cementite and other constituents of iron alloys may arrange themselves. Data as to the single potential of these various constituents are needed if we would express quantitatively the tendency of a certain combination to corrosion. At the present time our only knowledge of these potentials is of a qualitative kind and also very fragmentary. The available published data come from the records of the work done by the metallographists in their microscopic study of iron. Highly polished iron surfaces have been treated with various corroding acids and reagents, the purposes being to corrode the different constituents at different rates to make the outlines of the various materials apparent under the microscope. A study of the literature on metallography for the purpose of classifying these observations might constitute interesting and valuable work.

It is perhaps doubtful if the exact measurement of any one constituent could be made, at least, with the present methods of measurement, since in measuring the electrical potential of an iron or iron alloy, a value is obtained which may be the electromotive force given by the most positive constituent, or it may be that produced by the polarization phenomenon, or it may be some intermediate or composite value. W. H. Walker and associates (Journal of Am. Chem. Soc., Sept., 1907) have devised an ingenious method for determining the different potentials established by different portions of an iron surface, and they have shown "that in certain instances areas having marked difference in potential exist in far greater number upon the surface of a piece of iron prone to corrosion than upon iron which is resistant to corrosion." Whether this method would lend itself to the measurement of microscopic portions of an iron surface is problematical. An active electrochemical system can usually be detected wherever corrosion is observed, but whether corrosion can exist where no electrolytic action is possible is a matter which appears far more difficult to determine.

Assuming a similarity in chemical composition and metallographic constitution in different samples of iron or iron alloys, the question may be asked, "Can the single potential differ in different specimens or different parts of the same specimen?" The conditions which have been suggested under which differences of potential of this sort may be produced are those resulting from *mechanical working* or deformation of a metal, and by *inequality of temperature.*

Influence of Strain on Corrodibility.

Does strain in iron increase tendency to corrosion? This is a question which has been the subject of interesting discussion and upon which there is radical difference of opinion. Data obtained by different investigators are quite contrary, and it is natural then that contradictory conclusions have been drawn.

In referring to those radically different conclusions of different experimenters the writer disavows any desire to enter into a controversy. But it appears that unless errors which are allowed to creep into methods of measurement are recognized and then guarded against, the data obtained can be of little value, and these errors can perhaps be detected by comparison of the methods employed by different observers.

As a matter of scientific interest we may refer to that well-known riddle which runs as follows: Two steel clock springs are identical as to weight and quality of material, and differ only in that one of the springs is coiled and the other uncoiled. These are immersed in an acid solution and completely dissolved. What has become of the energy which was stored up in the coiled spring? The answer which most easily suggests itself is that this energy must have been liberated during the chemical process of solution, and manifesting itself as heat. Upon this supposition, in dissolving the coiled spring, more heat would be liberated than in dissolving the uncoiled spring. Further, the coiled spring would be more chemically active, and if so this chemical activity should be manifest as increased electrical contact potential existing between the metal and the solvent.

There are many instances coming under practical observation which seem to bear out the idea that a metal under strain is more subject to a dissolving or corroding action than is unstrained metal, this relation being particularly true in iron and its alloys. Mr. James Andrews, in 1894 (Proceedings of the Institution of Civil Engineers), described some experiments by which he attempted to demonstrate that strained iron has a higher potential in a corroding solution than has unstrained. He concluded, however, from the results of his measurements, that the *reverse* condition holds, and that unstrained metal is more rapidly acted upon by the solution than the strained metal. Mr. Carl Hambuechen, in 1900 (Bulletin of the University of Wisconsin, Engineers' Series), pursued an investigation which was, in a measure, a duplicate of that made by Mr. Andrews, with the exception that Hambuechen sought to eliminate some error in the former work by modifications and refinements in the method of measurement. He produced experimental data showing that the iron behaved as it should according to theory, and in fact, he was able to secure, in some cases, a remarkable similarity of stress-electromotive force diagrams with the stress-strain diagrams obtained simultaneously on the sample. He says "the application of stress to metal causes an increase in chemical activity, this increase being especially marked after the elastic limit has been reached."

In 1906, T. W. Richards and G. E. Behr, Jr., contributed a paper to the Carnegie Institution of Washington, Publication No. 61, entitled "The Electromotive Force of Iron Under Varying Conditions and the Effect of Occluded Hydrogen." This paper asserts the presence of regrettable errors in Hambuechen's work, and among the conclusions it is stated that "Measurements of the free energy change in iron during a pull upon wire great enough to cause rupture gave results showing that this change must be very small." The authors apparently conclude from their work that the changes in electromotive force actually produced are too small and the data too scanty and irregular to warrant conclusions of value from being drawn. This view apparently places some of Hambuechen's data under the charge of accidentally falling into a systematic order, which order would not have been shown had the alleged errors been avoided.

In 1907, Messrs. W. H. Walker and Colby Dill discussed "The Effect of Stress Upon the Electromotive Force of Soft Iron" before the American Electrochemical Society. In their summary the statement is made that "the magnitude of the potential suffered by soft iron when tested in a tension machine below the elastic limit is exceedingly small. . . . The change, when great enough to be measured, was negative: the strained metal had a slightly lower potential than the same metal unstrained. . . . Somewhere above the elastic limit the potential rises suddenly several hundredths of a volt."

It may perhaps be not unprofitable to enter into a consideration of the cause of the marked differences of the results obtained by different observers and the diametrically opposite conclusions which were drawn therefrom. Of the various authorities mentioned, Hambuechen has apparently secured results which uphold that plausible theory that iron upon which mechanical work has been done retains some of the energy in a potentialized form capable of being measured by electromotive force readings. The other authorities discredit these results. It is probable that none of the results referred to have been obtained under conditions which are free from all sources of error. Hambuechen's work was done under the supervision of the writer, who therefore feels justified in discussing some criticism of his methods and conclusions. Mr. Hambuechen pointed out in his bulletin that chances for error existed in Andrews' work by reason of the fact that the surfaces whose potential was being measured were not protected from action of the air. He devised a cup-shaped arrangement which surrounded the sample of iron in the testing machine and carefully protected all of the parts of the iron from the air and the electrolyte except such portion of the surface as was being immersed in the electrolyte and whose potential was being measured. He recognized that the amount of potential changes were exceedingly small and that the potential established by a metal in contact with an electrolyte is easily upset by the flow of exceedingly small amounts of current. The use of an ordinary galvanometer used in connection with the compensation method was believed to allow the flow of sufficient current to materially polarize the small surface under measurement. He therefore used a capillary electrometer, which acts as a condenser of small capacity and does not allow the steady flow of current through it. This electrometer had a sensitiveness of .0007 of a volt, and in addition to this sensitiveness it was unaffected by vibration and magnetic disturbances and could be mounted in close proximity to the testing machine.

Messrs. Richards and Behr employed a d'Arsonval galvanometer sensitive to 0.001 volt, and they apparently did believe it necessary to guard fully against polarization phenomena. Walker and Dill likewise took this view as to the precautions deemed necessary, for they employed a d'Arsonval galvanometer of fairly high resistance, but provided with a shunt "to protect the galvanometer from too heavy currents during the preliminary adjustment of the resistances."

In both papers referred to, that by Richards and Behr, and by Walker and Dill, objection is made to Hambuechen's results on account of his use of ferric chloride as the electrolyte against which the potential of the iron was determined. The former writers say that "this unfortunate choice" (of ferric chloride) "completely invalidates all the results. The reason is very simple. Ferric chloride is always hydrolized to a considerable extent—that is, it contains acid. * * * There exists in the electrolyte a continually changing concentration of ferric, ferrous and hydrogen ions and reliable work is out of the question. The effect of these influences combined would cause the electromotive force to change steadily, quite independently of any stress and strain effects." Data are given showing that in two cases the electromotive force of iron rose 0.192 and 0.123 volts in about seventeen hours, and they say that this rise would have been ascribed by Hambuechen to strain.

While it is perhaps true that a solution better than ferric chloride might be chosen, the criticism of Hambuechen's work for this reason is perhaps too severe, since he did recognize the fact that the electromotive force was subject to change, regardless of any strain effect. The change becomes so slow after a half-hour that a stress-strain diagram could be run through in a sufficiently short time that the natural change would have little effect in masking the changes produced by strains. In fact, in producing the autographic record of the stress-strain diagrams, Figure I, the testing machine was run continuously and the electromotive force measurements had to be taken with some rapidity. The writer believes that these observations of varying electromotive force are more probably the results of potentialized energy in the iron than the effects of hydrolysis of the ferric chloride solution, as emphasized by Richards and Behr.

The feature which at first sight might discredit more than any other the accuracy of Hambuechen's results is that he found changes in electromotive force which were materially greater than those calculated on the assumption that all of the energy applied to an iron rod in pulling it apart is thereby potentialized.

Barus has studied the disposition of energy applied in rupturing a piece of iron. ("The Energy Potentialized in Permanent Changes of Molecular Configuration," U. S. Geological Survey Bulletin, No. 94, 1892), and quoting from him we read: To summarize, it appears that as much as one-half of the work done in stretching up to the limit of rupture may be stored up permanently." Calculation of the increase of electromotive force by the potentializing of energy in iron involves the application of the formula

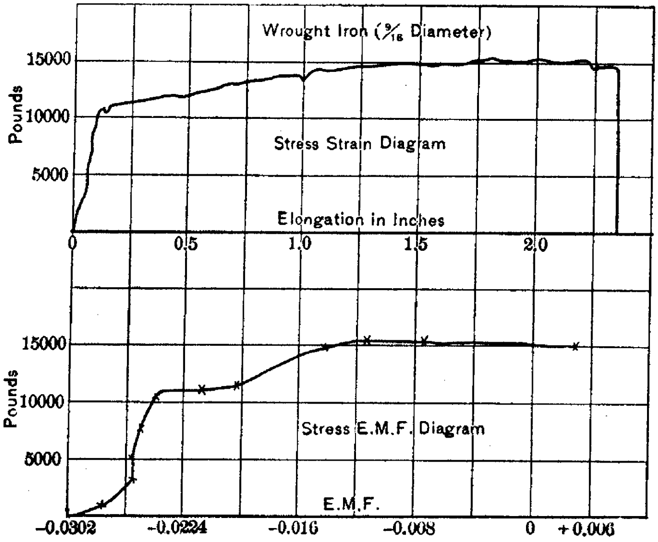

FIG. 1.
Stress-strain and Stress-E.M.F. Diagrams on Wrought Iron.

$$E = \frac{W \times c}{96540 \times g}$$

where

E is increase of electromotive force in volts.

W is energy stored, expressed in Watts-seconds.
c is the chemical equivalent.
g is weight in grams of the iron in which the energy is stored.

From measurements of stress and deformation Hambuechen calculated that the possible increase in electromotive force on a particular sample was .0126 volt (on the erroneous assumption that *all* of the applied energy was potentialized). He found in some of his measurements values two or three times as high as were apparently theoretically possible, to explain which he assumed an excessive storing of energy in the outer layer of iron as compared with that at the center. Richards and Behr were justified in considering this an erroneous assumption. They have apparently overlooked the possibility, however, of a non-uniform distribution of such energy as may be potentialized by strain, for in their calculations of electromotive force they have assumed the energy to be equally stored in all particles of the sample of iron.

Ewing and Rosenhain, in a paper on "The Crystalline Structure of Metals" (Phil. Trans., Royal Soc., Vol. CXCIII), have given results of miscroscopic study on the effect of strain on metals. Figure II. shows the results of strain in Swedish iron, the black lines through the grains being slip-bands. It is well-established in their work that the influence of strain is not uniformly distributed throughout the mass. It appears that the shape of the grains is altered, but that the crystals making up the grains are not deformed. "The conception that metals adapt themselves to the new shapes imposed upon them when they undergo plastic deformation by means of slips along cleavage or gliding planes within each crystalline grain, leads naturally to the supposition that the crystalline elements themsleves undergo no deformation in the process."

Energy is expended in overcoming the adherence or attractive force between crystals, and if there is a storage of this energy it might well be considered as being stored in the portion of metal adjacent to these surfaces. As this metal containing potentialized energy is exposed to the electrolyte, the electromotive force of this portion will be greater than that of the remaining portions. To calculate this electromotive force according to the formula given requires a knowledge of the actual weight of that portion of the metal in which the energy is stored, which obviously would be less than that obtained by weighing the entire mass. This weight is, of course, impossible to determine by known methods of measurement.

The electromotive force of the most electropositive particles is then greater than the *average* electromotive force calculated. The question then arises as to which value—the maximum, the minimum or average value, or some value of over-voltage of hydrogen, is obtained by experimental measurement of contact potential. Richards and Behr have described their determination of the single potential of small globules of iron around which were wrapped platinum wires to make contact. Their voltages are given as being the values for iron even though it is in contact with the more electronegative platinum. Likewise we have in a zinc amalgam the electromotive force of the zinc almost unaffected by the electronegative mercury. From analogy we might expect, therefore, that the potential would be that set up by the most electropositive particles on its surface. And if this line of reasoning is correct, we can easily explain why Hambuechen's measured values of electromotive force were higher than

FIG. 2.
Strained Swedish Iron, Magnified 300 Diameters.

those calculated, and we may perhaps wonder why the differences were not even greater than found.

It should be recognized, in comparing the results of different investigators, that the materials designated as iron may, in fact, be different grades of iron. Richards and Behr confined their attention to highly purified iron, while Hambuechen used the term more loosely as designating the commercial grades of the metal. He found that the increase of potential by strain is more marked in steel than in pure iron, and a microphotograph of steel reveals the presence of various constituents. In all probability there is a difference in the storage of energy in the various constituents, and consequently the possibility of higher electromotive forces.

It may be emphasized again, and in this connection, that the microscope is a useful device in studying the phenomena pertaining to the corrodibility of iron.

Additional Experiments Showing Corrodibility of Strained Iron.

As bearing upon the question whether strained iron has a greater tendency to corrode than the unstrained metal, the following experimental observations may be of interest. These are abstracted from a compilation of results recently obtained by John Thickens, in the Applied Electrochemistry Laboratory of the University of Wisconsin, and also from work carried on under a grant from the Carnegie Institution.

Test rods of mild steel were treated as follows: The rods, 8" long and ¾" in diameter, were turned down at the middle section for a length of ⅜" to a diameter of ½". These were subjected to a stress in a testing machine until the elastic limit had been exceeded and the narrow portion had necked down to a diameter of about 0.4". The entire bars were then turned down to uniform diameter, this being done under running cold water to prevent heating. Bars 3" long were cut from the central portion of the longer bars, and including the strained portion. Some of these bars were subjected to corrosion by suspension in dilute hydrochloric acid solutions, and others by making them the anode in neutral solutions of ammonium chloride, and causing current to flow under low current density. In all cases a marked difference was noted in the rate at which the strained portions corroded as compared with the unstrained, and although the sample looked absolutely uniform before corrosion the decrease in diameter of the strained portion after corrosion is marked. Some of these specimens before and after corrosion are shown in Figure 3.

Differences of potential of from 5 to 9 millivolts were noted between two electrodes, one of which constituted the strained portion and one the unstrained.

Another set of samples were strained beyond the elastic limit by torsion. The original bars were 3" x 1" x 1"; they were turned down for a length of one inch at the center to a diameter of ⅝", the ends being left square. They were subjected to a torsion through 180°, after which the entire length was turned down to a uniform diameter, the specimen in this condition having a uniform appearance on the entire surface. Three grades of iron were employed, and are designated by the terms wrought iron,

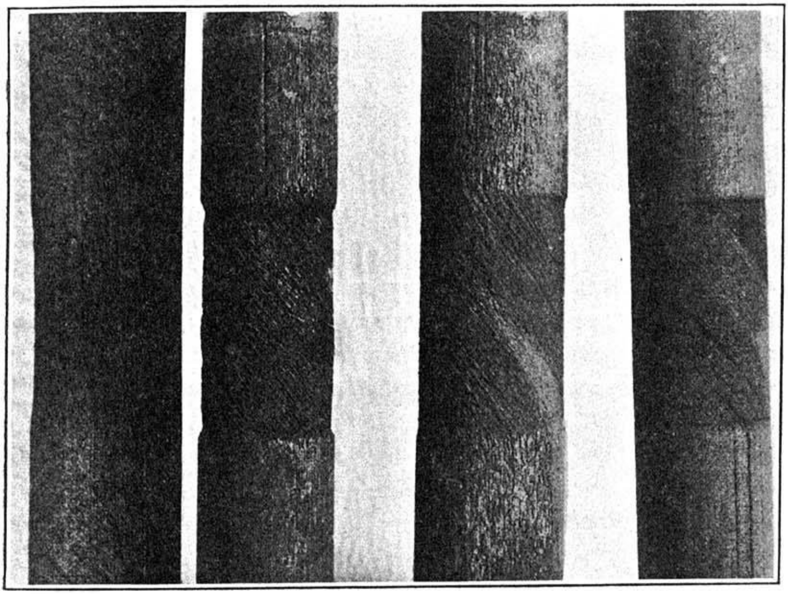

FIG. 3. FIG. 4.

FIG. 3.—Mild Steel Tension Specimen, Corroded Electrolytically 263 Hours 0.04 amperes.

FIG. 4.—Mild Steel Specimens, Strained by Torsion and Corroded.

mild steel and electrolytic iron. The last one was prepared from electrolytic iron which had been melted and forged.

These were subjected to corrosion by suspension in dilute acids, as well as by making them the anode in neutral solutions and corroding electrolytically, using a low current density. In all cases a greater corrodibility of the strained metal was noted, as shown by the reduction in diameter, as well as by the general appearance of the corroded surfaces. The greatest difference was noted in the mild steel, it was less marked in the wrought iron, and least with the electrolytic iron. The results of some of these tests are shown in Figure 4.

The more rapid electrolytic corrosion of the strained portion appears to be due to the fact that the strained metal is electropositive to the unstrained, the current finding the easier path through the surface of the electropositive metal. Another phenomenon which points to the fact that the strained metal is the more electropositive is noted in immersing the machined test samples in dilute hydrochloric acid. There is a liberation of hydrogen bubbles on the unstrained portion. This is not a temporary condition, but it persists, and indicates that there is electrolytic action, the strained portion serving as the anode and the unstrained as the cathode. It was noted that the purer the iron, the less pronounced is the phenomenon, and in the case of the electrolytic iron, the corrosion as well as the distribution of the evolved hydrogen bubbles was nearly uniform. Figure 5 shows non-uniform distribution of the hydrogen bubbles.

The effect of annealing a previously strained bar was noted by heating a machined bar imbedded in iron filings to a temperature of 900° F. for five hours. The difference in corrodibility between the strained and unstrained portions was then shown to have been completely eliminated by this treatment. In the dilute acid solutions the distribution of the hydrogen bubbles was uniform.

An instance where the increased corrodibility of steel is a matter of practical importance is in the use of punched metal. It is a universal specification in boiler construction that the rivet holes shall be drilled and not made by the cheaper method of punching. The reason for this is that the former method gives

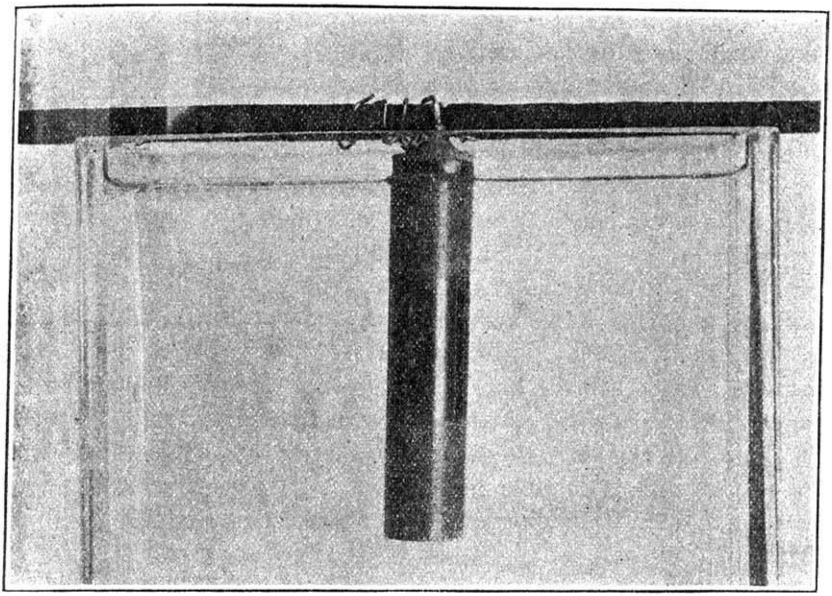

FIG. 5.
Hydrogen Bubbles on Strained Specimens.

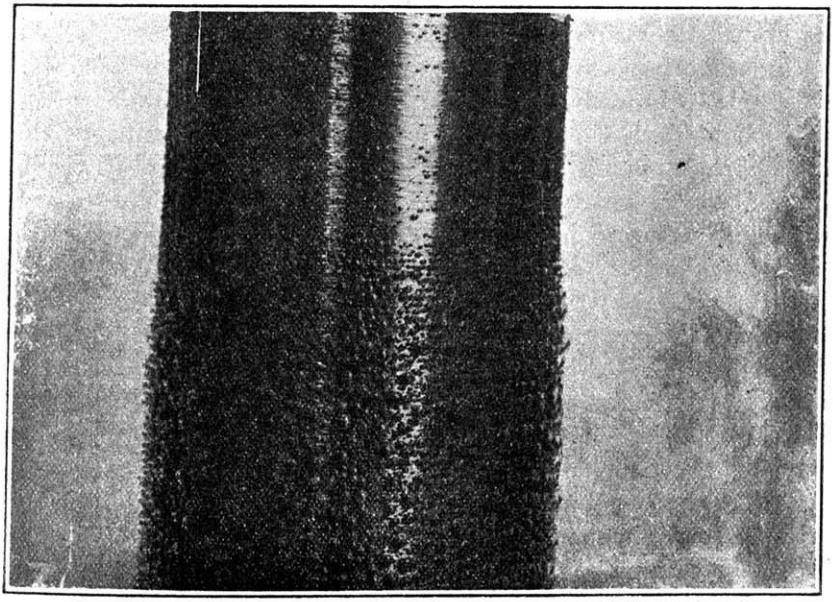

FIG. 5A.
Same as Fig 5, Magnified.

better results as far as durability and freedom from corrosion is concerned. In addition to the liability of cracking or otherwise mechanically damaging the metal surrounding the punched hole, it has been found that rivets inserted in punched holes tend to become loose and leaky.

In the process of punching, straining both by compression and tension is produced, the punched disc being compressed, and the walls of the hole and the disc having been subjected to tension of shearing. According to those who hold that unstrained metal is more subject to corrosion than the strained, the corrosion around a punched rivet hole will proceed some distance away from the hole; on the other hand, if it is true that the strained portion is electropositive to the unstrained, then the metal nearest the hole should corrode the more rapidly. This is a matter which is capable of settlement by experimental demonstration, and the following experiments were carried out with this object in view.

Some steel plates ¾″ thick were punched cold, the punchings having a diameter of 1″. The punched plates were subjected to corrosion, both electrolytic and by dilute acids. It was noted that the corrosion was most rapid on the sides of the hole and in the immediate vicinity.

Figure 6 shows one of a number of plates which had been etched electrolytically, and acid etching produces a similar effect. This photograph does not clearly show the corrosion inside the punched hole, but it shows that the effect of the strain extends some distance, nearly two inches from the hole. The curved grooving, radiating from the center, is taken by the observer as indicating the lines of strain in the surrounding metal. .

Some of the punchings were attached to wires and suspended in various corroding solutions. The suspension wires and the point of contact with the iron pieces were protected from the solution by paraffine. It was shown that the sides of the cylinders had a far greater rate of corrosion than had the circular surfaces, as illustrated in Figure 7.

One of the punchings, and a piece of similar size cut from the original steel plate, were suspended as electrodes in a ¼ normal HCl solution and connected to a mil-ammeter. The current was constant at about ½ milampere for several days, the punching

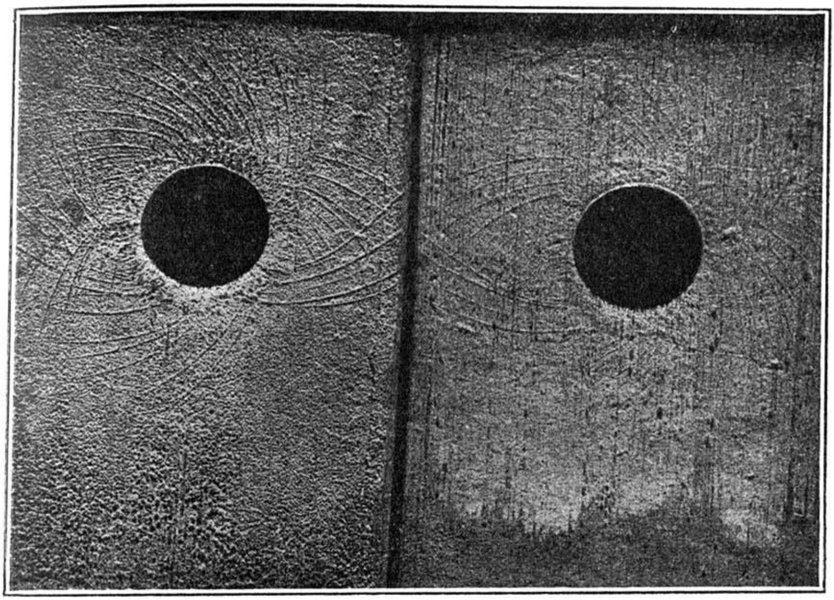

FIG. 6.
Corrosion of Punched Boiler Plate.

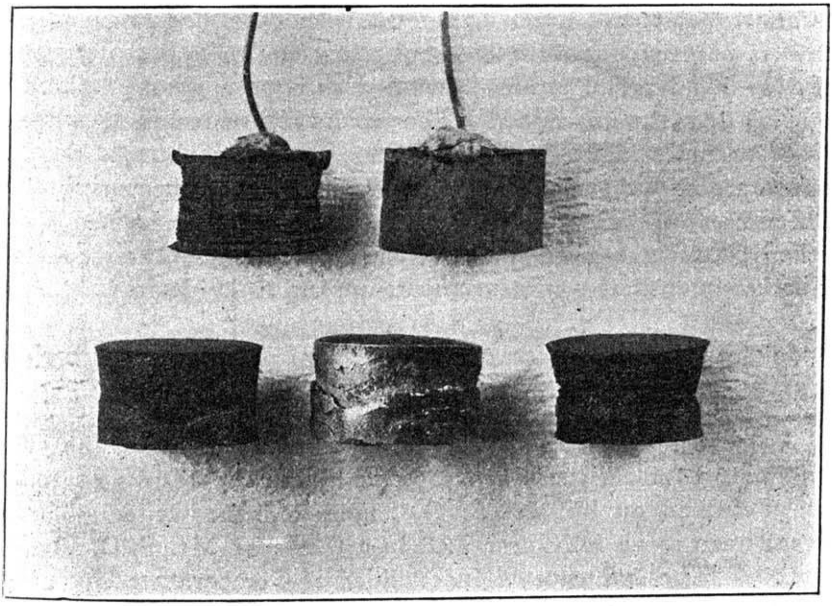

FIG. 7.
Corrosion of Punchings.

being the anode, and corroding the more rapidly. Similar results were obtained by immersing in a normal KCl solution, the current remaining constant at 0.75 mil-amperes. In both solutions it was noted that on first immersion the current was much higher than the constant value subsequently maintained, this decrease being due to polarization as manifested by an accumulation of hydrogen on the unstrained cathode.

Upon momentarily lifting the two electrodes into contact with the air, and again immersing, the flow of current greatly increased. By blowing air through the solution a similar result was attained, and by adding a very small quantity of sodium peroxide the current quickly rose from 0.75 mil-amperes to over 30 mil-amperes. The effect of oxygen in all of these cases was apparently due to its depolarizing action on the cathode, which allowed more current to flow, and which consequently increased the corrosion of the strained metal anode. This appears to be in confirmation of the important discovery made by W. H. Walker, that oxygen causes oxidation, not by uniting with the iron, but by depolarizing, and allowing other corrosive agents to become active.

The experiments which have just been described are qualitative rather than quantitative, but show in an apparently conclusive manner that strained metal *does* have a greater solution tension than the unstrained. The results are of technical as well as of scientific interest, and the effects are so pronounced that it appears obvious that our available methods of measuring the differences of potential between strained and unstrained iron when properly applied should yield accurate quantitative data. Further quantitative measurements appear to be desired.

Influence of Inequalities of Temperature Upon the Corrosion of Iron.

As bearing upon the influence of temperature upon the corrodibility of iron, there are presented here the results of some work carried on by Mr. S. G. Engle and the writer. These results are more fully described in a thesis by Mr. S. G. Engle, entitled "The Influence of Inequalities of Temperature Upon the Corrosion of Iron." This investigation was originally taken up in connection with the study of certain peculiar corrosion pheomena which are commonly found in locomotive boilers.

To one familiar with the corrosion produced by stray currents in underground pipes, the pitting and grooving of boiler tubes has the appearance of being electrolytic action. A place where corrosion is particularly noticeable in locomotive boilers is just inside the end shells where the tube is expanded. At one end of the boiler a copper shim is placed between the tube and the end plate, the purpose being to utilize the ductility of the copper in making a tight joint. At the other end the tube is expanded directly to fill the hole in the end plate. If copper shims were used at both ends of the tubes a logical explanation of the fact that tubes corrode in the immediate neighborhood would be that a voltaic couple is set up between the copper and the iron. It appears, however, that the corrosion is just as marked at the end where copper is not used, and other explanation must therefore prevail. The one most commonly accepted is that the iron tube on being expanded is thereby strained and this strained metal corrodes more rapidly than does the neighboring unstrained metal. There is not enough data to absolutely fix this point.

There is also an irregular pitting in the tubes, the rapidity of the action depending upon the care taken of the boiler, upon the kind of feed water used and perhaps upon other factors. Among the results of this kind of corrosion is the frequent puncture of the tubes, the extinguishing of the fire, the stalling of trains between stations and the retirement from commission of valuable machinery. The pitting may be somewhat general in distribution, but usually there are a few deep pits with the surrounding metal apparently intact. It is a matter of general observation that the pitting is more marked on the tubes nearer the shell of the boiler, rather than on those farther toward the interior—in fact, the interior tubes may last as long as several sets of tubes renewed on the lower row. This is explained commonly by the supposition that the circulation of water, also the introduction of fresh feed water, is such as to emphasize corrosive action.

The object of the investigation previously referred to was to determine if possible whether the equivalent of galvanic cells is established in locomotive boilers, due to inequalities of temperature in the different portions. The most highly heated metal in the boiler are the tubes which are exposed to the hottest products of combustion. The lower tiers of heated tubes are probably subjected to this heat. The direction of the flow of heat is from the interior of these tubes to the water which in turn is in contact with the cooler shell of the boiler. If the boiler tube is, by being hotter, rendered more electropositive than the boiler shell, we would expect a galvanic action resulting in the corrosion of the tube. We would expect the corrosion to be at such places as the current finds the most ready path between the anode and the cathode. The shortest path between the hot anode and the cooler cathode would be between the lower and the side tubes and the interior of the boiler shell.

TABLE I.

Time.	Temp.	Contact Potential.
4.17	20 C.	0.085
4.19		0.064
4.21		0.070
4.23		0.085
3.25		0.085
4.30		0.102
4.35		0.114
4.40		0.143
4.45	38	0.143
4.50		0.150
4.55	38½	0.143
5.00		0.158
5.05	39½	0.165
5.10	41	0.172
5.15	42	0.172
5.20	42	0.187
5.21	42	0.187
5.22	42	0.187*
5.23	42	0.187
5.25	42	0.202
5.28	41	0.202
5.38	37½	0.202
5.44	34½	0.202
5.50	32	0.202
5.55	31	0.202

* Heating current cut off.

Tests were first made to determine the effect of heating of the single potential of iron. It has been previously noted by various authorities that a slight heating does not appreciably change the electromotive force of iron. The purpose of these experiments was to determine what electromotive force changes take place when there is a high rate of transfer of heat from the iron to water. An iron ring was immersed in water contained in a glass dish. The ring was heated by currents induced by a solenoid placed below. The ring acted as a one-turn secondary of the transformer. The purpose of this method of heating was to avoid trouble of introducing heat by conduction through terminals passing through the walls of the containing vessel or through the surface of the solution.

TABLE II.

Time.	Temp.	Contact Potential.
3.15	21° ½ C.	0.085
3.18	21 ½	0.085*
3.20	33	0.106
3.25	50	0.137
3.30	61	0.165
3.35	71	0.188
3.40	79	0.203
3.45	82	0.225
3.50	84	0.240
3.55	85	0.246†
4.10	71	0.246
4.15	86	0.250
4.20	94	0.262
4.25	95	0.276
4.30	96	0.276
4.35	96	0.276‡
4.40	79	0.268
4.50	53	0.232
5.00	43	0.224
5.10	37	0.218
5.25	32 ½	0.212
5.30	31 ½	0.212
5.32	31	0.144**
5.33	30 ½	0.202
5.34		0.212

* Began the test.
† Took the burner away for four minutes.
‡ Turned the lamp out.
** Took this reading directly after shaking the solution.

The water used was that taken from a locomotive boiler, and had a specific resistance of 332 ohms at 23.2° C. Measurements were made by comparison against the normal electrode having the assumed value of -.56 of a volt, the method of measurement being similar to the Oswald Potentiometer Method.

Table I gives the results of one series of measurements, being one of three runs. The results of each of these were almost identical. The maximum temperature was 42° C., it being impossible to go beyond that value on account of the limited current capacity of the solenoid which was used.

In another test the dish containing the ring immersed in water was heated by means of a burner placed below it. The results of this are given in Table II. These data also show the fall of potential during the cooling.

An interesting peculiarity in the electrical heating is shown in the decrease of potential which is first produced by the heating and the subsequent rise after the minimum point has been reached. This minimum was not observed in the test where the external heat was applied.

It was desired to carry the temperatures of the iron surface beyond that which was possible by the former methods of heating, and this was accomplished by bending a soft iron wire into a "U" shape, immersing it in the water and heating it by the passage of an alternating current through it. Voltage readings were taken between this electrode and another one of the same material which was not heated by the passage of the current. It was found that there were certain irregularities in the measurements, due to the fact that the wire dipped down through the surface of the electrolyte. This was remedied by passing the wires out through the bottom of the vessel, which contained an asbestos stopper. Water taken from the locomotive boiler was again used as the electrolyte. It was found that the heated wire first became more electropositive, then became steadily negative as the heating progressed, until the wire became fused. This tendency for the heated wire to become negative in this case is ascribed to the fact that the wire became hot enough to oxidize when in contact with the water, coating itself with the more electronegative iron oxide.

Another experiment consisted in using two steel tubes of similar composition, one tube being one inch in diameter and the other four inches. The inner tube was fastened through a rubber stopper passing through an inverted glass jar, above which rested the larger iron tube. The joint between the glass bottle and the large iron tube was closed by means of a cement joint. A Bunsen burner was placed inside the inner tube and served to heat this metal. Electrical connections were made between the lower part of the tube extending below the stopper and outside of the iron jacket. Locomotive boiler water again was used as the electrolyte between these tubes. The results of one of these tests are given in Table III. Instead of measuring the electromotive force between these tubes, connection was made through a milli-ampere meter to determine the amount of current which flows under the conditions given. It was to be noted in these tests that the inner tube was the anode, and therefore the one to be corroded; also that the corrosion current increases as the diameter increases until the water begins to boil. It is to be noted that after the maximum current has been reached the current begins to decrease slowly. This increase of current to a maximum and its subsequent decrease, regardless of the fact that the temperature conditions are maintained, is a characteristic which has been noted in many experi-

TABLE III.

Time.	Amperes.	
12.20	—0.0009	Inner tube anode.
12.30	—0.0020	
12.40	—0.0026	
2.54	—0.0026	Began the test.
2.55	—0.0032	
2.56	—0.0035	
2.58	—0.0045	
2.59	—0.0050	
3.00	—0.0055	
3.05	—0.0091	
3.10	—0.0115	
3.13	—0.0123	
3.15	—0.0123	Water boils. Put in more water.
3.20	—0.0105	
3.25	—0.0100	Water boils freely.
3.30	—0.0075	
3.35	—0.0060	
3.40	—0.0045	
3.45	—0.0040	
3.49	—0.0027	
4.06	—0.0027	
4.25	—0.0026	
4.45	—0.0026	Turned gas off.
4.45½	—0.0028	
5.05	—0.0010	
5.40	—0.0004	

ments, and it appears that the flow of current produces an increase of resistance, either on the electrode surfaces or in the electrolyte itself, which serves to increase the amount of current flowing. This is merely a suggestion, and the explanation of it requires further study.

The experiments thus far indicate decided tendency for a heated surface to become electropositive, as compared with the cooler piece of metal in the same solution. This is a condition which may exist in locomotive and other boilers, although direct conclusions could not be drawn from these experiments without recognizing the fact that these were carried out under atmospheric conditions, while the water in a boiler is usually under high pressure.

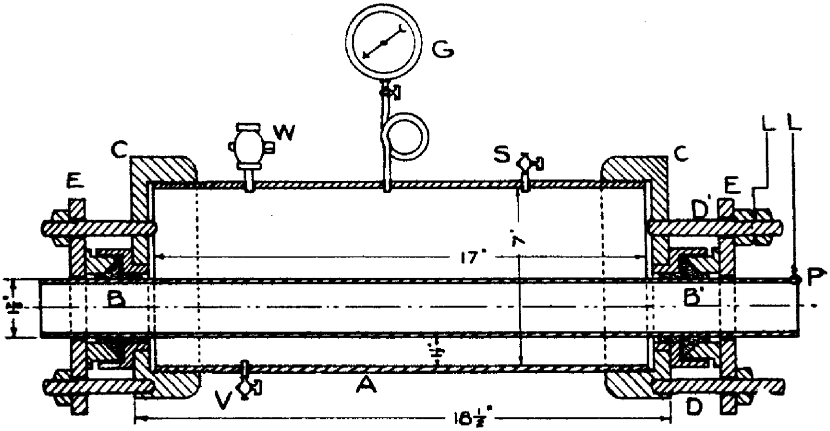

FIG. 8.
Apparatus for Studying Boiler Corrosion.

To conduct laboratory tests upon conditions which would more clearly approach the conditions found in a locomotive boiler, an apparatus, as illustrated in Figure 8, was constructed. This consisted of an iron pipe "A," 7 inches in diameter, and 17 inches long, closed by iron caps screwed on the ends. "B" and "B¹" are stuffing boxes placed below the center of the caps through which the pipe "P" passes. The purpose of this stuffing box is to insulate the pipe from the steel cylinder, at the same time allowing this joint to stand a high steam pressure. Asbestos packing was found to serve this purpose admirably. The cylinder was fitted with a steam gauge and steam cock for the release of pressure, and another opening for the introduction and drawing off of water and sediment. Heat was applied to the apparatus by means of a blast flame inside of the smaller tube. The interior of the apparatus was first thoroughly boiled in caustic solution and rinsed in water.

Electrical connections were made between the inside and outside tubes through the electrical measuring instruments consisting of mil-ammeter and mil-voltmeter. A large number of tests were made by means of this apparatus, employing various kinds of boiler water and operating under a variety of conditions as regards pressure, rapidity of heating, cleaning out of the apparatus, etc.

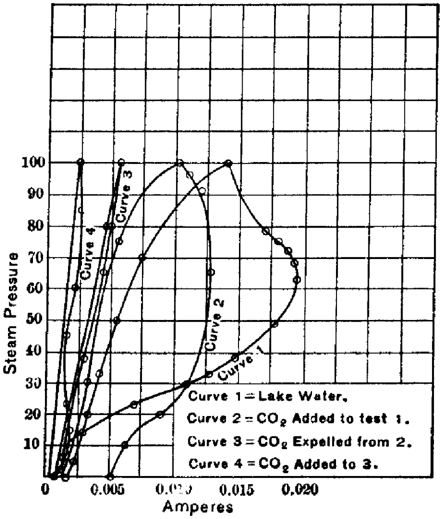

FIG. 9.
Corrosion Curves in Steam Boiler.

In each of the runs the apparatus was first completely filled with water and then 2½ pints of solution were withdrawn in order that the same amount of liquid and air space be present each time. As an illustration of some of the data obtained by this device, reference may be made to Curves 1, 2, 3 and 4, Figure 9, showing graphically the data recorded in Tables IV., V., VI. and VII. These results are given, not for the purpose of describing completely this investigation referred to, but to call

TABLE IV.

Time.	Amperes.	Volts.	Lbs. Pressure.
3.25	—0.0012	—0.0003	0*
3.28	—0.0012	—0.0003	0†
3.30	—0.0014	—0.0003	0
3.35	—0.0012	—0.0002	0
3.40	—0.0020	—0.0004	0
3.45	—0.0070	—0.0014	14
3.50	—0.0128	—0.0025	33
3.55	—0.0148	—0.0036	49
4.00	—0.0192	—0.0039	63
4.01	—0.0192	—0.0039	68
4.02	—0.0189	—0.0038	72
4.04	—0.0180	—0.0036	75
4.05	—0.0170	—0.0034	78
4.10	—0.0140	—0.0028	100‡
4.20	—0.0076	—0.0016	70
4.30	—0.0055	—0.0012	50§
4.35	—0.0041	—0.0008	33
4.40	—0.0032	—0.0007	20
5.05	—0.0018	—0.0004	5

* Heated tube anode.
† Began test.
‡ Gas off.
§ Opened steam cock.

TABLE V.

Time.	Amperes.	Volts.	Lbs Pressure.
9.15	—0.0012	—0.0003	0*
9.20	—0.0012	—0.0003	0†
9.22	—0.0010	—0.0002	0
9.25	—0.0032	—0.0007	0
9.30	—0.0050	—0.0010	0
9.35	—0.0063	—0.0011	10
9.40	—0.0090	—0.0014	20
9.45	—0.0110	—0.0016	30
9.50	—0.0122	—0.0017	50
10.00	—0.0120	—0.0017	91
10.01	—0.0120	—0.0015	96
10.02	—0.0102	—0.0013	100‡
10.05	—0.0055	—0.0010	75
10.10	—0.0036	—0.0014	32
10.18	—0.0012	—0.0002	0

* Heated tube anode.
† Began test.
‡ Turned gas out. Opened steam cock to let CO_2 and pressure off.

TABLE VI.

Time.	Amperes.	Volts.	Lbs. Pressure.
10.18	0.0012	0.0002	0*
10.21	—0.0015	—0.0003	5
10.25	—0.0025	—0.0004	15
10.30	—0.0030	—0.0006	38
10.35	—0.0042	—0.0008	65
10.37	—0.0049	—0.0009	80
10.40	—0.0056	—0.0010	100†
10.45	—0.0047	—0.0008	80
11.45	—0.0008	—0.0001	0‡

* Continued test of Table No. 5, and water still hot.
† Turned Gas off.
‡ Opened the steam cock and the current went to 0.0010 (-).

TABLE VII.

Time.	Amperes.	Volts.	Lbs. Pressure.
2.45	—0.0016	—0.0004	0*
2.57	—0.0020	—0.0005	0
3.00	—0.0020	—0.0005	0†
3.01	—0.0008	—0.0002	0
3.01½	—0.0005	—0.00005	0
3.15	—0.0010	—0.0002	2
3.21	—0.0015	—0.0003	13
3.25	—0.0020	—0.0003	25
3.30	—0.0023	—0.0004	85
3.32	—0.0023	—0.0004	100‡
3.33	—0.0018	—0.0003	98
3.34	—0.0020	—0.0004	98
3.35	—0.0022	—0.0004	98
3.37	—0.0025	—0.0004	98
3.40	—0.0025	—0.0004	98
3.46	—0.0020	—0.0003	80
5.00	—0.0004	—0.00005	0

* Heated tube anode.
† Began test.
‡ Opened steam cock to regulate the pressure.

attention to this form of apparatus and method of investigation as a means for studying corrosive action of different kinds of boiler feed water. It is possible that measurements of this sort may be useful in determining the efficacy of various materials which may be used to improve boiler feed water and for getting quantitative as well as qualitative information regarding boiler corrosion.

Curve 1 was obtained by first cleaning out the apparatus and using lake water which had first been boiled and then saturated with oxygen by bubbling this gas through the water while in place in the testing apparatus. As the pressure increased, due to the application of heat, the current gradually increased up to a maximum of 19.2 milliamperes, with a corresponding open-circuit voltage of .0039 volts. This occurred at a pressure of about 68 pounds. The current and voltage then slowly decreased until at 100 pounds pressure the heat was turned off. The current curve on cooling is shown by means of the dotted lines. The introduction of the oxygen appeared to have a decided effect in increasing the amount of current and consequently the amount of corrosion.

While the pressure was decreasing during the cooling the steam cock was opened so as to allow the oxygen to be expelled from the water and from the gas space above it, and when completely cold the same solution was saturated with carbon dioxide, likewise filling the gas space above the water. Another run similar to the former was then made, Curve 2 giving the results. If conclusions might be drawn from this data they would be to the effect that the presence of oxygen has a greater influence than has the presence of carbon dioxide in promoting the corrosive action. To compare the corrosive action in the solution as used in the last test to the same solution freed from carbon dioxide, this gas was expelled by opening the steam cock while the apparatus was under a certain amount of pressure. Another run was made on this same solution by again applying heat and raising the pressure to a hundred pounds. Results are given in Curve 3. Curve 4 shows the subsequent test on the same solution through which carbon dioxide had again been passed, and this in turn showed apparently that the carbon dioxide has practically no influence on the corrosion current.

The effects of the addition of various other dissolved substances were observed; thus treating lake water with one gram of soda ash per 5 gallons of water, a method commonly employed for treating boiler feed water, gave potentials in the *opposite* direction, the heated tube being the cathode. This same result was found in a more pronounced way by increasing the percentage of soda ash. However, with a solution obtained from a locomotive boiler which had been treated with soda ash and in which the soda ash had been concentrated by repeated evaporation, the inner tube became the anode. The heated tube was likewise found to be the anode when using 1 gram of magnesium sulphate or magnesium chloride per gallon. Barium hydrate, caustic soda, dilute acids and other materials were used, but the results need not be given here in full.

It was always noted that no matter what electrolyte was used, the current gradually increased to a certain point and then decreased. It was also noted that in repeating tests without otherwise changing the solution, the successive results always gave lower values of current and pressures. In other words, a fresh solution always causes apparently a higher current and more corrosion than one which has been used. This would coincide with the general belief that it is the fresh feed water in boilers which has the greatest corrosive action. This fact, and the one that each curve shows the current to reach a maximum, after which it decreases—even if the heat be kept constant—requires an explanation. Among the suggested explanations is the influence of the formation of a high resistance coating on either the anode or the cathode, formed from the corrosion products, and a second factor might be the partial decomposition of the electrolyte or a decrease of such materials in the electrolyte which might promote corrosion. For example, the presence of oxygen acts as a depolarizer at the cathode and facilitates the flow of current as long as there is any oxygen present. It is natural to expect, therefore, that as the oxygen in the boiler water is eliminated, either by escaping with the steam or uniting chemically with other materials, the polarization will increase, and consequently the measured voltage and current will decrease.

That both these factors apply in part should undoubtedly be recognized. From the testing apparatus the tube was removed at frequent intervals and in all cases a coating of more or less adherent scum or incipient scale was observed. Upon removing this and again making the test an increased current was noted. An examination of the surface of the tube after various runs revealed the fact that the corrosion had not been uniform but was in the form of pits which could be readily distinguished by the naked eye.

W. H. Walker has given us his opinion that the presence of oxygen in a solution promotes corrosion by acting as a depolarizer and in this way allows a more ready passage of galvanic or corroding currents. His views can undoubtedly find confirmation in the study of boiler corrosion, for it has been repeatedly noted that water which has been thoroughly saturated with air and consequently with oxygen, is especially corrosive when used as feed water. In fact, some of the most injurious cases of corrosion can be found where distilled water is used—distilled water having been allowed to become saturated with oxygen from the air.

The question naturally arises, "Do the currents, as measured in the tests referred to, reach a sufficiently large value to indicate a serious amount of corrosion?" Various of the laboratory tests have shown current of .01 ampere. In 24 hours this is equivalent to a corrosion of ¼ gram of metal; and since this corrosion is not evenly distributed but is confined to a few localities, it is obvious that these laboratory experiments will give basis for the belief that pitting of locomotive boiler tubes is galvanic action, and that the galvanic action is sufficiently rapid to cause perforation of the tube in a few months, or weeks, or even days.

When we view the rapid deterioration of modern iron structures and at the same time call to mind that famous iron shaft at Delhi which has endured with practically no deterioration for a time dating back toward the beginning of the Christian era, we are perhaps led to wonder whether our efforts toward increasing the life of iron is a step toward the restoration of a lost art. But whether or not a non-corrodible iron has ever been produced, there is much reassurance that improvement will result from systematic and scientific study of corrosion phenomena.

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DISCUSSION.

MR. E. G. ACHESON: I would make a few remarks in regard to this paper. I think I can give some information bearing on the subject treated. I have found the presence of graphite in water would prevent the water from causing the steel to rust, but on removing the steel from that particular water and putting it into another quantity of clear water, it would rust. I had hoped to be able to cure the steel and prevent corrosion, but I found that continued soaking in the water would not affect it. Water containing defloculated graphite was proven to be an efficient compound for some purposes, as in screw cutting, where one could use the water and get the high specific heat of the water, in conjunction with the non-rusting quality of the graphite.

Recently I received a letter from a gentleman who was placing on the market a lapping machine. The machine, as described to me, was particularly designed for lapping shafting. He said very definitely in the letter that, after grinding a piece of shafting, the pores were all opened up, but that after lapping with deflocculated graphite for a period of five minutes there was a great difference between it and a piece of shafting that had not been treated in this manner. One would corrode in moist atmosphere and the other would not corrode. He did not tell me in what form he used the graphite, whether in oil or water, but I presume it was in water.

MR. R. H. GAINES: Is anything known of the composition of the shaft in India that seems to be perpetual?

PRESIDENT BURGESS: The composition is known, analyses having been published, but I do not remember what the results are.

MR. J. F. MCELROY: I want to add one word which may not be pertinent to this discussion, but at the same time may be of interest in connection with it.

I regard Prof. Burgess' paper as a most excellent one and as of great interest in showing how electrochemical effects are changed by the internal strains of the metals themselves. I have for some time been testing the conductive power of sheets of perforated iron with different styles of perforation. These sheets have been about 4″ wide and from 14 to 20 mils thick and carrying current of about 300 amperes. The results of these tests seem to indicate that there is a zone around the hole in the perforated metal in which the metal is highly strained by the act of perforation and that the electrical resistance of the metal in this zone had been increased. Whilst my tests on this have not yet been completed, sufficient work has been done to show that in closely perforated metal the increase of resistance of the metal is greater than can be explained by the cross section and length of the path through the conducting perforated metal. In sheet metal with widely distributed perforations, I have not noticed this effect; but in closely perforated metal the increase is apparently 30% higher than what can be accounted for by the cross section of metal and length of the conducting path through it.

DR. F. A. WOLFF: Could not the effect last described be accounted for by a change in the shape of the cross-section. The average cross-section would not determine the resistance, but the average resistance would be greater than the cross-section, and it might be modified greatly by having a large number of holes which would take up fifty per cent. of the whole area. There is probably an effect due to same, but that other factor must be considered.

MR. MCELROY: I would say that the metal between the holes when figured up, and the length of the path when considered, does not account for the increase of the resistance. That has been carefully gone over.

MR. F. A. LIDBURY: Does that increase of resistance disappear when the metal is annealed?

MR. MCELROY: I have not discovered that that could be reduced by annealing.

PROF. W. D. BANCROFT: The President has referred to the electromotive force as being the cause of corrosion. It is a cause, but it does not determine the whole behavior of the metal, provided you are dealing with anything more than infinitesimal corrosion. The other factor is whether a surface film has formed. You can compare a bar of zinc and a bar of iron. There is a greater potential difference between zinc and solution than between iron and solution. Zinc corrodes only to a slight extent, aluminum still less, and then the corrosion stops. Iron goes on rusting indefinitely under most circumstances. It is important to keep in mind that the only thing which the measurement of electromotive force gives you is the first initial tendency to corrosion, and does not show in the least that the metal will actually corrode, using corrosion in the ordinary sense of the word.

DR. CLAYTON H. SHARP: I would like to inquire whether anything is known as to the reason why deflocculated graphite acts as a protector of an iron surface, whether it is because it covers the iron with a coating of material which itself will not go into solution, which carries the current from the iron to the electrolyte as an intermediate metallic conductor between the iron and the electrolyte, or whether there is something else to account for its action.

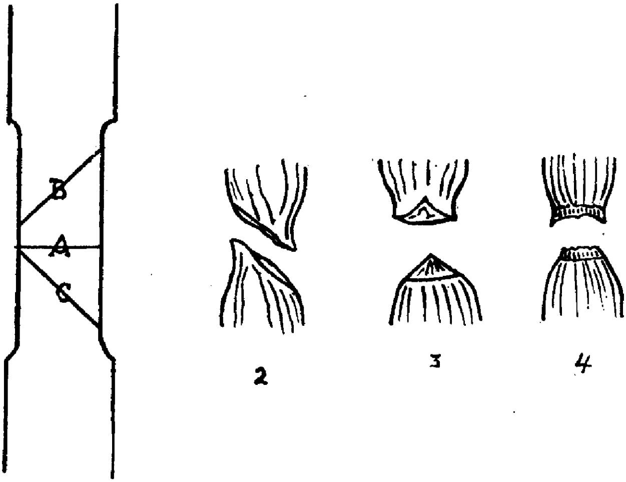


FIG. 1.

I should like to know if there is any possibility of the application of this method of protecting iron to protecting underground pipes, and so forth.

MR. GEORGE G. GROWER: There has been no reference made to thermo-electricity; it seems to me that part of the current observed might be of thermo-electric origin, iron ranking very high among metals in this respect.

On several of the slides shown the lines of corrosion are very marked, the speaker does not appear to be quite sure that these are lines of strain. I do not think there is much doubt about it. It might be interesting to refer to the lines of strain produced in breaking a sample of metal in a testing machine. In Fig. 1, representing the usual shape of the test-piece which is being pulled apart, it would at first appear as though the lines of strain would be at right angles to the axis, as at A, but in reality they are diagonal as at B or C. These lines can sometimes be seen forming on the sample under test, and they generally begin at the shoulders and work toward the center. When the sample breaks it will not break straight across but at an angle as in Fig. 2, or a double angle forming a cone as in Fig 3; frequently the cone is truncated forming what is called a cup as in Fig. 4. Almost invariably samples will break in one of these forms, or a combination of them, showing that the lines of strain are in two directions crossing each other at an angle.

MR. CARL HERING: I have been greatly interested in this paper which I think is one of the most instructive papers which has been presented to this Society. Professor Burgess referred to a case in which the iron was corroded when it was a cathode. I would be very much interested if he would say something further about it, as it seems to me that this is very important; we usually assume that the iron is free from danger of corrosion when the current enters it. If this is not true we ought to know it.

PROF. H. S. CARHART: I suppose the extent to which the electrolytic corrosion of iron takes place is undoubtedly understood by all the members of this Society.

But this is a very noticeable fact—if you have examined water pipes that have been corroded electrolytically, you must have noticed a scale on the pipes which you can cut off readily with a knife, consisting almost entirely of graphite or oxide; you will find it in spots, or in holes, so you can take a knife and by twisting it run it through the pipe. The metallic iron has disappeared. I think corrosion in water pipes generally takes place that way. These facts support what Professor Burgess has said, that the action in part, at least, may be voltaic action. We can see that in cast iron the graphite would be left there, if the iron is taken out, of course, but it is difficult to see why the corrosion takes place in spots in this way, unless there is more graphite in certain places than in others. Of course, the iron is not homogeneous, and the corrosion set up at any point would naturally continue there until the greatest damage is done.

I recently examined a water pipe which had been down only a little over two years, and which showed a marked amount of scale on the outside. I must confess that this occurred at a point where the street railway has been accustomed, at a crossing, to put salt on the street for the purpose of removing ice; and the earth is probably saturated with salt water, and that increases the corrosion. It may not be known the extent to which vertical pipes or rods or columns in the earth are injured by electrolytic action. I know a case where an iron pipe is down in the ground to a very considerable depth, and in a period of a few years there has been so much corrosion that the pipe has been eaten through, so that holes developed in it, and the pipe could not be employed for the purpose for which it was put down.

Another point occurred to me, and that is that this appreciable electromotive force, which Professor Burgess describes as having been obtained between strained and unstrained iron, may be explained, I think. Perhaps Professor Burgess has not had his attention called to the thermo-electromotive force, which is a source of electromotive force in addition to the energy of the strained iron. Say we had two sources of electromotive force (Professor Cahart then drew the Helmholtz equation on the board).

The thing which has been talked about is this first term, which may be heat of reaction, heat of hydration, heat of solution, heat stored as potential energy, due to the twisting of the spring, etc.; or it may be a variety of other things, small quantities of energy stored in the material. The second term is thermo-electric, because it is proportioned to the absolute temperature; that is evidence enough. In this case it is electrolytic thermo-electromotive force, as in a concentration cell, which is different from ordinary thermo-electromotive force between metals. Unless the experiment has been tried, of course, I have no evidence as to the direction of it, whether positive or negative in the case of the stretched iron. I have no doubt there is an electrolytic thermo-electromotive force there. If it is positive, the two terms can be added together and we get an electromotive force higher than the one calculated from the potential energy alone.

Another point is, in this case of the steam boiler, the electromotive force rose with the temperature. It would enter here as due to pure chemical action, but it may be due in part to this electrolytic thermo-electromotive force. We should take that into account and see whether it is there.

It seems to me these experiments show we have voltaic action or electrolytic action taking place, which corrodes the iron.

PRESIDENT BURGESS: Professor T. W. Richards has written me a letter in which he makes a comment and suggests it be read as his discussion of this matter. He says: "As far as my experience goes, electrodes which are not in equilibrium do not give constant results. Referring to the use of the ferric chloride, which is criticised, I have tried several other cases lower down, for example, in the hope that the kind of metastable form might be obtained, but without success. I should be interested to hear by what device you can give iron satisfactory results in ferric chloride, for of course, there must be some condition or circumstance which determines the difference between our experience."

In regard to Mr. Hering's question as to how current flowing toward the cathode will produce corrosion, I will say it does not, but sometimes it does, depending on conditions, but it will take too much time to go into that. That will be a subject for a paper. I might say briefly, however, that if there is a film effect which Dr. Bancroft speaks of, a film effect which will stop the corrosion, then this film can be broken up, if you have current flowing toward that as a cathode. Taking the case of ——— that will not corrode, unless you make it in the form of a cathode, and it will corrode freely. That is present in marked degree in iron, especially when exposed to certain acids.

A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

ELECTRIC FURNACE CONVERSION OF IRON PYRITES INTO A MAGNETIC FORM.

BY O. L. KOWALKE.

One of the important problems in preparing mixed sulphide zinc ores for the smelting operation is the removal of iron pyrites. A method commonly employed for removing the iron pyrites is first to convert the non-magnetic sulphide to a magnetic form by roasting the ore in a furnace where the products of combustion come in direct contact with the ore. After cooling, the roasted product is treated by a magnetic separator. In this roasting process some of the ore frequently becomes heated to an excessive temperature, and in the presence of oxidizing gases, red oxide of iron is formed which is non-magnetic. The purpose of the investigation described in this paper was to determine the temperature and the various atmospheric conditions under which iron pyrites can be made magnetic; also the loss of sulphur necessary for the attainment of this condition.

The Furnace.—A granular carbon resistance furnace proved to be the most feasible arrangement for heating the materials to the desired temperature.

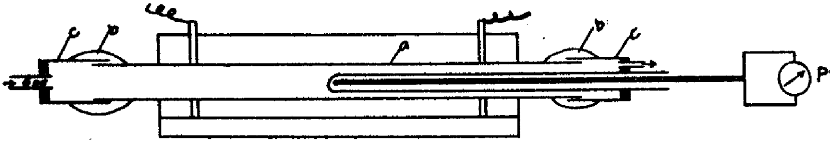
The furnace, whose inside dimensions were 3″ x 2½″ x 13″, was built of fire brick. A Royal Meissen porcelain tube (a) 26 inches long, one inch internal diameter and glazed on the inside served as the chamber in which the ore was treated. This tube, surrounded by the graphite resistor, lay lengthwise in the furnace. The furnace terminals were graphite slabs straddling the tube. To provide for suitable stoppers for the ends of the tube, glass sleeves (c) about 3 inches long, were slipped over the ends of the porcelain tube and cemented on by a mixture of magnesia and water glass (b). Besides providing for a stopper of sufficient size to admit the placing of inlet and outlet tubes;

these glass ends served also to prevent heat conduction from the porcelain to the stopper.

A thin layer of charred paper around the tube served to prevent any pitting action on the porcelain by the hot resistor particles even at temperatures above 1,000° C.

An alternating current at about 33 volts was sufficient to give the heat desired. The voltage, when applied to the furnace, brought the tube up to temperature quickly, and then by regulating the voltage, the temperature was maintained easily within 10° C. of the point desired.

Pyrometer.—A Le Chatelier platinum and platinum-rhodium couple standardized by the Reichsanstalt, and a Kaiser and Schmitt galvanometer served as an instrument for the measurement of the temperature. The pyrometer couple (P) Fig. 1, encased in a porcelain tube projected through the stopper and extended to the middle of the heating chamber and touched the boat containing the ore.



Gas Generator.—A Kipp generator about 3 feet high served as a means of supplying the gas necessary for the various tests.

Electromagnet.—The electromagnet used was 2½ inches external diameter and 6 inches long. With a magnetizing current of 6.2 amperes, flowing in the winding, a flux was obtained sufficient to hold up 4,830 grams of soft iron.

Procedure of Tests.—In all cases the material used was pure marcasite. This was crushed and sized, and that portion which passed a 20 mesh sieve and caught on a 40 mesh was used for the tests. The weight of marcasite for each test was determined on an analytical balance, then the charge was placed in a porcelain boat 2" x 3/16" deep x ¼" wide and put into the furnace. After sealing the furnace the gas in which the ore was to be tested was passed through for at least 20 minutes to insure complete expulsion of air before the current was applied. The surface was heated slowly to insure an even distribution of heat; this usually took an hour or more. When the desired temperature was attained it was kept at that value within about 10° C. by regulating current and voltage on the furnace. After the ore had been treated a sufficient length of time the current was cut off, but the gas allowed to pass through the tube until the temperature had fallen to at least 180° C. before the tube was opened. The ore was then removed and tested under the magnet for magnetic qualities. In all cases the magnetizing current was kept close to 6.2 amperes. The magnetic and non-magnetic portions were again carefully weighed.

In computing the percentage of magnetic portions the amount taken from the furnace served as a basis. The percentage loss is based on the amount taken for the test.

Tests in Air.—The procedure varied somewhat in this test from the general scheme—the heating tube was open to the air at one end and the ore was roasted in a closed cylinder to avoid too much exposure to oxidation. A cylinder of iron ⅜" diameter and 1" long, closed at both ends with the exception of a small hole to allow the escape of fumes, proved unsatisfactory. The sulphur vapors which were driven off attacked the iron and a fluxing action between the iron and ore took place so that it became impossible to account for losses. A porcelain cylinder of the above size whose ends were closed by stoppers each with holes of 1/32" in diameter gave the best results. Thus an atmosphere composed of sulphur vapors and air was attained.

The furnace was first brought up to temperature and then the charged cylinder put in the tube. After heating the cylinder and charge this was taken out into the air and left to cool. When cool the separation tests were made with the magnet. The magnetic portion varied in color from a black to blue-black, while the non-magnetic residue was yellow.

The results of tests 1 to 10 in Table I will be omitted, as the loss could not be determined, and hence only the results of tests in a porcelain cylinder will be given.

Tests Under Reduced Pressure.—In this series of tests an open porcelain boat, as before described, held the ore. After placing the ore in the furnace, all openings were securely closed and an aspirator bottle attached. The pressure was reduced about 55 m.m. of mercury, when the furnace was cold, and about 45 m.m. when hot, for at the high temperature the leaks were somewhat larger.

TABLE I.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
11	Marcasite	1 8155	45	669-674	1.0400	0.6405	1.6805	60.47	0.1350	7.43	Porcelain boat.
12	"	2.1030	60	679-679	1.2305	9.6785	1.9090	64.45	0.1940	9.22	
13	"	1.6380	120	677 680	1.2525	0.0745	1.3270	94.38	0.3110	18.48	Rolled boat.
14	"	1.2665	120	703 705	1.0445	0.0115	1.0560	98.91	0.2105	16.62	

Table II shows the results, and it is interesting to note that the ore becomes magnetic at 150° C. lower than under atmospheric pressure and in half the time.

The appearance of the roasted ore particles was a bluish black. Only the outside layer of the particles had changed color, for the inside was yellow and apparently unaffected. Run No. 37 was made under the best vacuum and here a loss of only 8.58 per cent. is shown.

TABLE II.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
36	Marcasite	1.2725	60	579-592	1.1775	0.0000	1.1755	100.00	0.0970	7.62	
37	"	1.2725	60	542-554	1.1633	0.0000	1.1633	100.00	0.1092	8.58	Best Vacuum.
38	"	1.2725	60	477-492	1.1705	0.0180	1.1885	98.48	0.0840	6.67	

Tests in Hydrogen.—The hydrogen for the tests was made in a Kipp generator from electrolytic iron and hydrochloric acid. From the generator the gas passed successively through wash bottles containing solutions of potassium hydrate, potassium permanganate, potassium pyrogallate, concentrated sulphuric acid, and fused calcium chloride, then through the furnace over the ore and finally through a bottle containing lead acetate acidified with acetic acid. Before the heating current was turned on, hydrogen passed through the above train for at least 20 minutes.

At a temperature of 494° C. in the furnace a black precipitate appeared in the lead acetate bottle. The precipitate increased in volume with an increase in temperature, so that at 507° C. the precipitate was formed in large amounts. In run No. 18 the test was allowed to proceed at a temperature between 503° and 522° C. until no more precipitate appeared in a fresh bottle of lead acetate. In this run there was a loss of only 2.93 per cent

TABLE III.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
15	Marcasite	1.2915	30	584-632	0.8550	0.1030	0.9580	89.40	0.3335	25.80	**Put in boat at 507° C.**
16	"	1.3425	160	508 657	0.9910	0.0205	1.0115	97.97	0.3510	32.92	**Couple parted.**
17	"	0.9905	928	494-1172	0.6365	0.0000	0.6365	100.00	0.3540	35.74	**Hydrogen gone at 1172° C.**
18	"	0.9710	100	503 522	0.9410	0.0015	0.9425	99.85	0.0285	2.93	

The resultant grains were blue-black in color, due to a thin magnetic layer, for the inside was still yellow. It takes heat, evidently, to crack the particles of ore open so that the hydrogen can get at the inner portions, for an increase in the temperature produces a further formation of lead sulphide in the bottle of lead acetate. To see how high a temperature would have to be attained beyond which no more hydrogen sulphide is given off, the product of Run No. 16 was used for No. 17 and heated to 1,172° C. At this point the supply of hydrogen gave out and the precipitate was still being formed. The product was a metallic appearing mass which was highly magnetic. In iron pyrites there is 46.6 per cent. iron, and the iron content in the amount taken for Run No. 16 is 0.6254 grams. The residue in

No. 17 weighed 0.6365 grams, hence the resultant product was within 1 per cent. of being metallic iron.

It is interesting to observe that hydrogen reduces marcasite to a magnetic sulphide at the low temperature of 494° C., and further, that hydrogen suphide seems to exist at the high temperature of 1,172° C. Meyers, in Annalen der Chemie, 159, p. 124, claims that hydrogen sulphide is decomposed at 400° C., while on the other hand, Watt's Chemical Dictionary claims that hydrogen sulphide is formed from hydrogen and sulphur vapors at 400° C.

Tests in Carbon Dioxide.—Carbon dioxide gas was generated in a Kipp generator from marble and hydrochloric acid, and before being used in the furnace was washed in the following train: water, silver sulphate solution, concentrated sulphuric acid and calcium chloride. The air in the entire train was displaced by carbon dioxide before heating was begun.

At about 507° C. free sulphur vapors appeared and at 567° C. an odor of sulphur dioxide was detected. In Run No. 39, three liters of gas coming through the furnace at 592° was passed successively through two bottles each containing 15 c.c. of 1/10 N. iodine solution. The excess of iodine was titrated with sodium thiosulphate and it appeared that 5.95 c.c. of sulphur dioxide had formed. It might seem that the following reaction took place: $x\,FeS_2 + 2\,CO_2 = Fe\,x\,Sy + 2\,COS + SO_2$, but since no test for COS could be obtained the explanation does not appear to be a sound one. No test was made for free oxygen in the incoming gas. It is probable that there was a little oxygen in the pores of the marble, and since no provision was made for the removal of oxygen, the small amount of sulphur dioxide probably was formed from the free sulphur and this oxygen.

In comparing the results of these tests as shown in Table IV, it is seen that the loss is variable at temperatures that do not differ so widely. It is seen that a magnetic product can be attained as in run No. 34 with a loss of only 7.76 per cent.

Tests in Carbon Monoxide.—Carbon monoxide was generated by passing carbon dioxide over charcoal heated to redness. Before feeding the gas into the furnace it was purified in a train consisting of two bottles of saturated solution potassium hydrate, a bottle of saturated solution of barium hydrate, and some calcium chloride.

The ore and furnace were prepared in the usual manner. The gas after having passed through the furnace was bubbled through a column of distilled water. According to Watt's Chemical Dictionary carbon monoxide and sulphur combine: $CO + S = COS$, and the product again decomposes in water: $COS + H_2O = CO_2 + H_2S$. These reactions were found to take place. At the end of a run after the waste products had bubbled through the bottle of water during the entire test, the bottle was stoppered and set aside over night. In the morning a distinct test for H_2S was obtained by holding a paper moistened with lead acetate at the exit of the bottle as the gas in it was displaced.

TABLE IV.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
19	Marcasite	1.1670	60	479-494	0.4415	0.7075	1.1490	47.28	0.0180	1.54	
20	"	1.5250	60	579-602	1.2495	0.1085	1.3580	92.01	0.1670	10.95	
21	"	1.4725	60	592-595	1.1612	0.1843	1.3455	86.30	0.1270	8.61	Tested for SO_2.
22	"	1.4445	60	650-655	1.1175	0.0000	1.1175	100.00	0.3270	22.65	SO_2 estimated.
23	"	. . .	. .	. .	. . .	. . .		. .	. . .		Couple parted.
24	"	1.6905	60	622-632	1.2235	0.0190	1.2425	98.43	0.4480	26.50	Iron pyro. tube.
25	"	1.7030	60	622-632	1.3272	0.0045	1.3317	99.67	0.3713	21.75	" " "
26	"	1.3505	60	614-624	1.0960	0.0000	1.0960	100.00	0.2545	18.85	Porc. " "
27	"	1.5495	60	514-524	0.8000	0.6905	1.4905	53.67	0.0490	3.19	
28	"	1.2890	60	579-602	1.1865	0.0065	1.1950	99.28	0.0960	7.44	
29	"	1.3065	60	542-550	0.9595	0.2825	1.2420	77.25	0.0645	4.93	
30	"	1.2678	60	587-607	1.1190	0.0025	1.1215	99.78	0.1463	11.54	
31	"	1.3889	90	582-602	1.2155	0.0000	1.2155	100.00	0.1734	12.48	Slow stream CO_2.
32	"	1.2405	90	591-594	1.0328	0.0000	1.0328	100.00	0.2077	16.74	CO_2 shut off at 400° C.
33	"	1.3362	25	562-567	0.2660	1.0510	1.3170	20.19	0.0912	1.43	
34	"	1.4455	90	592-592	1.3325	0.0007	1.3332	99.94	0.1123	7.76	Rapid stream CO_2
35	"	1.5595	30	567-567	0.3380	1.1915	1.5295	22.12	0.0300	1.92	" " "
39	"	1.2725	60	590-609	1.0428	0.1025	1.1453	91.00	0.1272	10.00	Took sample Gas.
40	"	1.2725	30	704-712	0.9640	0.0000	0.9640	100.00	0.3085	24.24	

Table V shows the marcasite can be made magnetic in an atmosphere of carbon monoxide at a temperature about 80° C. lower than in carbon dioxide. The loss in Run 43 is only 11.70 per cent. The product from Runs 41 and 42 was black, soft and homogeneous. The large loss in Run 42 in the short period of time seems to indicate that FeS_2 can also be reduced to metallic iron by carbon monoxide.

TABLE V.

No. of Test.	Kind of Material	Grams Taken.	Time in Minutes.	Range of Temperature in Degrees C.	Grams Magnetic.	Grams Non-magnetic.	Grams Total Taken from Furnace.	Per cent. Magnetic.	Grams Lost.	Per cent. Loss.	Remarks.
41	Marcasite	1.2725	60	547-547	0 9552	0.0000	0 9552	100.00	0.3173	24.93	
42	"	1.2725	30	592-592	0.9468	0.0000	0.9468	100.00	0.3257	25.60	
43	"	1.2725	60	507-517	1.1172	0.0065	1.1237	99.41	0.1488	11.70	

Temperature at Which Sulphur is Given Off.—The tests on marcasite heated in air and sulphur vapors did not permit the determination of the temperature at which sulphur begins to distill. A special muffle and condenser of graphite was prepared. A cavity 4" x 4½" x 8" was machined out of a graphite block and a cover fitted. A cylindrical condenser 3½" x 8" communicated with the cavity by a one inch round passage way 2½ inches long. A hole in the side of the graphite block or muffle served as a receptacle for a pyrometer. The muffle was packed in a granular carbon resistor to be heated, and the condenser was outside the furnace walls. Pure marcasite was heated in the muffle and the temperature observed at which sulphur appeared in the passage from the muffle to condenser. The following is a log of this determination:

Time.	Temp.	Remarks.
9:08	22° C.	Started.
9:26	382 "	Faint crackling in muffle.
9:35	512 "	Odor of SO_2 appeared.
9:40	582 "	Sulphur vapors visible at opening into muffle.
9:43	612 "	" " coming freely. S. flame maintained
9:48	662 "	" " " "
10:10	697 "	" " stream getting smaller.
10:20	682 "	" " " almost ceased.
10:25	702 "	" " " coming rapidly again.
10:30	732 "	" " " still " "
10:45	732 "	" " " " slowly.
10:53	752 "	" " " " more rapidly.
11:00	762 "	" " " just visible.
11:18	822 "	" " " increased, but soon stopped
11:27	826 "	" " white.
11:45	832 "	" burning in small flame in condenser.
12:18	872 "	No vapors of sulphur and no flame—stopped.

Run No. 50.—Put 700 grams of marcasite crushed to about a 6-inch mesh in the muffle and heated.

The residue was soft, blue-black in color, wholly magnetic and not sintered. The weight of the product was 546 grams, thus showing a loss of 154 grams, or 22 per cent. This loss agrees very well with Run No. 40, where the loss is 24.2 per cent. at a slightly lower temperature.

CONCLUSIONS.

The following conclusions may be drawn from these tests:

1. That it is not necessary to roast pyrite or marcasite to a homogeneous mass in order to obtain a magnetic product. A loss of sulphur of from 3 to 12 per cent. is sufficient to produce a coating, such that its magnetic properties will cause the whole particle to be picked up.

2. Roasting in a reducing atmosphere and under a slightly reduced pressure requires a lower temperature than in a neutral atmosphere, and causes a smaller loss of sulphur to form a magnetic product.

3. That, in a neutral atmosphere, sulphur begins to distil from FeS_2 at about 510° C. and continues to come off up to about 680° C. The roasting could be stopped slightly above 600° C., as shown by tests 31 and 34, providing the atmosphere is neutral. If the temperature is increased beyond 680° C., the sulphur is driven off until FeS results.

4. Marcasite can be reduced to a metallic iron in an atmosphere of hydrogen.

In conclusion the author wishes to express his appreciation to Prof. C. F. Burgess and Prof. O. W. Brown for the many helpful suggestions and the criticisms they made during the progress of the work.

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A paper read at the Thirteenth General Meeting of the American Electrochemical Society, at Albany, N. Y., May 2, 1908; President C. F. Burgess in the Chair.

THE PREPARATION OF CALCIUM ALLOYS FOR ALUMINOTHERMIC WORK.

By O. P. Watts and J. M. Breckenridge.

The use of thermit for the welding of pipes and rails, and for the repairing of broken machinery, has become so general throughout the world, that these applications of the aluminothermic process to engineering need no description. The uses of aluminothermy in chemistry and in metallurgy are, however, not so generally known, and a brief account of the process as applied in these sciences, and of some of the improvements made in it up to the present, may, perhaps, be necessary as an introduction to the experiments which form the subject of this paper.

When a mixture of an oxide with granulated aluminum in chemically equivalent proportions is strongly heated at one spot, a vigorous reaction often occurs, at the end of which the oxygen has combined with the aluminum, and the other metal has collected as a single mass in the bottom of the crucible. When neither the crucible nor the reacting materials contains carbon, the metal produced is, of necessity, carbon-free. Because of the almost universal tendency of aluminum to form alloys with other metals, it is necessary that this element be rather finely divided, and that the oxide to be reduced be slightly in excess of the amount required by theory for complete reaction. This reaction is usually started by placing in the top of the charge a small amount of a mixture of pulverized aluminum or magnesium with some peroxide. The mixture is conveniently kindled by thrusting a few inches of magnesium ribbon into it to serve as a fuse.

In this manner over 100 tons each of chromium and of manganese are produced annually, as well as considerable quantities of other metals and alloys.

It is necessary that the reaction shall furnish enough heat to melt both the metal and the alumina formed so that the scattered particles in which the metal is first formed may collect into a single mass. The temperature produced depends upon the difference between the heats of formation of the oxides to be reduced and of alumina, and to some degree upon the amount of charge used.

It is evident from these considerations that a successful reduction of those oxides having a heat of formation nearly as great as that of alumina cannot be obtained by the ordinary "Goldschmidt process." If the metal desired has an extremely high melting point, like tantalum, titanium, tungsten and some others, success is doubly difficult. For these reasons Dr. Goldschmidt had, up to 1902, failed to obtain in reguline form the elements barium, beryllium, boron, cerium, silicon, thorium, titanium, tungsten and uranium.

Several ingenious and more or less successful attempts have been made to overcome the difficulties just mentioned. In general these improvements have consisted in

(a) Supplying heat from an external source;
(b) Increasing the amount of heat liberated by the reaction;
(c) Rendering the slag more fusible.

Attempts have also been made to lessen the cost of the reducing agent by substituting cheaper materials for a part or all of the aluminum.

External heat has been applied in two ways: By preheating the whole charge to the ignition point, and by adding the heat of the electric arc to that of the reaction.

Although the oxides of boron, titanium and several other elements are not successfully reduced by aluminum, Dr. Goldschmidt, by substituting for a part of the above oxides, those of iron or manganese, has obtained alloys of these metals with boron, titanium and vanadium. Success is attained by the greatly increased heat of reaction and the lower melting point of the metallic product.

Holleman,[1] in order to obtain silicon, added sulphur and extra aluminum to the usual charge of that metal and silica, thus in-

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[1] Rec. Trav. chim. Pays-Bas, 23, 380 (1904).

creasing the heat obtained from the reaction. K. A. Kuhne[2] added potassium chlorate, and later various peroxides[3] and persulphates, and to secure a highly fluid slag, added fluor spar and lime to the charge. E. Maemecke[4] substituted a compound of silicon or ferro-silicon and magnesium for aluminum, and also claimed the use of aluminum, calcium, barium, strontium and sodium mixed with the reducing agents above mentioned. It is evident that some, at least, of these claims had never been tried by the patentee. In 1905, H. Goldschmidt[5] patented a mixture of calcium and silicon as a reducing agent for the purpose of securing a very fusible slag, and later[6] mixed calcium with the aluminum used in thermit. Attempts have been made to use calcium carbide and silicon in place of aluminum in such reductions, but with very limited success. F. M. Perkin[7] has recently experimented quite extensively with calcium and calcium hydride as reducing agents, and claims to have obtained a regulus of fused tungsten by the reaction of calcium with wolframite. If the mineral were of average composition the ingot must have contained about 76 per cent. tungsten alloyed with iron and manganese, and in consequence have possessed a melting point much below that of pure tungsten. Even so, its production is a distinct achievement.

The aluminothermic process has also been applied very successfully by A. Colani,[8] by Matignon and Trannoy[9] and others to the preparation of silicides, borides and other chemical compounds which had previously been considered as belonging exclusively to the domain of the electric furnace. At first the only compounds obtained were those of moderately low melting point, and of metals whose oxides are fairly easy to reduce, but more recently silicides of tantalum, titanium, tungsten and zirconium have been produced by the aluminothermic process.[10] This means that experimental research upon the most refractory metals and

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[2] British patent 20,884 of 1905.

[3] U. S. patent 878,210, Feb. 4, 1908.

[4] British patent 3,089 of 1906.

[5] French patent, 361,197.

[6] British patent 926 of 1906; U. S. patent 875,345, Dec. 31, 1907.

[7] Electrochem. & Met. Ind., Jan., 1907, p. 276; 1908, p. 31.

[8] Comptes rendus, **141**, 33-35 (1905).

[9] Comptes rendus, **141**, 190.

[10] O. Hönigschmid, Monatsch, f. Chem., **27**, 1069-81 (1906), and Comptes rendus, **143**, 224-6; Ed. Dufacqz, Comptes rendus, **144**, 848-50 (1907).

compounds can now be carried on by those who have not an electric furnace at their disposal.

The preparation of alloys of alumium, calcium, magnesium and silicon for aluminothermic work, was undertaken with the hope of obtaining reducing agents which would possess a somewhat higher heat of oxidation per unit of oxygen than aluminum, and whose mixed oxides would form a much more fusible slag than alumina. It was also thought that there would be a decided advantage, so far as fluidity of the slag is concerned, in having the particles of the different oxides produced in intimate contact. This will be the case, to a far greater degree when the metals are alloyed, than when the different oxides are formed from isolated particles of each metal, as in a mechanical mixture.

From previous experiments with aluminum-copper alloys, it was believed that several alloys could be produced from the above-mentioned elements, which would be brittle enough to be pulverized to any degree of fineness required. This is a decided advantage over aluminum, as the size of the reacting particles is an important factor in the velocity of reaction.

To what extent these anticipations were realized, and what unexpected difficulties were encountered, will be shown in the following brief account of the experiments.

Twenty-three different alloys of calcium with one, two or all three of the elements—aluminum, magnesium and silicon, have been prepared. Their composition is shown in the table opposite:

The alloys were made in an electric furnace of the granular-resistor type, by melting the constituents together in crucibles of Acheson graphite. The method of operation was as follows: The crucible was set in the furnace, sufficient calcium chloride added to form a layer over the metals when melted, and the elements put in in the following order: Aluminum, silicon, magnesium, calcium, each as soon as the one previously put in had melted. Since the temperature was always much below the melting point of silicon, this element was taken up only by solution. This was a rather slow process until the calcium or magnesium was added, when the silicon quickly dissolved. The alloy was stirred very thoroughly, and poured into a cast iron mould. There was little trouble from burning of the calcium until this exceeded seventy per cent. In two attempts to prepare a calcium-aluminum alloy of over eighty-five per·cent. calcium, the alloy took fire and was lost. The time required to melt and pour a charge of about a pound varies from five to twenty minutes, depending on whether the furnace was hot or cold when the charge was put in, and upon the amount of calcium added. Ten to twelve kilowatts was used for heating, although the current was often interrupted for a considerable portion of the time in order to keep the temperature to the lowest limit that would melt the metals. The alloys containing only calcium and magnesium were troublesome to prepare, as they were less dense than the protective layer of calcium chloride.

No. of Alloy.	Formula.	Aluminum.	Calcium.	Magnesium.	Silicon.
1	......	75.	25.	......	......
3	......	74.5	25.5	......	......
4	......	45.	55.	......	......
5	......	......	30.	70.	......
6	......	60.	......	40.	......
7	$CaMg_2$	......	45.5	54.5	......
8	......	50.	30.	20.	......
9	$AlCaSi$	28.4	42.	......	29.5
11	$AlCaMg$	29.7	43.9	26.3	......
12	$AlCaMg_2$	23.5	34.8	41.7	......
14	$Al_4CaMgSi_3$	41.4	15.8	9.4	33.8
15	$AlCa_2Mg_2$	17.4	51.6	31.	......
16	......	93.8	6.4	......	......
17	......	90.	10.	......	......
18	......	84.	10.	6.	......
19	......	67.1	12.9	......	......
20	......	80.	20.	......	......
21	...	80.	12.5	7.5	......
22	......	27.2	72.8	......	......
25	......	60.	......	40.	......
31	......	65.	......	......	35.
32	......	45.	......	20.	35.
33	......	60.	40.	......	......
34	40% Al+60 $CaSi_2$	40.	25.	......	35.
35	$Al_2Ca_3Mg_2$	24.3	54.1	21.6	......

In appearance these alloys vary greatly, from the homogeneous glass-like structure of No. 6 (60% Al, 4% Mg), to the coarsely crystalline structure of No. 9 (28.4% Al, 42% Ca, 29.5% Si), which appears to be a mass of flat crystals ⅛"x½". Their luster is metallic, and in most cases brilliant. They all decompose water at rates depending mainly on the amount of calcium or magnesium present. The addition of three drops of concentrated hydrochloric acid to 15 c.c. of water containing the alloys causes a considerable increase in the rate of evolution of hydrogen, and with the silicon alloys, yields a spontaneously inflammable gas, probably partly SiH_4. This causes sharp explosions in the test tubes.

The stability of the alloys in air is remarkable. After two weeks exposure in the laboratory, only one has disintegrated to an appreciable extent. As this alloy, No. 22, contained 73 per cent. of calcium, its disintegration was to be expected. The other alloys appeared as bright as when made. This is in striking contrast to the rapid disintegration of copper-calcium alloys.

All of the above alloys, which contained 25 per cent. or more of calcium or magnesium were readily pulverized in ordinary crushing and grinding machinery. Nos. 11 and 15 took fire in the grinder at first, but with a little care, gave no further trouble. A series of calcium-aluminum alloys was made to determine the least amount of calcium which would render the alloy brittle enough to pulverize readily. At 20 per cent. calcium the alloy was not sufficiently brittle for this purpose. The upper limit of the brittle alloys was not reached, as the highest in calcium of all the alloys prepared was the most easily broken. This was not tried in grinding machinery as the quantity made was small.

The percentage composition given is that calculated from the amounts of the constituents originally weighed out, and is subject to errors of 2 to 3 per cent., as the balance used was for rough weighing only, and there was a variable amount of calcium chloride adhering to the sticks of calcium. Determinations of calcium in two alloys containing a high percentage of this metal showed the errors to be within the limits mentioned.

Experiments in the use of these alloys are now in progress, but are not sufficiently advanced to draw final conclusions in regard to them.

Attempts have been made to reduce the compounds MoO_3, MoS_2, WO_3, SiO_2, Fe_3O_4, Mn_3O_4, TiO_2 and mixtures of SiO_2 with MnO_2, of TiO_2 with MnO_2 and of TiO_2 with Fe_3O_4. The alloys so far tried are Nos. 8, 11, 14 and 15.

The first experiment was an attempt to reduce MoO_3 by alloy No. 8. The oxide was the usual fine powder of commerce and the alloy a mixture of all sizes that would pass a 20-mesh sieve. The reaction was very rapid, and was accompanied by the projection of melted material, flame and much smoke. At the end of the reaction the crucible was nearly empty, and contained no metal. Thinking that the sudden expansion of air contained between the particles of the charge might be responsible for much of the loss of material, the experiment was repeated in a vacuum cylinder constructed from a piece of 8-inch steam pipe. Less material was projected than before, but the loss was still great. Forty grams of well-fused molybdenum was obtained.

Several other experiments were tried in vacuo. SiO_2 was only partially reduced, yielding a brown product resembling silicon monoxide in appearance. A mixture of MnO_2 and SiO_2, reduced by alloy No. 11 ($AlCaMg$), gave an excellent ingot of silicon-manganese, well separated from the slag. The yield was only 22 per cent. of the theoretical, probably due to the large amount of material projected from the crucible. In order to reduce the velocity of reaction, pulverized fluor spar and lime were added to several charges, with a slight improvement in the yield of metal. After eight trials in the vacuum cylinder, experiments under atmospheric pressure were resumed.

Reduction of a mixture of MnO_2 and TiO_2 by No. 15 ($AlCa_2Mg_2$), in pieces ¼ to ⅛ of an inch in length, was violent, with much flame and smoke, and the projection of some slag. Only a few globules of metal were obtained. Other reactions were tried with quite similar results. The only alloy that gave quiet reactions was No. 14 ($Al_4CaMgSi_3$). This acted much like aluminum itself.

As a last resort the charges were fired inside a closed steel cylinder, designed to withstand a pressure of 10,000 pounds per square inch. With this apparatus, several difficult reductions were carried out. Mixtures of the alloys with molybdenite in theoretical proportions failed to react, but on adding a large excess of alloy and enough calcium peroxide to oxidize it, an ingot of well fused metal was secured.[11]

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[11] This addition of a mixture containing an alkaline-earth peroxide with the reducing agent to assist in difficult reductions, devised by one of the authors in 1905 (Bull. of Univ. of Wisconsin, No. 145, p. 313), has recently been patented by Kühne, as already cited.

The most difficult reduction carried out was that of rutile. By the use of calcium peroxide, a single button weighing 15 grams, and many groubles were obtained. The metal is hard, though not sufficiently so to scratch glass. It is not in the least malleable, and is broken by severe pounding with a hammer. In appearance it resembles freshly broken Goldschmidt manganese. A qualitative test shows the presence of aluminum, apparently in rather small amount. It is hoped that further experiments may lead to the elimination of this impurity. Until this is attained the reduction cannot be considered a success.

All attempts to obtain tungsten from WO_3 failed.

The cause of the violent nature of the reductions by aluminum-calcium-magnesium alloys, whether carried out in air or in vacuo, whether the materials were coarsely or finely pulverized, was, for some time, very puzzling. The following explanation is offered:

When all the products of reaction are non-volatile, and no gases are present, it would seem that mere rapidity of reaction should not throw half the material from the crucible. If the cause does not lie in the volatile nature of some product, nor in the speed of the reaction, it must be sought in the original charge, and it is here that the authors believe that the difficulty lies—in the low boiling points of calcium and magnesium. The boiling point of the latter is given at 1100°C,[12] and that of the former as about 1300°.[13]

Besides confining the charge in a gas-tight cylinder, another method of preventing this vaporization of calcium was tried. Since calcium silicide is a product of the electric furnace, it ought to be stable at a very high temperature. It should follow that if all the calcium put into a thermit charge is in the form of calcium silicide, none of the metal can be vaporized until the silicide is decomposed by oxidation. When a molecule is broken up by attraction from outside, that element in it which has the greater affinity for the destroying agent is not the one which will "get left" in the struggle for oxygen. It was therefore expected that the calcium would all be burned to lime without vaporizing.

Alloy No. 34 (40% Al, 60% $CaSi_2$), was prepared to test this

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[12] Landolt & Börnstein's Physikalisch-chemische Tabellen.

[13] The Alloying of Iron and Calcium, A. Hirsch and J. Aston, this volume.

theory. In two reactions with Fe_3O_4, in open crucibles, there was no projection of material, and the reduction was very successful. The presence of this amount of silicon in the reducing agent, either free or combined, would greatly reduce the temperature attained. It is possible that the effect observed was entirely due to a diminished heat of reaction rather than to the reason assigned; yet the fact that the temperature was high enough for iron to be perfectly fluid, leads us to consider these experiments as evidence in confirmation of our theory. Further experiments are in progress upon the prevention of this supposed vaporization of calcium and magnesium from such alloys.

Several alloys have been used in the ignition mixture instead of aluminum or magnesium, and have proved more reliable for that purpose than either of those metals. This is probably due to their possessing a lower kindling point.

The cost per pound of materials entering into the alloys was: Aluminum, $0.43; calcium, $1.50; magnesium, $1.25; silicon, $0.15. The cost of materials in three of the alloys was: $1.14 per pound for No. 11, $1.36 for No. 15 and $0.58 for No. 14. Silicon appears to be the only cheapening material at present available for addition to aluminum or its alloys, when they are to be used for aluminothermic processes.

SUMMARY.

The results so far obtained in these experiments may be summed up as follows:

Alloys of calcium with aluminum and magnesium can be easily prepared up to a calcium content of 70 per cent.

Alloys containing 25 per cent. or more of calcium or magnesium can be readily pulverized.

In the absence of any considerable amount of silicon, alloys containing much calcium or magnesium react very violently in the reduction of oxides, and the yield of metal is small.

So far as tested, the addition of silicon to alloys of aluminum and calcium in the proportions necessary for the formation of $CaSi_2$, renders the reactions quiet, and greatly increases the yield of metal.

Experiments along the lines indicated are being continued.

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DISCUSSION.

Prof. J. W. Richards: It is a great satisfaction to me to see the aluminothermic process a commercial success. It may be well to recall that the first to reduce metallic oxides by an aluminothermic operation were the Tissier Brothers, who in 1858 made experiments in reducing metallic oxides by aluminium. They made the very natural mistake, however, of heating the whole mass to the ignition temperature in a furnace, and when they did so the reaction was so violent it blew the crucibles and furnace all to pieces. Goldschmidt modified that reaction so that it proceeded quietly and quite a safe operation resulted.

I wish to add what I can to the proposition to call this class of processes by another name. We have alumino-thermic, we have silico-thermic and we have calcio-thermic. I think the whole operation should be called metallo-thermic, or generally a metallo-thermic reaction. It is a solecism to apply the word "alumino-thermic" to reactions of calcium and silicon. The idea is to apply the reaction to thermic processes, using a metal as the reducing and heat supplying reagent, and I think it would be an improvement in our nomenclature to call them generally metallo-thermic operations, and hope it will be done before it is too late.

Mr. Henry D. Hibbard: I might say a word in addition to this. Messrs. Greene and Wahl (Mr. Wahl is secretary of the Franklin Institute of Philadelphia) did some reduction of metals by aluminum, I think in the early 90's. I used to have a pocket piece of metallic manganese that was made that way. Manganese and silicon is what they were chiefly after. This piece of manganese was different from what I get now. It was a bright metallic metal, about the color of silver, I would say, but it broke with a conchoidal fracture, and not a granular fracture; it was so hard it would scratch glass. I do not think that it was ever made on a commercial basis, but it was very interesting at the time to some of us who were interested in metallic manganese, especially manganese which contained no carbon. I believed that they were the first to make manganese practically free from carbon. Two of the processes were patented at that time, and the patents have about expired, I think. I was surprised, from what Professor Richards said, to hear it had been done a good many years before that.

Mr. Watts: I found the process was not commercially successful, and, judging from the description of the manganese, I should think, judging from the description of their product, that it was probably an alloy of manganese containing aluminum, which Messrs. Greene and Wahl produced. I should judge that from its great brittleness and the whiter color than the manganese which we have to-day.

Replying to Mr. Betts' question, in regard to the possible use of these alloys mechanically, I do not see any particular use for them. They are too brittle. The object of this work was to get alloys that were brittle, and these are not what one would expect to find useful for mechanical purposes, although no doubt alloys can be made by changing the proportions very much which will be applicable to mechanical use.

Prof. J. W. Richards: Dr. Wahl used a considerable amount of cryolite as a flux, and that contains a great deal of silica. Undoubtedly there was silicon introduced into the alloy that way, which would give it a conchoidal brittle fracture. I ask Dr. Watts whether the use of this as a flashlight powder would possibly not be practicable.

Mr. Watts: I think that would be very practicable. I think it would react violently, and give an intense heat and light, and I think it would be quite possible to use it for that purpose.

Prof. A. W. Smith: If there are two names for this process, inasmuch as the substances are not metals, why not call it elemento-thermic, and that would cover the whole thing.

Mr. Richards: The word elemento-thermic is rather too clumsy for ordinary use, and, in fact, covers far too much to be properly used in this connection. I think "metallo-thermic" really covers the needs of the case, and would be a satisfactory improvement on the too limited term "alumino-thermic."

REPORT OF COMMITTEE ON CALORIMETRY.

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3. Principles of Gas Calorimetry.
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CHAPTER I. GAS CALORIMETRY.

1. PRACTICE IN AMERICA AND EUROPE:

Ten years ago gas calorimetry in the United States was practically unknown; that is, calorimetry as a general practice in a commercial business, and it has only been recently that a few of the larger gas undertakings have been making the calorific value of the gas a regular test at the works. Probably a half dozen of our larger companies have been making readings systematically or experimentally for some years, but it is only since the state and civic authorities have enacted measures governing the heating value of gas delivered, that the calorimeter has been adopted as an instrument to be used daily in our works, and a systematic record made of the heating value of the gas manufactured.

In Germany the gas calorimeter has been in more general use, as the authorities and companies there have appreciated the importance of the heating quality of the gas.

The English authorities and supplying companies have demanded spasmodically that the gas be of a certain heating value, but readings have not universally been made in England, although the heating value has been recorded for some time by the larger companies.

The candle power of gas supplied in both Germany and England has been generally lower than in the United States, owing to the fact that the greater percentage of the gas manufactured is coal gas. The tendency has been in England during the last four or five years to reduce gradually the illuminating value, as it is known that the heating value is not proportionately lowered; so, while reports of the heating value have not been generally demanded, many of the larger companies have been making and recording calorific readings.

In Germany in some instances the authorities have demanded continuous reports of the calorific value of the gas, and, therefore, readings are systematically made and recorded in many of their cities, occupying an importance equal to, if not exceeding, that of the illuminating value.

2. REASONS FOR INCREASING DEMAND FOR CALORIMETRY:

Reports from many of our companies show that from 80 per cent. to 90 per cent. of the total gas consumed has been used under such conditions, that the measure of its heating value closely approximates its usefulness for the purpose whether used in stoves, ranges or incandescent lighting. This fact has naturally demanded, to a more or less extent, that the heating value of the gas should be given, as well as the illuminating power. We appreciate that in some gases, particularly coal gas, the illuminating value may be reduced without a corresponding reduction in the calorific value, which fact has caused to be embodied in some of our state and civic regulations a demand for the reading of the calorific value.

In industries using producer gas and by-product gases, where the illuminating value of the gas is practically negligible, the sole determination of quality has been the calorific value. The extensive development and use of the gas engine to-day has incited the engine manufacturers to make guarantees upon heating value of the gas, although the constituent gases themselves modify somewhat the serviceability of the gas for engine purposes.

If these various industries are determined to measure the calorific value of the gases, it seems important that the gas industry of the country should undertake to determine and describe systematic methods for general use in determining the calorific value of gases.

If our state and civic authorities are likewise undertaking to measure the calorific value of urban gas by some method, this method should be universally constant, and should be approved by the American Gas Institute.

3. PRINCIPLES OF GAS CALORIMETRY:

Gas calorimetry may be defined as a process of determining the quantity of heat developed by the complete combustion of a unit volume of gas. The common and most successful method of accomplishing this is through the use of an instrument known as the "Calorimeter," its auxiliary meters, thermometers, regulators, scales and weighing tanks. An exact quantity of gas can be burned under prescribed conditions and the heat developed in the combustion absorbed by a known weight of water passing through the instrument. It is possible, knowing the weight of the water passed through the instrument and the rise in temperature, to calculate the entire quantity of heat absorbed by the water.

This type of instrument is so much the simplest in design and application that your Committee have adhered to it in all their experimental and test work on which this report is based. Other gas calorimeters, designed on different principles intended to measure a part or all the heat developed in the combustion, have been put forward in great variety, but none of them seem to be as easily adapted to our general commercial requirements as those of the water heater type.

4. ENGLISH UNITS:

The British Thermal Unit is the quantity of heat required to raise one pound of water at its maximum density one degree Fahrenheit, the maximum density being at a temperature of 39.1 degrees. The amount of heat absorbed by water in being raised one degree at normal operating temperatures, say from 60 degrees to 90 degrees F., is, however, practically the same as when it is at its maximum density, the error being, at 90 degrees F., only .016 per cent., and less at lower temperatures. Therefore, no correction is considered necessary in our operation. The discrepancy would account for a difference of only .096 of a B. T. U. in a 600 B. T. U. gas.

Based on the fact that all gas in this country is sold by the cubic foot, and that the British Thermal Unit has been in general use as expressing the unit of heat; your Committee believe that it is proper to recommend the use of the Fahrenheit thermometer, the cubic foot and the pound, the results being expressed by direct multiplication in British Thermal Units.

If all our members in future in ordering calorimeter outfits will specify cubic foot meters, Fahrenheit theremometers, scales graduated to one-hundredths of a pound, to weigh the heated water passing from the calorimeter, all the inconvenience of using a mixture of metric and English units, or a reduction of a portion of their data from metric to the English system, will be avoided.

5. CALORIFIC VALUE CALCULATED FROM ANALYSIS:

The calorific value of a gas is often expressed as being calculated from anaylsis. Such an expression may or may not closely approach the value determined by the calorimeter. The analysis of a simple gas containing but few hydrocarbons is easily made, and its heating value easily calculated, but the gas as supplied in our urban distribution is so complex in its character that the determination of its hydrocarbons is a matter of great difficulty, and as these hydrocarbons constitute the important or more compact heating elements, it necessarily makes it difficult to accurately calculate the true heating value.

In the hands of the best and most experienced gas analysts, however, we believe that gas analyses can be made to give comparative results, and the average composition of the illuminants approximately determined. Nevertheless, before the calculated heating value of a gas is accepted, the accuracy of the analysis should be investigated.

6. COMMERCIAL CALORIMETRY:

By employing extraordinary precautions in calibrating the thermometers, weighing the water, in the adjustment of meter, and in obtaining correspondence between the temperature of the water and that of the room, as well as in making corrections for atmospheric temperatures and pressure, it is possible to obtain an accuracy higher than that necessary for commercial purposes.

For ordinary commercial work the same amount of care need not be taken in the determination. The ordinary wet test meter, familiar to all through its use in photometric work, checked and manipulated in the usual way, is sufficiently accurate.

7. FACTORS UPON WHICH ACCURACY DEPENDS:

The accuracy of operating depends upon several factors. The instrument should be installed in a well ventilated, light room, free from draughts and vibration, and of normal temperature. The gas should be measured at the temperature of the atmosphere, and the exhaust products should leave the calorimeter as nearly as practicable at this same temperature. With the temperature of gas, inlet water, air and exhaust products the same, there will be no reasons for making corrections for the sensible heat absorbed or lost. The temperature of the water should be practically the temperature of the operating room, and should be uniform. With the temperature of the water the same as that of the room, the exhaust products may be made to approach closely to the temperature of the air and gas without difficulty.

In the measurement of water by volume, owing to the large surface exposed and to the irregularities commonly found in the bottom of graduates, it is impossible to read the quantity of water by the eye within a small limit of error. As weighing is not open to these disadvantages, the determination of the quantity by weight largely avoids such errors.

The accuracy of the instrument also depends upon the constancy of operation; that is, the rate of flow of gas should be constant, the heat transmitted should be uniform, and with unvarying temperature of inlet water, there should be no variation in the temperature of outlet water.

CHAPTER II. CALORIFIC VALUE AS RELATED TO HEAT UTILIZATION

By this we mean the heating value of the gas, as determined by the calorimeter, and the available heat in the gas that is applicable for various uses in the arts. Many misunderstandings have arisen from the use of the words "gross" and "net," as applied to heating values. The "gross" heating value is that value which is obtained by the calorimeter when the gas, air and exhaust products from the calorimeter are at the same temperature. This condition strikes a thermal balance for the calorimeter, and the heat absorbed by the water passing through the calorimeter is all the heat developed by the combustion of the gas. This result, under normal conditions, is not exact, as the entrained moisture in the air and gas, and the moisture found in the products of combustion, do not balance, but the errors in absorbed heat are slight.

For example, the gas having passed through a wet meter is apt to be saturated. The air may have a saturation of 70 per cent.; while the exhaust products leave the instrument saturated. This means that some of the water vapors formed by combustion complete the saturation of the products leaving the instrument. This error is small, and the Committee are of the opinion that for commercial practice, at least, it may be entirely disregarded, as these errors ordinarily in actual practice would be a small fraction of 1 per cent. Hence, the calorific value as determined by the calorimeter is the "gross" or true heating value developed by the combustion of the gas. The "net" heating value, so called, is the "gross" heating value, less the latent and sensible heat of the water vapors condensed in the calorimeter. Where there is a large percentage of free or combined hydrogen this condensation is greater, and in certain gases the difference between "gross" and "net" may be as high as 10 per cent. In other commercial gases it may be as low as from three to five per cent. But this latent heat is not completely lost unless the products of combustion leave the apparatus at such a temperature that the moisture formed during combustion will be carried off as vapor. Under ordinary conditions this might be 130 to 150 degrees, while under some conditions it would be much higher.

Now, if the latent heat and sensible heat of the condensed water from the products of combustion are deducted there is just as much reason for deducting the sensible heat of the uncondensed portion of the products of combustion, since it is necessarily lost at the same time; and if the temperature of the exhaust products leaving the appliance is very high, this sensible heat may be several times that deducted in obtaining the so-called "net" value. In other words, there would be a different true "net" value for each change in conditions of the utilization of the gas, and none of them determinable by direct test by a calorimeter or any other known instrument. Therefore, the Committee are of the opinion that the heating value of a gas should be expressed only in that which is determinable as the "gross" or total heating value, the value of the gas as given by the calorimeter.

This use of the total heating value of the gas has been objected to seriously by the manufacturers of some appliances, notably of gas engines, as they claim that it is impossible for them to utilize the latent heat of the products of combustion. Their engines exhaust at such high tempeartures that the latent heat is never available, and in making guarantees they are inserting clauses whereby the "gross" value, less the latent heat, is considered as the heating value of the gas. If such a condition is to be met, it is only fair, too, that some method should be adopted whereby the "gross" heating value alone is expressed and the available heat for the given purpose is figured in some other way.

Gas has become a competitive fuel in many of our industries. All other fuels are rated by their total heating value. Why not gas?

The argument for a correction is based on the claim that all of the heat developed cannot be utilized, but that varies widely with the appliance. With some appliances a great loss is experienced through sensible heat of waste products and latent heat of water vapors. With other appliances this loss is reduced to very small magnitude and water heaters, or similar types of appliances can be made, as in the calorimeter itself, to utilize it all. In what an absurd position we would find ourselves if, advocating the use of "net" values, we tried to figure the efficiency of such an appliance.

CHAPER III. CALORIMETERS.

1. CALORIMETERS—GENERAL:

The only calorimeters considered by your Committee were of the Junkers or water heater type, measuring the gas and determining the calorific power by transferring the heat developed to a known quantity of water, and determining the rise in temperature of this water.

This we think is the only practical type of commercial calorimeter on the market, and at this writing your Committee disapproves of the adoption for commercial practice of any instrument which determines the heating value by raising the temperature of metals, or that records the heating value by measuring the density of liquids, or by which the heating value is deduced from the quantity of air required for combustion.

We also disapprove of the use of calorimeters which do not measure the total heating value of the gas. There have been designed calorimeters that allow the products of combustion to leave at temperatures such that the water vapors formed in the products of combustion will not be condensed in the instrument. This method of operating a calorimeter allows for many chances of error, and it does not provide for measuring the sensible heat that is lost in these products of combustion, and also increases the error occasioned by the presence of moisture in the atmosphere.

2. JUNKERS:

The Junkers gas calorimeter, designed by Hugo Junkers, of Germany, is probably the best known available instrument. It has been extensively used in the gas works of Germany and England, and to-day is used in the United States by the gas industry, and by users of producer and blast furnace gas. Gas engine manufacturers have depended almost entirely on this instrument for observations to check the guarantees of their engine economies. It was probably the first and most accurate calorimeter to be put into general service, and deserves entirely the credit it has received.

An improvement may be made in this instrument by having the water inlet and outlet on the same level and adjacent, so that the thermometers may be more conveniently observed. The construction of the meter is such that it is impossible to adjust the water level. The entire equipment, to conform to American practice, may be made more convenient if arranged with English units of measurement.

The capacity of the Junkers calorimeter is such that it may be used for testing either low or high heating value gas.

3. BOYS:

The Boys Calorimeter, designed by C. V. Boys, of London, is an instrument which has been adopted by the London Referees for determining the heating value of London gas. This instrument is of limited capacity, and, while it may be made to give very accurate readings with some gases, under certain conditions, it is exceedingly inconvenient in operation. Its construction necessitates taking the calorimeter apart to light or extinguish the burner. The flame adopted is of the illuminating style, and under certain conditions, with rich gas, is apt to smoke and deposit carbon on the interior of the calorimeter.

4. SIMMANCE-ABADY:

The Simmance-Abady Calorimeter is an English instrument, and is little known in the United States. This instrument is mounted on a platform, which makes its use as a portable instrument inconvenient. There were several difficulties encountered in its manipulation that appeared like defects in the design of the instrument. The outlet water temperature was very difficult to control, and led us to believe that the average reading of the outlet thermometer did not record the average temperature of the outflowing water. This was partly caused, we believe, by the trapping of air around the outlet thermometer and partly by the low rate of water flow, due to the small gas capacity of the burner.

Great care must be taken in starting this instrument to prevent this forming of an air pocket, which is due to the siphoning off of some of the water from the top of the instrument by the curved overflow pipe. The operating directions of this instrument also indicated that fractional revolutions of the drum of the meter should be taken in making observations.

The instrument was not provided with a water outlet of constant head. The calorimeter was jacketed with wood, which was found by the Committee to be unsuitable and not as satisfactory for accurate work as a polished metal jacket.

5. SARGENT:

The Sargent was the only American Calorimeter examined by the Committee. The first instrument tested was found faulty in design and gave irregular readings. A second instrument was submitted by the makers, which gave better comparative readings with the other calorimeters.

This calorimeter embodies arrangements intended to assist in making rapid and accurate observations. The principal point of difference in the Sargent Calorimeter is in the adoption of the English units entirely, and of weighing the water instead of measuring it in glass graduates. The instrument is further provided with an automatic electric device that changes the water supply from one measuring vessel to another at fixed revolutions of the meter.

6. OTHER CALORIMETERS:

No other calorimeters than the above were examined by your Committee, but the various designs as illustrated in our engineering publications were studied carefully, and as they did not embody the simple principles of the water heater type of calorimeter, it was not thought desirable, owing to the limited time for our work, to make an investigation of these instruments.

CHAPTER IV. TESTS.

1. TESTS MADE BY COMMITTEE:

The tests made by your Committee consisted of readings at Philadelphia, further readings at the laboratories of the Milwaukee Gas Light Company, and finally of an extended series of readings in the laboratories of the University of Wisconsin, at which special equipment was provided for the purposes of this investigation.

The calorimeters were erected and operated according to the instructions of their makers, so far as practicable. Changes from the prescribed methods of operation were only made when it became evident that such changes would lead to better results with the given instrument.

They were then operated to determine the capacity of each calorimeter for the absorption of heat. They were further checked to determine the effect of varying quantities of water being raised to different temperatures. They were then checked to see what effect varying the quantity of air supplied to the burner of the calorimeter would have. Further tests were made to determine the actual efficiencies and the rate of combustion at which the maximum efficiency occurred.

2. THE IDENTITY OF THE INVESTIGATORS:

In the investigations of this subject made by your Committee, they were assisted to a great extent by the work and observations made by Messrs. C. O. Bond, Chief Photometrist, Philadelphia Gas Works, at Philadelphia, by A. C. Wilke, Chemist, Milwaukee Gas Light Company, at Milwaukee, and by O. L. Kowalke, Instructor in Department of Chemical Engineering, U. of W., R. C. Cornish, Asst. Engineer of the Milwaukee Gas Light Company, and D. A. Powell, Cadet Engineer with the Madison Gas and Electric Company. These latter men devoted an entire month at the University of Wisconsin to the calibration and checking of all instruments used and to the actual tests.

3. PURPOSE:

The purpose of the investigation was to secure information on which to base recommendations to the American Gas Institute as to calorimeters for general commercial practice; also, to determine the accuracy and efficiency of calorimeters in common use, and to formulate and prescribe rules and methods of operating.

4. CALORIMETERS TESTED:

1. Standard Junkers Calorimeter, with pressure regulator, belonging to Chemical Engineering Department of the University of Wisconsin.

2. Junkers Calorimeter, modified so that the inlet and outlet thermometers are at the same height. This instrument

has been in daily use for about one year and is the property of the Milwaukee Gas Light Company.

3. New Sargent Calorimeter, using wet pressure regulator from a Junkers outfit and not using the electrical dumping device.

4. Standard Boys Calorimeter with wet pressure regulator from a Junkers outfit.

5. Standard Simmance-Abady Calorimeter.

A few preliminary tests were made at the West Side Works of the Milwaukee Gas Light Company, but it was impossible to maintain uniform conditions for more than one calorimeter at a time, on account of small sampling holder and limited water supply. Accordingly, all apparatus was sent to the Chemical Engineering Building, at Madison, Wis., where it was possible to maintain a constant water and gas supply for a series of tests.

5. CALIBRATION OF INSTRUMENTS:

Before making any tests all thermometers and meters were carefully calibrated. Two standard thermometers were used, one, No. 4,180, belonging to the Chemistry Department of the University of Wisconsin, certified August 9, 1902, and No. 2,620, from the Physics Department of the University of Wisconsin, certified by U. S. Bureau of Standards January 14, 1908. No. 4,180 has a range from 0 to 100 degrees C., reading 1/10 of a degree, and No. 2,620 has same range, reading to 2/10 of a degree. These two thermometers were carefully compared through range from 10 to 50 degrees, using a micrometer telescope to read the latter, and an ordinary reading glass, the former. It was found that they did not agree, so the ice point was determined and No. 2,620 was found correct and No. 4,180 was .08 degree high. After making this correction, scale readings were found to agree. As No. 4,180 was more easily read it was used to calibrate the calorimeter thermometers, making the correction for 0 point.

Each calibration was made as follows: The standard and two thermometers to be calibrated were suspended side by side in a bucket of water, which was surrounded on the outside with excelsior to prevent radiation. The water was agitated by means of a stirrer operated by a motor. Bulbs of thermometers were immersed to the depth they would be used on calorimeters and correction was made for length of stem exposed. A piece of plate glass was set up in front of thermometers to prevent the observer's breath striking them.

In this way curves were obtained for six of Sargent Steam Meter Company thermometers and two Centigrade thermometers furnished with the M. G. L. Co. Junkers instrument. A copy of one of these correction curves is shown in appendix.

In order to facilitate our calculations, four meters reading to 1/10 of a cubic foot per revolution were selected. Three of these meters were made by the Sargent Steam Meter Company, and the fourth was an American Meter Company meter, No. 458.

These four meters were calibrated at the rate of flow at which they were later used, with a ¼ cubic foot bottle, making five complete revolutions of the meter by filling the bottle twice. The calibration of the bottle was carefully checked to deliver ¼ cubic foot of distilled water at 62 degrees Fahrenheit.

All meters were adjusted to within .05 of one per cent. After the correct water level was obtained a strip of paper was pasted around the gauge glass to show proper level. Gas was taken from a five-foot prover and a constant pressure of 14/10 on inlet of meter maintained. Water for meters and bottle had been previously saturated with gas.

6. TESTS AND COMMENTS:

Water for tests was obtained from a large tank, located above the level of the table on which the instruments were set up. A constant level was maintained in the tank by using a float valve, thereby maintaining a uniform head on the apparatus and supplying water of constant temperature.

Gas tested was run from the city gas mains into two holders, each having capacity of about 60 cubic feet. These holders were located in the basement of the Chemical Engineering Building, and were connected in parallel, so that they could be filled and emptied at the same time. The holders were counterweighted to give 25/10 inches of pressure, and this was reduced to 15/10 by means of a governor. No. 1 holder was built with an annular space for the water, thereby cutting down to a minimum the surface of water exposed to the gas. No. 2 holder was built with an open tank and care was taken to use water thoroughly saturated with gas in filling it. No. 1 holder was provided with a fan to agitate the gas. The gas made by the Madison Gas and Electric Company was entirely carburetted water gas.

All the apparatus was set up on a bench in a room which could be kept free from draughts.

Each calorimeter had its own water and gas connections.

In order to operate the calorimeters under more nearly uniform conditions, some changes were made from the arrangement of apparatus provided by the manufacturers.

All meters registered 1/10 of a cubic foot per revolution. Water was caught in copper tubs and weighed on scales sensitive to ½ gram in 5 kg.

Float pressure regulators of Junkers make were used on three instruments and a similar regulator on the Simmance-Abady. All copper tubs were carefully counterbalanced against a lead weight. This was done with the inside of bucket wet, so that no correction would be required during tests. Tubs were filled with water, emptied and then shaken in an inverted position for about five seconds.

In setting up the instruments, it was our aim to reduce the number of joints where leakage might occur, to a minimum. After apparatus was all connected up, gas pressure was turned on and burner shut off to test for leakage, and no observations made until meter showed no movement.

The humidity was determined by means of a wet and dry bulb thermometer, upon which a constant current of air was impinged by a small motor driven fan.

All tests were run in series, and tests of the same series number on different instruments were run at very nearly the same time. A new series was started with each new sample of gas, at the same time being indicated by a new letter.

All tests were recorded on special blanks which were printed for this investigation, and which is shown in the typical calculation.

The series of tests as made extended consecutively from A to N.

Series A to F, inclusive, were made with an idea of becoming more familiar with the operation of the several calorimeters, and to find out the effect of varying the gas, water and air supply.

Series G and H were made to determine the most efficient rate of combustion of gas in the several calorimeters, maintaining a constant water supply. With the gas used for these tests it was found that for the Boys Calorimeter a rate of combustion from 3½ to 4½ cu. ft. per hour was the most advantageous; for the Sargent about 5 feet; for the Simmance-Abady and Junkers calorimeters 5 to 7 feet.

Series I and P were run using these different rates of combustion, and comparative results were obtained. The accompanying diagrams show graphically these determinations. In these diagrams the times of making the test are plotted as abscissae and the heating value plotted as ordinates. Throughout the I series there was a gradual decrease in the heating value of the gas with time. This was possibly due to absorption of some of the illuminants, as the water used to fill the No. 2 holder was taken from one of the holders of the Madison Gas Company, and was saturated with coal gas; whereas, at this time the gas made by the Madison Company was water gas. These series of tests show the relative efficiency of the various calorimeters.

Series S gives results of tests on Simmance Abady calorimeter, when a burner of larger capacity was substituted, which allowed an increase in the flow of water to be made, thereby obtaining more uniform readings.

Comparison of results in series P, between the Junkers and the Simmance-Abady instruments, on gas, shows the Simmance-Abady about 10 per cent. above the Junkers.

Similar tests "T" and "U" were made on Simmance-Abady in conjunction with the Sargent, and the same high efficiency readings of the Simmance-Abady were obtained. We believe, however, that had we been able to increase the heat input from our electric heater to the same degree that was done in series "S" on gas by a change of burners, a small discrepancy in efficiency noted would have resulted.

Owing to the great fluctuations in the outlet temperature, we are not at all certain that we obtained an actual average of the temperature of the water leaving the instrument. However, based on the two series of tests, one with the electric coil heater and the other on gas, both showing better than 100 per cent. efficiency, we concluded that the construction, as shown in this particular Simmance-Abady instrument, which is about five years old, could not be considered satisfactory.

In series J a comparison was made between the U. W. Chem. Engineering Junkers and the Milwaukee Gas Light Company's modified Junkers. Both calorimeters were run at approximately the same rate of gas consumption, and the same rise in temperature of the outlet water and the same amount of water. A subsequent check on meters used for this test showed that the meter used on the Milwaukee Gas Light Company's Junkers was about .4 per cent. fast. Making this correction on the average reading of this series by the Milwaukee Gas Light Company's Junkers, it leaves a difference of but .4 per cent. between the readings of the two instruments.

7. EFFICIENCIES:

The purpose of tests K and L was to determine the efficiency of the absorption of heat in the calorimeter. To determine this efficiency, a known quantity of heat energy was supplied electrically for a known interval of time, and the quantity of heat absorbed was determined in the usual way.

The apparatus for supplying this heat energy consisted of a coil of nickel wire wound on a mica frame. The current from a 120 volt storage battery was passed through this coil and measured by standard electrical instruments. The electrical measuring instruments were of the Weston Laboratory standard type, and had recently been calibrated. The heating coil was made of two pieces of mica, 2 inches wide, 5 inches long and 3/32-inch thick, set at right angles to each other. This frame was mounted on a brass axis, such that it would fit into the ordinary holder for the Bunsen burner of a Junkers calorimeter. The accompanying photograph will show details of construction of this coil. The current through the circuit was regulated by means of a lamp bank placed in series in the circuit, and the amount of energy put into the coil was regulated to give a rise in temperature equal to that which had been used in the tests with the gas.

In making this test, three operators were employed, one to observe the readings of the voltmeter, the second to observe the readings of the ammeter and the third to operate the calorimeter.

The time for each test extended over three minutes. During this time readings of voltage and current were taken as rapidly as the observer could record them. Likewise, observations of temperature of inlet and outlet water were taken as rapidly as the data could be recorded. The water passed through the calorimeter during the period of test was carefully weighed to within one gram, and all results were expressed in small calories. Series of tests of this kind were made on the U. W. Chemical Engineering Junkers and the Simmance-Abady. The results of Series K show an average efficiency of over 99½ per cent Junkers calorimeter.

Series L was made similarly on the Simmance-Abady. The results of this series show that there is something wrong in this test. The efficiency of the instrument shows about 108 per cent. In looking over the temperatures of the outlet water, an explanation for this apparent discrepancy can be found. In this series of tests the observer recorded the observations of temperature as fast as it was possible to do so, and he also attempted to give the extreme variation of such temperature indications. At no time was the temperature as indicated by the thermometer constant for even a second, but the mercury thread kept moving up and down continually. It would seem that the water as it comes out of the instrument and passes over the dome of the combustion chamber, is unevenly heated and not thoroughly mixed to a uniform temperature before reaching the thermometer, and thus the thermometer records not a uniform temperature of water, but water which comes in unevenly heated currents.

Series M was a repetition of the tests of Series J. Before making this series of tests, the two meters were again carefully calibrated. Then the M. G. L. Company's Junkers was run against the U. W. Chemical Engineering Junkers. A series of five tests was made with this arrangement. Then another series of five tests was made, running the M. G. L. Company's Junkers against a second Junkers, belonging to the University of Wisconsin. These results show a very close agreement between the three instruments.

CHAPTER V. SPECIFICATIONS AND RECOMMENDATIONS.

Your Committee recommend the adoption of a calorimeter of the water heater type.

In determining the calorific value of the gas, we recommend the adoption of English units; the measuring of the gas in cubic feet; the correction of the volume of the gas to standard volume, as expressed when measured under a standard temperature of 60 degrees Fahrenheit, and standard barometric pressure of 30 inches of mercury.

We recommend taking all temperatures of air, gas and water with Fahrenheit thermometers, and expressing the result in Fahrenheit degrees.

We recommend weighing the water used with balances reading in pounds and hundredths of a pound.

We recommend expressing the result of all calorific determinations of gas in British Thermal Units, or B. T. U.'s, which is the natural product of a pound degree.

As not one of the calorimeter outfits supplied was entirely satisfactory, and as several improvements suggested themselves during the experiments, we consider the following specifications and recommendations necessary for the best results:

I. METERS:

For a meter, we recommend one registering 1/10 cubic foot per revolution.

The large dial should be graduated into 100 equal parts, with every 10 parts distinctly marked to facilitate reading. In addition to the large dial, there should be a smaller dial to register the number of revolutions of the large hand. This dial will register 10's, units and 10ths of a cubic foot.

The face of the meter should be enameled, and no glass used on the front, thereby reducing the error due to parallax. The face of the meter should be easily removable, in order to get at the shaft and the stuffing box on the shaft. This stuffing box should be of a size large enough to be easily packed.

The large hand of the meter should be well pointed and not extend to the outer end of graduations of the meter dial. Several of the meters tested had very wide pointers, and these pointers extended beyond the graduations, so that it was difficult to get accurate readings. The meter should have three leveling screws, two in front and one in the center at the back of the meter.

Two level tubes should be securely fastened to the top of the meter, placed at right angles with each other.

The meter should have an outside gauge glass showing the water level. This glass should not be less than 3/8 inch, nor more than 3/4 inch, inside diameter, as it is necessary to have the glass large enough to be readily cleaned, and small enough that the meniscus formed by the water can be accurately read. The opening through gauge bodies to the meter should be unobstructed, and of a size to correspond with the size of the gauge glass. A pointer to show the correct water level, reading to the bottom of the meniscus, should be put on all water level gauge glasses.

For convenience, a standard 3-light meter union should be used on all meters, and hose nipples for 3/8-inch hose should be furnished with the unions.

The meter should be provided with an opening for the addition of water when needed. This can be done by using a pet cock with a small funnel mounted on top, connected to the top gauge glass body.

An opening must be left for a thermometer in or near the gas outlet. This thermometer should be a chemical thermometer in a metal case, reading to one degree Fahrenheit, with a range of from 50 to 100 degrees, and accurate to within ½ degree. Some of the thermometers furnished with the apparatus read to two degrees, and there were variations on three thermometers furnished by one company of 1½ degrees. Another criticism of the same thermometers was that the glass tubing was not round, making the thermometers difficult to read.

An opening with a plug connection should be left on the bottom of the meter to drain it when the meter has to be transferred from one place to another.

In general, we would say that the number of joints liable to cause leakage should be reduced to a minimum. We found that several of the meters which had faced joints were very difficult to keep tight, even by using carefully made gaskets.

2. REGULATOR:

The pressure of the gas when burning in the calorimeter should be absolutely uniform, to obtain the best results, and any small regulator that will maintain this uniform pressure will be satisfactory. We recommend the use of a small wet governor, as supplied with Junkers Calorimeter, as giving excellent regulation, and which will operate without chattering. Such a regulator should be constructed so as to be readily weighted for altering the pressure.

3. CALORIMETER:

The calorimeter should be designed to give a constant head of water on the apparatus. This head can be maintained by having a weir overflow on the inlet at some distance above the top of the calorimeter, and a weir overflow on the outlet. The rate of flow through the apparatus should be regulated by means of a cock on the inlet water. It was necessary, in case of the Boys Calorimeter, to use a screw cock on the rubber tubing to get variations in the rate of flow. This was not used on this calorimeter, except during very low consumption of gas, as at higher consumption the coil was not large enough to give an amount of water capable of reducing the temperature to the desired range.

A calorimeter should be so built that the water will circulate freely and that there will be equal distribution of water throughout the apparatus. Baffle plates should be so arranged that the water will be thoroughly mixed before coming in contact with the bulb of the outlet thermometer, thereby giving correct readings. The design should be such that air pockets will not form in the water space. It was found in several tests that considerable variations in temperature arose from neglect in this particular.

The calorimeter should be made of bright polished metal, air jacketed in all its parts. We found a reduction in heating value by one of the calorimeters on spilling water over the wooden jacket, due to evaporation of water from the jacket, and since the accidental wetting of the jacket is always liable to occur, we consider that the use of an absorbent jacket a serious defect in design.

There should be a damper in the exhaust gas flue which can be easily adjusted, and which will not be moved by a slight jar.

The calorimeter should be mounted on four legs, with a spread great enough to give a firm base, at a height sufficient to make it easy to put the burner in place.

Thermometers should both be on the same level to facilitate readings. This is a desirable feature of the Sargent, and there is no reason why Junker instruments made in the future should not conform to it. The openings for thermometer corks should be large enough to take a No. 4 rubber stopper.

4. BURNERS:

The Boys Calorimeter was provided with a burner with an illuminating flame, and while this was found satisfactory for small gas consumption, it was replaced with a Bunsen flame, which was equally satisfactory under all of the same conditions, and in addition had a wider range for the rate of flow. The burners provided with the other instruments tested were solely of the Bunsen type, which is the type that we recomment for general use.

The burner should be a long tube Bunsen, having a spreader on top, an adjustable air mixer which can be easily reached when burner is in position in the calorimeter. The burner should be provided with a stop-cock to change the regulation. The burner should be attached to the calorimeter in such a way that its position cannot be accidentally shifted, and also so that the condition of the flame may be observed by the operator, either directly or by the means of a reflecting mirror.

5. THERMOMETERS:

Accurate thermometers are the most important accessories to good calorimetry.

In supplying many of the thermometers with calorimeters up to the present time, cost has apparently had a large influence, and some very poor thermometers have been supplied with commercial calorimeters.

Your Committee believe that the thermometers (particularly those for reading water temperatures) are one of the most important adjuncts, and should be of such a quality as to read accurately within 1/10 of a degree Fahrenheit.

The thermometers should be graduated from 60 to 110 degrees Fahrenheit, each degree to be divided into 10ths with short, distinct graduations. The thermometer should be accurately made, so that in ordinary commercial work corrections may be neglected. With each thermometer should be provided a calibration curve, which would enable very accurate results to be obtained whenever it was deemed necessary to make these corrections. Thermometer cases should not be more than ½ inch in diameter and be made of thin glass. This will prevent reflection and parallax in reading. The bore of the thermometer tubing must be carefully made, as it was found that of six (6) thermometers of one make, compared with a standard thermometer, there was a considerable minus (—) correction in the lower portion of the scale, and a very abrupt plus (+) correction in the upper part of the scale.

Telescopic sights for reading of thermometers should be provided, as much more accurate readings can be obtained in this way.

Where disputes arise as to results, we recommend the certification of thermometers by the United States Bureau of Standards at Washington. They are prepared to do this work promptly and at a reasonable expense.

6. BAROMETER:

Corrections for variation in barometer readings should be made in measuring the volume of the gas. These readings should either be made by means of a mercury column barometer or by a recently calibrated aneroid barometer. Where it is possible, barometer readings should be checked occasionally with readings of the Government Weather Bureau of the city in which the readings are made. It is possible to get fairly accurate readings where no barometer is available by obtaining from the Weather Bureau the barometer readings for the day, and correcting for variations in elevation.

7. WATER SUPPLY AND MEASUREMENT:

The control of the temperature of the water supply is a very important adjunct to accurate calorimetry, and this temperature should be approximately the temperature of the room or atmosphere in which the observations are being made. Water obtained from an ordinary house piping system is apt to be variable in pressure, and also very variable in temperature, due to the uneven consumption in other parts of the building, and possible exposure of the water main to the extreme temperatures of the ground or atmosphere. This control of temperature and pressure may be readily obtained by providing a permanent water supply tank in the upper part of the room or building that will contain enough water to enable the readings for the day to be made. A flat tank of large horizontal area is preferable to a deep vertical tank. The exposed surface allows the water to come to the temperature of the room more readily, while the shallow depth affects the head less as the water is being used.

Water may be collected and weighed in thin sheet metal containers, holding about 8 pounds of water. This size container will hold all the water required in burning .2 of a cubic foot of ordinary illuminating gas with a range of about 15 degrees in temperature between the inlet and outlet water. The scales, or balance, employed should have a capacity of about ten pounds, should read to 1/100 of a pound, and should be calibrated and certified to as being correct by proper authorities.

8. GAS PIPING AND TUBING:

The piping for a calorimeter should consist of as much metallic piping as possible, and the lengths of rubber tubing used in conducting the gas should be as short as possible, and when used should be saturated with the benzine vapors and other illuminants. The absorption of the illuminants by the tubing, however, has less effect upon the calorific readings than it has upon the photometric readings.

9. HUMIDITY:

It may be desirable to have the state of the humidity of the atmosphere during the test, in which case percentage readings may be made from wet and dry bulb thermometers. For accurate work these wet and dry bulb thermometers should be arranged so that the average humidity of the room may be obtained. This may be done by having a whirling wet thermometer, or having a constant current of air impinging upon the wet bulb from an electric fan; or, a more perfect instrument in the form of an Assman Psychrometer may be obtained. The percentage of saturation of the gas itself may be obtained by readings made with a gas hygrometer. These humidity readings of the gas and atmosphere are not necessary in commercial calorimetery, but may be found useful if it is desired to make corrections for heat absorbed or evolved in saturating the products of combustion.

10. REMARKS AND CRITICISMS CONCERNING SPECIFIC INSTRUMENTS BASED ON EXPERIENCE DURING TESTS:

THE JUNKERS: The design of this instrument is such that it is jacketed by a polished metal surface, containing an air chamber. This has proved by experience to practically prevent radiation. The water circulates but once through the instrument from bottom to top, and opposite in direction, as it should be, to the products of combustion.

The water content is comparatively small, about one and one-half pounds, but large enough for the efficient absorption of all heat through a wide range of gas consumption, and ample to enable gas of greatly varying heating values to be readily measured.

The small fixed weir for maintaining a constant head of water on the calorimeter, and the controlling cock with a quadrant arm for indicating its position, are admirable, and necessary for the best work. The overflow is so arranged that syphoning is impossible. When not in use the instrument is easily drained of its water content.

The location of the thermometers gives accurate readings of the average temperature of both the inlet and outlet water.

One objection to Junkers Calorimeter is that the thermometers are not on the same level, which makes rapid readings awkward and inconvenient.

The instrument as now mounted on three legs is somewhat unstable, and it is rather difficult to insert the lighted burner when the instrument is set up.

The gas meter supplied with the Junkers Calorimeter was open to serious objection. It has an inside fixed overflow, which cannot be adjusted when out of proof, and a meter which cannot be adjusted is certainly unfit for this service.

The interior of the calorimeter allowed for draining the condensate as well as any instrument tested.

The supply of air through the calorimeter could be readily regulated by the damper in the waste products flue, a convenient and necessary arrangement for efficient work.

The workmanship on the entire Junkers Calorimeter was good and commendable.

THE SIMMANCE-ABADY: The Simmance-Abady is mounted on a large, cumbersome stand, and is not convenient as a portable instrument. It is jacketed with wood, which is not considered as serviceable as polished metal. The water content is large, being twelve and one-half pounds, which necessarily takes a longer time to strike a thermal balance, and renders short readings more liable to error.

This is in direct contradiction to the claims for the instrument, which were that the calorimeter could be used for quick readings, the dial of the meter being divided so that fractional revolutions of the drum should be taken. This is another objection, and is in opposition to careful and accurate work.

The circulation of water through the Simmance-Abady Calorimeter does not seem to be such that the heat is absorbed from the waste products of the gas with any uniformity. The water courses up and down through the instrument several times, while the gases go through once. This causes an uneven heating, which is augmented by the construction of the last water pocket above the combustion chamber. This arrangement made the outlet water temperature very difficult to control, and led us to believe the average reading of the outlet thermometer did not record the average temperature of the outflowing water.

The water inlet pressure was designed to be controlled by a water gauge, instead of the usual weir overflow. The outlet was controlled by a three-way cock. The waste from this cock caused a syphoning effect in the calorimeter, and altered the head of water through the instrument.

The shifting device for operating the water in the outlet was not adapted to our use, and it was necessary to remove it and support the overflow from a stand to get a more constant head.

THE BOYS: The Boys Calorimeter was found to be unsatisfactory for American practice, it being too inconvenient to operate and of too limited capacity.

The water content was only about .7 of a pound, which limited the rate of flow of gas capable of being burned, and eliminated the use of this calorimeter for our richer gases.

This calorimeter is quite different in construction from the other types tested. It is in two parts, the lower base and burner being mounted together, while the water coil and envelop are fastened together and easily removable by simply lifting from the base.

The water courses through the calorimeter in double coiled pipe, ending in a baffling compartment over the combustion chamber.

The use of an illuminating flame in the Boys was open to some objections. It would smoke if turned too high, or used with a rich gas, thereby causing a deposit of carbon on the water coils, decreasing the efficiency. A Bunsen burner was substituted by your Committee, which gave more satisfactory results and increased the capacity of the calorimeter. The illuminating flame was selected by the designers because its reflected light could be seen through the opening above the base, showing the operator that it was still lighted. Better facilities should have been provided for this purpose.

There was no way of regulating the supply of air through the calorimeter, either by burner adjustment or dampers. In case any adjustments have to be made on the burner or on the rest of the apparatus, it is necessary to lift off the heavy coil and place it on some sort of a support arranged nearby, as it cannot be moved far without disturbing water connections. If the test were made according to the instructions of the London Referees it would be necessary to lift out the coil and shut off water in order to make more than one run, as the shifting device for throwing the water in the glass graduate is mounted directly on the graduate. While testing we avoided this by supporting this shifting device by means of a clamp, and maintained a constant head on the apparatus by supporting an overflow from another clamp above the shifting device. In this way we were able to make a number of successive tests, and could vary the rate of water and gas supply to the apparatus without lifting off the coil.

In the Boys Calorimeter the inlet and outlet thermometer openings are not large enough to use even a No. 3 rubber stopper, and the connections are so short that a stopper which has been firmly placed in the connection will extend down far enough to throttle the flow of water, or even a thermometer with a large bulb will throttle the flow.

The pressure regulator furnished with the Boys instrument is complicated, and has a large number of joints which are difficult to get tight. We had so much trouble with this regulator that we finally abandoned it and used a regulator from a Junkers instrument.

The meter furnished with the Boys instrument registered 1/12 cubic foot per revolution, and the large dial was divided into 100 equal parts. To facilitate calculations, this meter was not used. The water line on the meter is shown by an outside gauge. The gauge is so large that accurate readings are difficult.

THE SARGENT: The Sargent Calorimeter is wood jacketed, an objection, as stated before. The water content of the first instrument is almost twelve pounds, too large for general purposes, although if the operator has sufficient time at his disposal accurate readings may be made with a calorimeter of this capacity, but slight fluctuations in the quality of the gas are less likely to be caught.

The course of the water, as in the Simmance-Abady, is up and down the calorimeter three times, while the gas products pass through in a single course. We understand this has been improved and a single circulation of water substituted.

The thermometers on this instrument are on the same level, which enables the temperature of both inlet and outlet water to be conveniently read.

The air supply is easily regulated by a damper in exhaust flue.

An ingenious device, enabling the water to be turned on and off the measuring tub, was supplied with this calorimeter. This device is operated electrically by contacts on the gas meter hand.

Arrangement is made for weighing the water with scales indicating pounds and hundredths of a pound.

A diaphragm regulator was mounted on the meter, but owing to leakage through the leather, and a slight chattering, this was not used, but a wet governor substituted.

The Sargent meter is of the wet type, with drum one-tenth of a cubic foot per revolution, the dial being divided into hundredths of a foot. The meter has the outside gauge glass, but the lower part of the glass is obstructed by a screw, which was designed to show the proper height of water. This screw has a large, flat head, which interfered by holding the water down by a capillary action, so that the correct level of the water in the meter was not determinable.

II. SELECTION OF CALORIMETER:

The calorimeter selected should be an instrument that is portable, conveniently handled and easily adjusted, and one that will give results that may be transcribed to English units with the least difficulty.

It should have sufficient heating surface to transmit to the water all the heat developed by the combustion of the gas at the desired rate.

The course of the water should be direct through the calorimeter, and oppose the flow of the products of combustion. This will tend to prevent any irregular heating of the water column, and should give uniform temperatures passing the outlet thermometer.

The exterior surface of the calorimeter should be of such a nature that the radiation from it and the adherence of dust and fumes to it shall be a minimum. Preferably a polished metal exterior.

The inlet and outlet thermometers should be located at about the same level, and close together.

The water connections to the calorimeter, especially at the points of location of the thermometers, should be so arranged and constructed that there is no possibility of heat being transferred or conducted from the outlet water to the inlet water, and thus affect the true temperature readings.

The auxiliary apparatus should follow in general the recommendations and suggestions made in the earlier paragraphs of this chapter.

12. INSTRUCTIONS FOR OPERATING A CALORIMETER:

The calorimeter should be set up in a quiet, light and well ventilated room, which is free from draughts and in which the temperature can be maintained constant between 60 and 80 degrees Fahrenheit. The room should be provided with a bench and sink and with a good supply of running water. It is advisable to have a large shallow open tank suspended from the ceiling, from which the water supply can be taken. This tank should be large enough to supply the calorimeter for a series of a dozen or more tests. By having the tank shallow the water is brought more quickly to the temperature of the room. In order to take care of the difference in head as the tank is emptied, it is advisable to have a weir overflow on the outlet. If only a single test is desired, gas may be taken from the house piping, but if average value is required a small holder, or averaging tank, should be set up, and the gas flowing into holder adjusted to just fill it in the time during which the sample is to be taken. Care should be taken to have the service, from which this holder is filled, short and of small piping, in order that average sample may be obtained, or that the sample be taken from a line on which there is considerable consumption.

On unpacking the apparatus, see that it is clean and free of packing material.

Set up the calorimeter so that the overflow and outlet water can be easily led to the sink. Make water connections with rubber tubing, being careful not to cramp the tubing. To avoid air currents, caused by the movement of the observer's body, set up the calorimeter so that the water supply may be easily adjusted and that all temperatures may be readily observed. Lead the outlet water to a funnel a little above the top of the copper container used in collecting the water, so that the water can be shifted from the funnel to the container without spilling.

Set up meter facing the observer and level it carefully. Fill it with water slightly above the level mark on gauge glass. Connect inlet of meter to gas supply with rubber tubing.

Fill pressure regulator with water, then connect it with outlet of meter, and from outlet of pressure regulator to calorimeter burner. All rubber tubing used to connect meter, pressure regulator and burner should be as short as possible. Note: When fresh water or new gas tubing is used for the first time, gas should be passed through meter and all gas connections for one or two hours before test is made. This is necessary to insure saturation of water and tubing with gas.

Turn on gas and allow it to burn for 5 or 10 minutes. Shut off gas at burner and watch hand on meter for leakage. Be sure that all leaks are stopped before attempting to make a test. Shut off gas, remove pressure and draw off water from the meter until it is exactly at the point shown by gauge. Start water running through the calorimeter, light burner and insert it in the calorimeter. Then regulate the burner to burn at the rate of 4 to 7 feet an hour, as may be found by experiment to give the highest result with the gas to be tested, admitting enough air so that the flame shows a faint luminous tip.

Water should be regulated so that there is a difference between the inlet and outlet temperatures of about 15 degrees Fahrenheit. The temperature of the inlet water should vary but little, if an overhead tank is used and no water added during the test.

Before making the test the barometer, temperature of the gas at the meter, temperature of room and temperature of waste gas should be recorded. It is desirable to have the temperature of the inlet water and temperature of waste gases as nearly as possible at room temperature, in order to establish more nearly a thermal balance.

Next allow gas to burn in the calorimeter for a period of from 20 to 30 minutes. The test may now be started by shifting the outlet water from the funnel to the container just as the large hand on the meter passes the zero point. Readings are then made of inlet and outlet thermometers, making the readings as rapidly as the observer is able to record them during the consumption of 2/10 of a cubic foot of gas. At least ten readings should be made. Water is again shifted from the container to funnel as the hand passes the zero point the second time. Water is then weighed. The uncorrected heating value per cubic foot is obtained by multiplying the difference of the averages of inlet and outlet temperatures, by the number of pounds of water and dividing by 2/10ths. This quantity is divided by the correction factor for barometer and temperature, obtainable from tables, to give the heating value at 30 inches pressure and 60 degrees Fahrenheit. The weight of container should be obtained while the inside is wet. This may be done by filling it with water, emptying and shaking for about five seconds in an inverted position. This will do away with any correction where several consecutive tests are required with same container.

13. Care of Instruments:

The calorimeter, being a delicate and sensitive instrument, should be very carefully cared for when not in use. If the instrument is set up permanently, provision should be made that it be not disturbed by anybody except the operator. If the instrument is not erected permanently, when dismantled it should be carefully cleaned inside and out and the thermometers removed and carefully packed in cotton.

It seems hardly necessary that instruction should be given for the care of such an instrument, but certain precautions should be noted.

14. Capacity or Intelligence of Operator:

Any chemist or young man capable of making close observations of thermometers and meter readings, and having experience and patience necessary with the simpler laboratory operations, should be a successful operator for commercial observations.

15. PRECAUTIONS—"DON'TS":

Don't place lighted burner in calorimeter when water is not running through it.

Don't shut off water while gas is burning, and if water is accidentally shut off, shut off the gas quickly, to avoid breaking thermometers.

Don't move suddenly near instrument during test. Slight draughts thus caused will vary outlet readings and vitiate test.

Don't forget to test meter and all connections frequently for leakages.

Don't make the test with inlet water very much below temperature of room.

Don't erect the calorimeter too close to any heating or lighting appliance, where radiant heat might affect the readings.

16. TYPICAL CALCULATION (EXAMPLE):

Test Record Milwaukee Junker Calorimeter No. J-1

Date July 9 1908 3 P.M.

Barometer 29.26 Temp. of Gas 72.68

Correction Factor 0.9423

Humidity 66 %

Room Temp. 72.6 Exhaust Temp. 75.2

Condensed Water Collected per cu. ft. Gas.

Time one Rev. Meter 52 sec. = 6.92 cu. ft. per Hr.

Gas Consumed During Test 0.2 cu. ft.

Weight Water Heated 7.5728 lbs.

Temperatures

	Ther. No. U.W Inlet IIII	Ther. No. U.W. Outlet III
1	72.91	88 03
2	72.91	88.00
3	72 91	88.00
4	72 91	87 97
5	72.91	88.00
6	72 91	88.00
7	72 91	88.01
8	72 91	87.97
9	72 91	87.97
10	72.91	88.00
Av.	72 91	87.995
Cor.	− 0.174 72.736	+ 0.100 88.095

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          15.359
          7.5728
         122872
         30718
       107513
       76795
     107513
0.2) 116.3106352
0.9423) 581.553176 (617.16
        56538
          16173
           9423
           67501
           65961
            15407
             9423
             5984
```

Rise in Temp. 15.359

B. T. U. 617.16

Remarks

R.C.C. Observer

17. USE OF COMPUTER:

The labor of making the calculations for determining the heating value from observations of a calorimeter may be lessened by the use of a heating value computer, which has been designed by one of the members of the Committee. The computer consists of a circular slide rule, with divisions corresponding to the readings made on the calorimeter. This computer gives the corrected heating value of a cubic foot of gas in B. T. U's, having the barometer and temperature of the metered gas, and the difference in temperature between the inlet and outlet water and the pounds of water passed. This computer is designed to operate within the limits recommended by the Committee and will give corrected heating value of the gas of from 300 to 800 B. T. U's. Should a gas of a lower or higher heating value than 300 to 800 B. T. U's be measured, the computer can still be used by dividing or multiplying one of the other factors in its computation.

18. SUGGESTIONS FOR FURTHER INVESTIGATION:

Your Committee, knowing that much could be learned by further investigation of the subject of Calorimetry, suggests the following topics, not with the idea that their investigation is necessary as an adjunct to commercial calorimetry as at present practiced, but as a means of further enlightenment on the general subject as affecting close and scientific determinations:

Effect on calorific readings resulting from a varying atmospheric humidity.

Effect on heating value resulting from a difference in temperature between the inlet water and room atmosphere.

Determination of heat lost through the products of combustion leaving the calorimeter above or below the atmospheric temperature.

Respectfully submitted,

R. B. BROWN, *Chairman*
C. F. BURGESS,
J. B. KLUMPP,
Sub-Committee on Calorimetry.

APPENDIX A.

THE JUNKERS GAS CALORIMETER.

This apparatus consists essentially of a combustion chamber, the walls of which consist of an annular copper vessel. Inside this annular space a large number of copper tubes are fitted, through which the products of combustion escape by flowing down from the top of the chamber to an outlet closed by a throttle valve at the bottom. A current of cold water surrounds the tubes, and, flowing upwards, escapes through a suitable outlet at the top of the apparatus. The coldest water, therefore, meets the coldest gases. As a consequence, products of combustion are completely reduced to atmospheric temperature before they escape to outer air. Thermometers are fitted both at the point where the water enters and at that where it escapes. The rate of flow is maintained constant by leading the supply into a small tank with an overflow, whilst the heated water escapes from a second overflow. The heat-producing flow is thus kept constant, but the rate can be adjusted to any desired speed by means of a cock at the inlet to the calorimeter. The water supply required is from one-fifth to two-thirds of a gallon per minute. The gas supply to burner is measured through any accurate meter, and it is well to introduce an efficient governor between this and the burner. The water supply tube is connected to the nipple, and adjusted so that the rise of temperature in the outflowing water is from 10 degrees to 20 degrees Cent. The tightness of the gas connections is ascertained by turning off the burner, when the meter index should remain perfectly stationary. The height of the flame should be so adjusted that not more than 6,000 British thermal units are produced per hour. In taking the readings, the hot water discharge is turned into the measuring glass, when the pointer of the gas meter passes the zero mark. The temperature of the discharge is noted five or six times whilst measuring glass is filling, which takes from one to six minutes. When full, the gas is turned off, and the quantity used read. Having obtained this, and knowing the quantity of water used, and the number of degrees through which it has been raised, the calorific value per cubic foot of gas is readily obtained.

THE BOYS GAS CALORIMETER.

This calorimeter, which has been designed by Mr. Boys, is shown in vertical section. It consists of three parts, which may be separated, or which, if in position, may be turned relatively to one another about their common axis. The parts are (1) the base A, carrying a pair of burners B, and a regulating tap. The upper surface of the base is covered with a bright metal plate held in place by three centering and lifting blocks C. The blocks are so placed as to carry (2) the vessel D, which is provided with a central copper chimney E and a condensed water outlet F. Resting upon the rim of the vessel D are (3) the water circulating system of the calorimeter attached to the lid G. Beginning at the center where the outflow is situated, there is a brass box which acts as a temperature equalizing chamber for the outlet water. Two dished plates of thin brass KK are held in place by three scrolls of thin brass LLL. These are simply strips bent round like unwound clock springs, so as to guide the water in a spiral direction inwards, then outwards and then inwards again to the outlet. The lower or pendent portion of the box is kept cool by circulating water, the channel for which may be made in the solid metal, as shown, on the right side, or by sweating on a tube as shown on the left. Connected to the water channel at the lowest point by a union are five or six turns of copper pipe, such as is used in a motor car radiator of the kind known as Clarkson's. In this a helix of copper wire threaded with copper wire is wound round the tube, and the whole is sweated together by immersion in a bath of melted solder. A second coil of pipe of similar construction surrounding the first is fastened to it at the lower end by a union. This terminates at the upper end in a block, to which the inlet water box and thermometer holder are secured by a union as shown at O. An outlet water box P and thermometer holder are similarly secured above the equalizing chamber H. The lowest turns of the two coils MN are immersed in the water which in the first instance is put into the vessel D.

Between the outer and inner coils MN is placed a brattice Q, made of thin sheet brass, containing cork dust to act as a heat insulator. The upper annular space in the brattice is closed by a wooden ring, and that end is immersed in melted rosin and beeswax cement, to protect it from any moisture which might condense upon it. The brattice is carried by an internal flange, which rests upon the lower edge of the casting H. A cylindrical wall of thin sheet brass, a very little smaller than the vessel D, is secured to the lid so that when the instrument is lifted out of the vessel and placed upon the table, the coils are protected from injury. The narrow air space between this and the vessel D also serves to prevent interchange of heat between the calorimeter and the air of the room.

The two thermometers for reading the water temperatures and a third for reading the temperature of the outlet air are all near together and at the same level. The lid may be turned round into any position relatively to the gas inlet and condensed water drip that may be convenient for observation, and the inlet and outlet water boxes may themselves be turned so that their branch tubes point in any direction.

A regular supply of water is maintained by connecting one of the two outer pipes of the overflow funnel to a small tap over the sink. The overflow funnel is fastened to the wall about one meter above the sink and the outer pipe is connected to a tube in which there is a diaphragm with a hole about 2.3 mm. in diameter. This tube is connected to the inlet pipe of the calorimeter. A piece of stiff rubber pipe long enough to carry the outflow water clear of the calorimeter is slipped on to the outflow branch and the water is turned on so that a little escapes by the middle pipe of the overflow funnel, and is led by a third piece of tube into the sink. The amount of water that passes through the calorimeter in four minutes should be sufficient to fill the graduated vessel to some point above the lowest division, but insufficient in five minutes to come above the highest division. If this is not found to be the case, a moderate lowering of the overflow funnel or reaming out of the hole in the diaphragm will make it so. The overflow funnel should be provided with a lid to keep out dust.

The thermometers for reading the temperature of the inlet and outlet water should be divided on the centigrade scale into tenths of a degree, and they should be provided with reading lenses and pointers that will slide upon them. The thermometers are held in place by corks fitting the inlet and outlet water boxes. The positions of these thermometers should be interchanged every month. The thermometers for reading the temperature of the air near the instrument and of the effluent gas should be divided on the centrigrade scale into degrees.

The flow of air to the burners is determined by the degree to which the passage is restricted at the inlet and at the outlet. The blocks C which determine the restriction at the inlet are made of metal 3/16 inch or about 5 millimetres thick, while the holes round the lid which determine the restriction at the outlet are five in number and are ⅝-inch or 16 millimetres in diameter. The thermometer used for finding the temperature of the effluent gas is held by a cork in the sixth hole in the lid so that the bulb is just above the upper coil of pipe.

The calorimeter should stand on a table by the side of a sink so that the condensed water and hot water outlets overhang and deliver into the sink. A suitable change-over funnel may be constructed as follows:

A piece of india-rubber tube reaching nearly to the base should be attached to the waste water-pipe so as to avoid splashing, and another piece may conveniently be slipped on to the condensed water outlet so as to lead the condensed water into a flask, but care should be taken that the small side hole is not covered by the tube. A glass vessel must be provided of the size of the vessel D, containing water in which is dissolved sufficient carbonate of soda to make it definitely alkaline. The calorimeter after use is lifted out of its vessel D and placed in the alkaline solution and there left until it is again required for use. The liquid should not, when the calorimeter is placed in it, come within two inches of the top of the vessel. The liquid must be replenished from time to time, and its alkalinity must be maintained.

The above description of the Boys Calorimeter was taken from "The Notification of the Metropolitan Referees for the Year 1908."

THE SIMMANCE-ABADY GAS CALORIMETER.

This instrument consists of an outer casing, the interior of which is divided into a series of annular spaces, through which the hot gases from a Bunsen burner may pass. These gases flow out at a point at which a thermometer is placed for registering the temperature of the outflowing gases. A small damper is fitted to regulate the size of the opening past the thermometer. Each alternate annular space is closed at the bottom so as to form a container for the water inside the vessel. These water spaces are connected together at the top and bottom by small radial pipes. The hot gases from the burner rise and then pass down the spaces. The inflowing water enters at the cock and passes the thermometer, where its temperature is taken. From there it travels down the outer annular space, then through the radial pipes, up the next space, through the top radial pipes, down once more, then again through the radial pipes at the bottom, and up the last space to the top of the instrument, where its temperature is taken by another thermometer. After this it flows out through a pipe where there is a movable funnel, by means of which the water can be directed either into a graduated measure or can run to waste. There is a tube at the top of the instrument which forms a gauge to indicate the height of the water in the apparatus. At the point where the hot gases issue from the calorimeter, there is a small pipe, which conveys the water formed by combustion into a small graduated measure. The calorimeter is connected to a small ball-valve cistern, thus insuring a practically constant flow, and this flow should go on unceasingly, a pipe leading it away to waste, after it has traversed the instrument. The gas passes through a central dial meter (having a long pointer and a plainly marked dial), through a sensitive balance-valve governor (to take up unusually violent pulsations), and thus to the burner, constantly burning in the calorimeter, and imparting the whole of its heat to the flowing water. Large, distinctly scaled thermometers show the temperatures of the inlet and outlet water, and, the water and gas being both practically constant in flow, the temperature indications are reliable guides.

THE SARGENT CALORIMETER.

The Sargent Calorimeter consists essentially of a water heater, so arranged that the heat developed by the combustion of the gas will be entirely absorbed by a quantity of measured water.

The outer casing of this calorimeter is jacketed with wood to prevent the radiation of heat. The interior is a combustion chamber for the gas, surrounded by a compartment containing the jacket water. The combustion chamber is high enough to allow a suitable flame to be inserted without its impinging upon any part of the instrument. The products of combustion rise to the upper interior, then are diverted down through a series of small tubes to the bottom, and pass out through an opening, the size of which is controlled by a damper. The water enters in an opening at the top of the calorimeter. In the first Sargent instrument the water passed down through and just inside of the outer shell, then up and down several times, surrounding the small tubes carrying off the products of combustion of the gas, and finally leaving at the top on a level with the inlet. In the second instrument the course of the water was down adjacent to the outer shell, then up once, surrounding the combustion tubes, and passing in a direction opposite to the flow of the products of combustion.

The water head was originally controlled by a gauge on the outlet, but later a fixed elevated weir was adopted for this purpose.

The outflowing water also leaves the calorimeter through a weir overflow, after passing through a controlling cock. The overflow passes to an automatic dumping bucket, which is divided into two parts, one part connecting to an overflow or waste, the other passing the water to a measuring vessel. This dumping bucket is held in position by a keeper. The weight of the water in the full side tends to oscillate the bucket, so that the water will flow into the empty side and through another outlet to the empty receptacle. When the hand of the gas meter passes the zero point an electrical circuit is completed, which, passing through the solenoid, draws down the keeper, and allows the outlet water to automatically change from the full to the empty pail. With such a device the personal error is not only eliminated, but much of the work of the operator is done automatically, thereby allowing him more time for observing the temperatures and weighing the water delivered.

The Gas Meter is of the wet type, with a drum of one-tenth of a cubic foot capacity per revolution. The dial is divided in hundredths of a cubic foot.

The flow of gas from the meter to the burner is regulated by a small leather diaphragm governor, mounted on the top of the meter, at the gas outlet.

The thermometers indicating the temperature of both the inlet and outlet water are side by side, on the same level, at the top of the calorimeter, thus enabling both to be easily and quickly read. These thermometers read in Fahrenheit degrees, and are subdivided to read to one-tenth of one degree. There is a thermometer placed near the outlet damper to register the temperature of the outflow products of combustion.

The water after passing through the calorimeter is caught in a copper vessel and weighed on platform scales.

By weighing the discharged water and using Fahrenheit thermometers, no transformation of units is necessary to get the result in British Thermal Units.

APPENDIX B.

NOTIFICATION OF THE METROPOLITAN GAS REFEREES FOR THE YEAR 1908.

AS TO THE MODE OF TESTING THE CALORIFIC POWER OF THE GAS.

(Refers to use of Boys Calorimeter.)

This testing shall be made on such days as the Controlling Authority shall direct.

The Calorimeter to be used in testing the calorific power of the gas shall be one which has been examined and certified by the Gas Referees. A description of the Calorimeter is given in Appendix.

In order to test the gas for calorific power, the gas shall first pass through a meter and a balance governor of the same construction as those on the photometer table. It shall then be led to the gas inlet in the base of the Calorimeter. The gas shall be turned on and lighted, and the tap of the Calorimeter shall be so adjusted as to allow the meter hand to make one turn in from 60 to 75 seconds. The water shall be turned on so that when the regular flow through the Calorimeter has been established a little may pass the overflow of the funnel and trickle over into the sink. Water must be poured in through one of the holes in the lid until it begins to run out at the condensation outlet. The Calorimeter may then be placed upon its base. The measuring vessel carrying the change-over funnel shown in Figs. 16 and 18, pp. 42 and 43, should then be placed in position in the sink so that the outlet water is led into the sink. The hot water outlet tube of the Calorimeter should be above but should not touch the change-over funnel. After an interval of not less than 30 minutes the Gas Examiner, after bringing the reading glasses into position on the thermometers used for measuring the temperature of the inlet and outlet water, shall then make the following observations. When the meter hand is at 75 he shall read the inlet temperature; when it reaches 100 he shall move the funnel so as to direct the outflow into the measuring vessel and at the same time he shall start the stop-clock or a stop-watch. When the meter hand reaches 25 he shall make the first reading of the outlet temperature. He shall continue to read the outlet temperature at every quarter turn until fifteen readings have been taken. The meter hand will then be at 75. He shall also at every turn of the meter except the last make a reading of the inlet temperature when the meter hand is between 75 and 100. When the meter hand reaches 100 after the last outlet temperature has been read, the Gas Examiner shall shift the funnel so as to direct the outlet water into the sink again and at the same time stop the clock or watch. The barometer and the thermometers showing the temperatures of the effluent gas, of the air near the Calorimeter and of the gas in the meter, shall then be read. The time shown by the stop-clock shall be recorded. The mean of the four readings of the inlet temperature is to be subtracted from the mean of the fifteen readings of the outlet temperature and the difference is to be multiplied by 3 and by the number of litres of water collected and the product is to be divided by the tabular number. The difference in degrees centigrade of the temperature of the effluent gas and of the surrounding air shall be taken, and one-sixth of this difference shall be added to the result previously found if the effluent gas is the warmer of the two, or subtracted if the effluent gas is the cooler of the two.* The result is the gross calorific power of the gas in Calories per cubic foot.

In addition to the observations described, the amount of condensed water resulting from the combustion of the gas shall be measured. For this purpose the condensation water shall be led into a flask not less than twenty minutes after the Calorimeter has been placed in position. The amount collected in not less than thirty minutes shall be measured, the time of collection having been accurately noted.

The number of cubic centimetres collected shall be multiplied by the number of seconds in the time indicated by the stop-clock and by the number 1.86. The number of seconds in the time during which the condensed water was being

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*This correction has been found by experiment.

collected shall be multiplied by the tabular number. The first product shall be divided by the second. The quotient is to be subtracted from the gross calorific power. The difference is the net calorific power in Calories per cubic foot. The gross and net calorific power in British Thermal Units can be obtained by multiplying the corresponding numbers of Calories by 3.968.

APPENDIX C.

TESTS OF DR. IMMENKOTTER.

See "Ueber Heizwertbestimmungen mit besonderer Beruecksichtigung gasfoermiger und fluessiger Brennstoffe," by Theodor Immenkotter.—Press of R. Oldenbourg, Berlin, 1905.

From a series of tests on the Junkers gas calorimeter, Dr. Immenkotter arrives at the following conclusions:

1. That the combustion is perfect.
2. That the influence of radiation from the flame downwards is negligible, being at the most about ¾ B. T. U. per cubic foot.
3. That the conduction of heat by the burner stem plays no appreciable part, the stem being cool.
4. That the loss of heat to the surrounding air effects the heating value to the extent of no more than .03% per degree temperature difference between air and warmed water.
5. That heat carried off by the products of combustion (apart from water vapor), affects the readings of heating values only by .027 per cent, with an exact supply of air, to .12 per cent., with a 4-fold supply of air, per degree difference between the air and the spent gases.
6. That with regard to the moisture in the spent gases, these are found not to be saturated, but their temperature of saturation is found to be approximately the same as the temperature of the feed water.
7. That errors in the time of opening or shutting stop cocks mostly offset one another.
8. That weighing the water can be done quite exactly;

that errors in temperature reading need not come to more than .01, which on a raise of 20 degrees represents not more than .05 per cent.

9. The meter for measuring the gas burned needs to be verified.

10. That the estimation of the amount of water formed (which serves as a datum for computing the lower heating value of the gas) requires that the gas should be burned in the calorimeter for, say, one-half hour, 200 liters of gas burned in that time giving about 200 grammes of water contents.

11. That there is a combination which favors uniformity of heating of the water in respect that any water tube which happens to be colder than the rest has the colder portions of the waste products falling past it more rapidly, and vice versa.

12. That slight variations in the temperature of the feed water, or in the quantity of gas admitted, are slow in affecting the thermometers.

13. That the height of the flame should be watched, for it must not be allowed to vary.

U. W. CHEM. ENG. JUNKERS.—SERIES I.

	1	2	3	4	5	6	7	8	9	10
Barometer..	29.23	29.23	29.23	29.22	29.22	29.22	29.22	29.22	29.21	29.22
Temperature Gas.....	73.6	73.8	73.9	73.9	74.1	74.3	74.3	74.3	74.3	74.5
Correction Factor.....	0.938	0.9376	0.9371	0.9367	0.9362	0.9357	0.9357	0.9357	0.9354	0.9353
Humidity............	59.	61.	61.	61.	63.	63.	63.	63.	63.	63.
Room Temperature...	74.	74.2	74.6	74.5	74.2	74.9	74.7	74.6	74.6	74.
Exhaust Temperature.	77.	77.5	77.5	77.5	78.	78.	78.	78.	78.	79.
Gas Rate Cu. Ft. Hour.	7.2	7.06	7.06	6.97	7.14	7.12	7.13	7.12	7.2	7.05
Gas Consumed Cu. Ft.	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water Heated—K'gms.	3.442	3.441	3.452	3.439	3.452	3.381	3.385	3.373	3.374	3.371
Inlet Temperature....	74.254	74.357	74.458	74.56	74.852	74.946	75.039	75.349	75.803	76.082
Outlet Temperature...	89.734	89.778	89.848	89.996	90.175	90.573	90.584	90.968	91.409	91.702
Rise in Temperature..	15.48	15.421	15.390	15.436	15.323	15.627	15.545	15.619	15.606	15.62
B. T. U..............	626.1	623.85	624.92	624.7	622.8	622.49	619.89	620.6	620.49	620.60

7-1-08.

APPENDIX D—TABLE OF TEST DATA NO. 1.

BOYS CALORIMETER.—SERIES I.

	1	2	3	4	5	6	7	8	9
Barometer............	29.23	29.23	29.23	29.22	29.22	29.22	29.22	29.21	29.22
Temperature Gas "F"	73.6	73.8	73.9	73.9	74.3	74.3	74.3	74.3	74.5
Correction Factor.....	0.938	0.9376	0.9371	0.9367	0.9357	0.9357	0.9357	0.9354	0.9353
Humidity	59.	59.	61.	61.	63.	63.	63.	63.	63.
Room Temperature...	74.	74.2	74.6	74.5	74.9	74.75	74.65	74.8	74.7
Exhaust Temperature.	77.5	78.	78.	78.4	78.8	79.	79.	79.3	79.5
Gas Rate Cu. Ft. Hour	3.75	3.69	3.72	3.80	3.73	3.72	3.70	3.66	3.66
Gas Consumed Cu. Ft.	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water Heated—Lbs...	7.281	7.416	7.3699	7.233	7.3986	7.421	7.451	7.491	7.5419
Inlet Temperature "C"	23.449	23.544	23.615	23.649	23.917	23.872	24.138	24.266	24.51
Outlet Temp. "C"....	32.143	32.077	32.198	32.385	32.424	32.358	32.592	32.633	32.818
Rise in Temp. "F"...	15.649	15.359	15.449	15.724	15.312	15.274	15.217	15.060	14.954
B. T. U...............	607.4	607.4	607.5	607.1	605.4	605.8	606.3	604.1	602.4

Luminous Flame Used in All Tests.

7-1-08.

APPENDIX D—TABLE OF TEST DATA NO. 2.

U. G. I. SARGENT (NEW).—SERIES I.

	1	2	3	4	5	6	7	8	9
Barometer............	29.23	29.23	29.23	29.22	29.22	29.22	29.22	29.21	29.22
Temperature Gas......	73.6	73.8	73.9	73.9	74.3	74.3	74.3	74.3	74.5
Correction Factor.....	0.9380	0.9376	0.9371	0.9367	0.9357	0.9357	0.9357	0.9354	0.9353
Humidity %...........	59.	61.	61.	61.	63.	63.	63.	63.	63.
Room Temperature...	74.	74.2	74.6	74.5	74.8	74.7	74.6	74.6	76.6
Exhaust Temperature.	76.	76.	76.	76.5	77.	77.	77.	77.	78.
Gas Rate Cu. Ft. Hour	5.14	5.14	4.96	4.87	4.93	5.00	4.93	4.93	4.89
Gas Consumed Cu. Ft.	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water Heated—K'gms.	3.415	3.450	3.490	3.479	3.403	3.379	3.363	3.360	3.364
Inlet Temperature....	74.303	74.405	74.556	74.609	75.096	75.006	75.552	75.738	76.19
Outlet Temperature...	89.617	89.568	89.55	89.665	90.394	90.409	91.01	91.102	91.509
Rise in Temperature..	15.314	15.163	14.994	15.056	15.298	15.403	15.458	15.364	15.319
B. T. U.............	614.6	615.0	615.5	616.4	613.38	613.13	612.56	608.34	607.3

APPENDIX D—TABLE OF TEST DATA No. 3.

U. W. JUNKERS.—SERIES E.

At Varying Gas Consumption per Hour with Rise in Temperature maintained constant.

	1	2	3	4	5	6	7	8	9
Barometer	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3	29.3
Temperature Gas	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5	77.5
Correction Factor	.9307	.9307	.9307	.9307	.9307	.9307	.9307	.9307	.9307
Humidity	57.	57.	57.	57.	57.	57.	57.	57.	57.
Room Temperature	78.2	78.3	78.3	78.2	78.6	78.6	78.6	78.7	78.9
Exhaust Temperature	76.	76.5	76.0	76.5	76.3	76.5	76.	76.	76.
Gas Rate Cu. Ft. Hour	2.15	3.27	4.00	5.00	5.80	6.93	8.17	9.22	10.3
Gas Consumed Cu. Ft.	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water Heated—Lbs.	7.233	7.7554	7.193	7.361	7.502	7.400	7.509	7.550	7.131
Inlet Temperature	72.915	72.731	72.549	73.441	72.766	72.71	72.651	72.63	72.529
Outlet Temperature	89.149	88.434	89.073	89.644	88.760	88.723	88.479	88.535	88.945
Difference	16.234	15.703	16.524	16.203	15.994	16.210	16.018	15.905	16.416
B. T. U.	630.8	637.3	638.5	640.75	644.6	644.4	646.2	645.1	628.9

6-26-08 P. M.

APPENDIX D—TABLE OF TEST DATA No. 4.

BOYS CALORIMETER.—SERIES H.

	1	2	3	4	5	6
Barometer..................	29.00	29.22	29.22	29.00	29.00	29.00
Temperature of Gas........	70.25	72.9	72.0	70.9	71.6	72.0
Correction Factor..........	.9401	.9404	.9402	.9384	.9366	.9356
Humidity..................	65.	61.	61.	69.	69.	69.
Room Temperature.........	72.5	74.0	74.0	72.85	73.8	74.25
Exhaust Temperature......	72.6	72.5	74.5	74.5	75.5	75.8
Gas Rate—Cu. Ft. Hour....	2.08	2.34	2.79	3.61	5.12	5.46
Gas Consumed—Cu. Ft.....	.2	.2	.2	.2	.2	.2
Water Heated—Lbs.........	6.938	7.714	8.5141	7.961	5.997	5.67
Inlet Temperature "C".....	22.2	21.773	21.807	22.47	22.559	22.61
Outlet Temperature "C"....	30.8645	29.6765	29.092	30.313	32.949	32.415
Difference "F"	15.596	14.2263	13.113	14.1174	18.702	19.449
B. T. U....................	575.4	583.5	593.7	598.7	598.7	589.3

Impossible to maintain constant rise in temperature on account of size of coil.

APPENDIX D—TABLE OF TEST DATA No. 5.

U. W. CHEM. ENG. JUNKERS.—SERIES K.

	1	2	3	4	5
Room Temperature.......	74.65	74.65	74.9	75.2	75.3
Exhaust Temperature.....	79.5	79.5	79.5	79.5	79.5
Time of Test in Minutes...	3.	3.	3.	3.	3.
Water Heated in Grams...	4140.	4139.	4142.	4133.	4137.
Temperature Inlet "F"...	72.679	72.662	72.692	72.71	72.68
Temperature Outlet "F"..	87.646	87.657	87.671	87.671	87.642
Rise in Temperature "C"	8.315	8.3305	8.322	8.312	8.312
Volts on Heating Coil.....	86.643	86.70	86.6977	86.645	86.555
Amperes on Heating Coil	9.295	9.2956	9.295	9.290	9.285
Small Calories put in.....	34602.5	34627.52	34624.4	34593.3	34530.19
Small Calories observed...	34424.1	34479.9	34469.7	34353.49	34386.7
Efficiency	99.48	99.57	99.55	99.30	99.58

7-2-08.

APPENDIX D—TABLE OF TEST DATA NO. 6.

SIMMANCE-ABADY.—SERIES L.

	1	2	3	4	5	6
Room Temperature.........	75.	75.	75.5	76.	75.5	76.
Exhaust Temperature......	76.5	76.5	76.5	76.6	76.7	76.8
Water Heated—Grams......	4069.	4061.	4068.	4062.	4064.	4065.
Inlet Temperature "F".....	73.139	73.654	73.662	73.659	73.677	73.697
Outlet Temperature "F"....	86.857	86.861	87.002	86.934	87.009	86.943
Rise in Temperature "C"...	7.625	7.337	7.411	7.375	7.4066	7.3589
Time of Tests in Seconds...	180.	180.	180.	180.	180.	180.
Volts....................	94.8	94.73	94.70	94.65	94.6304	94.60
Amperes..................	6.8594	6.86	6.8619	6.861	6.862	6.862
Small Calories put in......	27939.55	27921.36	27920.25	27901.85	27900.14	27891.17
Small Calories observed.....	31009.84	29796.369	30147.95	29957.25	30100.42	29915.92
Efficiency.................	110.99	106.72	107.98	107.36	107.88	107.26

July-7-1908.

APPENDIX D—TABLE OF TEST DATA No. 7.

SERIES M.

	M. G. L. CO. JUNKERS.					No. 2, U. W. JUNKERS.				
	6	7	8	9	10	6	7	8	9	10
Barometer............	29.21	29.21	29.21	29.21	29.21	29.21	29.21	29.21	29.21	29.21
Temperature Gas......	76.37	76.37	76.37	76.37	76.37	76.37	76.37	76.37	76.37	76.37
Correction Factor.....	.9308	.9308	.9308	.9308	.9308	.9308	.9308	.9308	.9308	.9308
Humidity %...........	61.	61.	61.	61.	61.	61.	61.	61.	61.	61.
Room Temperature...	76.4	76.4	76.4	76.5	76.5	76.4	76.45	76.4	76.5	76.5
Exhaust Temperature.	77.	77.	77.	77.	77.	77.2	77.2	77.3	77.3	77.3
Gas Rate Cu. Ft. Hour	7.12	7.12	7.06	7.00	7.07	7.07	7.07	7.07	7.07	7.07
Gas Consumed Cu. Ft.	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Water Heated—Lbs....	7.2774	7.2377	7.2686	7.2708	7.2619	7.478	7.372	7.363	7.403	7.374
Inlet Temperature....	74.276	74.285	74.307	74.341	74.404	74.188	74.19	74.228	74.254	74.304
Outlet Temperature...	89.833	89.886	89.892	89.953	90.007	89.467	89.658	89.755	89.749	89.861
Rise in Temperature...	15.557	15.601	15.585	15.612	15.603	15.279	15.468	15.527	15.495	15.557
B. T. U..............	608.15	606.55	608.51	609.75	608.65	613.75	612.55	614.16	616.19	616. 7

7–8–1908.

APPENDIX D—TABLE OF TEST DATA NO. 8.

SERIES M.

	M. G. L. CO. JUNKERS.					U. W. CHEM. ENG. JUNKERS.				
	1	2	3	4	5	1	2	3	4	5
Barometer............	29.23	29.23	29.23	29.23	29.23	29.23	29.23	29.23	29.23	29.23
Temperature of Gas...	75.92	75.92	75.92	75.92	75.92	75.92	75.92	75.92	75.92	75.92
Correction Factor.....	.9344	.9344	.9344	.9344	.9344	.9344	.9344	.9344	.9344	.9344
Humidity	56.	56.	56.	59.	59.	56.	56.	56.	59.	59.
Temperature Room...	76.	76.	76.	76.	76.1	76.	76.	76.	76.	76.1
Temp. Exhaust Gas...	76.0	76.0	76.0	76.0	76.1	76.8	76.8	76.8	77.0	77.0
Rate of Gas Cu. Ft. Hr.	7.06	7.06	7.06	7.13	7.02	7.01	7.00	7.02	7.02	7.01
Gas Consumed Cu. Ft.	.2	.2	.2	.2	.2	.2	.2	.2	.2	.2
Water Heated—Lbs...	7.3612	7.3545	7.3633	7.3369	7.3520	7.372	7.392	7.3656	7.3788	7.3678
Inlet Temperature....	73.557	73.601	73.638	73.702	73.712	73.488	73.532	73.577	73.620	73.655
Outlet Temperature...	88.980	89.034	89.060	89.188	89.2147	89.012	89.059	89.127	89.153	89.202
Difference............	15.423	15.433	15.422	15.486	15.503	15.524	15.527	15.550	15.533	15.547
B. T. U..............	607.51	607.35	607.63	607.98	609.89	612.39	614.17	612.88	613.31	612.95

7-8-1908.

APPENDIX D—TABLE OF TEST DATA NO. 9.

JUNKERS.—Series P.

	1	2	3	4	5	6
Barometer..................	29.09	29.09	29.09	29.09	29.09	29.09
Temperature Gas............	73.04	73.13	73.22	73.31	73.4	73.4
Correction Factor..........	.9359	.9355	.9353	.935	.9348	.9348
Room Temperature..........	74.65	74.9	74.9	74.9	74.95	75.0
Exhaust Temperature......	74.0					
Gas Rate—Cu. Ft. Hour....	7.07	7.07	7.07	7.07	7.07	7.07
Gas Consumed—Cu. Ft......	.2	.2	.2	.2	.2	.2
Water Heated—Lbs.........	6.8717	6.8563	6.8519	6.8563	6.8585	6.8695
Inlet Temperature..........	69.888	69.98	70.064	70.182	70.306	70.395
Outlet Temperature	85.572	85.66	85.758	85.873	85.991	86.065
Difference "F"	15.684	15.68	15.694	15.691	15.685	15.670
B. T. U...................	575.8	574.6	574.8	575.3	575.2	575.7

APPENDIX D—Table of Test Data No. 10.

SIMMANCE-ABADY.—Series P.

	1	2	3	4	5	6
Barometer	29.09	29.09	29.09	29.09	29.09	29.09
Temperature Gas	73.04	73.13	73.22	73.31	73.4	73.4
Correction Factor	.9359	.9355	.9353	.935	.9348	.9348
Room Temperature	74.65	74.9	74.9	74.9	74.95	75.0
Exhaust Temperature	75.0	75.0	74.9	74.9	74.9	74.9
Gas Rate—Cu. Ft. Hour	4.08	4.08	4.08	4.08	4.08	4.08
Gas Consumed—Cu. Ft.	.2	.25	.2	.2	.2	.2
Water Heated—Lbs	7.2046	8.9926	7.2046	7.2068	7.1782	7.1826
Inlet Temperature	69.948	70.022	70.118	70.283	70.380	70.454
Outlet Temperature	86.455	86.331	86.331	86.651	86.836	86.777
Difference "F"	16.507	16.309	16.213	16.368	16.456	16.323
B. T. U.'s	635.3	627.1	624.4	630.8	631.8	627.1

APPENDIX D—Table of Test Data No. 11.

SARGENT.—SERIES T.

	1	2	3	4
Room Temperature........	71.	71.	71.	71.
Exhaust Temperature......	77.	77.	77.	77.
Water Heated—Grams.....	3223.	3187.	3168.	3182.
Inlet Temperature "F"	64.954	64.493	64.375	64.248
Outlet Temperature "F"...	80.468	80.098	80.0	79.889
Rise in Temperature "C" ..	8.519	8.6694	8.6805	8.689
Time of Test in Seconds....	180.	186.	180.	180.
Volts....................	95.332	95.027	94.919	94.844
Amperes..................	6.82	6.8	6.79	6.785
Small Calories put in.......	27934.956	27763.925	27691.587	27653.407
Small Calories observed	27779.057	27629.378	27499.824	27448.398
Efficiency °/o	99.5	99.5	99.3	99.2

SARGENT.—Series S.

	1a	1b	2a	2b	3a	3b
Barometer................	29.38	29.38	29.38	29.38	29.38	29.38
Temperature of Gas	68.7	68.9	69.6	69.6	69.6	69.6
Correction Factor.........	.9569	.9563	.9545	.9545	.9545	.9545
Temperature Room.........	70.0	70.1	70.1	70.1	70.3	60.3
Temperature Exhaust	67.7	70.7	67.5	67.5	67.5	67.5
Rate of Gas Cu. Ft. Hour..	3.0	3.0	4.07	4.04	5.15	5.15
Gas Consummed Cu. Ft....	.2	.2	.3	.2	.2	.2
Water Heated—Lbs.......	7.844	7.985	7.985	7.3325	7.705	7.6918
Inlet Temperature	65.052	65.012	64.982	64.940	64.902	64.902
Outlet Temperature.......	80.048	79.770	80.951	80.958	80.308	80.223
Difference	14.996	14.758	15.969	16.037	15.406	15.321
B. T. U.	614.5	616.1	613.4	616.1	621.8	617.0

SARGENT.—SERIES S (Continued.)

	4a	4b	5a	5b	6a	6b	7a	7b
Barometer......	29.38	29.38	29.38	29.38	29.38	29.38	29.38	29.38
Temperature of Gas....	69.6	69.6	69.6	69.6	69.6	69.6	69.6	69.6
Correction Factor......	.9545	.9545	.9545	.9545	.9545	.9544	.9545	.9545
Temperature Room....	70.2	70.3	70.3	70.1	70.1	70.0	69.6	69.6
Temperature Exhaust..	67.5	67.5	67.5	67.5	67.7	67.5	67.7	97.7
Rate of Gas Cu. Ft. Hr.	6.10	6.10	7.2	7.2	8.00	8.00	9.3	9.24
Gas Consumed Cu. ft...	.2	.2	.2	.2	.2	.2	.2	.2
Water Heated—Lbs....	7.5309	7.5618	7.3303	7.2973	7.5121	7.5507	6.8717	6.8563
Inlet Temperature......	64.902	64.902	64.902	64.902	64.824	64.803	64.748	64.704
Outlet Temperature....	80.545	80.535	80.943	81.06	80.484	80.446	81.823	81.804
Difference	15.643	15.633	16.041	16.158	15.66	15.643	17.075	17.1
B. T. U..............	617.1	619.2	615.9	617.6	616.2	618.7	614.6	614.1

SIMMANCE-ABADY.—SERIES S.

	1a	1b	2b	3a	3b	4a	4b
Barometer.............	29.38	29.38	29.38	29.38	29.38	29.38	29.38
Temperature of Gas....	68.7	68.7	68.6	69.6	69.6	69.6	69.6
Correction Factor.......	.9569	.9569	.9569	.9569	.9569	.9569	.9569
Temperature Room.....	70.0	70.0	70.2	70.1	70.1	70.2	70.2
Temperature Exhaust...	70.0	70.0	69.0	70.0	70.0	70.0	70.0
Rate of Gas Cu. Ft. Hr.	2.9	2.9	4.0	4.9	4.9	6.07	6.07
Gas Consumed Cu. Ft..	.2	.2	.2	.2	.2	.2	.2
Water Heated—Lbs....	7.5507	7.5706	7.5618	7.8969	7.8991	6.9996	6.9798
Inlet Temperature......	65.142	65.142	65.042	65.042	64.962	64.942	64.942
Outlet Temperature....	80.506	80.35	80.482	79.93	79.754	81.553	81.651
Difference.............	15.364	15.208	15.360	14.888	14.792	16.611	16.709
B. T. U...............	606.2	601.6	607.6	615.9	612.1	609.1	610.9

Regular Junkers burner without spreader was used in place of Simmance-Abady bunsen. Burner rest was removed and new burner held in place on block of wood so that top of burner entered instrument same distance as regular burner. All tests made after adjusting damper in exhaust to give maximum reading on outlet water thermometer.

SIMMANCE-ABADY.—SERIES S. (Continued.)

	5a	**5b**	**6a**	**6b**	**7a**	**7b**
Barometer................	29.38	29.38	29.38	29.38	29.38	29.38
Temperature of Gas.......	69.6	69.6	69.6	69.6	69.6	69.6
Correction Factor.........	.9545	.9545	.9545	.9545	.9545	.9545
Temperature Exhaust	70.0	70.2	70.0	70.2	70.0	70.0
Rate of Gas Cu. Ft. Hour..	7.0	7.0	8.0	8.0	8.95	8.95
Gas Consumed Cu. Ft......	.2	.2	.2	.2	.2	.2
Water Heated—Lbs.......	7.5948	7.6015	7.2509	7.220	7.0746	7.0768
Inlet Temperature.........	64.892	64.892	64.841	64.841	64.731	64.69
Outlet Temperature	80.323	80.272	81.01	81.122	81.125	81.173
Difference................	15.431	15.380	16.169	16.281	16.484	16.483
B. T. U	613.9	612.4	614.1	615.7	610.9	611.0

SIMMANCE-ABADY.—SERIES U.

	1	2	3	4	
Room Temperature......	67.5	67.5	67.5	67.5	
Exhaust Temperature....	68.5	68.5	69.	69.	
Water Heated Grams.....	3532.	3521.	2149.	2159.	
Inlet Temperature "F"...	64.391	64.512	64.891	64.901	
Outlet Temperature "F"..	74.403	74.522	80.82	80.953	
Difference "C"	5.562	5.561	8.849	8.918	
Time of Test, Seconds....	120.	120.	120.	120.	
Volts	93.63	93.41	93.186	93.15	
Amperes.................	6.8553	6.8436	6.83	6.83	
Small Calories put in.....	18385.488	18311.518	18246.771	18223.728	
Small Calories observed...	19644.984	19680.281	19016.501	19253.962	
Efficiency...............	106.8	107.4	104.2	105.6	106.0

Oct. 9, 1908

APPENDIX E.

Order of Cuts

Fig. 1—General view of Junker's Calorimeter, with accessories.

Fig. 2—Junker's Calorimeter—Sectional views and elevation.

Fig. 3—Boys' Calorimeter—Sectional view.

Fig. 4—Simmance-Abady Calorimeter—Sectional views.

Fig. 5—General view of final Sargent Calorimeter, with accessories.

Fig. 6—The first Sargent Calorimeter—Sectional views and elevation.

Fig. 7—The first Sargent Calorimeter—Sectional view.

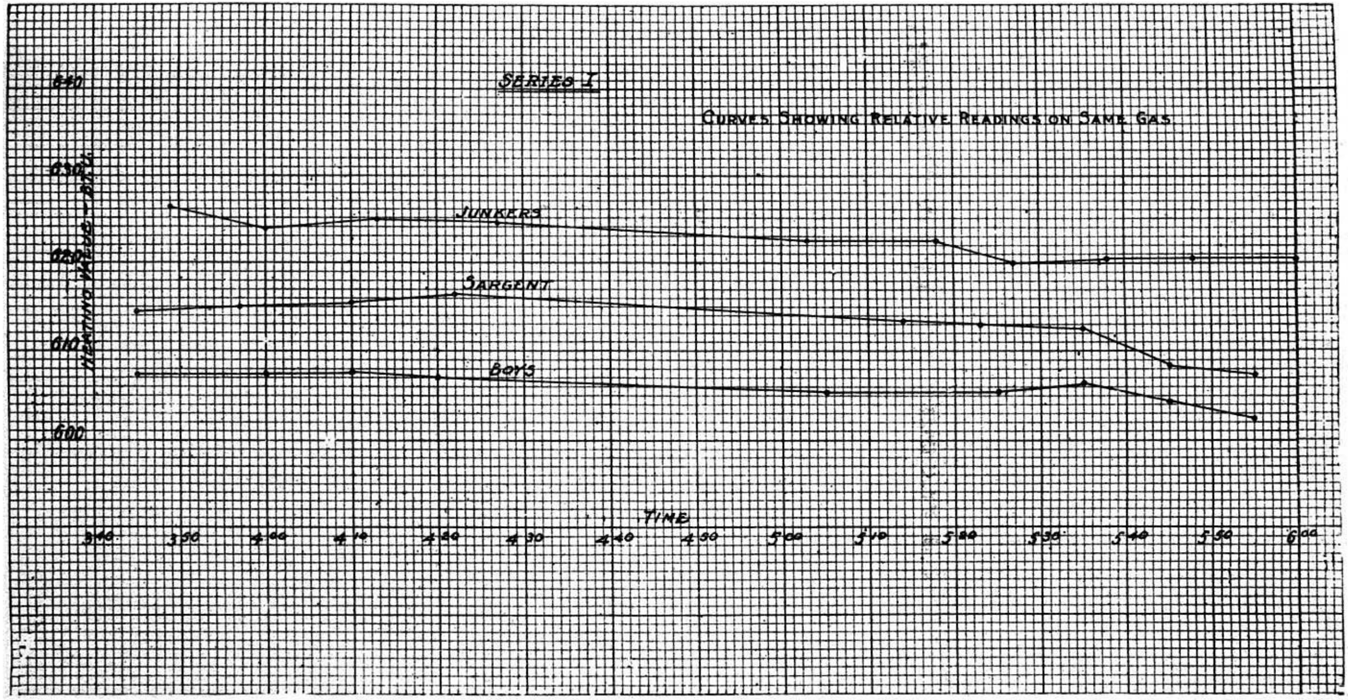
Fig. 8—Electric heater used in efficiency tests.

Fig. 9—General view of modified Junker's Calorimeter, with accessories. Laboratory of Milwaukee Gas Light Co.

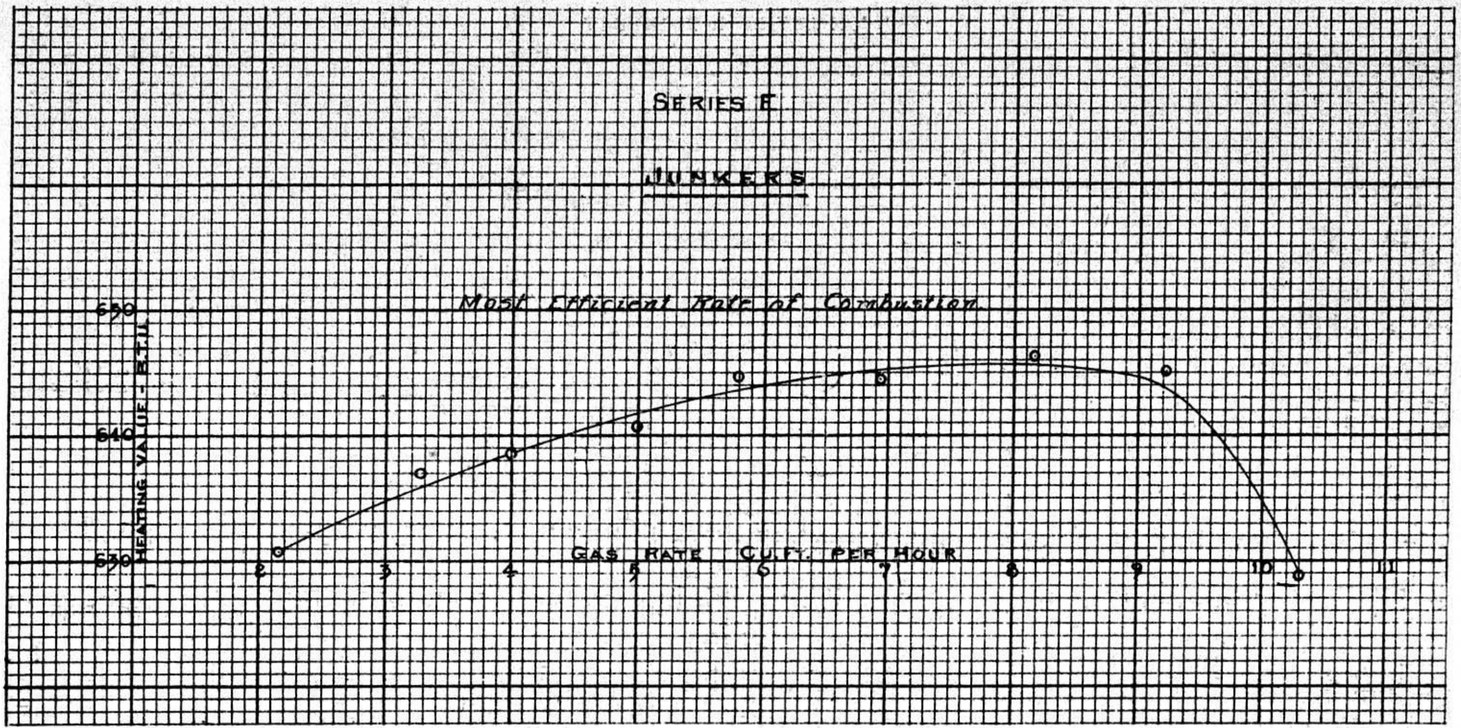
Fig. 14—Heating value computer—For calculating the corrected heating value of a gas from calorimeter readings.

Fig. 15—Correction factors for temperature and pressure.

Fig. 16—Curves showing Percentage of Relative Humidity from Wet and Dry Bulb Thermometer Readings.



APPENDIX E—CHART NO. 1.



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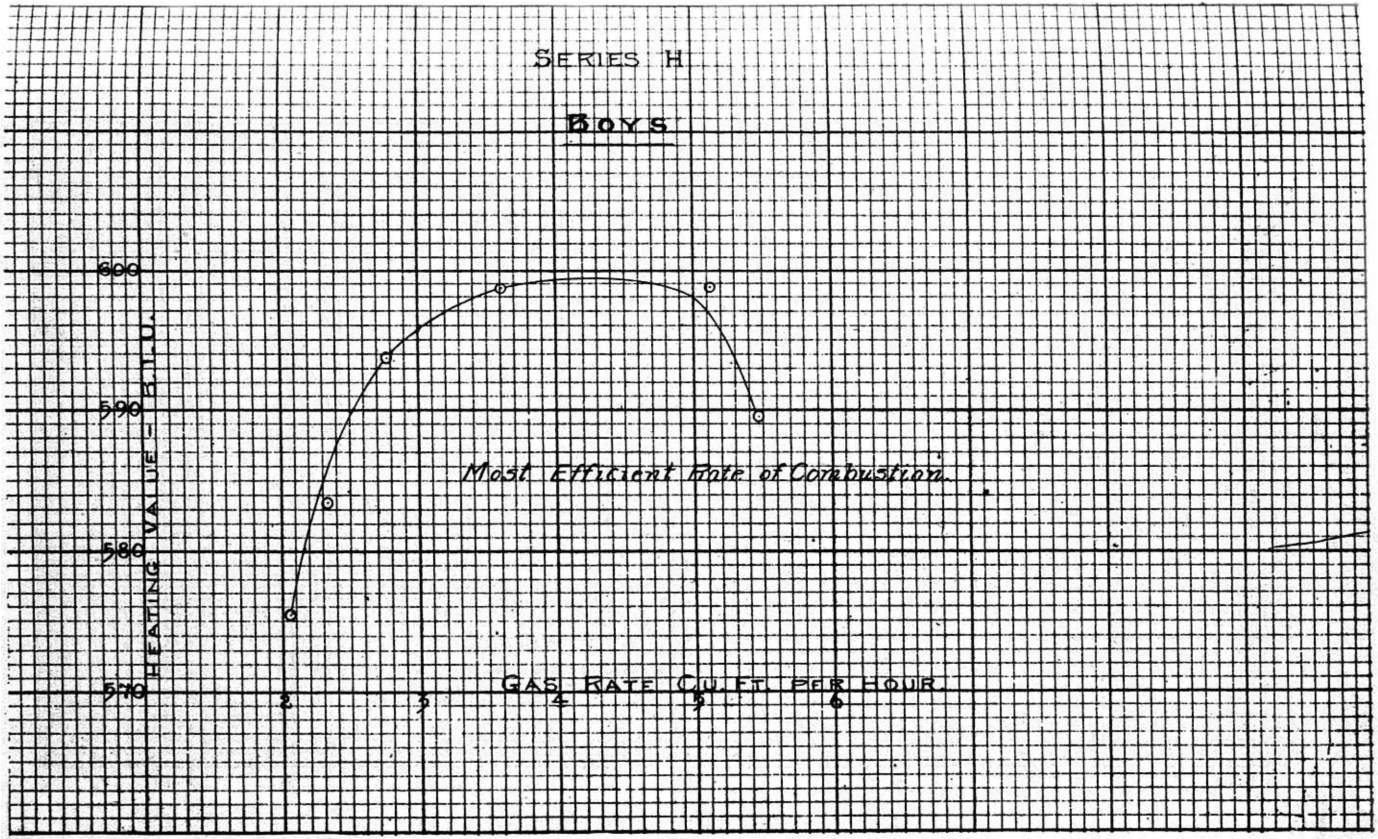

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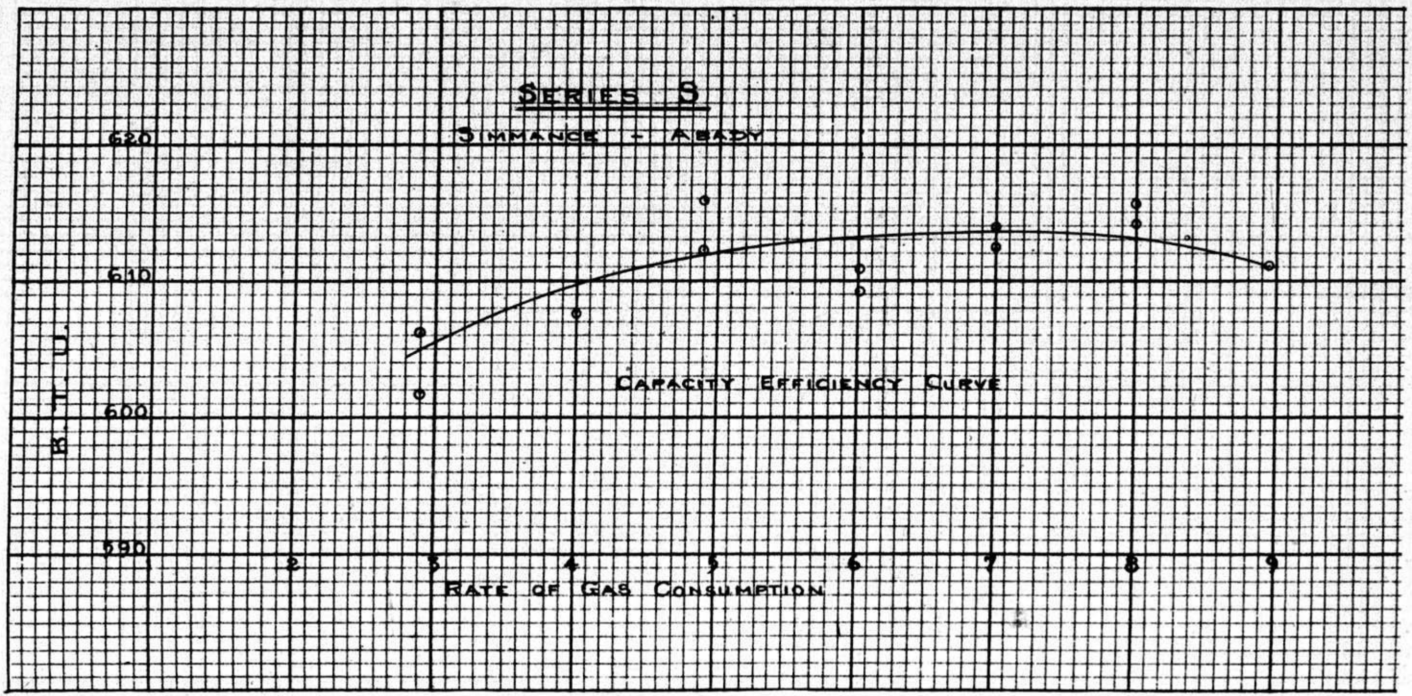

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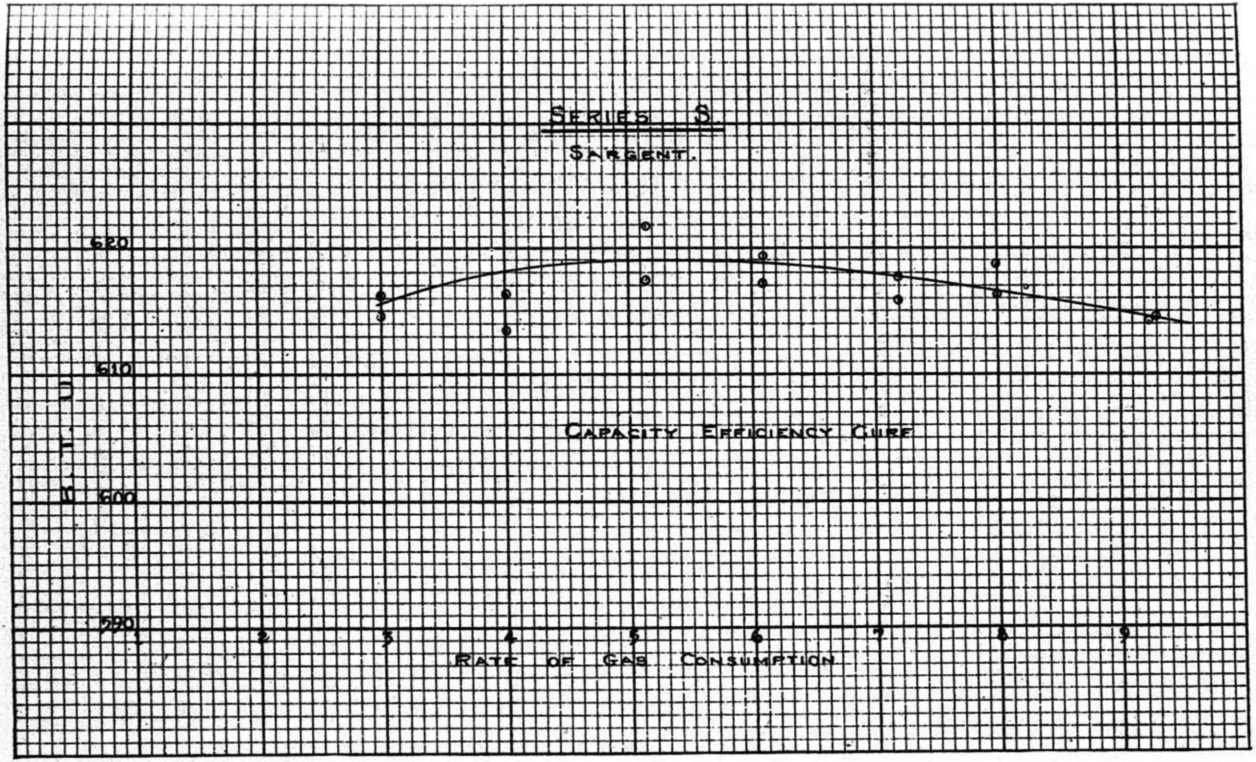

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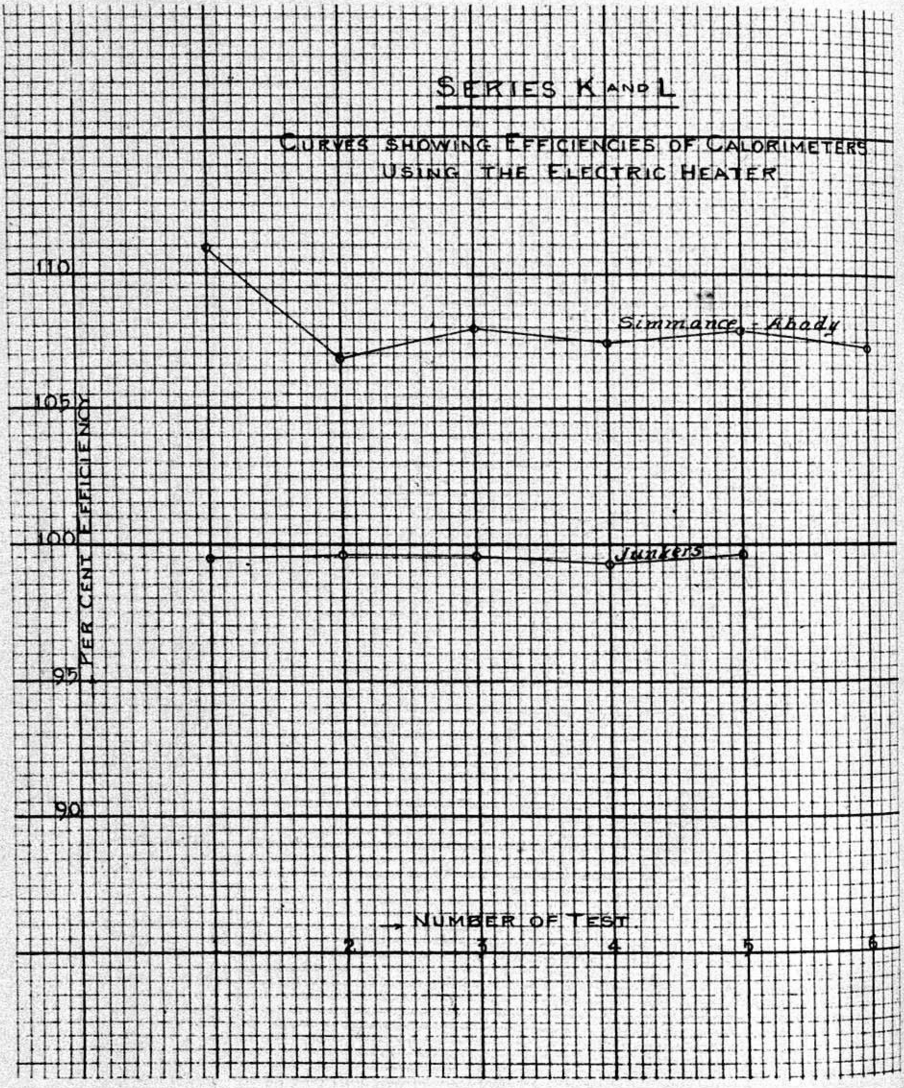

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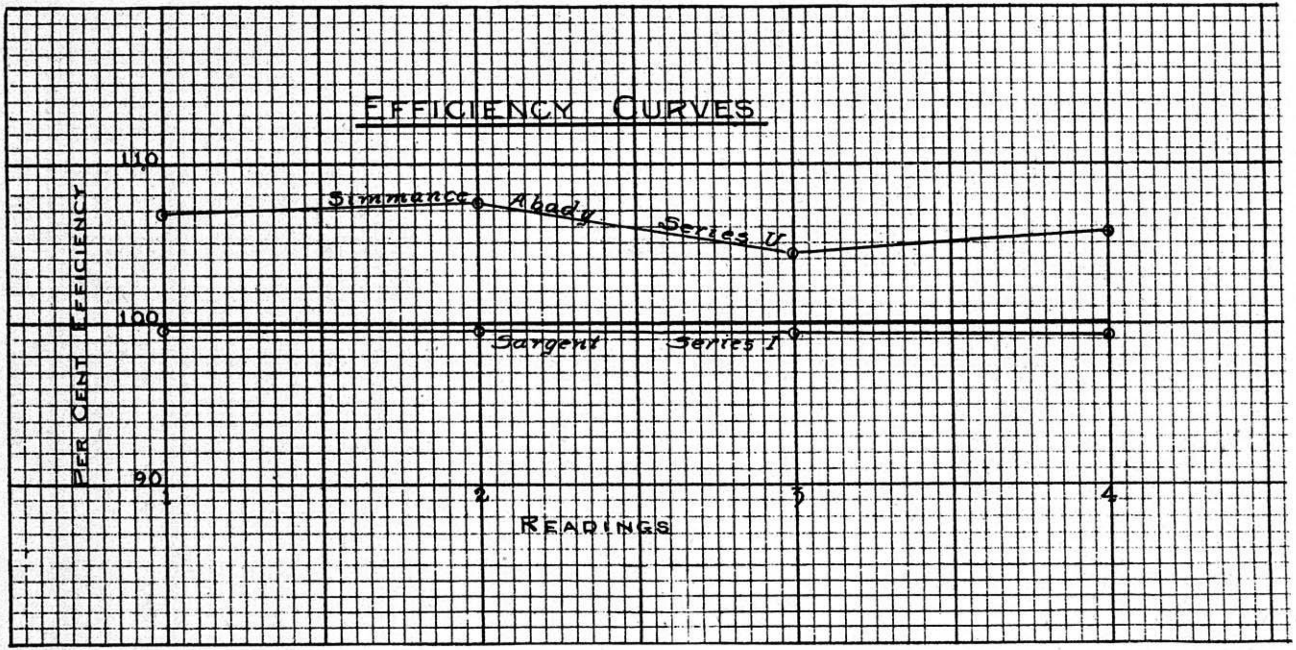

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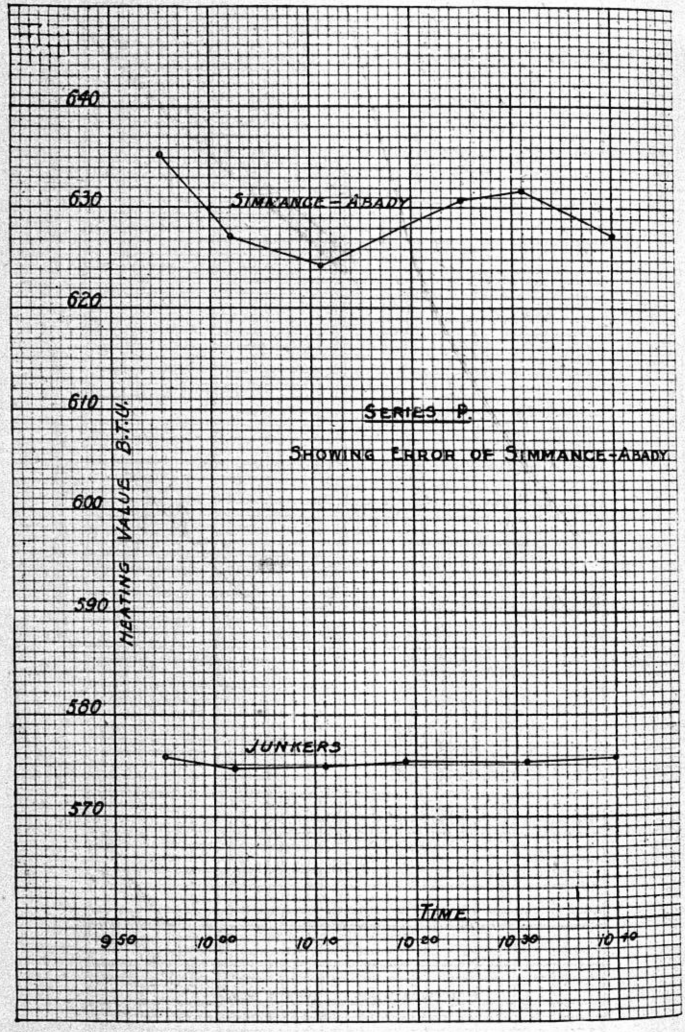

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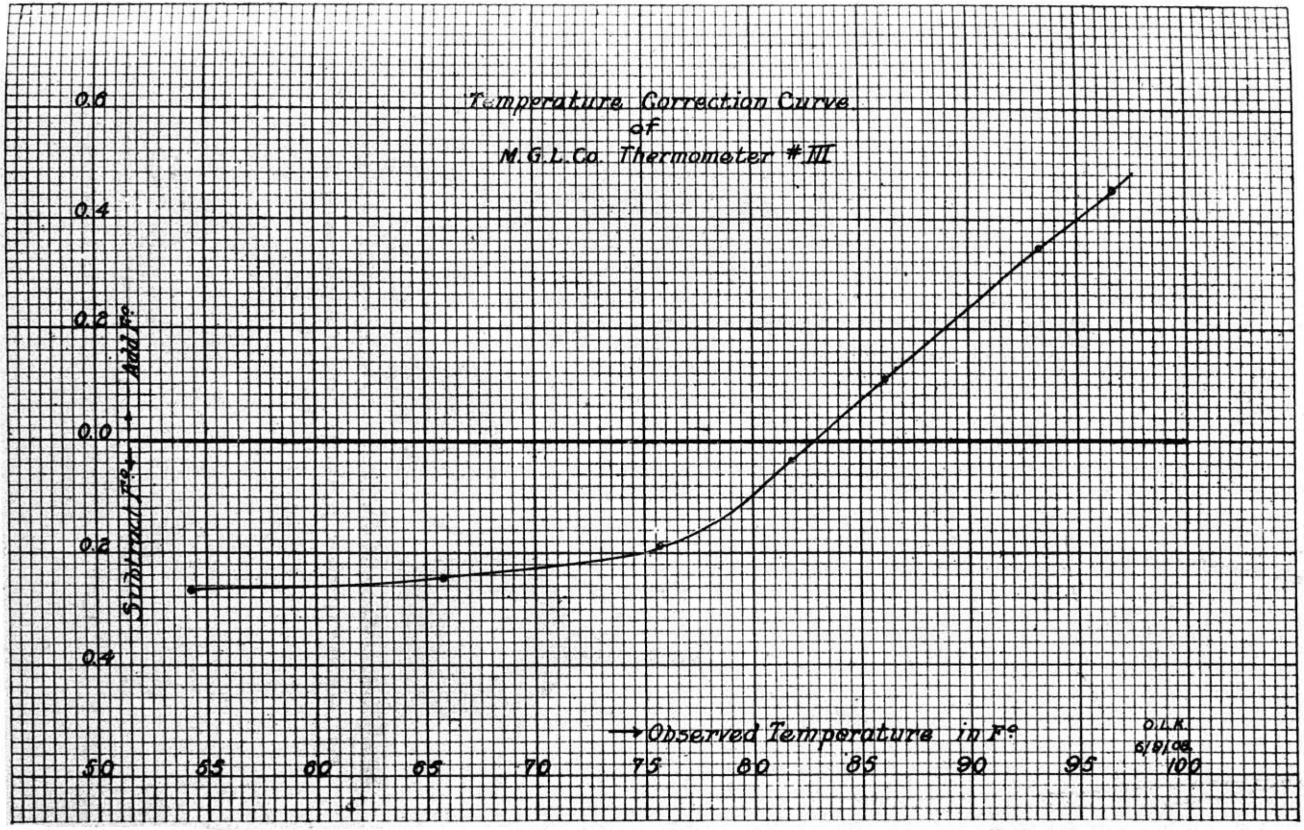

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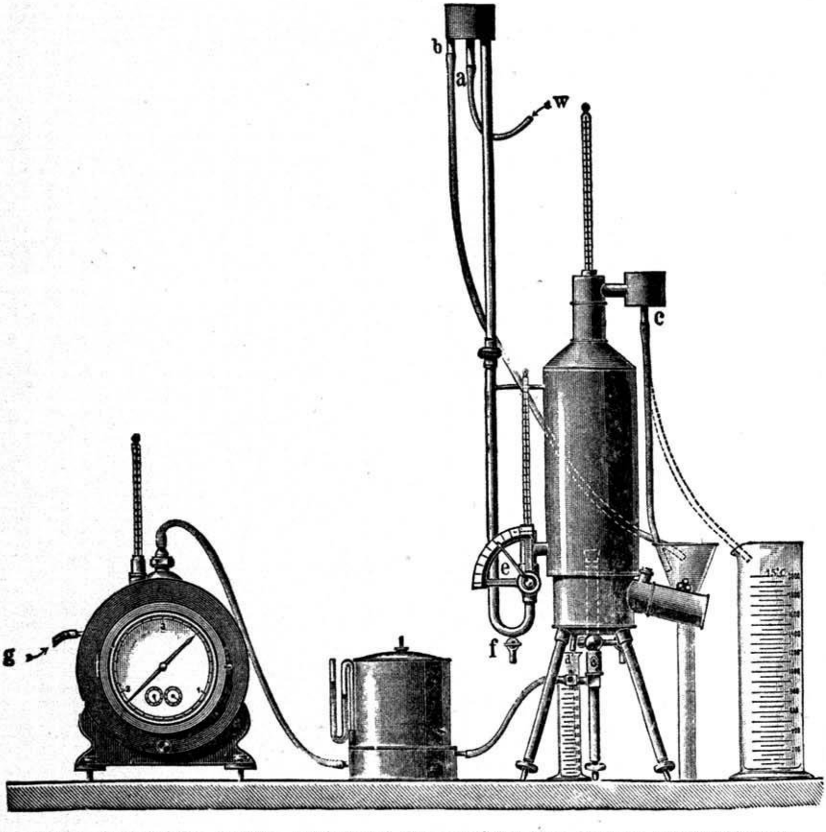


FIG. 1—GENERAL VIEW, JUNKERS CALORIMETER, WITH ACCESSORIES. APPENDIX E.

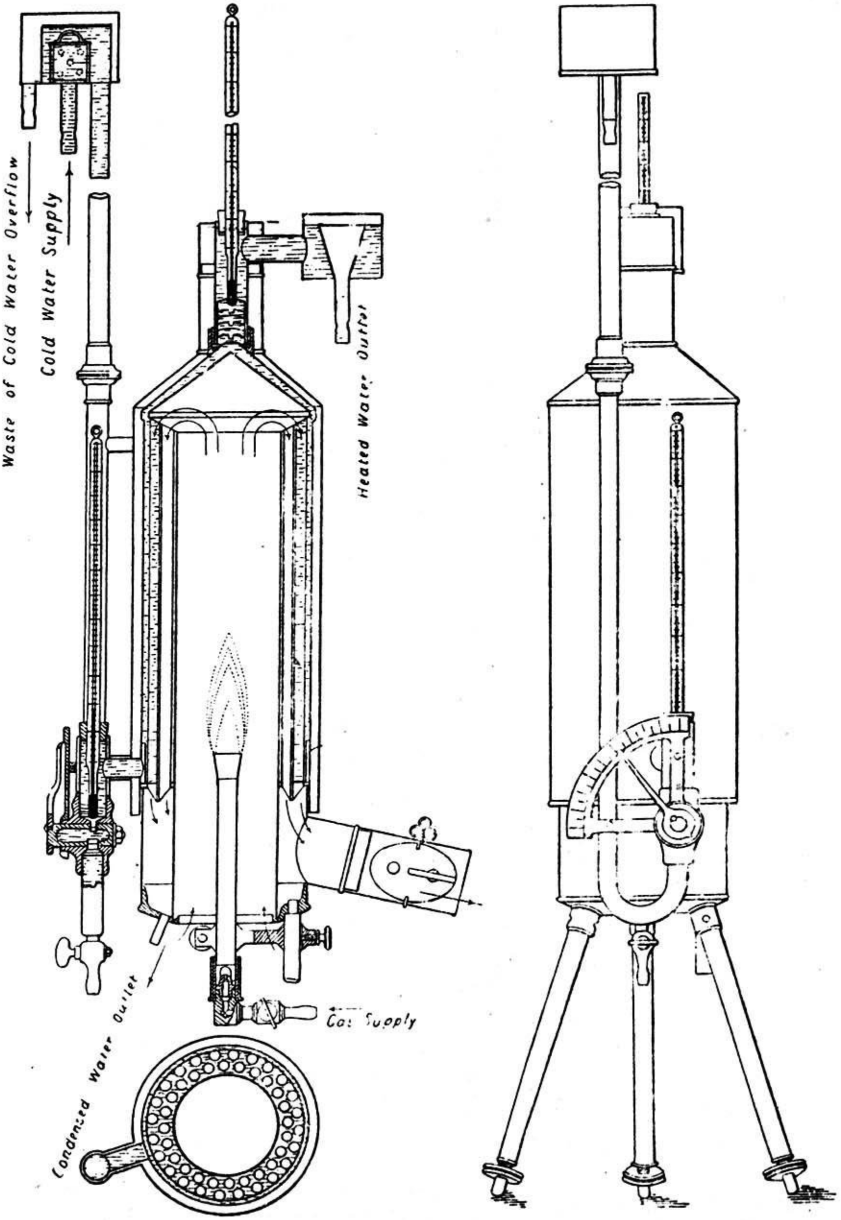


FIG. 2—JUNKERS CALORIMETER. SECTIONAL VIEWS AND ELEVATION. APPENDIX E.

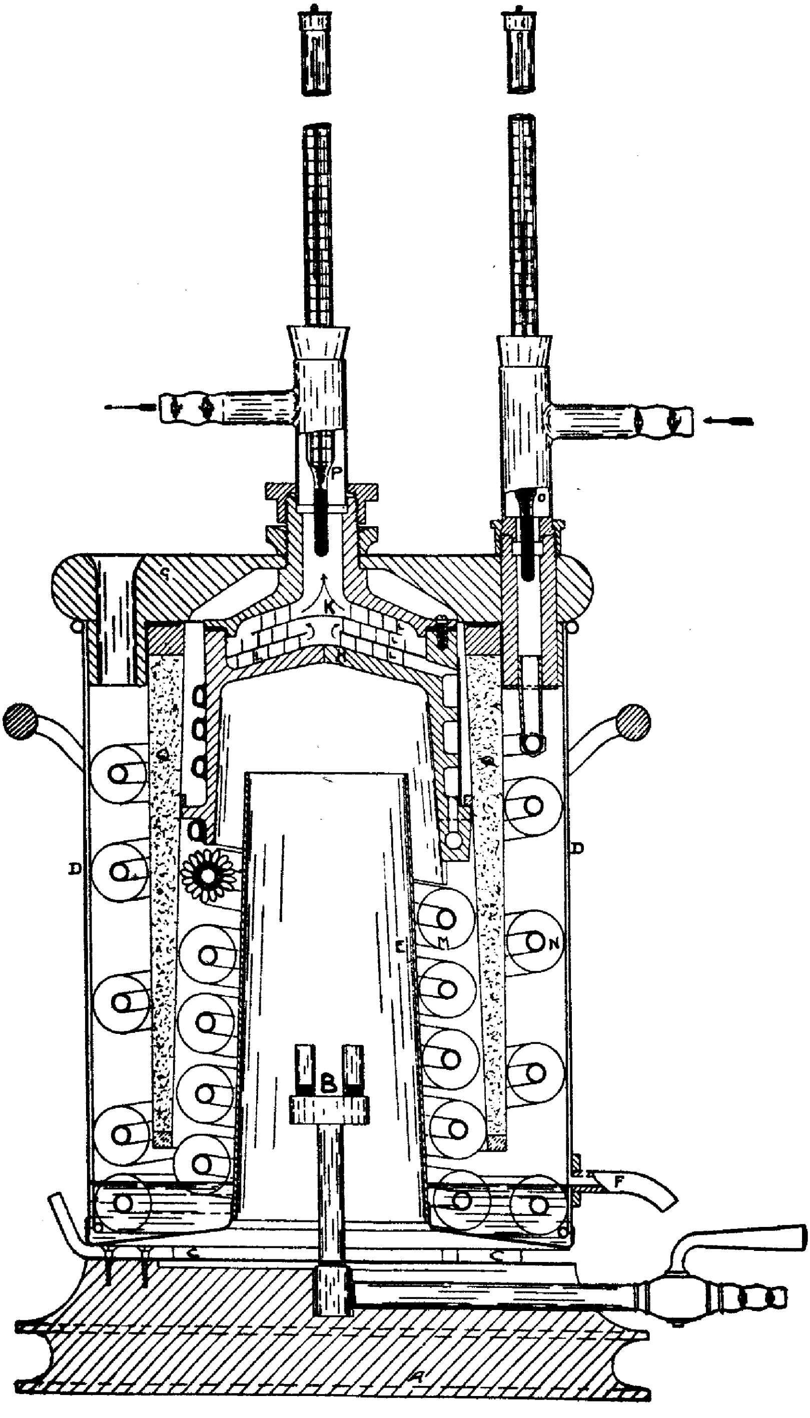


Fig. 3—BOYS CALORIMETER. SECTIONAL VIEW.
APPENDIX E.

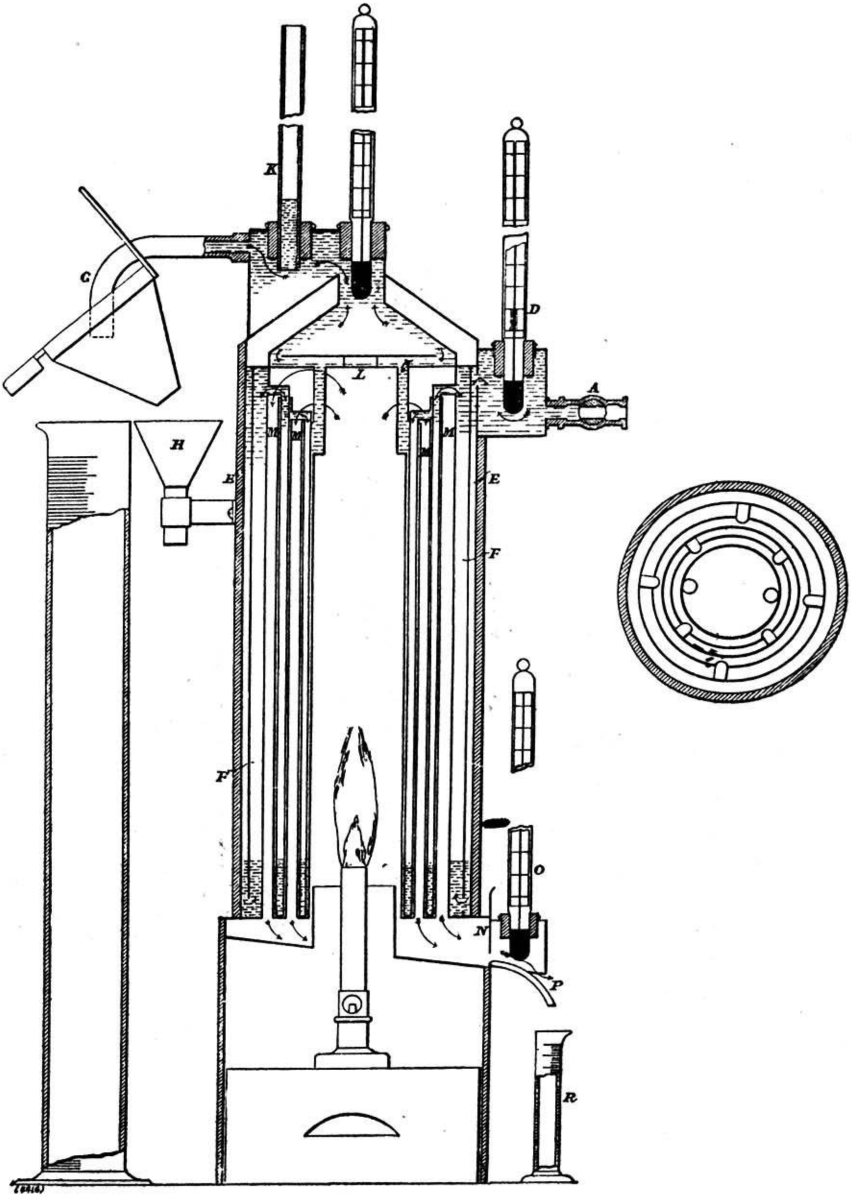


FIG. 4—SIMMANCE-ABADY CALORIMETER. SECTIONAL VIEWS. APPENDIX E.

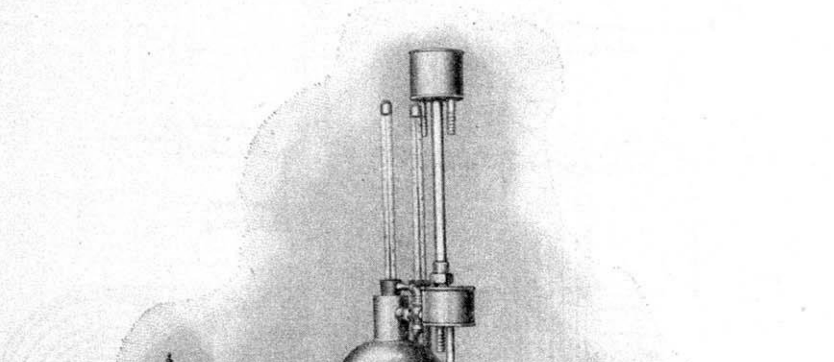


FIG. 5—THE FINAL SARGENT CALORIMETER, WITH ACCESSORIES. APPENDIX E.

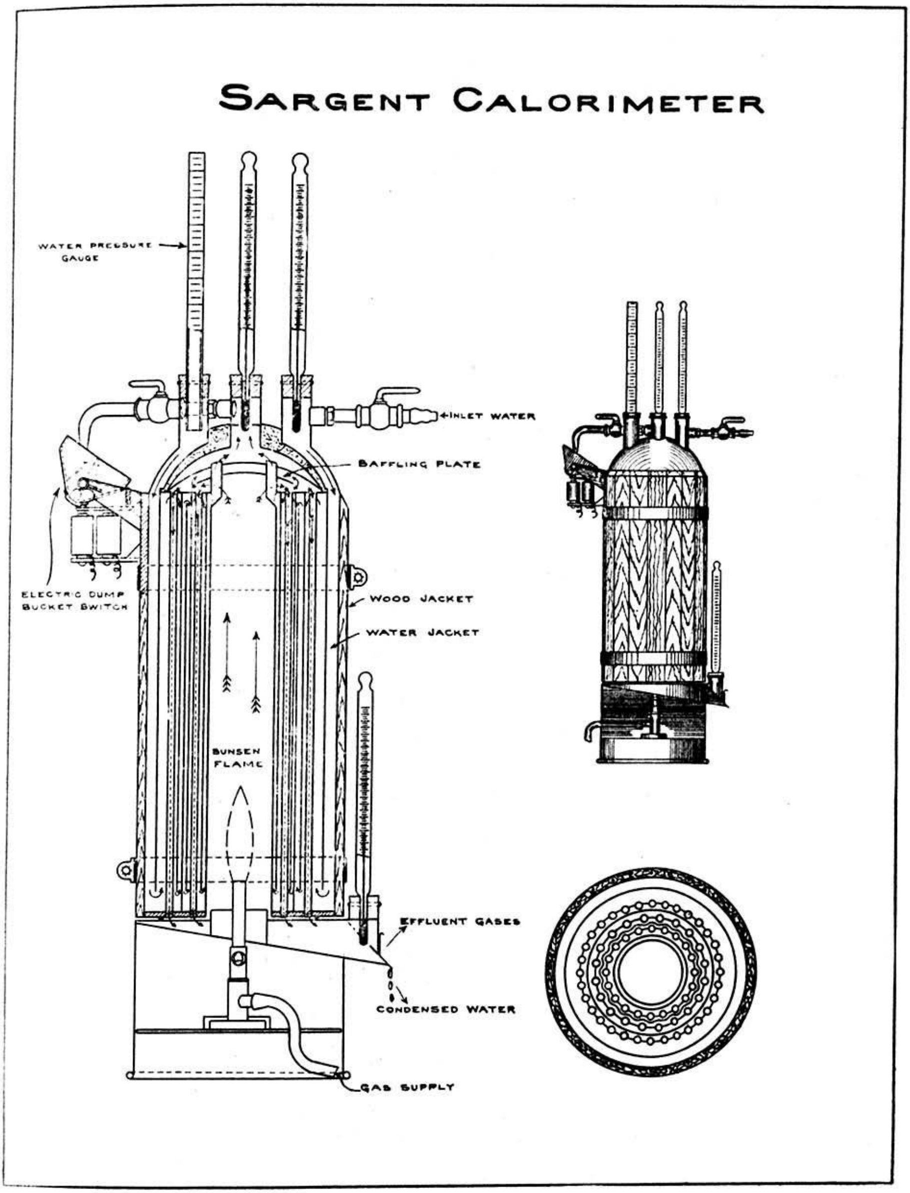


FIG. 6—FIRST SARGENT CALORIMETER. SECTIONAL VIEWS AND ELEVATION.
APPENDIX E.

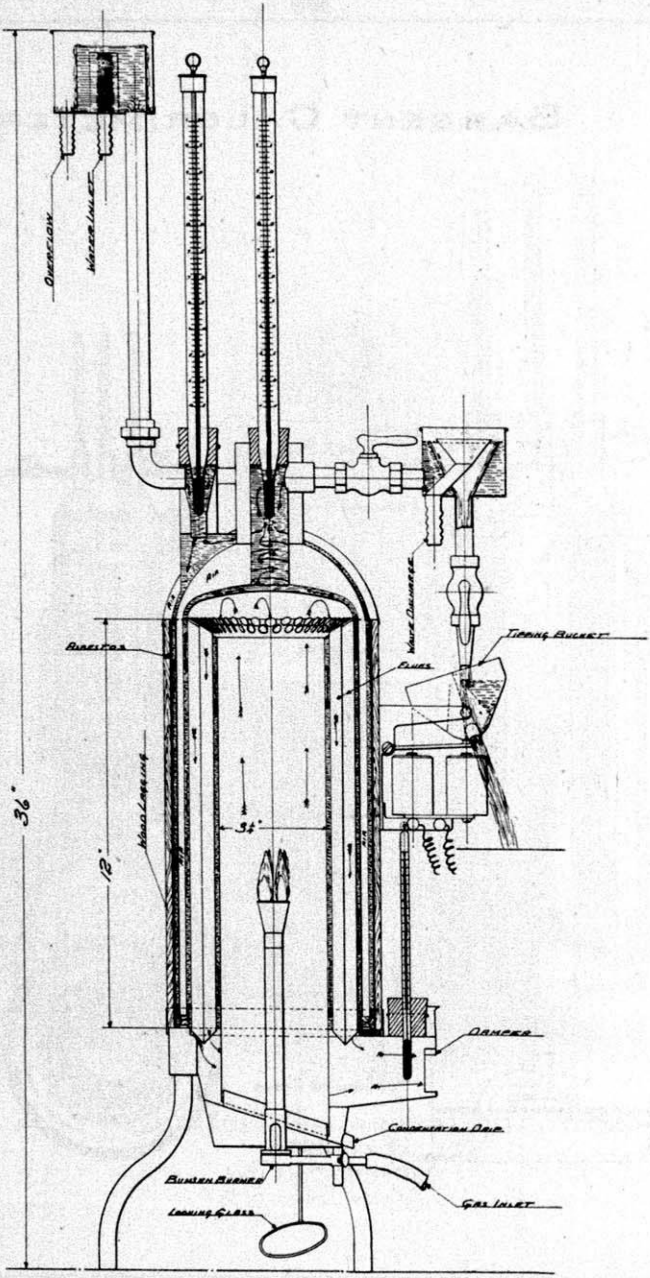


FIG. 7—THE FINAL SARGENT CALORIMETER. SECTIONAL VIEW. APPENDIX E.

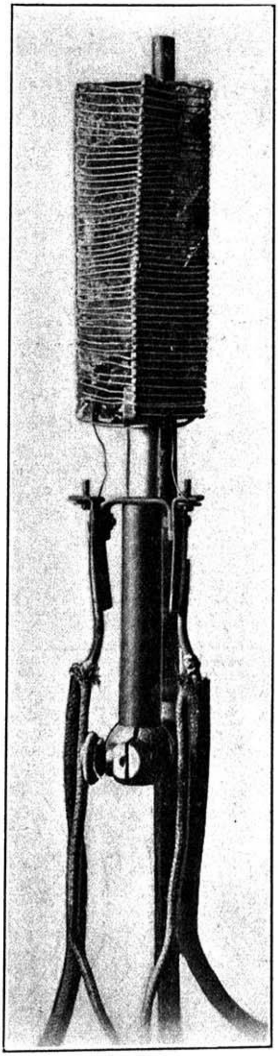


Fig. 8—ELECTRIC HEATER. USED IN EFFICIENCY TESTS. APPENDIX E.

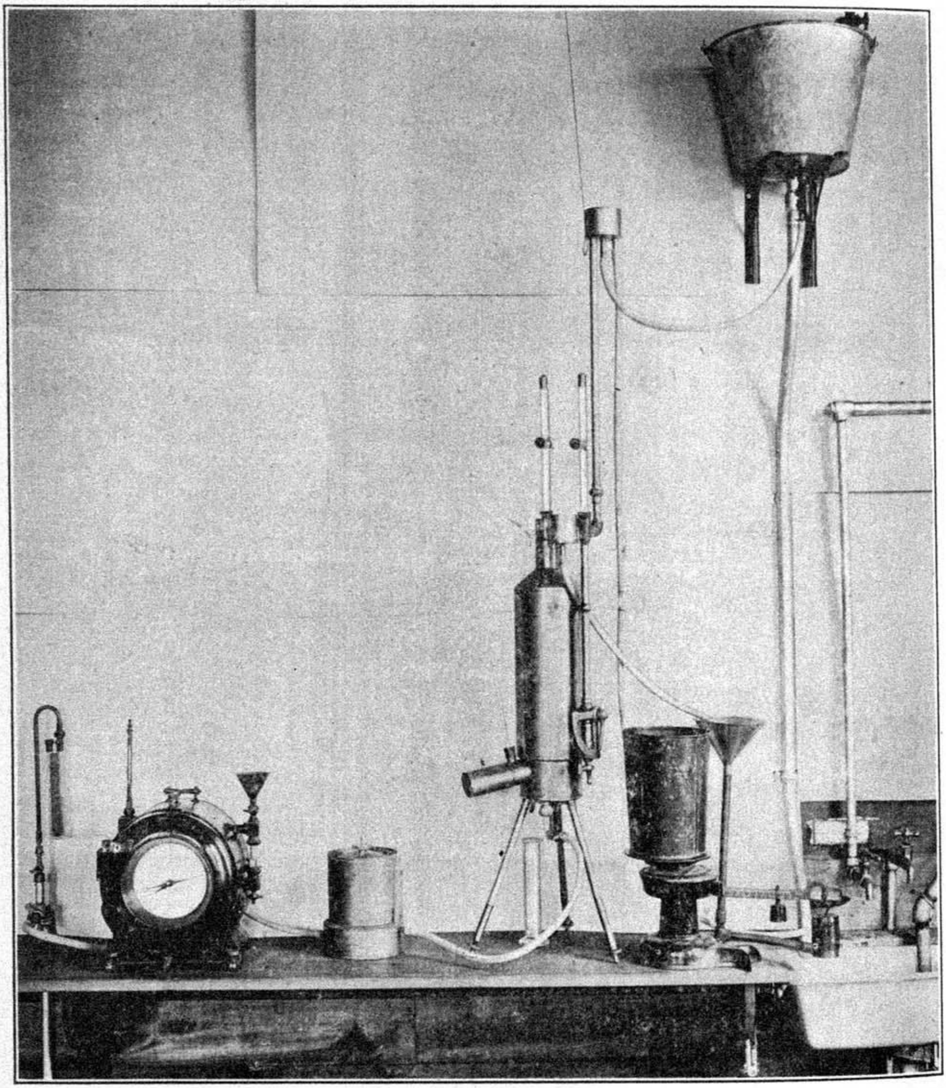


FIG. 9—GENERAL VIEW OF MODIFIED JUNKERS CALORIMETER, WITH ACCESSORIES. LABORATORY OF MILWAUKEE GAS LIGHT COMPANY. APPENDIX E.

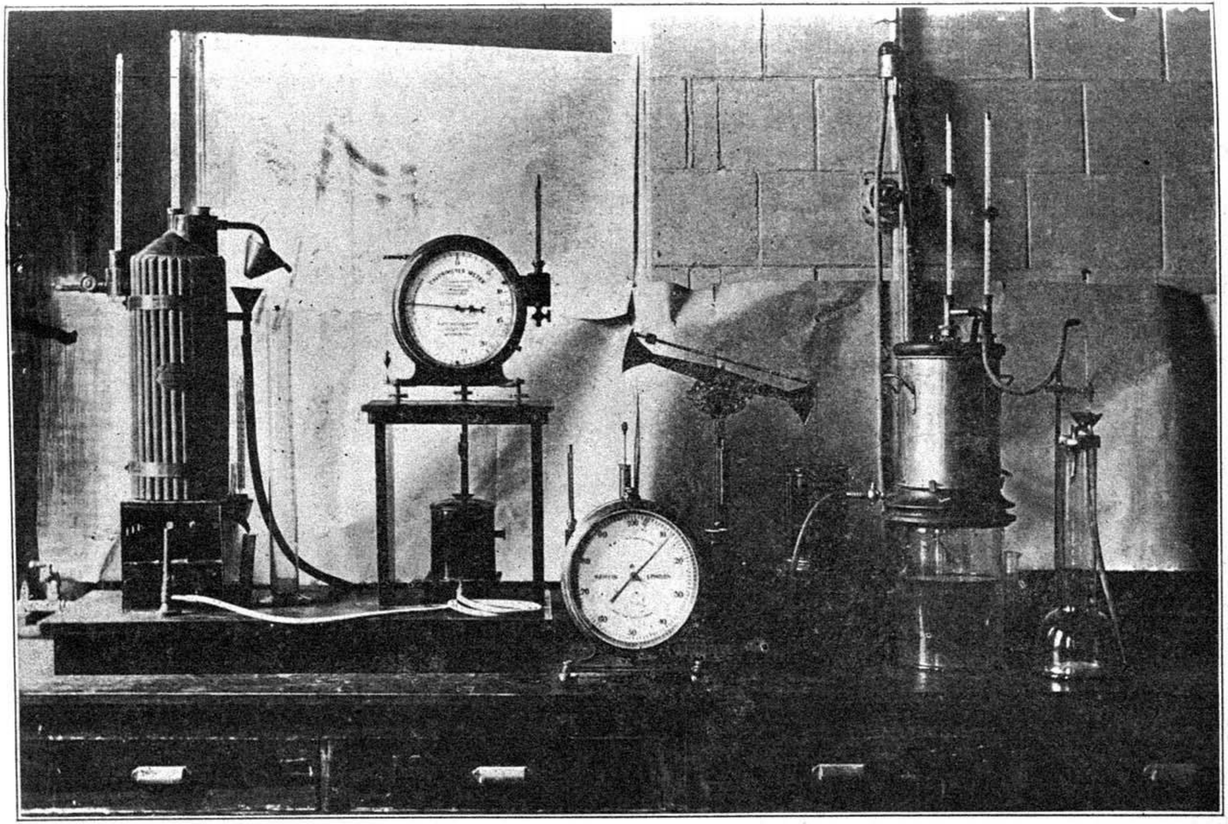


FIG. 10—APPENDIX E—GENERAL VIEW OF SIMMANCE-ABADY AND BOYS CALORIMETERS, WITH ACCESSORIES.

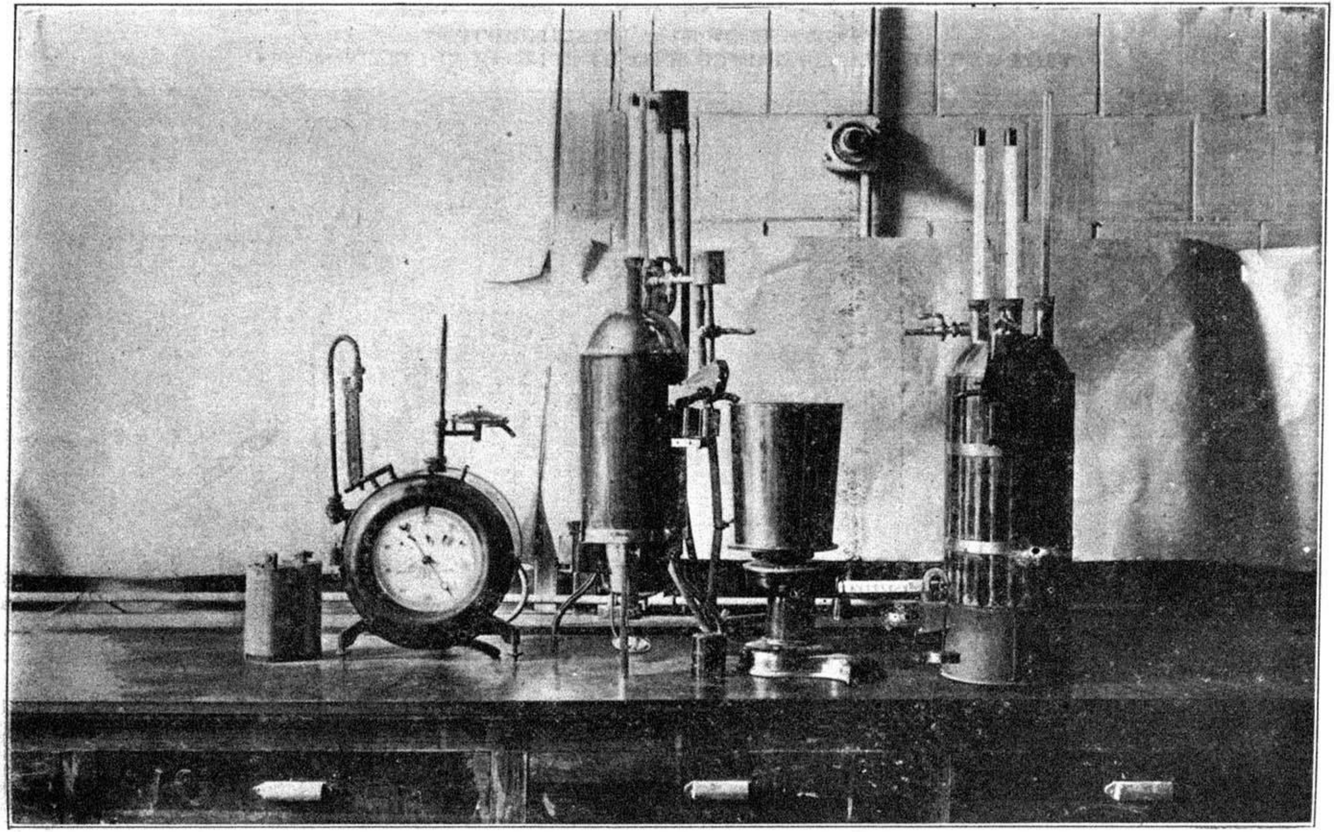


FIG. 11—APPENDIX E—GENERAL VIEW OF SARGENT CALORIMETERS, NEW AND OLD, WITH ACCESSORIES, SHOWING WATER WEIGHING APPARATUS.

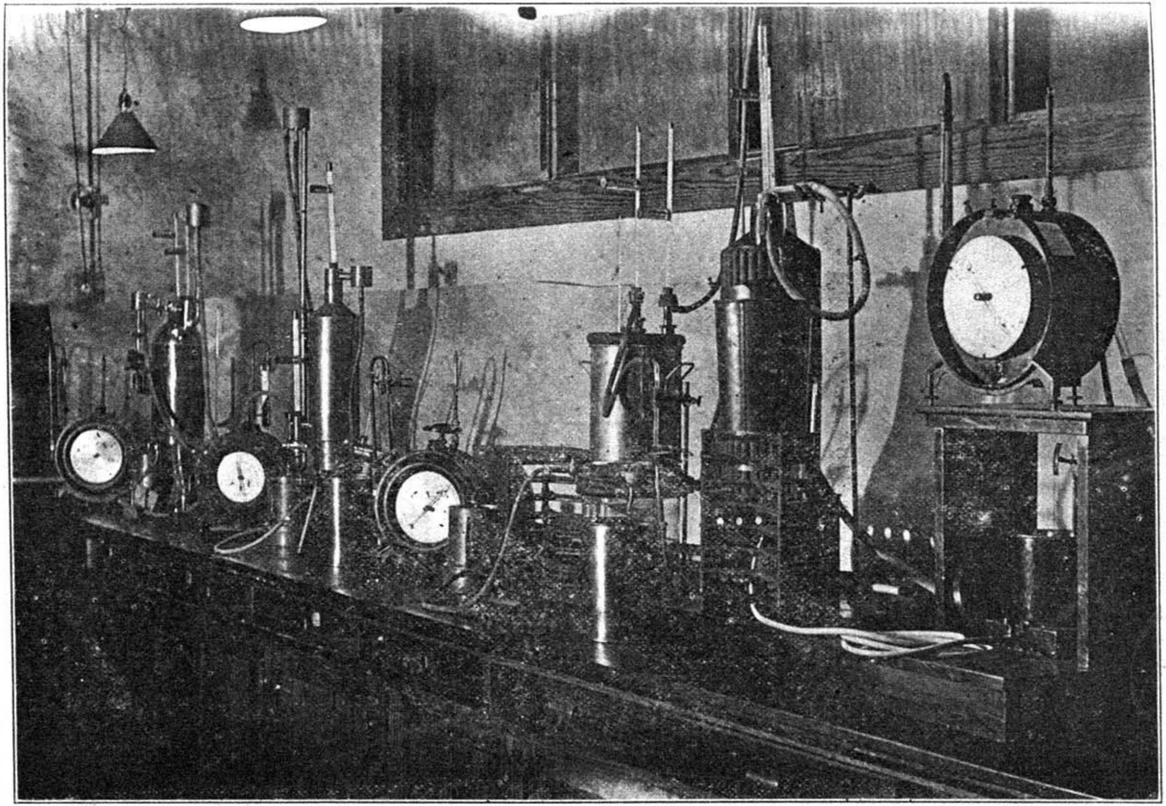


FIG. 12—APPENDIX E—GENERAL VIEW OF CALORIMETERS AS CONNECTED FOR COMPARATIVE TESTS AT LABORATORIES OF UNIVERSITY OF WISCONSIN.

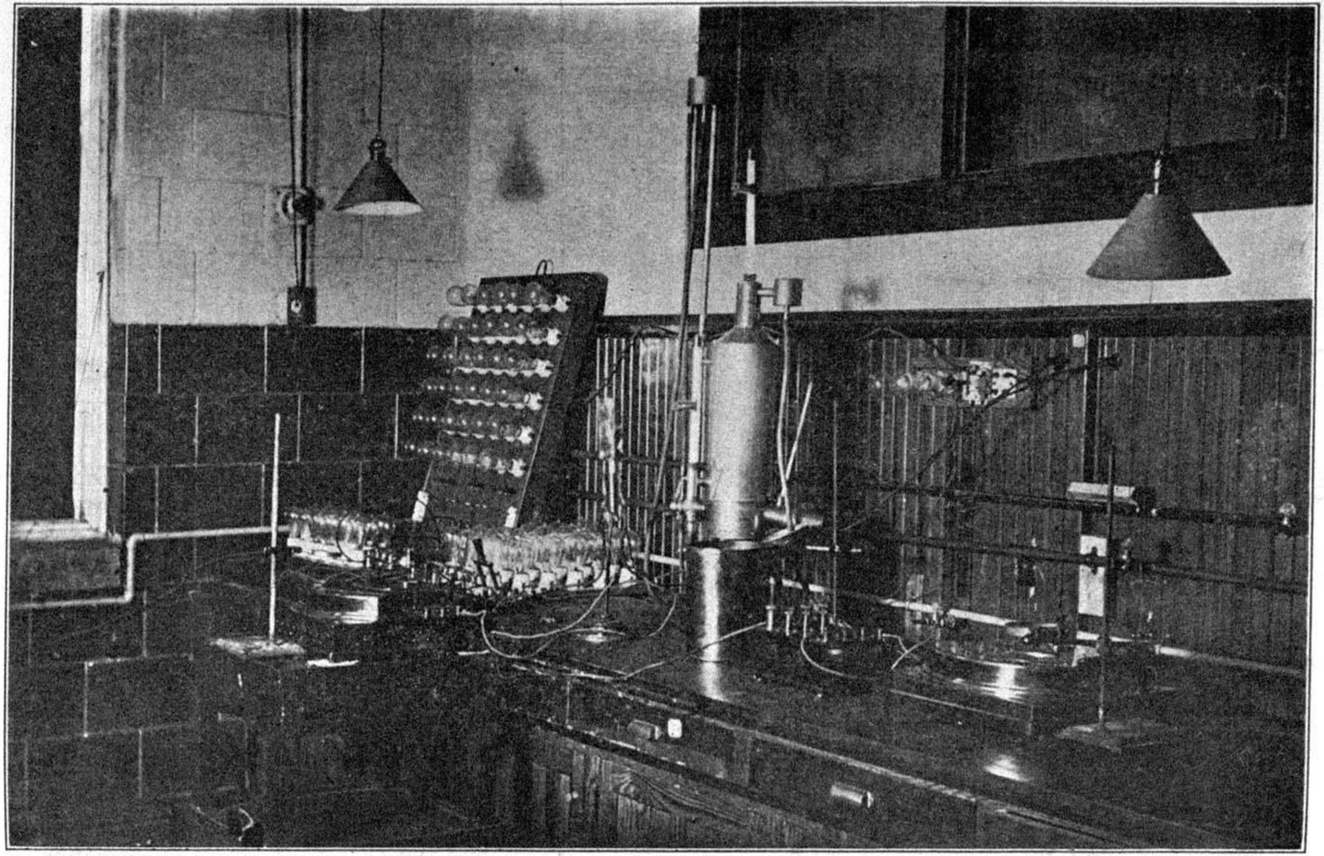
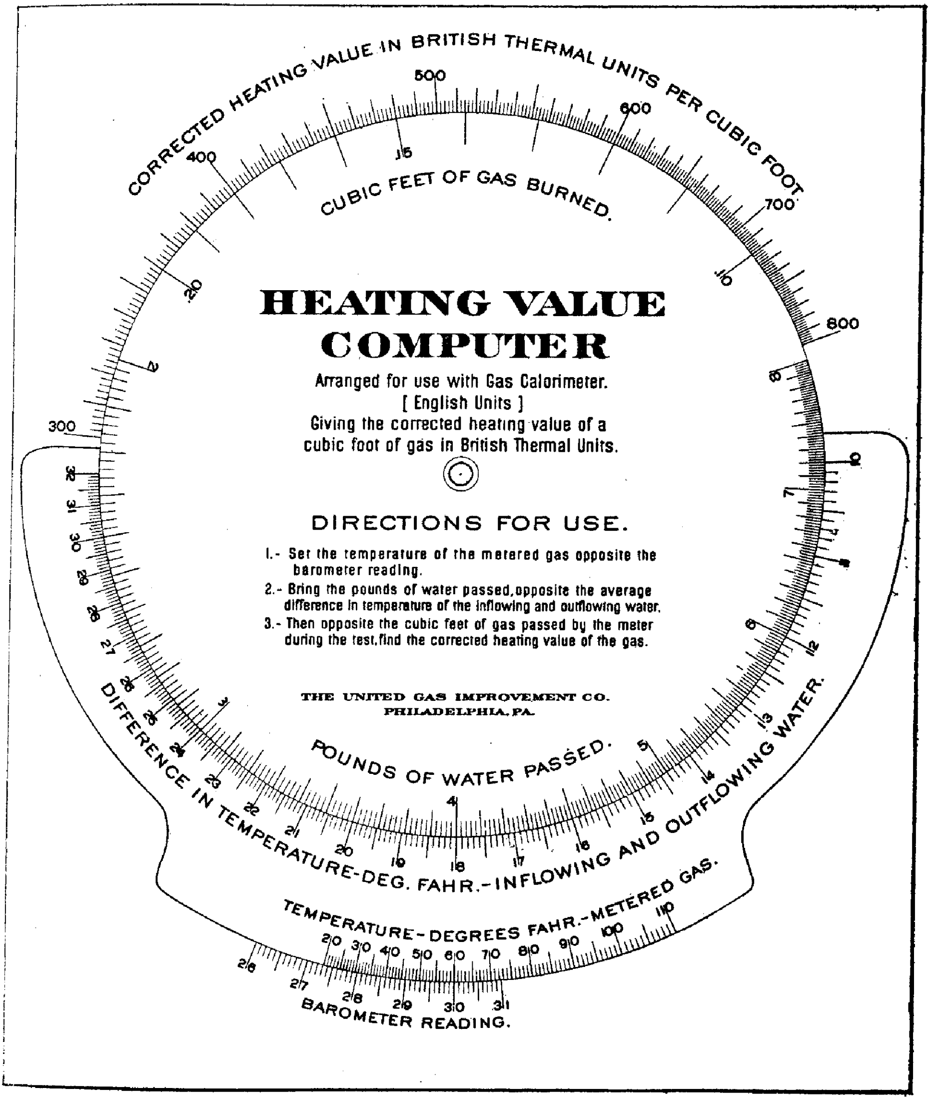


FIG. 13—APPENDIX E—JUNKERS CALORIMETER EQUIPPED WITH ELECTRIC HEATER FOR EFFICIENCY TESTS.



Arranged for use with Gas Calorimeter.
[English Units]
Giving the corrected heating value of a
cubic foot of gas in British Thermal Units.

DIRECTIONS FOR USE.

1.- Set the temperature of the metered gas opposite the barometer reading.

2.- Bring the pounds of water passed, opposite the average difference in temperature of the inflowing and outflowing water.

3.- Then opposite the cubic feet of gas passed by the meter during the test, find the corrected heating value of the gas.

THE UNITED GAS IMPROVEMENT CO.
PHILADELPHIA, PA.

FIG. 14—HEATING VALUE COMPUTER. FOR CALCULATING THE CORRECTED HEATING VALUE OF A GAS FROM CALORIMETER READINGS. APPENDIX E.

APPENDIX F.

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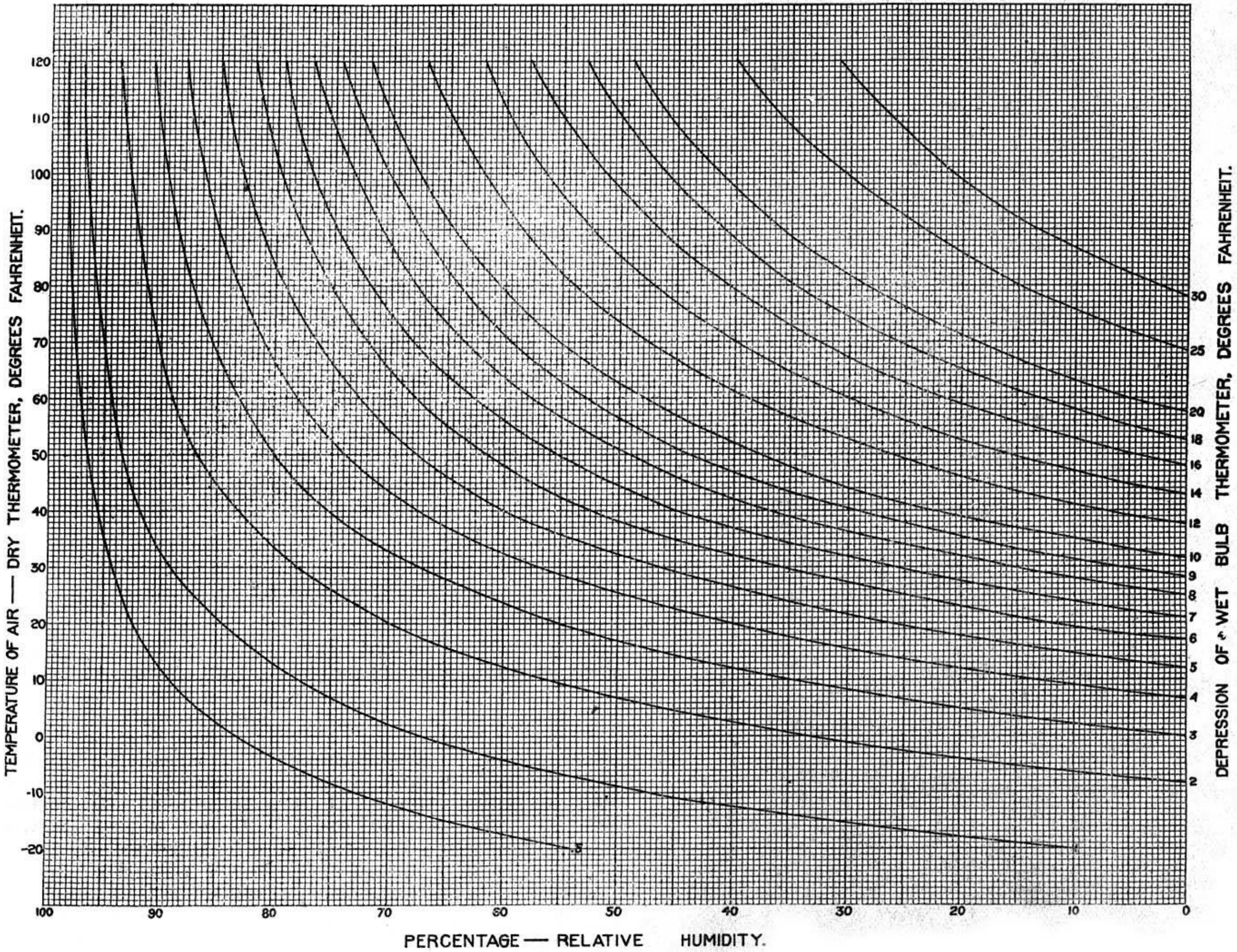
CORRECTION FACTORS FOR TEMPERATURE AND PRESSURE

TEMPERATURE	BAROMETER																			
	28.6	28 7	28.8	28.9	29.0	29.1	29.2	29.3	29.4	29.5	29.6	29.7	29.8	29.9	30.0	30.1	30.2	30.3	30.4	30.5
95	.857	.860	.863	.866	.870	.873	.876	.879	.882	.885	.889	.892	.895	.898	.901	.904	.908	.911	.914	.918
94	.860	.863	.866	.869	.873	.876	.879	.882	.885	.888	.892	.895	.898	.901	.904	.907	.911	.914	.918	.921
93	.863	.866	.869	.872	.876	.879	.883	.886	.889	.891	.895	.898	.901	.904	.907	.910	.914	.918	.921	.924
92	.866	.869	.872	.875	.879	.882	.885	.889	.892	.894	.898	.902	.904	.907	.910	.914	.917	.921	.924	.928
91	.869	.872	.875	.879	.882	.885	.889	.892	.895	.898	.902	.905	.908	.911	.914	.917	.921	.924	.928	.931
90	.872	.875	.878	.881	.885	.888	.892	.895	.898	.901	.905	.908	.911	.914	.917	.920	.924	.927	.931	.934
89	.875	.878	.882	.885	.889	.892	.895	.898	.901	.904	.907	.910	.914	.917	.920	.923	.927	.931	.934	.937
88	.878	.881	.885	.888	.892	.895	.898	.901	.904	.907	.910	.913	.917	.920	.923	.926	.930	.934	.937	.940
87	.881	.884	.888	.891	.895	.898	.901	.904	.907	.910	.913	.916	.920	.923	.926	.929	.933	.937	.940	.943
86	.884	.887	.890	.894	.898	.901	.904	.907	.910	.913	.916	.919	.923	.926	.929	.932	.936	.940	.943	.946
85	.887	.890	.893	.896	.900	.903	.906	.909	.913	.916	.919	.922	.926	.929	.932	.936	.939	.943	.946	.949
84	889	.893	.896	.899	.903	.906	.909	.912	.915	.919	.922	.925	.928	.932	.935	.939	.942	.946	.949	.952
83	.892	.895	.899	.902	.906	.909	.912	.915	.918	.921	.924	.928	.931	.935	.938	.942	.945	.949	.952	.955
82	.895	.898	.901	.905	.908	.911	.914	.918	.921	.924	.927	.931	.934	.937	.941	.945	.948	.951	.954	.958
81	.898	.901	.905	.908	.911	.914	.917	.921	.924	.927	.930	.934	.937	.940	.944	.948	.951	.954	.957	.960
80	.901	.904	.907	.910	.914	.917	.920	.923	.927	.930	.933	.937	.940	.943	.946	.950	.954	.957	.960	.963
79	.904	.907	.910	.914	.917	.920	.923	.926	.930	.933	.936	.939	.943	.946	.949	.953	.956	.960	.963	.967
78	.906	.909	.913	.916	.919	.923	.926	.929	.932	.936	.939	.942	.946	.949	.952	.956	.959	.962	.966	.969
77	.909	.912	.915	.919	.922	.925	.928	.931	.935	.938	.942	.945	.948	.951	.955	.958	.962	.965	.968	.972
76	.911	.915	.918	.921	.925	.928	.931	.935	.938	.941	.944	.948	.951	.954	.958	.961	.964	.968	.971	.975
75	.914	.917	.921	.924	.928	.931	.934	.937	.940	.943	.947	.950	.954	.957	.960	.963	.967	.971	.974	.978
74	.917	.920	.924	.927	.930	.933	.937	.940	.943	.947	.950	.953	.957	.960	.963	.966	.970	.973	.977	.980
73	.920	.923	.926	.930	.933	.936	.940	.943	.946	.949	.953	.956	.960	.963	.966	.969	.972	.976	.980	.983
72	.922	.925	.929	.932	.935	.939	.942	.945	.949	.952	.955	.959	.962	.965	.968	.972	.975	.979	.982	.986
71	.925	.928	.931	.935	.938	.941	.945	.948	.951	.954	.958	.961	.965	.968	.971	.975	.978	.981	.985	.989
70	.927	.931	.934	.937	.941	.944	.947	.950	.954	.957	.960	.964	.967	.970	.974	.977	.980	.984	.988	.991
69	.930	.933	.937	.940	.944	.947	.950	.953	.957	.960	.963	.967	.970	.973	.977	.980	.983	.987	.990	.994
68	.932	.936	.939	.942	.946	.949	.952	.956	.959	.962	.966	.969	.972	.976	.979	.983	.986	.989	.993	.997
67	.935	.938	.942	.945	.949	.952	.955	.959	.962	.965	.968	.972	.975	.979	.982	.985	.989	.992	.996	1.000
66	.938	.941	.944	.948	.951	.954	.958	.961	.964	.968	.971	.974	.978	.981	.985	.988	.992	.995	.998	1.002
65	.941	.944	.947	.950	.954	.957	.960	.963	.967	.970	.973	.977	.980	.984	.987	.991	.994	.997	1.001	1.005
64	.943	.946	.949	.953	.956	.959	.963	.966	.969	.973	.976	.980	.983	.986	.990	.994	.997	1.000	1.004	1.008
63	.945	.919	.952	.955	.959	.962	965	.969	.972	.975	.979	.982	.985	.989	.993	.996	1.000	1.003	1.006	1.010
62	.947	.951	.954	.958	.961	.964	.968	.971	.975	.978	.981	.985	.988	.991	.995	.999	1.002	1.005	1.009	1.013
61	.950	.954	.957	.961	.964	.967	.971	.974	.977	.981	.984	.987	.991	.994	.998	1.001	1.005	1.008	1.011	1.015
60	.952	.956	.959	.963	.966	.969	.973	.976	.980	.983	.986	.990	.993	.997	1.000	1.004	1.007	1.010	1.014	1.017
59	.955	.959	.962	.966	.969	.972	.976	.979	.983	.986	.989	.992	.995	.999	1.003	1.006	1.010	1.013	1.016	1.020
58	.957	.961	.964	.968	.971	.975	.978	.981	.985	.988	.992	.995	.998	1.002	1.005	1.009	1.012	1.016	1.019	1.023
57	.960	.963	.967	.970	.974	.977	.980	.984	.988	.991	.994	.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025
56	.962	.966	.969	.973	.976	.979	.982	.986	.990	.993	.996	1.000	1.003	1.007	1.010	1.014	1.017	1.021	1.024	1.028
55	.965	.968	.972	.975	.979	.982	.985	.989	.993	.996	.999	1.002	1.006	1.009	1.013	1.016	1.020	1.023	1.027	1.030
54	.967	.970	.974	.977	.981	.984	.988	.991	.995	.998	1.001	1.005	1.008	1.012	1.015	1.019	1.022	1.026	1.029	1.033
53	.969	.973	.976	.980	.983	.986	.990	.993	.997	1.000	1.004	1.007	1.011	1.014	1.018	1.021	1.025	1.028	1.031	1.035
52	.971	.975	.978	.982	.985	.989	.992	.996	.999	1.003	1.006	1.010	1.013	1.017	1.020	1.024	1.027	1.031	1.034	1.038
51	974	.977	.981	.984	.988	.991	.995	.998	1.002	1.005	1.009	1.012	1.016	1.019	1.023	1.026	1.030	1.033	1.037	1.040
50	.976	.980	.983	.987	.990	.994	.997	1.001	1.004	1.008	1.011	1.015	1.018	1.022	1.025	1.029	1.032	1.036	1.039	1.043
49	.979	.982	.985	.989	.993	.996	1.000	1.003	1.007	1.010	1.014	1.017	1.021	1.024	1.028	1.031	1.035	1.038	1.042	1.045
48	.981	.985	.988	.992	.995	.999	1.002	1.006	1.009	1.013	1.016	1.020	1.023	1.027	1.030	1.034	1.037	1.041	1.044	1.048

Observed volume multiplied by factor corresponding to observed temperature and barometric pressure equals corrected volume.

Appendix E. Fig. 15.

CURVES SHOWING PERCENTAGE of RELATIVE HUMIDITY, FROM THE WET AND DRY BULB THERMOMETER READINGS.



Appendix E. Fig. 16.

Progressive Age:

April 15, 1907 Page 206
Sargent Calorimeter

Engineering:

May 3, 1895 Page 574
Junkers Calorimeter.

January 13, 1905 Page 66
Simmance-Abady Calorimeter.

July 12, 1907 Page 46
Beasley's Calorimeter.

Proceedings A. S. M. E.:

December 1900 Page 815
Testing Inflammable Gases, by C. E. Sargent

TEXTBOOKS:

Calorimetry	FRANK H. BATES
Calorimetry of Producer and Illuminating Gases	JOHN F. SIMMANCE
Calorific Value of Fuels	POOLE
Gas Works Chemistry	H. B. HARROP
Handbooks	

PATENTS.

No. of Patent	Title	Grantee	Date
555956	Calorimeter	Hugo Junkers	Mar. 10, 1896
723751	Apparatus for Indicating the Thermal Quality of Gases	Wilbur F. Steele	Mar. 24, 1903
808693	Calorimeter	Louis Schutte	Jan. 2, 1906
816042	Gas Calorimeter	Chas E. Sargent	Mar. 27, 1906
828306	Gas Calorimeter	H. L. Doherty	Aug. 14, 1906
832611	Process for Determining the Heating Power of Combustibles	Hugo Junkers	Oct. 9, 1906

THE MUTUAL ADVANTAGES TO BE DERIVED THROUGH CO-OPERATION BETWEEN ENGINEERING SCHOOLS AND THOSE ENGAGED IN THE GAS INDUSTRY.

BY MR. CHARLES F. BURGESS,

The primary object of technical education as developed in this country appears to be the elevation and development of the individual, while the promotion of greater material prosperity is secondary. In attaining this primary object the success has been phenomenal, and as the late Professor J. B. Johnson has said, "Engineering education to-day speaks for itself more forcibly than any one can speak for it."

In training young men in the fundamental principles of science and engineering, so that they may successfully handle many problems of industrial life, a certain and close relationship has been established between the technical schools and the industrial world, a relationship analogous to that of producer and consumer, both finding a common ground of interest in the product, the graduate of the technical school. The success of the technical educator's work is estimated largely by the degree with which the man who has taken the course of training which he offers meets the requirements of the employer, of the man whose efforts are concerned most directly with the promotion of material progress. In this mutuality of interests co-operation is possible, and it is the purpose of this paper to touch upon some of the features of co-operation between engineering schools and that branch of industrial life concerned with the production and utilization of gas.

James Watt and William Murdock, working at the same time and in the same shop, laid the foundations of those two branches of engineering which were to influence most profoundly the exterior forms of society—steam engineering and gas engineering, respectively.

These twin industries have developed along somewhat divergent paths; the former flourished more rapidly from the beginning, but during recent times gas engineering has made such rapid progress that it bids fair to attain ultimately the greater field of usefulness.

The transformation and utilization of steam power involved a complexity of mechanism which long ago gave rise to the need of technically trained men, and the technical schools co-operated by establishing courses in Steam and Mechanical Engineering to help in the training of such men.

That similar co-operation between the technical schools and the gas engineering profession was not effected until a much later period might be construed by some as demonstrating that progress in gas engineering did not require it. Though not within the scope of this paper, it is interesting to speculate as to the causes of the later recognition given by our technical schools to gas engineering. Whether it may be attributed to lesser relative importance of gas engineering to modern civilization, or to smaller amounts of capital involved, or to greater simplicity of problems connected with gas engineering progress, the demand in the gas field for technical graduates has been less until recent years than it has been in civil, mechanical or electrical engineering lines.

Not a great many years ago a presidential address before this association contained the statement that "Gas engineering can neither be taught successfully in schools, nor does the practice of it demand a scientific education as a requirement." It is possible to find men who will say that the efforts which certain technical schools are making to provide for a special training for the gas engineer are to a certain extent misdirected, and engendered by an over-enthusiastic attempt of educators to find profitable positions for the young men in their institutions.

It is scarcely more than a third of a century ago that engineering education had for its one object the training of the Civil Engineer. The growing industrial demands later led to the establishment of courses in Mechanical Engineering, then

Electrical, Mining, Sanitary, Municipal, Hydraulic, Structural, Metallurgical Engineering, and so many other kinds that a contemplation of them all will lead us to say that this is truly an age of specialization.

That this specialization has been brought about largely through the demands of industrial conditions is illustrated by a series of resolutions passed a few years ago by the Pittsburg Foundrymen's Association and later by the National Association:

"Resolved, That the foundry industry has arrived at a point where there is a demand for managers properly trained in the principles of scientific and commercial founding.

"Resolved, That a representative body, such as the American Foundrymen's Association, be requested to draw the attention of institutions of learning in this country to this fact, and to urge them to take the necessary steps to supply the demand."

Various other requests of a like nature might be cited. The gas industries have placed a similar request before the engineering colleges, perhaps not formally in the manner above outlined, but in a manner none the less insistent, by first offering employment to a large number of engineering graduates, and more recently by requesting more graduates than the supply affords. This is a condition which effectually disposes of arguments put forward from time to time disparaging college education as a path to highest success in the gas business, and it will not be attempted herein to justiy further the attempts which some of our technical schools are now making to train men for gas engineering.

For this profession the requirements are such that none of the older established courses meet them in a satisfactory manner, the principal shortcoming being insufficient attention to chemistry and chemical technology. Perhaps a half-dozen technical schools in this country are now offering courses in Chemical engineering, courses in which one of the purposes is to train men for the gas industry as well as for other analogous industries in which a knowledge of chemistry with other branches of technology is important. An outline of the course which was adopted at the University of Wisconsin a year ago is appended herewith, not as an example of an ideal course, but as being more specifically illustrative of what some of the technical schools are doing toward co-operation with the gas interests in training men for this profession.

In entering upon a discussion of the advantages to be derived through mutual co-operation between engineering schools and those engaged in the gas industry, it may be desirable to point out some of the various methods in which co-operation might be effective.

It would appear that much of the difference of opinion which exists between the technical school and the practical man would be removed, and much of the criticism which is made of the former would be rendered unnecessary if there were a thorough understanding upon the part of the industrial man as to just what the purposes of the technical school are. There are many who hold that the technical educator falls far short of success from the fact that his graduates can not step at once into the management of works, equipped not only scientifically and theoretically, but with a knowledge of technique, of business details, and with ability to handle men. The engineering graduate is not, and has never been, claimed to be a finished engineer. The purpose toward which the administrations of engineering colleges direct their efforts is to train young men into resourceful and exact thinkers, men with a fundamental knowledge of the laws of nature and the means to utilize nature's forces. In other words, the object is to produce not finished engineers, but young men of capacity for rapidly becoming engineers when thrown into industrial work.

That nothing more than this is claimed for our engineering graduates is demonstrated by various facts. The degree which the majority of our institutions bestow upon their four-year men is the Bachelor's degree. Such colleges recognize that professional attainments must supplement a college course before the recipient may be entitled to the designation "engineer,"and at the University of Wisconsin, as well as in the various other technical schools, one of the requirements is that a graduate must have had at least three years of professional work, one of which must have been in a position of responsibility, before his engineer's degree will be conferred upon him.

It is true that some technical schools bestow the title of "engineer" upon its students who have had four years of study. The writer believes this to be an unfortunate procedure so far as it places technical schools in somewhat the same position of a merchant who explains to a dissatisfied customer who found that the "genuine Spanish leather" which he had purchased was only a varnished burlap, that that is exactly what is meant by "genuine Spanish leather."

The criticism which has been so frequently raised against college men, that they are consumed with conceit of their attainments and thus set the practical men of the factory or workshop against them, is rapidly coming to have less ground. It is probably no exaggeration to state that there is not a technical school in this country that does not endeavor to impress upon its students that they have not passed the apprenticeship stage, and that the engineering graduate is not necessarily the man who is going to occupy the highest planes in his profession. In this effort the faculties have been highly successful in spite of various counteracting influences. The principal difficulty in inculcating this frame of mind is that the demand for graduates has become larger than the supply, and most of the members of the senior class have had several offers of employment made to them some months in advance of graduation.

That the average present-day engineering graduate has an appreciation of his limitations is amply demonstrated by the fact that a good percentage of the members of the graduating classes are entering the apprentice courses of various large industrial establishments at a wage hardly high enough to pay actual living expenses; it is testified to by the fact that it is very common to find men who have distinguished themselves in college life working beside Mexican laborers in a construction gang, or contentedly working in a man-hole as a helper and obeying orders from a practical man who may neither read nor write. In fact, as has been stated by a prominent British engineer, in reporting upon his investigation of educational conditions in this country, "The know-it-all college man has almost vanished from the workshop, though a tradition of him and his eccentricities still lingers."

The technical man can, therefore, co-operate to a considerable degree by acquainting himself with the purpose of the educator, with the claims which he makes for his product, and with the methods through which the product is manufactured.

The various courses in chemical engineering which are being given at several institutions in this country differ materially in character. Some are better than others. There have been no long years of practice leading to uniformity and the establishment of the best method. The courses have been laid out in accordance with the beliefs of the heads of the respective courses as to what the practical requirements are. The administrators of technical schools offering such courses are prevented from providing completely for the work in the manner in which they wish to carry it out, through various limitations set by local conditions. The funds available may be inadequate to equip an ideal laboratory, or to provide for the most efficient instructional staff, and the crowded conditions of our techical schools may make it difficult to secure suitable class room and laboratory space. These limitations will disappear with time, and through the co-operation which might be expected from and should be offered by the industrial men, our courses in chemical engineering are bound to take rank with the other important engineering courses which have been longer established.

The question of funds has been and always will be a vital question in the conduct and enlargement of engineering schools. While tax payers in many of our states are providing liberally for technical schools, and while large donations are being received from alumni and friends of endowed institutions, the demands are increasing at such a great rate that the funds for providing for the same are seldom in sight. When our universities are faced with a probable deficit or are in urgent need of additional funds to carry on their work, it is quite customary to look to the alumni for assistance, expecting that men who have obtained their educations at such universities and have gone out into industrial life and become wealthy, should be willing to give to their Alma Mater.

Another class of people may be looked to for assistance, namely, manufacturers and industrial people who are more or less directly benefited by the things accomplished through the technical schools. The form which the assistance takes from this class of contributors is varied. It may be funds for building, equipment, the endowment of chairs for specific lines of instruction, or for research work. There is scarcely an important engineering laboratory that has not been materially assisted through the donation of equipment from the manufacturer or the loan of machinery for a more or less indefinite period; and it is the exception rather than the rule, that a manufacturer is not willing to sell apparatus to an engineering college at a price not greater than the actual factory cost.

In the effort to turn out broadly educated young men for the chemical industries the management of the gas industries can lend assistance to the technical colleges in various ways other than the above mention. Most of our courses provide for about three months of vacation in the summer, during which time little or no supervision of the time of the students is exercised. At the University of Wisconsin the requirement has recently been inaugurated that engineering students shall spend at least six weeks during one of his vacation periods in the machine shop. He is also required to accompany an inspection party which makes a tour of large industrial establishments. If, on account of expense or for other reasons, a student is unable to take this trip, he is required to spend some time during the summer vacation in studying one or more industrial plants. It is suggested that for students who propose to enter the gas business a more profitable method of employing one or more vacation periods would be in working in subordinate positions in a gas works, and the writer would advocate the adoption of this as a requirement of the course if suitable arrangements could be made with gas works to take such young men for short periods of time before graduation. A plan similar to this has been put into successful operation in other lines of engineering work, and there appears to be no reason why the managers of gas works might not find it possible to co-operate with the universities in like manner. The kind of work which an undergraduate student might do during such period of employment would not probably be of great value to the gas works, though while it would be possible, it would not be advisable to require the student to work for no compensation, since he will take a greater interest in and profit more by his work if he sees that it has some value measurable in dollars and cents; since in some other lines of manufacture employers not only take on undergraduate students for vacation periods, but are actually soliciting them to accept employment at a fair living rate of pay, it would be an unpopular requirement that would force a student to work for no compensation in any particular line of work outside of the university laboratories.

As previously intimated, a fair percentage of our engineering graduates accept the advantages offered by apprenticeship systems for graduates which have been established by various manufacturers. Through the advantages which such systems afford the graduates are willing to accept employment at a lower initial salary than could be received where no such system prevails. Many concerns who employ large numbers of such students each year, have taken up this matter of apprenticeship for engineering graduates and, while in the subdivided gas industry such a system might be difficult to establish, through the co-operation of an organization such as this Western Gas Association a satisfactory plan might be worked out. There are various objections to apprenticeship systems as well as arguments for them, and while the writer does not at this time wish to advocate them in connection with gas work, it might be a matter worthy of consideration.

While the elevation and development of the individual is the primary aim of the ordinary college course, the technical schools have other highly important functions, one of them being the carrying on of research and investigation work. As our schools are at present run this research work is done by undergraduate students in the preparation of their theses, by graduate students who are specializing in certain definite lines of work, and by the instructional force. The usual character of the undergraduate research work is not such as to make it of great value to the industries, although valuable contributions are sometimes made. The primary object in requiring a student, before graduation, to carry on a piece of investigation is to throw him as largely as possible upon his own resources; to develope his capabilities of independent reasoning and thinking; to give play to his ingenuity, and to impress him with the importance of planning and laying out a piece of work in advance of its execution. Where a student shows marked ability in this respect, the results of his work may be of practical importance. In the carrying out of this work the gas industries may offer assistance and encouragement. The local company near the University of Wisconsin offers to students the privilege, not only of visiting and carefully studying the operation of the plant, but also of making any tests and investigations which are desired, the only restriction placed upon them being that the operation of the plant shall not be materally interfered with. A spirit of competition among thesis students may be advantageously fostered by award or some other formal recognition of work of exceptional merit.

The research work done by graduates under direct supervision of the instructional force, and the work done by the instructors themselves, may have for an incentive the advantage to be derived through a solution of technical problems or the hope of addition to scientific knowledge. The importance of this kind of investigation to the gas industry at large hardly needs argument, and the reason that so little of it has been done in this country is that the demand for operating engineers has been so great that it is much more difficult to induce competent students to remain in the research laboratory after graduation. For this reason research along technical lines does not compare favorably in amount and quality of work done with departments of physics, chemistry, botany and the line and with technical schools abroad. Industrial men have it within their power to assist in promoting this work by advocating its importance and by assisting in establishing equipment and facilities for efficiently carrying on investigation of the many problems constantly arising in industrial operations. The Michigan Gas Association has materially promoted this kind of work by establishing a graduate scholarship at the University of Michigan, and the quality of the work which has been done through this assistance and under the able direction of Professor White, appears to have amply justified the appropriations which have been made. Through the more general establishment of graduate scholarships at the various technical institutions in which the facilities are such that high grade work can be carried on, much encouragement could be given for advanced research. If such scholarships amounting to several hundred dollars per year be open to competition, not only to the graduates of the institution in question, but to others in the industrial field who are competent and desirous of carrying on investigations, it is quite probable that a considerable amount of talent might be put to work in acquiring information of which the gas industries are in need.

Coming, finally and briefly, to the advantages to be derived through co-operation above referred to, it is hardly necessary to enumerate them, since they are largely self-evident. Co-operation will enable the technical schools to more nearly attain the purposes for which the endowments and appropriations for the support of the same are made, i. e., the moral and material betterment of society. The industrial men while sharing in these larger benefits can, by the efficient conduct of technical schools, secure for the industrial needs a class of men competent to work into the management and development of gas interests. The development of research work may make it possible for the gas profession to profit through discovery, through added scientific knowledge, and through affording facilities whereby practicing engineers may carry on certain investigations which have an immediate bearing on their business. Advantages might accrue to them in much the same way that the agricultural interests have been benefitted by the magnificent work accomplished at our various agricultural experiment stations.

The summer apprenticeship system above referred to would help the work of the technical schools and incidentally acquaint the employer with the students in such a way as to enable him to make a satisfactory choice of future employees.

A criticism frequently made, especially by the utilitarian, upon the character of the work done in scientific laboratories, is that it is too theoretical, that it has not immediate value, that the study of "the condensation of succinylosuccinic acid diethyl ester with guanadine" should give way to a thorough investigation of the condensation of tar. If this criticism is justified it may arise through lack of suitable co-operation between the laboratory investigator and the technical man, and it is entirely conceivable that a "getting together" may benefit the scientist by impressing him more thoroughly that many problems await investigation which afford opportunities for highly scientific work and the results of which will at the same time have a marked utilitarian value That the advantages of such co-operation will have the element of mutuality in it is self-evident.

On the other hand, science for science's sake, is a motto, from the wearing of which no attempt at discouragement should be made, for many of the great blessings which come to mankind through discovery have resulted from the indefatigable labors of those men who have worked to increase the sum total of human knowledge and without the hope of immediate practical utility of such knowledge.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

OBSERVATIONS ON ALLOYS OF ELECTROLYTIC IRON WITH ARSENIC AND BISMUTH.

By Charles F. Burgess and James Aston.

It has been noted that the presence of arsenic in acid pickling solutions causes a marked diminution in the rate of attack by the acid, and the idea was suggested that if the presence of arsenic in a corrosive solution protected iron from corrosion by that solution, that the presence of arsenic in the iron itself might increase its durability. To test this possibility, such alloys were made, but they failed to show any marked advantage over iron and steel of ordinary grades in their ability to resist corrosion. From the arsenic alloys prepared primarily for this purpose, test bars were made and subjected to the various physical tests to which a large number of other alloys have been subjected in an extensive investigation on the properties of alloys made from electrolytic iron.

In this investigation, which has been made possible through a grant from the Carnegie Institution of Washington, some six hundred ingots of iron and iron alloys have been made, and from these about five hundred forged bars have been secured, these bars covering a considerable range of composition, over half of which are binary alloys.

In determining the magnetic properties of the arsenic alloys, some interesting and unexpected results were obtained, which in turn suggested the advisability of testing the influence of the analogous elements, antimony and bismuth, upon the magnetic quality of iron.

While the tests on these alloys are incomplete, being still in progress, and although the data is not sufficiently complete and extensive to warrant the derivation of positive deductions, the results of this work are given as showing the desirability of further investigation along this line.

The general idea upon which our investigation on iron alloys has been based is that comparatively little is known of the properties of iron alloys free from carbon, and, that the production and study of such alloys appears to offer an interesting field of work. The iron which has been used for this purpose is that which has been electrolytically refined from Swedish iron bars and this subsequently melted and then forged into bars of as high a purity as possible.

Some idea as to the purity of electrolytically deposited iron which has been employed may be taken from the following table, giving the results of analyses reported by Messrs. Booth, Garrett & Blair, of Philadelphia.

TABLE I.

	Single Refined.	Double Refined.
Sulphur	0.001	None
Silicon	0.003	0.013
Phosphorus	0.020	0.004
Manganese	None	None
Carbon	0.013	0.012
	0.037	0.029
Iron (difference)	99.963	99.971
Hydrogen	0.083	0.072

This material has been melted alone or with the desired alloying elements in an electric furnace using granulated carbon resistor material into which is embedded magnesia crucibles containing the charges, the crucibles being removed from the furnace after cooling. Special attention was given to preventing contamination of the crucible contents, by using dense electrically shrunk magnesia crucibles with a magnesia cover, and the crucibles in turn being placed in an Acheson graphite crucible with a graphite cover.

The atmosphere under which the melting takes place is one composed mainly of nitrogen and carbon monoxide, and that this atmosphere is not without influence in contaminating the molten charge is shown by the fact that subsequent analysis reveals a slight increase in the amount of carbon. This probably comes about through a reversible action, as indicated by the equation

$$Fe + CO = FeO + C.$$

Various analyses show that this increase in the amount of carbon is probably not more than 0.04 per cent. In the subsequent forging of the ingots into bars 20″ long x ⅝″ diameter, very little impurity is imparted to the bar.

In general, the ingots weigh about 500 grams, and the bars produced from them have been subjected to various tests for properties, and mainly those which do not destroy the bars during the process of testing. The determinations of the magnetic properties, including permeability, coercive force, retentivity and the measurement of electrical resistance, have received special attention, while comparatively few tests have been made upon tensile strength.

Among the various instruments available for testing the magnetic properties of iron, that designed by Professor Esterline has been adopted, and this after an investigation of the merits of the various methods had been made. The reasons for adopting the Esterline instrument lie in its ability to accurately reproduce results, in its ease and rapidity of working, and in the convenient form of sample test bar which it requires. The test bars are about 20 cm. long and 1 cm. in diameter. The Esterline instrument which was used was specially designed to meet our requirements. While the method employed in this instrument gives comparative results, we believe that it may be calibrated with such accuracy that the results may be as dependable as those secured in the ballistic-ring method. While the results which we obtained with this instrument may not necessarily be strictly comparable to results obtained by others using different methods, we are convinced that all data which we have secured is comparable in itself.

Comparatively little attention seems to have been given to the influence of arsenic on iron beyond the influence of the slight quantity of arsenic which may be met with in commercial iron. The work of Harbord and Tucker (Iron & Steel Institute, 1888, Vol. I); of Stead (Iron & St. Inst., Vol. I), and of Marchel (Bul. Soc. d'Encour, 1899), covers the mechanical properties exclusively, the general conclusions being that small percentages of arsenic not exceeding 0.20 per cent. have no material effect on the strength. Larger amounts result in the brittle material, but the hot working is not affected, even with 4 per cent. of arsenic. Friedrich's investigation (Metallurgie, 1907) is entirely a metallographic study, and shows that arsenic alloys with iron in all proportions up to 56 per cent., under his conditions of mixing.

The method employed in making the arsenic alloys was to place the arsenic, together with the iron, in the magnesia crucible and melt in the ordinary manner. Attempts have been made to produce alloys in various proportions up to 10 per cent. of arsenic. Subsequent analyses, however, showed that the maximum amount of arsenic taken up and retained by the iron was about 4 per cent. In addition to the alloys of arsenic with pure iron, alloys were made up adding 5 per cent. of arsenic to a high grade commercial transformer iron. Table II gives the series of arsenic-iron alloys which have thus been produced. This table shows the incompleteness of our data, in that check analyses have not as yet been obtained by quantitative analysis to show the probable amount of arsenic contained in those samples where the analysis is still lacking.

TABLE II—ELECTROLYTIC IRON.

Bar No.	Per cent. Arsenic		Per cent. Carbon	Remarks
	By Mixture	By Analysis		
117 A	0.00	0.000	0.047	
121 I	0.25	0.292		
121 H	0.50	0.430		
113 A	1.00	0.915		
113 B	2.00	1.810	0.042	
113 D	4.00	3.862		
113 F	6.00	4.141		Broken—not tested quenched.
113 H	10.00	3.563		
92 A	1.00	.....		Tested only in unannealed state, not yet complete.
113 C	3.00	.....		
113 E	5.00	.....		
171 L	4.00			Tested unannealed and lost in annealing.
172 B	5.00			Twice annealed but not quenched.

Commercial Transformer Iron.

171 O	0.00	Tested unannealed, lost in annealing.
171 P	5.00%	
172 C	0.00	Twice annealed, not quenched.
172 D	5.00%	

It has been found that all the arsenic ingots forged readily under normal forging temperatures. The odor of arsenic was very evident upon heating, even at the low temperatures produced by grinding, and this alliaceous odor was very intense during the forging.

It is evident from the analyses that under conditions of working, 4 per cent. of arsenic is about the maximum that may be counted upon, and below this percentage the arsenic is taken up in about the percentages calculated, showing no great loss by volatilization.

The forged bars of 20″ in length were cut into three test bars, two for tensile tests and one for the magnetic tests. The tensile bars were about 5″ long, and turned down over a clear length of 2 inches to about 0.4″ diameter. The tests were made in a Riehle 1,000,000 pound testing machine. No special difficulty was noticed in machining the bars, the higher arsenic seeming to be brittle, which brittleness is also confirmed by the following data on strength.

TABLE III—STRENGTH TEST.

Arsenic Alloys.

Bar No.	Per cent. Arsenic	Stress in ^{2} Ultimate	 Elastic limit	Per cent. Elongation	Per cent. Reduction of area
121 I	0.292	61,250	47,900	27.5	68.2 (flaw)
121 A	0.430	65,500	53,000	28.5	58.3
113 A	0.915		47,000		(flaw)
113 B	1.810	60,250	53,500	0.0	3.7
113 D	3.862	63,900	63,900	1.0	1.7
113 F	4.141				
113 H	3,563	61,250	61,250	1.0	0.65
		Electrolytic Iron.			
117 A	Elec. forg.	50,000	40,000	31.0	91.4 (greatest reduction of area.)

MAGNETIC TESTS.

The magnetic tests consisted in general of a magnetization curve and readings of the retentivity and coercive force for each bar, after being subjected to each of four different heat treatments; first, as forged; second, after heating to 675° C. and slowly cooling; third, after heating to 1000° C. and slowly cooling; fourth, after heating to 900° C. and quenching in water. All the heating was done in the electric resistor furnace, and the bars were packed in ground magnesia, in a magnesia-lined graphite box. The temperature readings were taken with a thermo-couple. The heating and cooling proceeded very slowly, in general about three to four hours being required to bring the temperature to the desired point; it was then held constant for one to two hours; after this the bars were allowed to cool in the furnace, about twelve hours being necessary for a temperature drop to 200° or 300° C.

We have taken as a reference standard an electrolytic iron bar No. 117 A, in its unannealed condition, since among the earlier tests on electrolytic iron this sample reached the highest maximum of magnetic density, and showed great uniformity throughout the length of the curve, having a steep slope in the early part of the curve, but a gradual bend as saturation was approached; also because annealing had little influence on the quality of this bar. The quality of this bar is indicated in Chart I, and in the accompanying Table IV, in which the magnetic flux density of this electrolytic material for different applied magnetizing forces is compared with a sample made from our Swedish anode bars, and which is representative of a good quality of wrought iron, as may also be seen from Table IV, where comparative figures are given for Hopkinson's classic wrought iron sample, formerly a standard of magnetic excellence.

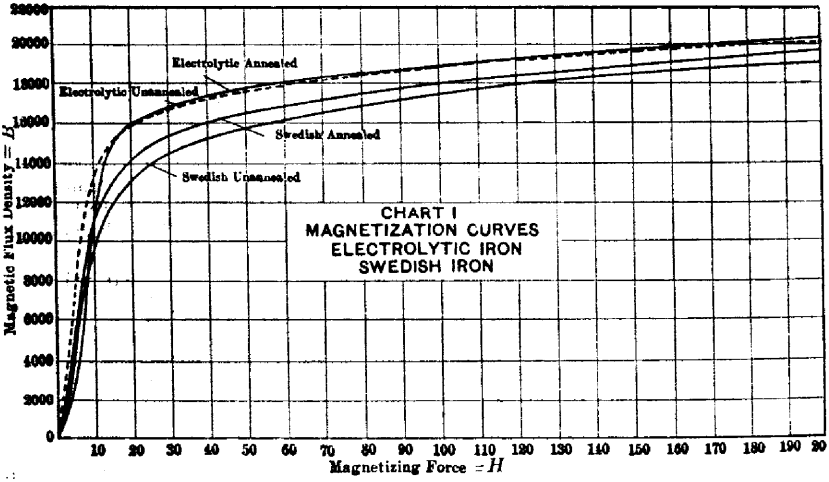


TABLE IV.

No.	Comp.	H = 10	H = 20	H = 50	H = 100
117 A..Electro. forged	unannealed...	13,100	15,750	17,600	18,850
NWS..Swedish anode.	unannealed...	9,500	13,200	15,700	17,450
	annealed 675..	10,000	14,200	16,500	18,000
Hopkinson's Wrought Iron	....	10,200	13,950	15,650	16,500

TABLE V—MAGNETIC TESTS DATA.

Bar	Comp. Per cent.	H = 10				H = 20				H = 50				H = 100			
		Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann d 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900
Iron																	
NSW	Anode	9,500	10,000	10,850	8,400	13,200	14,200	13,900	12,050	15,700	16,500	15,850	15,550	17,450	18,000	17,200	17,100
117 A	Elec. Forged	13,100	10,000	13,350	11,800	15,750	15,950	15,450	14,600	17,600	17,700	17,050	16,950	18,850	18,850	18,200	18,150
Antimony																	
172 E	1.15	8,800	10,000	7,700	. . .	12,800	13,350	11,600	. . .	15,300	15,750	14,800	. . .	16,950	17,100	16,400	. . .
Arsenic																	
121 I	0.29	10,500	13,200	10,800	11,200	14,750	15,550	14,100	14,750	16,900	17,250	16,500	16,700	18,350	18,550	17,850	17,950
121 H	0.43	7,000	7,800	10,400	8,100	13,000	14,000	13,750	12,750	16,300	16,600	15,950	16,250	17,800	18,100	17,250	17,600
113 A	0.[illegible]	6,200	6,250	11,950	12,600	13,200	14,050	14,750	15,300	16,450	17,000	16,650	17,050	17,950	18,550	17,950	18,250
113 B	1.81	8,300	11,850	12,600	10,300	13,950	15,750	15,150	13,800	16,700	17,450	16,850	16,650	17,950	18,750	18,150	18,250
113 D	3.86	13,850	15,050	14,850	13,600	15,350	16,300	15,750	15,450	16,450	17,550	16,850	16,900	17,600	18,650	17,850	18,100
113 F	4.14	13,300	14,200	14,650	. . .	15,500	15,900	15,750	. . .	17,000	17,250	17,050	. . .	18,200	18,450	18,150	. . .
113 H	3.56	12,400	14,200	12,300	13,450	15,000	16,100	14,600	15,450	16,700	17,550	16,650	16,900	17,950	18,750	17,950	18,000
Bismuth																	
172 G	1.0	7,000	11,550	6,300	. .	13,250	14,650	11,350	. . .	16,800	16,850	15,500	. . .	18,600	18,350	17,550	. . .
172 H	2.0	9,200	13,250	9,700	. . .	15,500	16,100	12,750	. . .	18,350	18,350	16,050	. . .	19,650	19,750	17,800	. . .
172 J	4.0	7,700	10,500	10,000	. . .	12,600	13,750	13,500	. . .	16,250	16,550	16,650	. . .	18,050	18,050	18,350	. . .
172 K	6.0	9,100	12,000	6,400	. . .	13,250	14,700	12,950	. . .	16,650	16,850	16,250	. . .	18,350	18,100	18,250	. . .
172 L	10.0	6,100	9,500	7,750	. . .	12,000	13,200	11,050	. . .	15,800	15,800	14,850	. . .	17,600	17,350	17,450	. . .
Special																	
172 C	Trans.	6,500	9,550	8,600	. . .	12,050	13,550	12,400	. . .	15,850	16,550	15,850	. . .	17,700	18,050	17,450	. . .
172 D	+ 5 AS	9,100	11,500	8,500	. . .	13,700	14,750	11,800	. . .	16,500	16,750	15,300	. .	17,950	18,000	16,950	. . .

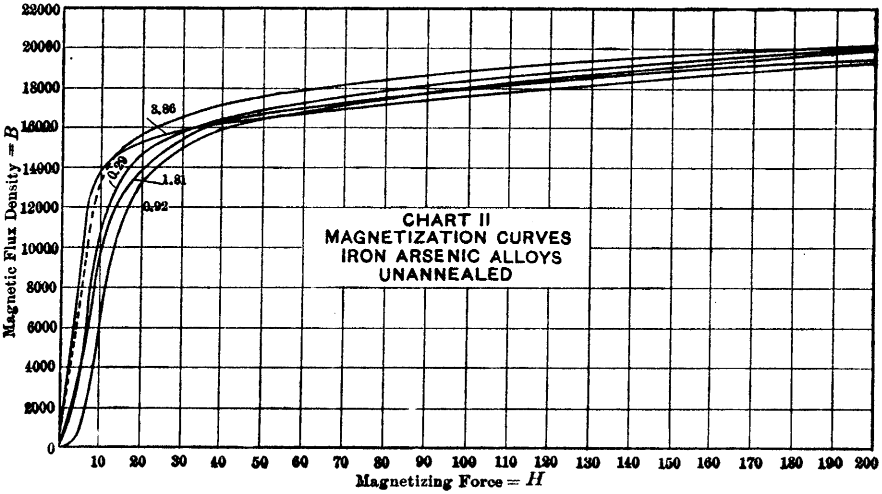
This standard reference curve for electrolytic iron is indicated in all drawings by a dotted curve. It does not represent the ultimate standard of quality of pure iron, since we have in our later tests found samples of electrolytic iron of presumably higher purity, which have shown somewhat higher magnetic qualities, but it is satisfactory as a standard reference curve in showing that if the alloys approach this curve they have exceptional magnetic qualities.

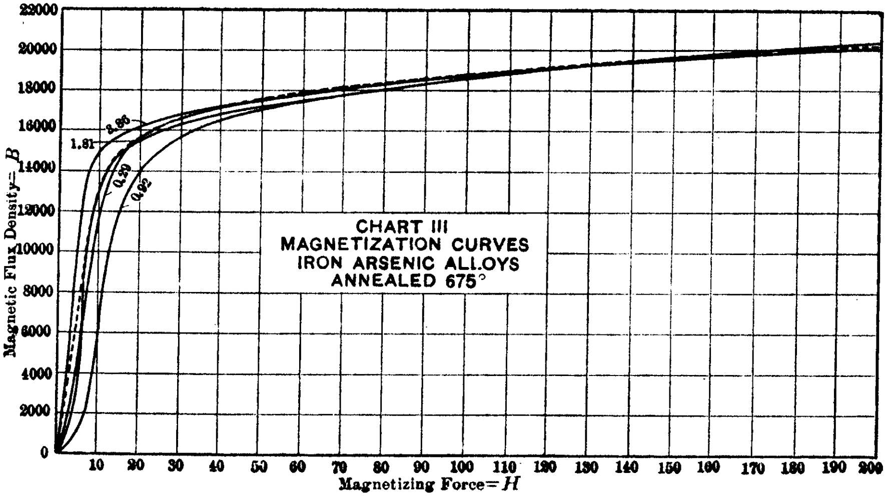
As is shown by Table II, magnetic tests have not been completed for all of the various heat treatments; also a few bars were lost by breakage and in annealing. It is also the intention to make additional series of similar alloys for further confirmatory tests, but the results as far as completed at the present time are given in the accompanying tables and curves.

TABLE VI—COERCIVE FORCE AND RETENTIVITY.

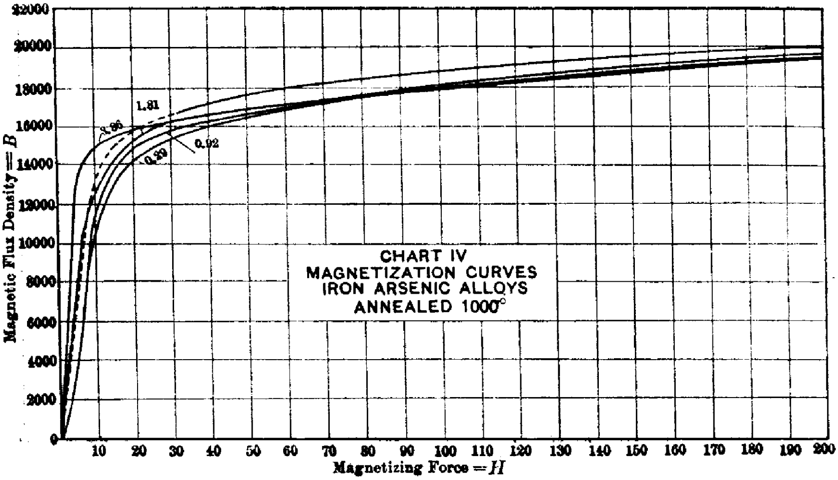
Bar	Comp. Per cent.	H (Max) = 200 COERCIVE FORCE				H (Max) = 200 RETENTIVITY			
		Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann d 1000	Quench 900
Iron									
NSW	Anode	5.5	4.8	3.9	5.0	11,400	12,700	9,000	8,500
117 A	Elec. Forged	5.5	6.2	3.1	2.5	12,300	13,800	10,000	8,000
Antimony									
172 E	1.15	7.3	5.0	4.0	. . .	12,000	8,700	6,900	. . .
Arsenic									
121 I	0.29	6.5	5.5	4.5	4.0	12,400	14,600	9,900	10,800
121 H	0.43	8.2	8.0	5.5	4.3	12,700	12,700	9,400	8,600
113 A	0.92	9.5	9.2	5.3	3.0	12,700	14,700	12,300	9,500
113 B	1.81	5.9	5.0	3.7	3.0	10,300	12,200	8,900	8,600
113 D	3.86	4.0	3.5	2.0	2.1	12,100	13,000	6,500	8,600
113 F	4.14	5.0	3.3	2.3	. . .	10,800	12,300	8,900	. . .
113 H	3.56	4.5	4.0	2.7	2.7	11,000	13,400	8,600	8,900
Bismuth									
172 G	1.0	8.3	4.6	7.3	. . .	12,900	10,800	10,300	. . .
172 H	2.0	7.0	4.2	4.5	. . .	13,200	11,000	8,500	. . .
172 J	4.0	8.0	5.0	4.3	. . .	12,200	11,200	7,600	. . .
172 K	6.0	7.5	3.9	6.2	. . .	12,400	9,700	10,800	. . .
172 L	10.00	8.7	5.0	4.7	. . .	12,900	10,300	8,900	. . .
Special									
172 C	Trans.	8.1	6.2	4.5	. . .	11,100	12,300	8,700	. . .
172 D	+ 5 AS	6.6	4.0	3.9	. . .	12,600	11,500	7,900	. . .

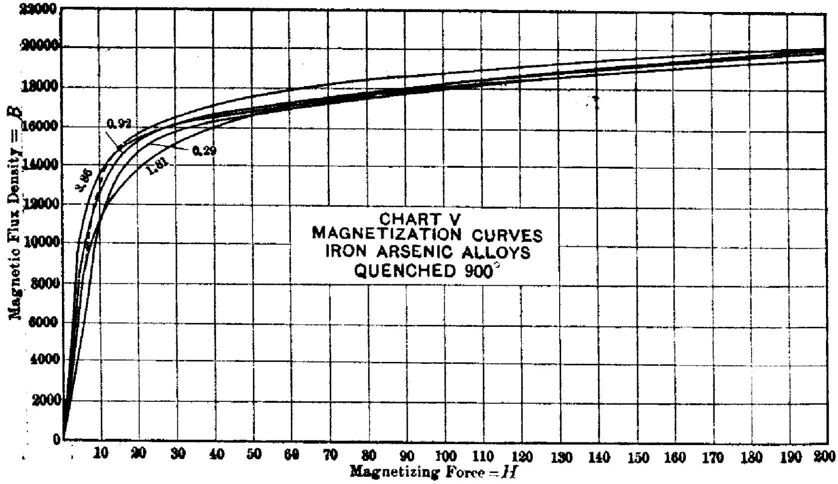
Magnetization curves for representative bars are plotted in Charts II, III, IV and V, and the data for comparison in Tables V and VI. For the lower values of the arsenic content there is nothing of particular interest. Bar 121 I, with arsenic content of 0.29 per cent. is very close to the standard electrolytic curve; bars 121 H and 113 A with 0.43 per cent. and 0.915 per cent., respectively, are poorer in quality. This is shown also in the relative coercive forces of 6.5, 8.2 and 9.5 for the unannealed state. Further increase of arsenic to 1.810 per cent in Bar 113





B shows an improvement in quality, and the coercive force has dropped to 5.9. But the most interesting features are noted with the higher arsenic alloys 113 D, 113 F and 113 H, with 3.862 per cent., 4.141 per cent. and 3.563 per cent. respectively. For lower values of the magnetizing force, the density reaches very high values for relatively small impressed field, being for 113 D and 113 F considerably higher than in the case of our electrolytic iron 117 A. The coercive forces also are the smallest noted in any of our tests of the unannealed bars, being 4.0, 5.0 and 4.5.





When H reaches 20, however, the curves fall below that of the electrolytic iron in the unannealed condition.

The effect of successive heat treatments is seen by inspection of the curves and tables. A marked improvement throughout the entire range of the curves is the result of heating to 675° C. and slowly cooling, due, no doubt, to the removal of all forging strains and the opportunity afforded for the grain size of the material to become normal; this improvement of the already good results observed place the arsenic alloys on an equality with the best electrolytic material for magnetizing forces, above H = 50, and below this value of H they are considerably superior, thus ranking with the very best magnetic material for which records are available. Comparing 117 A and 113 D, both annealed at 675° C, we note densities of 10,000 and 15,050 for H = 10, and for H = 20, the values are 15,950 and 16,300, respectively. At H = 50 the densities are practically equal, being 17,700 and 17,550.

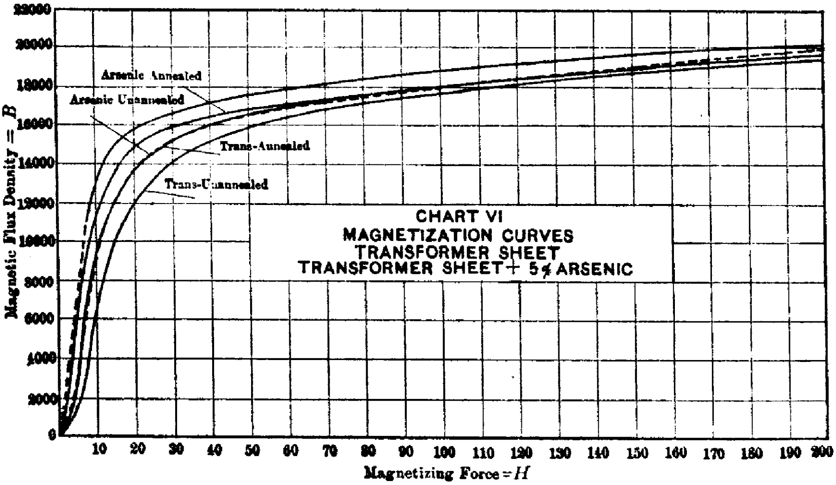
The second heating to 1000° C with slow cooling in general has been accompanied by an improvement of the quality in the lower ranges of the magnetizing forces, but there is a decided falling off throughout the upper ranges of the curve. Quenching from 900° C shows no hardening, there being but slight changes in the magnetization curves. Referring to Table VI, the tabulation of the coercive forces shows a continual falling off after successive heatings, and even after quenching. The low values of coercive force for the higher arsenic content are worthy of note, the mininum of 2.0 being reached by 113 D with 3.86 per cent. after annealing at 1000° C.

The retentivity data allows no deductions to be drawn. In general, it varies with the maximums attained by the magnetization curve increasing as the usual accompaniment of annealing at 675° and decreasing after a 1000° heating and after quenching.

To determine the effect of the addition of arsenic to ordinary iron, we have made the tests recorded in Chart VI and Tables V and VI. Ordinary transformer sheet steel was melted into ingots, alone and with the addition of 5 per cent. of arsenic, then forged and turned into test bars. Examination of the magnetization curves shows a considerable improvement of the quality in the arsenic bar, with both materials inferior to the electrolytic.

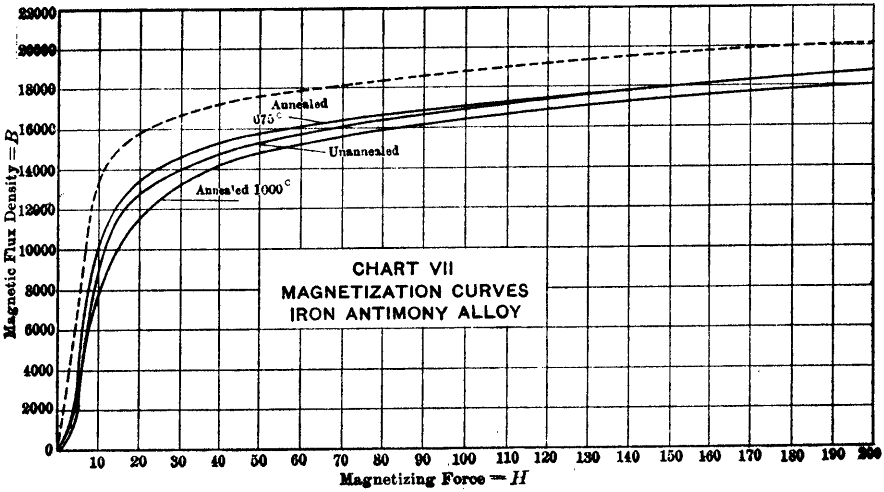
Annealing at 675° has improved both bars, the arsenic bar still being superior in the lower ranges of magnetizing force, and being but very little inferior to the electrolytic sample. Further heating to 1000° resulted in a marked falling off in both bars, and the material free from arsenic gave the better results.

Summarizing, we have in this arsenic series some most interesting and unexpected results. In the first place, this element, with a temperature of sublimation of 450° C, alloys with iron under conditions where it has passed this temperature long before the fusion of the iron, in practically the proportions of the solid mixtures up to a content of arsenic of 4 per cent. Also we note the more interesting feature that the presence of this large quantity of an element, which when present above 0.25 per cent. is most detrimental in its physical effects, imparts to the alloy magnetic qualities excelling those of the purest iron and on a par with the best material of which we have been able to obtain data.



ANTIMONY.

Two sets of alloys with proposed antimony content of 1, 2, 4, 6 and 10 per cent. were made up and resulted in good ingots. In each case, however, but one of these with the lowest content of 1 per cent. was forgeable, and that only with difficulty. As in the case of the arsenic bars, magnetic tests were made of the unannealed sample, and after successive annealings at 675° and 1000° C. A quenching test was not made. The magnetization curves are plotted on Chart VII and some of the data are collected in Tables V and VI. As compared with the electrolytic iron sample, the antimony alloy is of low grade. The same general effect of annealing is indicated as previously discussed; viz., an improvement upon heating to 675° and a deterioration after the second heating to 1000°. Also we note the same successive falling off in the coercive force, being 7.3, 5.0 and 4.0, respectively.



The antimony series, therefore, seems of little value, forming a difficulty workable product with no apparent value as a magnetic material.

Check analysis on the forged bar showed the presence of antimony of 1.15 per cent.

BISMUTH.

A third element in this analogous group, the effect of which has been investigated, is bismuth. Alloys were prepared to have a bismuth content of 1, 2, 4, 6 and 10 per cent. The 2 per cent. ingot was lost in the melting, and the others were made into test bars and magnetization curves taken in the unannealed condition. However, all of these bars were lost in annealing and a second series was prepared of like composition, all of the ingots being good. They were worked into bars with no special difficulty, either in forging or machining. Table VII gives the test numbers of these bars, together with the bismuth content.

TABLE VII.

Bar No.	Per cent. Bismuth As mixed	Per cent. Bismuth By analysis
172 G	1.0	.....
172 H	2.0	.....
172 J	4.0	.....
172 K	6.0	.....
172 L	10.0	.....

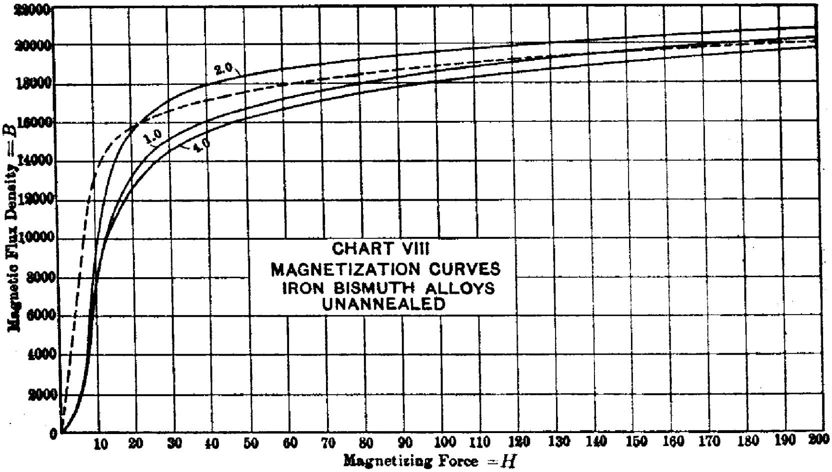


CHART VIII
MAGNETIZATION CURVES
IRON BISMUTH ALLOYS
UNANNEALED

The magnetization curves under two conditions, as forged and as annealed at 675° C are plotted in Charts VIII and IX, and comparative data is tabulated in Tables V and VI. For all tests the curves for a bismuth content of 1.0, 4.0, 6.0 and 10.0 per cent. present no features of particular interest, the quality being well below the standard electrolytic iron sample. But for the bismuth content of 2 per cent., the curve, while below the standard for values of H of less than 22, at this point crosses the electrolytic curve and reaches values of density from four to five per cent. higher throughout the rest of the range.

Annealing at 675° C has not had much effect in these upper ranges of magnetizing force, but has been most beneficial in the lower portions, by making the quality equal to the standard for these values of H, and lowering the crossing point to H = 10. The coercive force also has dropped from 7.0 as unannealed to 4.2 after heating. Further annealing at 1000° has caused a pronounced deterioration of the quality, and the 2.0 per cent. bismuth curve has taken a place in the midst of those of other percentages.

The general effect of the successive annealings is again the same as previously noted. The first heating to 675° C. has brought out the best magnetic qualities of the different alloys, with considerable improvement over the unannealed state; and further annealing to the higher temperature of 1000° C has resulted in a deterioration. The coercive forces also have been markedly lowered with the first heating, but their values are relatively varying at the higher heating.

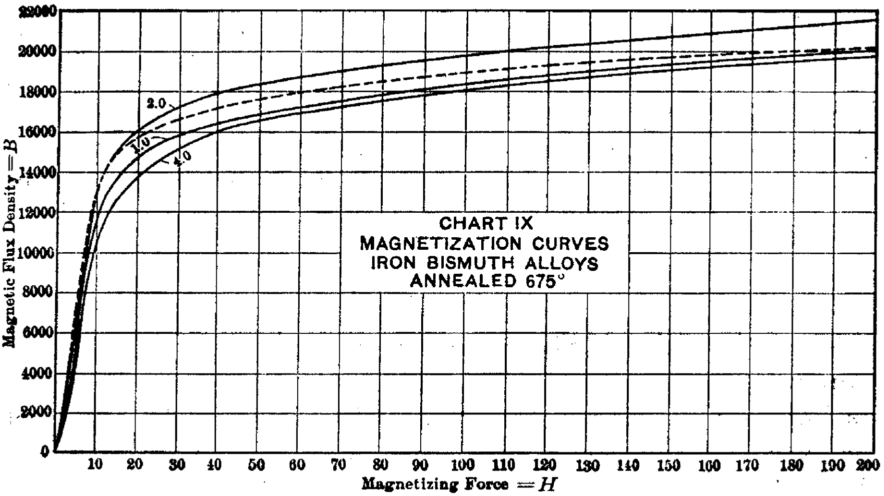


CHART IX
MAGNETIZATION CURVES
IRON BISMUTH ALLOYS
ANNEALED 675°

Summarizing, we have in this series the somewhat paradoxical condition of the addition of 2 per cent. of bismuth, the most diamagnetic element known, improving the already high quality of the pure iron. The density values reached with this material exceed those obtained with any of the several hundred different alloys which we have tested up to this time. Since analyses have not as yet been made to determine the amount, if any, of bismuth present in the alloys, it cannot be asserted that the intended content and actual content of bismuth are the same, Definite conclusions as to the quantitative influence of bismuth must therefore be reserved until later.

TABLE VIII—COMPARATIVE RANK OF MATERIALS ON VALUE OF B, AT H = 20.

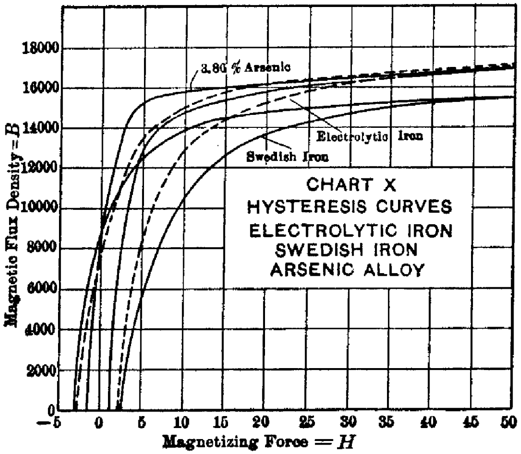
No.		Comp.	H = 10	H = 20	H = 50	H = 100
1	Kreusler's Annealed Rod of Dynamo Steel.....		15,680		17,100	18,280
2	Barrett-Hadfield's Alloy...	2¼ AL	15,300	17,000	18,000	
3	113 D	3.86 AS	15,050	16,300	17,550	18,650
4	172 H	2.0 Bi	13,250	16,100	18,350	19,750
5	113 H	3.56 AS	14,200	16,100	17,550	18,750
6	Sankey's Lohys Sheet.....		14,150	16,100	17,050	18,250
7	117 A	Elec.	10,000	15,950	17,700	18,850
8	113 F	4.14 AS	14,200	15,900	17,250	18,450
9	Hadfield's Magnet Steel...		12,150	15,900	17,350	18,200
10	Barrett Pure Iron........		14,000	15,900	17,200	
11	113 B	1.81 AS	11,850	15,750	17,450	18,750
12	121 I	0.29 AS	13,200	15,550	17,250	18,550
13	Allen's Cast Steel........		12,100	15,050	17,200	18,450
14	Barrett-Hadfield Alloy....	2½ Si	14,000	15,000	16,600	
15	High Grade Sheet........		13,100	14,800	16,300	17,600
16	172 D	(Trans + 5 As)	9,550	14,750	16,750	18,000

COMPARISONS.

Magnetic testing is not on such a basis that data from various sources can be assumed as absolute, and on this account comparisons are apt to be misleading. While recognizing this fact we have nevertheless collected published data and compared them with our results in Table VIII. In this table is given the comparative ranking of several of our alloys, together with material tested by other investigators and the data for which was published because of the excellent magnetic quality. The material is ranked on the relative densities reached for a magnetizing force of H = 20, this value of H being taken because it is beyond the bend of the magnetization curve. Among the outside data we note the results of Barrett's tests (Inst. Elec. Engrs. Vol. 31) on pure iron (10) and on Hadfield's alloys of this iron with 2¼ per cent. of aluminum (2) and 2½ per cent. silicon (14), the last being the basis of the present silicon alloys so largely used in transformer construction. In this tabulation of sixteen tests there appear eight of our electrolytic iron, arsenic and bismuth series.

TABLE IX—ELECTRICAL RESISTANCE.

		Microhms per cm.^{3}	Relative
NSW	Swedish anode	11.6	0.96
117 A	Electro forged	12.1	1.00
Antimony.			
172 E	1.15%	20.2	1.67
Arsenic.			
121 I	0.292%	14.7	1.22
121 H	0.430%	16.8	1.39
113 A	0.915%	19.5	1.62
113 B	1.810%	25.5	2.11
113 D	3.862%	37.1	3.07
113 H	3.563%	34.0	2.82
172 C	Trans. sheet.	18.7	1.55
172 D	Trans. + 5% As.	30.2	2.51
Bismuth.			
172 G	1.0%	13.4	1.11
172 H	2.0%	14.5	1.20
172 J	4.0%	15.3	1.27
172 K	6.0%	13.0	1.08
172 L	10.0%	16.6	1.38



HYSTERESIS TESTS.

On Chart X are plotted the hysteresis curves for bar 113 D, the 3.86 per cent. arsenic alloy; for the electrolytic iron sample, 117 A; and for the Swedish anode bar NSW. The half loop only is shown, with H (max.) = 50. Integration gives as the relative areas of the loops, 1, 1.7 and 2.1, respectively; and indicates the relative hysteresis losses per cycle of the materials in question.

ELECTRICAL RESISTANCE.

In connection with these investigations, measurements of the electrical resistance of the magnetic test bars were made, and in Table IX are enumerated the results for the materials discussed in this paper. The specific resistances are given in microhms per cubic centimeter, and in the last column are tabulated the relative resistances with electrolytic sample 117 A as the basis of unity. Its resistance is but little different from the Swedish iron bar, being slightly higher, as a result perhaps of the heat treatments which the bars had undergone.

The addition of 1.15 per cent. of antimony has increased the resistance very markedly, from 12.1 to 20.2 microhms per cubic centimeter, or an increase of 67 per cent.

Additions of arsenic to the iron have also increased the resistance most markedly, the increase being a function of the percentage of added element. Bar 113 D, with 3.86 per cent. of arsenic, has a specific resistance of 37.1 microhms per cubic centimeter, or 3.07 times the resistance of the electrolytic samples. Likewise, the addition of the arsenic to commercial transformer sheet iron has raised its electrical resistance form 18.7 to 30.2 microhms per cubic centimeter, an increase of 62 per cent.

The bismuth alloys show but little increase of resistance, but definite deductions cannot be drawn from these figures, since the chemical analyses have not yet been completed to confirm our intended bismuth content.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

DR. W. R. WHITNEY: Mr. President, I recognize the truth of what Prof. Burgess has said, that it is difficult for any one to discuss a subject of this kind, where the methods of obtaining the data are difficult of manipulation. It is, unfortunately, true that it is hard to make comparative tests of the electric and magnetic properties of steel. I should be very glad to assist such work as Prof. Burgess is doing in any way possible, or to answer any questions that I can answer on the methods of the treatment of steel, because I recognize that it is work that ought to be, and is likely to be, of very great value to the electrical industries of this country. Take the case of arsenic in steel for transformers—4 or 5 per cent. He has tested, as I understand it, the physical properties of that material, and found that it can be rolled and made into sheets. That is a very important matter, and possibly of great value to the electric industry of this country. All I want to say is that I for one appreciate, and have appreciated, the value of such work as Prof. Burgess is doing on iron.

MR. CARL HERING: I also wish to express my appreciation of the great value of this work of Prof. Burgess. I would be pleased to know how he alloys the arsenic with the iron, in given proportions, because the volatilization point of arsenic is lower than the melting point of iron, so that much of the arsenic would be volatilized before it is gotten into solution with the iron. I ask this because there are special methods for doing this, one of which I understand is patented.

I notice also that he finds some impurities in the electrolytic iron. I would like to ask whether that could not be overcome by the use of porous cups. I have noticed that some of the particles which are suspended in the solution, travel with the current, as I described in a paper read before the Society,[1] and it seems to me that this explains how the carbon gets over to the electrolytic iron; if a porous cup were used, it would seem that it might prevent some of those impurities from reaching the electrolytic iron.

Concerning the comparison of magnetization curves, it seems to me that the difficulties might be overcome if some one material were agreed upon as a standard, and a whole lot of samples made of it and sent to the Bureau of Standards to have their curves determined; then let those who are interested in such comparative curves get a sample of that material and run that sample through their own apparatus. In that way it becomes possible to compare all curves with one standard, which has been accurately determined by the Bureau of Standards.

MR. H. M. HIBBARD: Mr. President, in regard to the remarks

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[1] See "Visible Migration of Particles between Electrodes," Hering. Trans. Am. Electrochem. Society, Vol. X, p. 35.

of the last speaker about alloying iron and arsenic: It is very easy to alloy iron and sulphur. I believe sulphur in respect to its fusing point presents the same condition as arsenic does. Thirty years ago, when I was in the laboratory, I used to have to make sulphide of iron for the generation of sulphide of hydrogen. I took a crucible, filled it full of iron fragments, heated them red hot, added sulphur, and got sulphide of iron without any trouble. I dare say something like that could be done to make iron arsenic alloy, which then could be alloyed with the iron in any proportion that was desired.

PROF. C. F. BURGESS: Mr. President, the remarks of Mr. Hibbard will, I think, answer Mr. Hering's question in reference to the possibility of alloying arsenic with iron. Alloys can be made, although the arsenic has a lower volatilizing point than the iron melting point. We perhaps made an error, although we did it knowingly, in calling this an alloy of iron and arsenic. It may be a mixture of iron with arsenide of iron under the particular conditions of working which we employed, that is, mixing the granulated electrolytic iron with arsenic in a closed magnesia crucible, and heating it somewhat rapidly in an electric furnace; percentages of arsenic subsequently found in the alloy were 4 per cent. Some of the arsenic, of course, volatilized out when the amounts put in were greater than 4 per cent.

As to the purity of the electrolytic material being increased by the use of porous cups, that undoubtedly could be secured. Some of the resultant impurity is doubtless due to entrainment, or physical mixture, of the electrolyte with the iron. The difficulty I would see in carrying out the suggestion of Mr. Hering, that the Bureau of Standards have one material which may be standardized by their methods and then furnished to other investigators, is that the different methods of testing require different sizes of samples, and it is difficult to get comparative results on account of the errors due to these varying sizes and shapes. In other words, the method of testing would have to be standardized.

MR. E. S. SPERRY: What was the amount of reduction in the reluctance below and above the anneal?

PROF. BURGESS: In reference to the bismuth alloy, which has been designed as a 2 per cent. bismuth iron alloy—that is, a supposed 2 per cent. bismuth content—shows a magnetic density of 20,000 lines per square centimeter, while the pure or electrolytic iron had a magnetic density of 19,000 per square centimeter. It is not a large percentage of increase, but it is some increase, and this is not so significant a point as is the apparent showing that the presence of a diamagnetic material, such as bismuth, will not harm the material.

A paper presented at the Fifteenth General Meeting of the American Electrochemical Society, at Niagara Falls, Canada, May 8, 1909; President E. G. Acheson in the Chair.

FURTHER EXPERIMENTS WITH CALCIUM ALLOYS AS REDUCING AGENTS.

By O. P. Watts and E. R. Suhm.

At a previous meeting of this Society one of the members made a suggestion to the effect that an account of our failures might prove sometimes quite as helpful as an account of the successful researches usually described; so, although the results hoped for when these experiments were undertaken have not been realized, the methods used may perhaps be of value to others who are experimenting along similar lines.

The present paper is a continuation of one which appeared in Volume XIII of the Transactions of this Society, entitled "The Preparation of Calcium Alloys for Aluminothermic Work." In the few experiments tried at that time the reactions were violent and the yield of metal was small. One of the objects of the experiments about to be described was to suppress this violence of reaction.

Since the heats of oxidation per gram equivalent of calcium and of magnesium are greater than that of aluminum, and because in some proportions the mixed oxides melt at a lower temperature than pure alumina, it was expected that these alloys would prove more effective reducing agents than aluminum, and it was hoped that by their use it might be possible to obtain fused tungsten and titanium as reduction products.

Aluminum Versus Calcium-Magnesium-Aluminum Alloys as Reducing Agents.

At the outset a direct comparison was made between aluminum and an alloy consisting of 30 per cent. calcium, 20 per cent. magnesium, 50 per cent. aluminum in the reduction of a mixture of rutile and manganese dioxide in proportions calculated to yield a manganese-titanium alloy containing 35 per cent. of the latter. Charges of 250 grams were fired in the usual way by magnesium ribbon surrounded by an igniter of barium peroxide and finely powdered aluminum. The granulated aluminum gave an excellent reduction and a good ingot of manganese-titanium alloy, but the reaction of the calcium alloy was very violent, blowing part of the charge from the crucible, and the resulting alloy was scattered through the slag in globules about the size of peas.

Substitution of External Heat for that Produced by the Reduction of Manganese Dioxide in the Previous Experiments.

Experiment 10: A charge of 90 grams pulverized rutile and 81 grams of the calcium alloy previously mentioned, without the igniter, was heated in a graphite crucible for twenty minutes in a resistor furnace, using 20 kilowatts. The reaction was quiet, but the yield was only 26 grams, or 48 per cent. of metal in scattered globules. The temperature had not been high enough for a good separation of metal and slag.

Experiment 11: The experiment was repeated on a larger scale, heating for 10 minutes by 24 kw. a charge of 281 grams of rutile and 255 grams of alloy. Twenty-seven grams of metal was obtained in globules, but much metal was scattered throughout the slag in particles too small for collection. Analysis of the product gave 75.3 per cent. titanium and 25 per cent. aluminum. This indicated that more than the theoretical amount of rutile is required in the charge in order to completely oxidize the aluminum, and accordingly more than the theoretical proportion of rutile was used in later experiments.

Experiment 13: Two hundred and forty-five grams of alloy was mixed with an amount of rutile 40 per cent. in excess of that required by theory, and the charge heated by 17.5 kw. for fifteen minutes. The resulting metal was scattered all through the slag.

Experiment 14: As a comparison, the same weight of rutile mixed with an amount of comminuted aluminum chemically equivalent to the alloy previously used, was heated by 19 kw. for thirty minutes. There was no outward manifestation of reaction, but reduction had occurred. The metal settled through the slag and collected in several large globules. This reduction by aluminum was more satisfactory than similar ones in which calcium alloys were used.

Experiment 15: In the hope of attaining a higher temperature, an alloy consisting of 60 per cent. calcium and 40 per cent. magnesium was tried upon excess of rutile. The reaction was quiet, although flames came from the crucible for thirty seconds. There was no separation of metal and slag.

It was evident that some way must be found of heating the charge considerably above the temperature at which reaction begins in order that the heat added by the reaction should produce a fluid slag and a good separation of metal. An attempt to add the charge to a crucible previously heated to whiteness resulted in the ignition of the charge before it got inside the crucible, and the consequent burning of the product in the air.

In this juncture an article read a dozen years ago upon the effect of size and shape of grain upon the rate of combustion of the brown prismatic powder used in large ordnance suggested a possible solution. As a result of experiments with grains of various sizes and shapes, and with perforations to increase the amount of surface, it was determined that the combustion of gunpowder is purely a surface phenomenon, and that the rate of combustion depends on the ratio of surface to mass.

In the previous paper upon calcium alloys the violence of reaction was ascribed to the sudden vaporization of a part of the calcium or magnesium before it could combine with the oxide which was being reduced. Attemps to use more finely pulverized materials and to secure more intimate contact betwen alloy and oxide had resulted in the blowing of most of the material out of the crucible. The use of briquettes promised to give a fairly slow reaction, even though the reducing agent and oxide were used in a very fine state of division.

The Use of Briquetted Charges to Diminish the Speed of Reaction.

An alloy consisting of 23 per cent. aluminum, 35 per cent. calcium and 42 per cent. magnesium was ground as fine as possible in a disc pulverizer, mixed with pulverized rutile, and made into briquettes using a 10 per cent. solution of gum arabic in water as a binding material. The briquettes contained 10 per cent. of rutile in excess of the theoretical amount.

Experiment 17: A crucible of Acheson graphite with an electrically baked lining of magnesia was heated to whiteness in the resistor furnace and the briquettes added one at a time. They slowly settled in the crucible, but gave no other indication of reaction. As a result of this experiment there was on the bottom of the crucible a layer of very porous, yellowish metal, with slag above it, then another layer of metal. Near the top the briquettes could still be distinguished, each having a metallic core with slag on the outside.

The briquettes had proved satisfactory in suppressing the violence of reaction, but the temperature attained was still too low for a good separation of metal from slag.

Experiment 20: A similar experiment was tried using an alloy of the formula Al_2CaMg with the theoretical proportion of rutile. As binding materials solutions of gun damar, tragacanth, shellac and linseed oil were used. Graphite crucibles with magnesia linings were heated by 24 kw. for two hours before adding the briquettes. Reaction was quiet in each case. The briquettes made with gum damar gave sparks and some smoke, and those made with linseed oil gave off a thick black smoke for nearly a minute. The result was about the same as in experiment 17.

An attempt was now made to secure a higher temperature by adding to the charge a considerable excess of calcium alloy and enough barium peroxide to oxidize it, thus adding greatly to the heat of reaction, yet introducing no other metal into the product, as was done when manganese dioxide was used as the oxidizing agent. Briquettes were accordingly made of the alloy Al_2CaMg with 10 per cent. excess of rutile, to which different amounts of the heat-producing mixtures of alloy and barium peroxide were added.

(*a*) 60 per cent. charge and 40 per cent. heating mixture.
(*b*) 50 " " " " 50 " " " "
(*c*) 40 " " " " 50 " " " "

Experiment 21: A graphite crucible four inches in diameter and six inches high with a magnesia lining, was heated to whiteness in the resistor furnace and the briquettes were dropped in one at a time. All reactions were violent, increasingly so in proportion to the amount of fuel and oxidizer added to the charge. The product was a white, porous metal of rather high density, but poorly separated from the slag.

An attempt was now made to obtain fused tungsten by the use of the same alloy as a reducing agent.

Experiment 22: Briquettes were made of Al_2CaMg and WO_3, using 15 per cent. of the latter in excess of the theoretical amount to insure complete oxidation of the reducing agents. Two charges were made into briquettes, using shellac as a binder.

(*a*) 171 grams WO_3 + 51 grams alloy.

(*b*) 103 grams of (a) + 103 grams of BaO_2 and alloy.

Two graphite crucibles with magnesia linings were heated to intense whiteness by 50 kw. At the end of forty-five minutes heating the briquettes were dropped in.

(*a*) The reaction was rapid, but not violent, and resulted in a single mass of tungsten. The metal had sintered rather than fused and was a mere shell, having the form and nearly the size of the original briquettes. The metal was entirely free from slag.

(*b*) The reaction was very violent and much material was projected from the crucible. The product was a porous mass of intermingled metal and slag at the bottom of the crucible. The magnesia linings were in good condition.

Experiment 23: An arc at 40 to 50 kw. was substituted for the resistor furnace in the hope of getting a higher temperature. Briquettes were made with shellac of 297 grams rutile and 172 grams Al_2CaMg. A graphite crucible four inches in diameter and six inches high was placed upon a slab of graphite, which served as one terminal, and surrounded by finely pulverized carbon. The bottom of the crucible was covered with a layer of magnesia to prevent contact of the reduced metal with carbon. The arc was started by laying a small carbon rod on top of the magnesia and bringing the upper electrode down upon it. Pure alumina was added and thoroughly fused. When the current was interrupted for the purpose of adding the charge, the alumina at once solidified. To prevent this, barium carbonate and lime were added and the whole fused by the arc. The circuit was then broken and briquettes fed in until the slag began to freeze, when the arc was started again, and so on until all the charge had been added. On examining the crucible a few globules of metal were found resting on the magnesia bottom and well separated from the slag above. Half way up was a mixed mass of metal and slag, and near the top was a porous, reddish mass that appeared to be titanium nitride, with a thin layer of slag above it. The only good separation of metal and slag occurred at the outset when the original fusible slag was in large amount compared to the charge.

Adding the Charge to a Fused Slag.

In the hope of getting a better separation of metal a mixture of oxides was fused in the crucible and the charge dropped into the molten mass.

Experiment 24: Two Acheson graphite crucibles 4" x 6" with an inch of magnesia in the bottom were heated in the resistor furnace. Thirty-four hundred grams of a mixture having the composition $2CaO.BaCO_3.2Al_2O_3$ was prepared.

(*a*) The charge was composed of 65 parts of the mixed oxides to 35 parts rutile. When this was thoroughly fused, 100 grams of aluminum wire in a single piece ⅛" in diameter was slowly introduced into the crucible. There was a very marked increase in temperature and at times the slag boiled over the edge of the crucible. A thin layer of whitish metal was found at the bottom of the crucible. Its color would indicate that it contained aluminum alloyed with the titanium.

(*b*) $2CaO.BaCO_3.2Al_2O_3$ was fused and briquettes of 559 grams WO_3 + 149 grams Al_2CaMg were thrust into the fused mass. The reaction was violent, spattering fused slag several feet out of the furnace. There was no separation of metal. The product was dark gray and of high density.

Experiment 25: The reduction of rutile was tried on a larger scale. Twelve hundred grams of $2CaO.BaCO_3.2Al_2O_3$ was mixed with 800 grams of rutile and fused in the resistor furnace. Four hundred and fifty grams of aluminum wire was then added. After cooling, it was found that the layer of magnesia placed on the bottom of the crucible at the outset, had disappeared. A layer of titanium on the bottom had taken up carbon from the crucible. Higher up in the crucible there was a considerable mass of white metal, which was found to consist of 80 per cent. titanium and 20 per cent. aluminum. This method fails to produce pure titanium because of the latter's affinity for aluminum.

Experiment 26: It is well known that the oxides of tungsten and molybdenum are volatile at high temperatures. This experiment was tried to see if the vaporization of MoO_2 could not be prevented by causing it to combine with other oxides before the highest temperature was attained. Accordingly 200 grams of MoO_2 was mixed with 1200 grams of $2CaO.BaCO_3.2Al_3O_3$ and the mass fused in a graphite crucible in the resistor furnace. No vaporization occurred. Six hundred grams more of MoO_2, which is 150 grams in excess of the aluminum added later, was mixed with the oxides of calcium, aluminum, etc., and gradually added to the fused mass in the crucible. Much vaporization occurred. Before all of this mixture had been added aluminum wire was fed in, then more mixture, and so on alternately until the whole 182 grams of aluminum had been added. On opening the crucible, 248 grams of a white, dense metal with a conchoidal fracture was found on the bottom of the crucible. The layer of magnesia which was placed in the crucible had disappeared. Above the metal was a layer of crystalline slag. The separation of metal and slag was perfect. The yield of metal was 51 per cent. of theory. A quantitative determination gave 99.5 per cent. of molybdenum. This experiment would seem to show that loss of MoO_2 and WO_3 by vaporization can be prevented by admixture with other oxides, provided the entire charge be put into the cold crucible and heated gradually.

Several additional experiments were tried in the direct comparison of the efficiency of aluminum and Al_2CaMg upon Mn_3O_4 according to the regular Goldschmidt method.

Experiment 27: (*a*) Sixty-four grams Mn_3O_4 + 26.4 grams alloy gave an excellent separation of metal from slag, and a yield of 43.4 per cent. of the theoretical amount of metal. The reaction was steady and quiet.

(*b*) Seventy-four grams Mn_3O_4 + 25.4 grams granulated aluminum gave a slow, quiet reaction, but a very poor separation of metal from slag.

(*c*) Two hundred and fifty-six grams Mn_3O_4 + 105.6 grams alloy reacted quietly and yielded 70 grams of metal in a single ingot, a yield of 57 per cent. The metal was hard, dense, and resembled commercial manganese produced by the Goldschmidt process. The slag was greenish in color, showing a desirable amount of unreduced manganese oxide.

Experiments with Cr_2O_3 on a similar scale yielded only scattered globules of metal. This result is not surprising in view of the statement by L. Guillet[1], as a result of many experiments, that the reduction of Cr_2O_3 by aluminum is not successful in small charges up to 3 kilograms.

SUMMARY.

The direct comparison of aluminum with the alloys as reducing agents gave conflicting results. In the reduction of a mixture of MnO_2 and TiO_2 aluminum was superior, while in reducing Mn_3O_4 the alloy gave far better results. It is probable that the alloys are superior in all cases where none of the charge is blown out of the crucible. The alloys are distinctly superior to aluminum for the igniting mixture.

Attempts were made to supply enough heat to secure solid masses of tungsten and titanium.

(a) by rapidly heating a charged crucible in a resistance furnace.
(*b*) by heating with an arc of 50-60 kw.
(*c*) by feeding the charge into a mass of melted oxides,
(*d*) by adding BaO_2 and extra alloy to the charge.

All these methods failed.

Molding a charge of very finely pulverized material into briquettes was very effective in suppressing too great violence of reaction.

The vaporization of MoO_2 can be prevented by getting it into combination with other oxides before an extremely high temperature is attained.

Since the violence of reaction of the alloys increases with the amounts of calcium and magnesium, the most serviceable, as well as the cheapest, alloys will probably be those with only enough calcium or magnesium to be readily pulverized.

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[1] Les Alliages Metalliques, p. 18.

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THE SOLIDIFICATION OF ALLOYS AND MAGMAS

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In this consideration of possible analogies in the solidification of alloys and igneous rocks, the treatment will be from a knowledge gained in the study of alloys, and with a confessed ignorance of the subject from the viewpoint of the geologist.

That the value of the views to be advanced is clearly recognized, and that their applicability extends beyond the limited sphere with which the writer is familiar, is well shown in the following extracts from the writings of Dr. George F. Becker,[1] of the United States Geological Survey. He says,

> In a plan submitted to the director when the new physical laboratory of the survey was first contemplated, I laid special stress upon the study of isomorphism and eutexia.

Also,

> It would appear that the relation between liquids must be reducible to very general groups. Liquids must be either miscible or immiscible, and miscible liquids must exhibit either isomorphic properties or eutectic ones.

And again,

> The applicability of eutexia to rock-classification depends upon the fact that it makes the systematic discussion of magmatic mixtures possible. Inasmuch as the subject-matter of lithology consists of mixtures, their classification must be carried out in terms of definite or standard mixtures, while the only mixtures possessing appropriate distinguishing properties are the eutectics. Thus in dealing with magmas or other heteromorphous miscible liquids, the eutectics seem to afford not only the best but the only natural and rational standards of reference. With any eutectic as a basis, a series of magmas may be prepared, each differing from the eutectic by containing an excess of one or more constituents.

Here, then, is the key to the whole discussion—the comparison of alloys and igneous rocks from the standpoint of isomorphism and eutexia, a standpoint which has its rational foundation on the laws

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[1] Day and Allen, *Isomorphism of the Feldspars* (Publications of the Carnegie Institution). Introduction by Dr. George F. Becker.

of physical chemistry, more especially the theory of solutions and the phase rule of Gibbs. The application of these laws is of very recent date. In fact, it is hardly necessary to go back more than ten years to cover the period of their development. Because of this fact the drawing of well-worked-out analogies is very difficult; a considerable amount of investigation has been done with the simpler alloys, but in geology the field is practically barren. It will be necessary, therefore, to confine the discussion to the fundamental types of solidification from the viewpoint of their solubility relations, and to point out the application of these laws to certain alloys, and analogous minerals and rocks, wherever possible; leaving to the judgment and imagination of the reader the possibility of their further application to geological problems.

Proceeding from this viewpoint, it is at first essential to grasp a few fundamental facts. Alloys are solutions, and obey the same laws in freezing as aqueous solutions of salts do in crystallizing. It is merely a question of fluidity at a different range of temperature. Not only is this true, but it is likewise true that solubility is not limited to any particular state of the interacting substances. Thus we may have solubility in the solid state, or solid solutions. This is shown in the tendency for mutual diffusion of solid gold and solid platinum; or more well known, perhaps, in the harveyizing of armor plate, where carbon is absorbed by iron at temperatures well below the point of fusion. These solid solutions you are more familiar with as isomorphous mixtures or mixed crystals.

COOLING-CURVES

In obtaining the solubility curves for salts in solution, the usual procedure is to make analyses of the saturated solution at various temperatures, and in this way to obtain a series of points which may be plotted into a temperature-composition curve. In the case of alloys, this method is not so well suited, since we are working at higher temperatures; also we often have to deal with changes in the solid, as well as in the liquid state. For alloys we obtain the necessary data for individual mixtures by means of the cooling-curve, a curve which is a function of time and temperature, and shows the change in the rate of cooling as the temperature is lowered. Breaks in the curve or changes in direction indicate an evolution or absorption of heat, and denote a change of state or a transition in the substance. In practice, the general method is to heat a metal or alloy of known composition to a desired temperature, introduce a pyrometer, and record the temperature at stated time-intervals during cooling.

Such curves are shown in Fig. 1. The one on the left represents the cooling of pure platinum. Temperatures are plotted on the vertical axis, and time on the horizontal. Starting at o, our metal cools gradually, until we reach 1,775°. Here we have a jog in the curve, an arrest in the temperature change due to the freezing of the metal and the evolution of the heat of solidification. Freezing completed, the material cools to room temperature without further break in the curve.

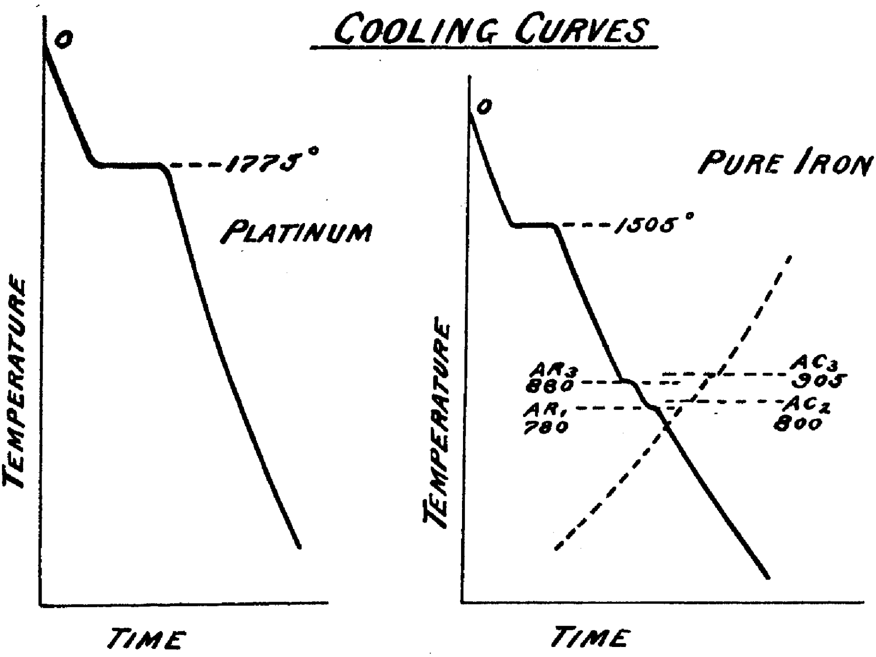

FIG. 1

On the right we have another cooling-curve, that of pure iron. Starting again at o, the metal cools to 1,505° when there is a break due to the solidification. On further cooling, we note a different condition from that observed in the case of platinum. There are two other jogs in the curve, at 880° and 780°, denoting changes in the solid state. These represent the transition points of the three allotropic modifications of pure iron, and are designated as the α, β, and γ states. These allotropic states represent changes in the properties of the iron without change of composition, and are analogous to some cases of pleomorphism in minerals; for example:

$$\text{Sulphur}\left\{\begin{array}{c}\text{orthorhombic}\\ \text{to}\\ \text{monoclinic}\end{array}\right\}96^\circ \qquad \text{Leucite}\left\{\begin{array}{c}\text{pseudo-isometric}\\ \text{to}\\ \text{isometric}\end{array}\right\}500^\circ$$

FREEZING-POINT CURVES

In the investigation of alloys, we consider three general types of solubility relations; with complete miscibility in the molten state it may after solidification be complete, partial, or nil.

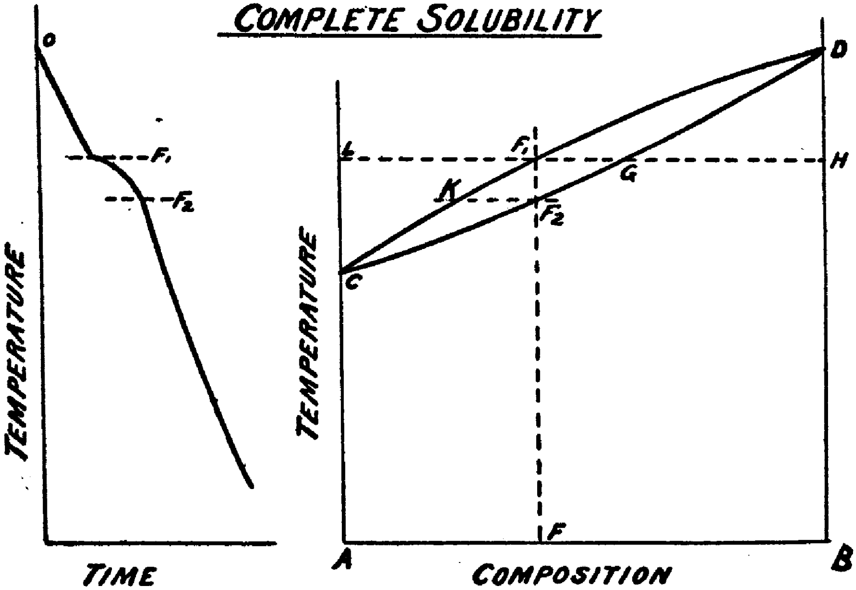

FIG. 2

Referring to Fig. 2, we have represented the type of complete solubility before and after solidification. On the left is the cooling-curve for a single mixture. We note two breaks, at F_1 that due to commencement of solidification, and at F_2 a change of direction due to its completion. With points for commencement and completion of solidification obtained from similar cooling-curves representing a complete series of mixtures, we may plot a new diagram with the composition on the X axis, and the corresponding freezing temperatures on the Y axis, and obtain the solubility curve as shown on the right of Fig. 2. In metallography this is usually designated the "freezing-point curve." CF_1D and CF_2D are the loci of the upper and lower transition points as obtained from the cooling-curves, and represent, therefore, the commencement and completion of solidification for the entire range of mixtures.

With this type of freezing, a mixture of composition F, for example, will commence to solidify at F_1 with a separating-out of the first frozen particle of composition G, a consequent relative enrichment of the molten metal in element A, and a lowering of the temperature of solidification. During freezing, therefore, the temperature-composition locus of the molten material will shift along the upper curve from F_1 toward C, and that of the solid material along the lower curve from G_1 toward C. If cooling is sufficiently slow because of the complete solubility in the solid, the equilibrium is completed by the diffusion of the different solid particles until finally the resultant alloy has a uniform composition F_2 the same as the original molten mixture.

With complete solubility, therefore, the freezing is selective but not rigid, and the initial heterogeneousness is effaced by diffusion. Under the microscope, the structure should be uniform throughout if diffusion is complete.

Of this type are the Sb-Bi, Ag-Au, Fe-Mn alloys.

The type of complete insolubility is shown in Fig. 3. On the left is the cooling-curve, with a break at K_1, indicating commencement of solidification, and a jog K_2K_2 denoting completion of freezing at a constant temperature. At the right is the freezing-point diagram, with FE_1G and CE_1D as the loci of commencement and completion of solidification. A mixture of composition K will commence to freeze at K_1. The solid separating out will be element A only, because of the complete insolubility; there will be a relative enrichment of the molten solution in B, and a gradual shifting of the temperature composition range from K_1 to E_1. At E_1 the whole of the remaining solution will freeze at this constant temperature; but because there is no solubility in the solid *A* and *B* will separate.

For a mixture of composition *E*, freezing will occur throughout the mass simultaneously, with a separation in the solid state of *A* and *B*. In like manner, for alloy *M*, freezing will be as explained above, except that element *B* will first separate out, with a gradual enrichment of mother metal in *A*, and a gradual lowering of the freezing temperature, until at E_1 there will again occur the isothermal solidification of the remaining solution, with separation of *A* and *B*.

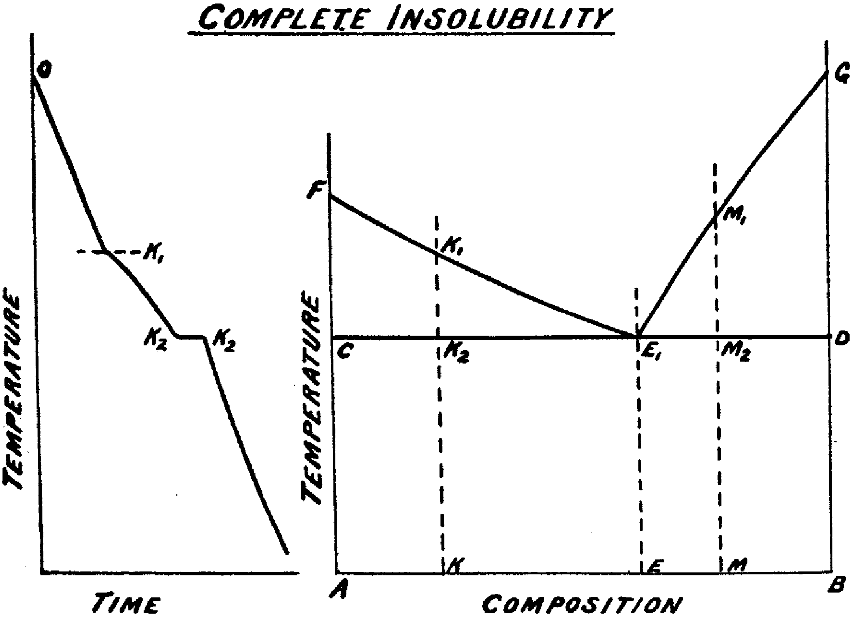

FIG. 3

The point of lowest freezing temperature E_1 is called the eutectic point, and the mixture of this composition, the eutectic mixture, or the eutectic.

Summarizing, we have in this type rigidly selective freezing, with alloys eutectiferous throughout the range of composition, and no tendency for mutual diffusion. Under the microscope we should expect to find a more or less segregated excess metal *A* or *B*, depending upon whether the initial composition was above or below the eutectic ratio; together with an intimate composite structure of *A* and *B* as the eutectic.

Of this type are the Sb-Pb, Pb-Sn, Cd-Zn alloys.

A third type of freezing-point curve is that of partial-solubility solid, as shown in Fig. 4. This condition is really a combination of the two types previously described. For mixtures between *JF* and *GK*, freezing will be of the type of complete solubility. Between *F* and *G*, the freezing will be selective, as in the complete insolubility type, except that, since there is partial-solubility solid, the excess metal to separate out will be saturated with the other element; and the eutectic will be a composite of *A* saturated with *JF* per cent. of *B* and *B* saturated with *GK* per cent. of *A*.

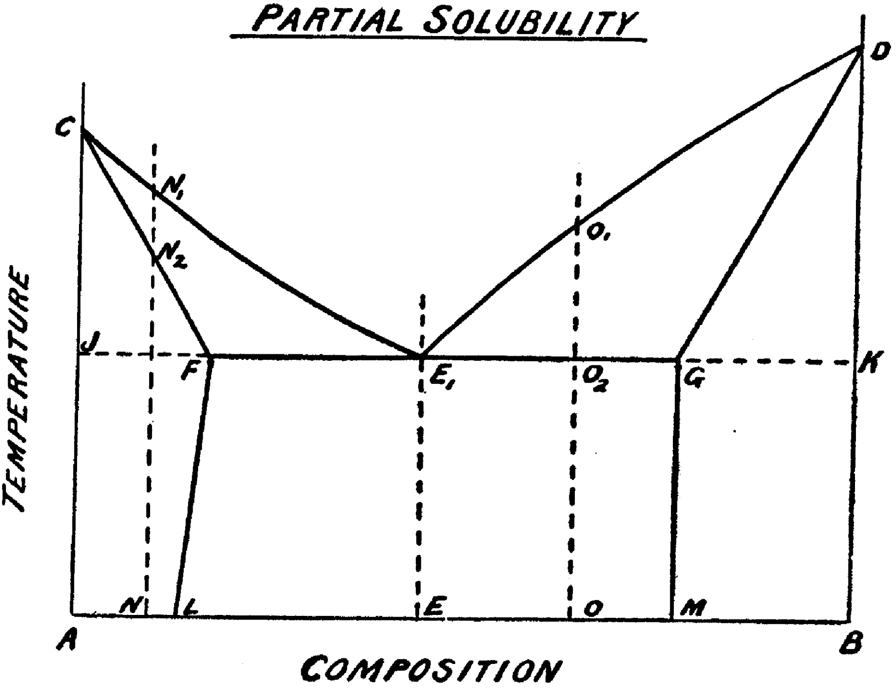

FIG. 4

With this type of freezing, therefore, we have freezing with complete solubility at the two ends of the series, and under the microscope we should find a homogeneous structure. For the intermediate mixtures there will be selective freezing and under the microscope we should expect a heterogeneous structure of an excess substance either *A* saturated with *B* or *B* saturated with *A*, depending upon whether the composition of the original molten mixture lay to the left or right of the eutectic ratio; and a composite eutectic *A* saturated with *B* and *B* saturated with *A*.

Of this type are the Sn-Zn, Au-Ni, Ag-Cu alloys.

Besides these three general types of solubility which we have considered, numerous others could be taken up in detail. For example, *A* and *B* might form one or more definite compounds, which compounds could have with *A* and *B* and with each other, independently different solubility relations. Or again, there might be only partial solubility while the alloy was still molten. However, all are really combinations and elaborations of the fundamental types to fit more complicated conditions.

ISOMORPHISM OF FELDSPARS

Referring now to one of the few investigations in this line which have been carried out in geological research, we have (Fig. 5) the

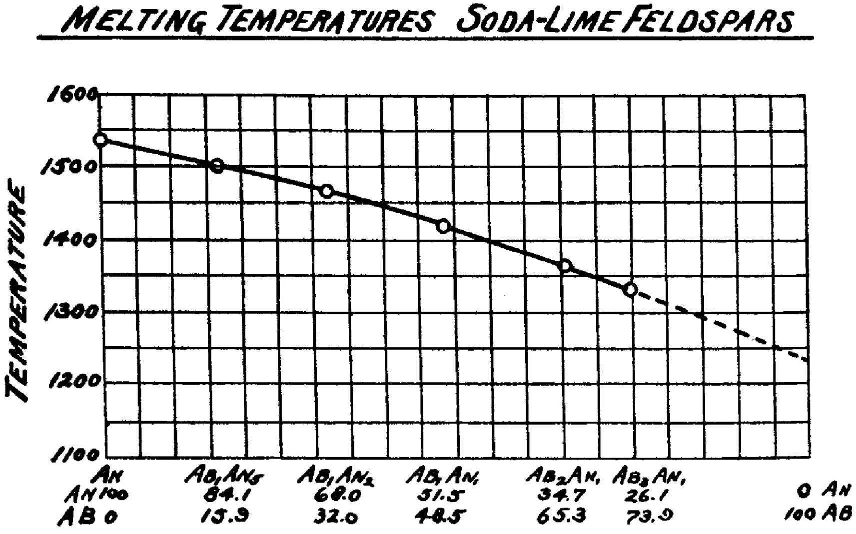

FIG. 5

freezing-point curve of the soda-lime feldspars, as determined by Day and Allen[1] at the Geophysical Laboratory of the Carnegie Institution. The work was conducted exactly as indicated for alloys, by time-

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[1] Day and Allen, *Isomorphism of the Feldspars* (Publications of the Carnegie Institution).

temperature records of the desired mixtures. Because of the undesirable supercooling, Day and Allen, however, recorded the heating, rather than the cooling, curve. As will be seen from the diagram, it is of the complete solubility type, with no indication of eutectics or intermediate compounds. It is conclusive evidence that between 100 per cent. of anorthite and 100 per cent. of albite we have an isomorphous series; and microscopic examination was entirely confirmatory.

IRON-SILICON ALLOYS

Fig. 6 shows the freezing-point curve of the iron-silicon alloy,[1] chosen because it represents a rather complex set of conditions. At A there is evidence of the formation of a compound, the silicide Fe_2Si. At C (50 atoms per cent. Si) another compound is indicated, of the composition FeSi. Up to $33\frac{1}{2}$ atoms per cent. of Si, the curve is of the type of complete solubility, with resulting solid solutions of iron and Fe_2Si. Between $33\frac{1}{2}$ and 50 per cent., Fe_2Si and FeSi are immis-

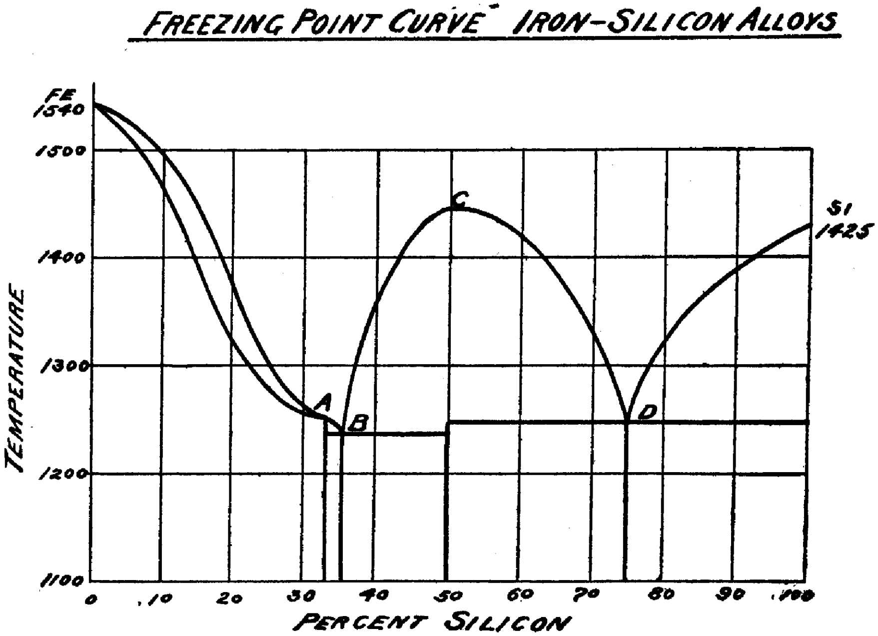

FIG. 6

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[1] W. Guertler and G. Tammann, "Ueber die Verbindungen des Siliciums mit dem Eisen," *Zeitsch. f. anorg. Chemie*, 1905.

cible, and we have completely eutectiferous freezing. This is also the case between 50 per cent. and 100 per cent. Si, with the two components FeSi and Si.

CALCIUM AND MAGNESIUM METASILICATES

Strictly analogous to this is the diagram (Fig. 7) of solidification of calcium and magnesium metasilicates, also determined at the Geophysical Laboratory of the Carnegie Institution by E. T. Allen and W. P. White.[1] As will be seen, at 47 per cent. $MgSiO_3 + 53$ per cent. SiO_3 there is indication of the formation of the compound $MgSiO_3$ $CaSiO_3$ the mineral diopside. This diopside breaks the diagram into two parts each of the partial-solubility type. For the left-hand side,

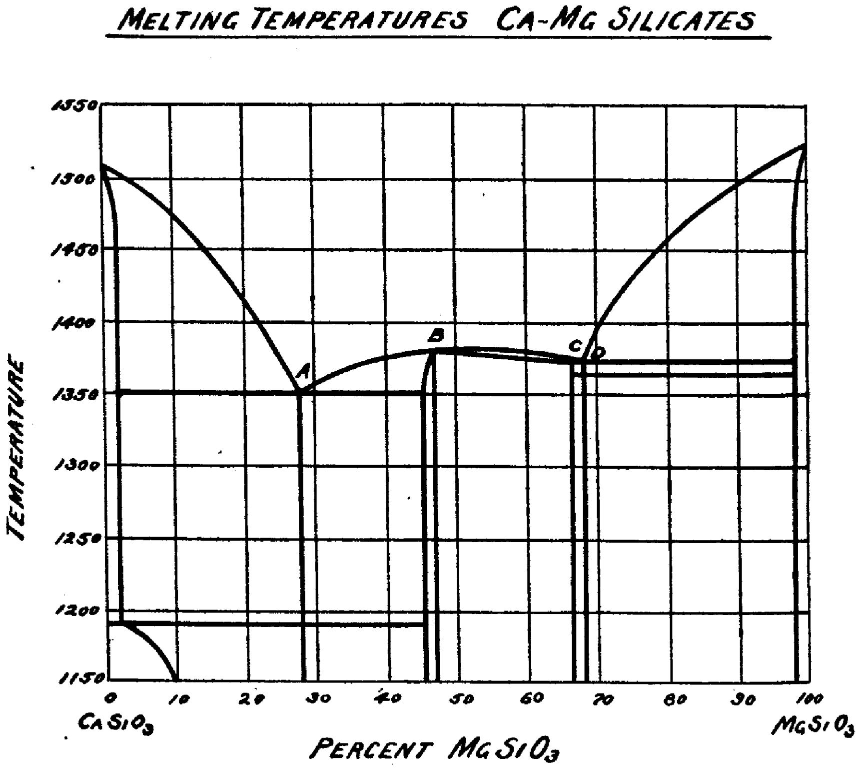

FIG. 7

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[1] Allen and White, "Diopside in Its Relations to Calcium and Magnesium Metasilicates," *Am. Jour. Sci.*, January, 1909.

solid solutions of $CaSiO_3$ and diopside will separate out between 0 and 2 per cent. and 46 and 47 per cent. of $MgSiO_3$. From 2 per cent. to 46 per cent., the structure will be a composite eutectic of $CaSiO_3$ + diopside, each saturated with a small amount of the other, and an excess substance of $CaSiO_3$ or diopside, each saturated with the other, depending upon whether the composition is below or above the eutectic composition of 28 per cent. $MgSiO_3$.

Likewise for the right-hand half of the diagram, isomorphous mixtures of diopside and $MgSiO_3$ are indicated between 47 and 67 per cent. and 98 and 100 per cent. of $MgSiO_3$. Between 67 and 96 per cent. a eutectic will form of $MgSiO_3$ and diopside each saturated with the other, and an excess substance diopside below the eutectic composition of 68 per cent. of $MgSiO_3$, and $MgSiO_3$ above this ratio. This diagram also furnishes an example of a condition frequently met with in alloys, that of allotropy, or transitions below the solidification range. Thus above 1,190° the α $CaSiO_3$, or pseudo-wollastonite, is the stable form, but is unknown in nature; below this temperature the β form, the mineral wollastonite, is stable. With $MgSiO_3$ the β form is magnesian pyroxene occurring in meteorites and intergrowths with enstatite. At 1,365° this is transformed into the orthorhombic α form distinct from enstatite and unknown in nature.

Microscopic examination confirmed these deductions except that the eutectic texture was rarely met with, probably due to the very slow cooling and consequent segregation of the constituents.

EUTECTICS AMONG ROCKS

Work of this general nature, but not so reliable and accurate, has been done by J. H. L. Vogt on the silicates, and he mentions a number of eutectic mixtures, as follows:

68 per cent. diopside	with	32 per cent. olivine
74 per cent. melilite	"	26 per cent. olivine
65 per cent. melilite	"	35 per cent. anorthite
40 per cent. diopside	"	60 per cent. akermanite
74.25 per cent. anorthite	"	25.75 per cent. quartz
75 per cent. albite	"	25 per cent. quartz

THREE COMPONENT MIXTURES

So far the discussion has been confined to the freezing of two component mixtures. However, more generally, particularly in rock magmas, three or more constituents will be present. This greater number of components will admit of the possibility of greater multiplication of the solid phases forming and results in a very much more complicated problem. Unfortunately, there have been published the results of but very few investigations along this line, and these only for very simple cases. To represent the equilibrium of a three-component mixture we make use of the property of an equilateral triangle that if from any point within perpendiculars be dropped upon each of the three sides, the sum of the lengths of these perpendiculars is a constant, and equal to the altitude of the triangle. Consequently with an equilateral triangle as a base, each apex of which represents respectively 100 per cent. of A, B, and C constituents, and temperatures plotted perpendicular to this base, we obtain a space-model, with the equilibrium between the solid and liquid phases, or, in other words, the locus of the solidification points of each particular mixture, represented by a set of warped surfaces, very much as topography is represented on a relief map. And just as we represent the elevations of this relief map on a plane surface by means of contour lines of equal elevations, so do we represent the temperatures of our space-model of solidification, by contour lines of equal temperatures, or, as technically called, by isotherms.

Such a representation is shown in Fig. 8, for the solidification of the Bi, Pb, Sn alloys.[1] These have the simplest relations for a three-component alloy, since no intermediate compounds are formed, and there is complete insolubility between the constituents. The dotted lines are the isotherms for the commencement of solidification. The altitudes at each angle denote 100 per cent. of each of the elements Pb, Bi, and Sn. The triangle is divided into three regions by the lines GE, IE, and HE, which correspond to our previous freezing-point loci representing the primary separation of one of the three pure components. Consider an alloy of composition A. The point denoting this alloy lies in the region Bi, GEI on the isotherm 175°. At this temperature, therefore, pure bismuth commences to separate out. The alloy becomes successively poorer in bismuth as the temperature is lowered, and, since the ratio of tin to lead must remain

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[1] G. Charpy, "Study of the White Alloys Called Antifriction," *Metallographist,* Vol. II, 1899.

constant, the composition shifts along the line *AC* from *A* to *C*. At 125° we meet the line *IE*. At this temperature, therefore, a binary eutectic mixture of bismuth and tin now separates out and the composition of the mixture is displaced along the line *IE* until finally at point *E* corresponding to a temperature of 96°, the ternary eutectic

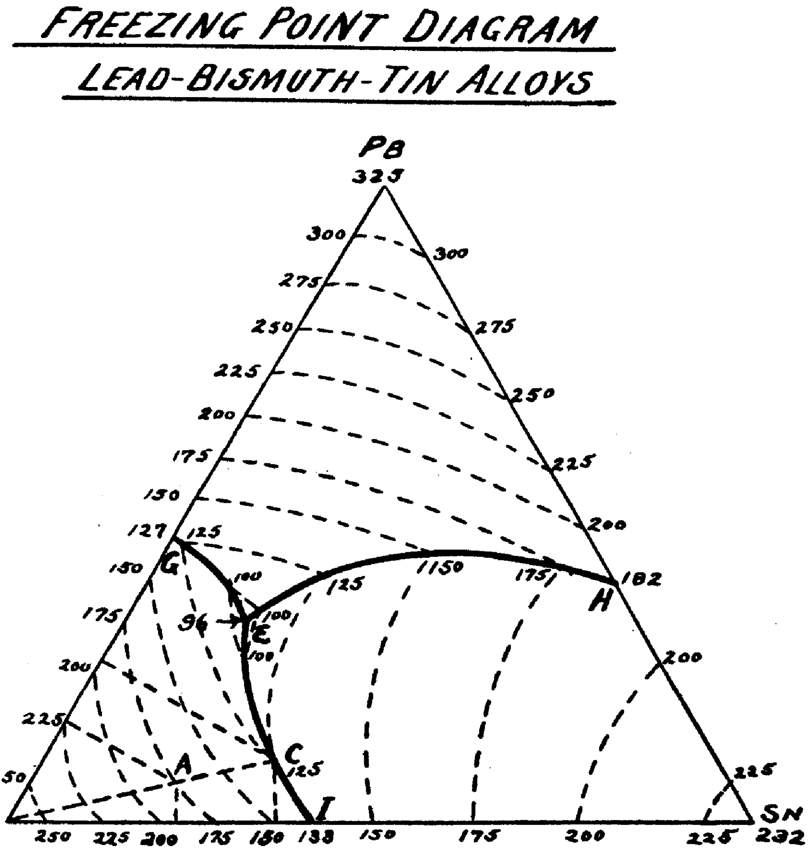

FIG. 8

51½ per cent. Bi, 15½ per cent. Sn, and 33 per cent. Pb freezes at constant temperature.

This is about the limit of our capabilities in indicating the solidification conditions. For a greater number of components, or where other factors enter, the representation becomes a space-problem of four or more dimensions, which is really beyond our powers.

COMPARATIVE MICROGRAPHS

Figures 9, 10, and 11 show the striking similarity between the structure of rocks and alloys as revealed by the microscope. In each case the rock-section is on the right, beside its analogous alloy-structure on the left.

In the upper left-hand corner of Fig. 9 is the structure of a three-component mixture of 74 per cent. Bi, $5\frac{1}{2}$ per cent. Sn, and 21 per cent. Pb. The excess bismuth has separated out into the white masses; surrounding these is the binary eutectic of bismuth and tin, and finally, as the central black constituent, we note the ternary eutectic. A somewhat similar rock-texture is on the right, a rhyolite with the white quartz, the dark orthoclase, and the finer remaining ground mass.

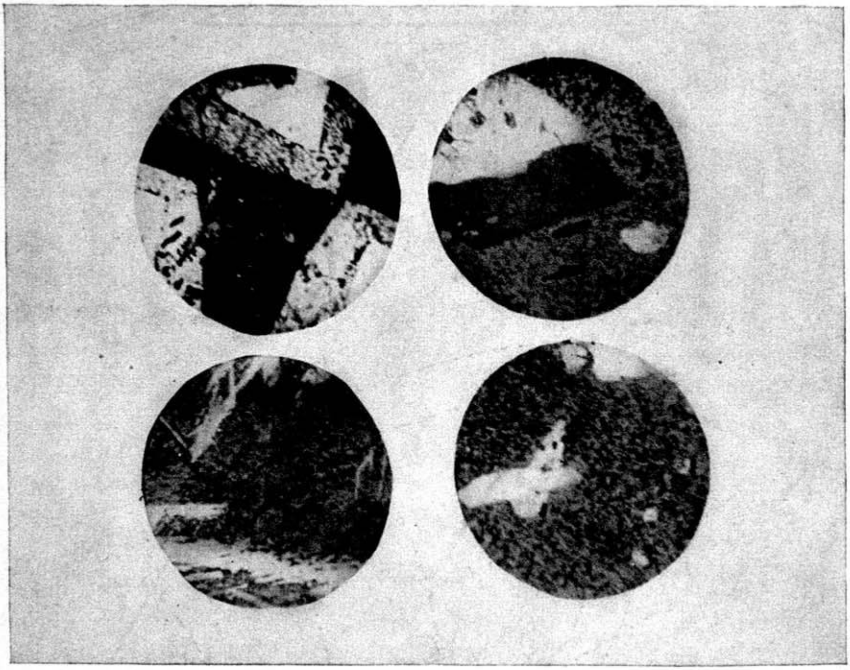

FIG. 9

Below on the right is a section of Augite porphyry, with the white plagioclase, adjoining this the gray augite, and inclosing all the fine texture of the ground mass of plagioclase and augite. It is very similar to the metal structure on the left, a steel with an excess cementite, and a eutectic pearlite, made up of this cementite and ferrite.

It is not the purpose of this article to discuss these sections in detail by trying to point out their methods of freezing; it is desired solely to show that two such classes of material as metals and rocks, widely different as they are ordinarily considered to be, in reality display the same peculiarities of texture.

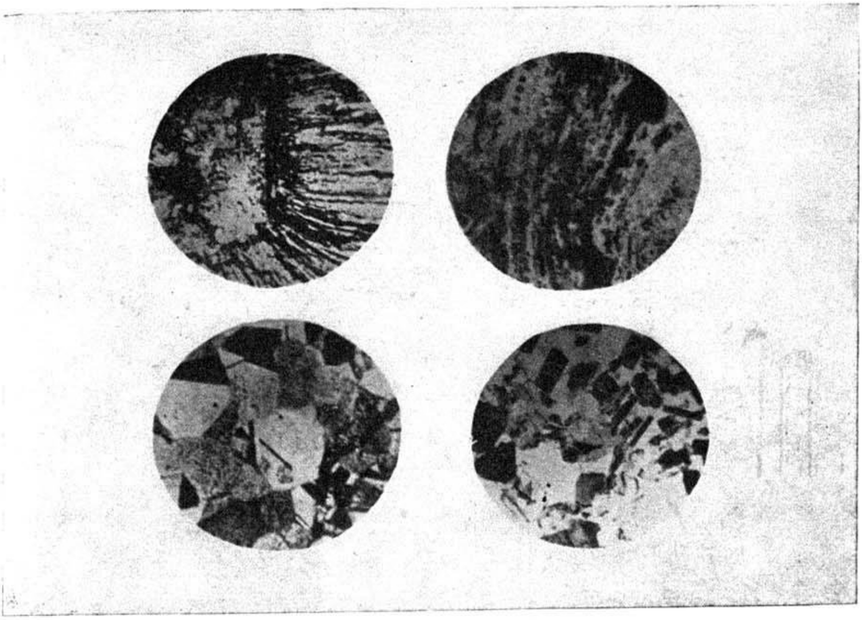

FIG. 10

APPLICATIONS TO IGNEOUS ROCKS

In endeavoring to point out the similarities in the solidification of certain alloys and magmas, one is limited to simple cases to which the theory of solubilities is easily applied. That the same considerations apply to the igneous rocks is indisputable; for it is not a question of drawing an analogy between the alloys and rock-masses. It is, rather, the application of broad general principles to specific problems; the application of general laws of equilibrium which must cover all possible cases of solution, even though as yet we may be unable to apply the details of their working. The igneous rocks are, as a rule, very complex, and may contain many component minerals or elements; also there is an additional complication in that solidification takes place very often under pressure. Pressure is of great importance in the consideration of vapors, and so difference of pressure may introduce additional complexity through the effect on the gases. Again, equilibrium conditions may not always be reached; for example, with rapid cooling of the magma, supersaturation may have occurred with a change in the order of deposition of the minerals, or differences in the microscopic structure.

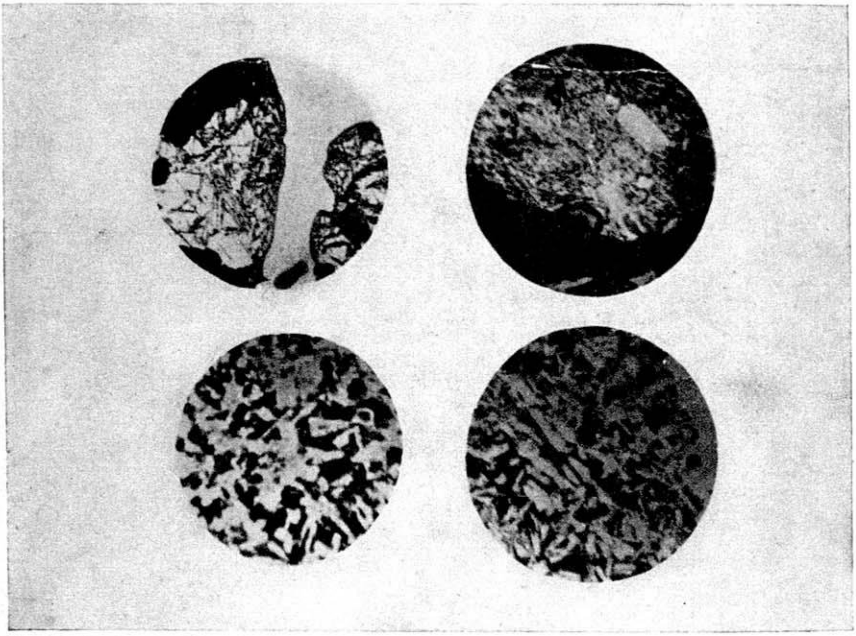

FIG. 11

In the solidification of magmas, also, we have certain conditions which do not occur in the metallic alloys. We have discussed the composite nature of the eutectic structure. Among the metals, where the cooling is normal, this intimate mixture of the constituents is very common; with the slow cooling of the igneous rocks (especially when enhanced by their poor conductivity of heat) the long sojourn just below the temperature of transition may cause a segregation of the eutectic constituents, and an elimination of the composite texture.

Furthermore, we do not make alloys in which the components are not perfectly miscible when molten, because in this case there will be separation by liquation and a defeat of the object sought by the mixture of the metals. But igneous-rock mixtures are not of man's choosing. Consequently there will very likely often be encountered the case of mixtures of imperfect miscibility, with a first separation of the components of saturation, and their final solidification according to the laws of freezing.

To clear up the intricacies of the problem, it is essential that extended research be conducted along the line of the few cases already worked out, beginning with the simpler conditions and extending the scope as circumstances warrant. With the electric furnace, desired minerals or rocks could be melted and could also be synthesized under any pressure; the pyrometer would give us the thermal reactions; finally with the microscope we could compare the structure of our artificial material with the natural rock in its original and remelted states. An investigation of this kind may reduce cases of seeming complexity to ones of comparative simplicity, by fixing a certain few of the components as of primary importance, and the rest of a secondary modifying nature. For example, while steel is a many-component alloy of Fe, C, Si, S, P, and Mn, we treat it as a two-constituent mixture of Fe and C as of greatest importance; the other elements have their influence mainly in their effect on the transition ranges of the carbon and iron.

At any rate, the thermal investigation has the great advantage of getting at the internal reactions, and can be backed up by our present methods with the microscope, and otherwise, which are suitable only for the end reactions.

In conclusion, it is well to bear in mind that the laws of equilibrium of solutions show that the melting-points of the constituents are of no service in predicting the order of their separation in the solidification of the magma. And is it going too far to predict that the study of the freezing-point diagrams of the conditions of this separation may result, as did Van't Hoff's application to the carnallite deposits at Strassburg, in economies in the recovery of the metals from their ores?

A paper read at the Sixteenth General Meeting of the American Electrochemical Society, in New York City, October 30 1909; President L. H. Baekeland in the Chair.

PHYSICAL PROPERTIES OF IRON-COPPER ALLOYS.

By Charles F. Burgess and James Aston.

The influence of copper on iron and steel has for long been a subject of controversy and contradiction. It is only comparatively recently that the effect has been investigated systematically and some of the doubt eliminated.

The prevalence of appreciable quantities of copper in the ores of certain districts makes important a knowledge of its effect, detrimental or otherwise, when present in small amounts. Also, the intimate relation of copper, nickel and iron, and the beneficial effect of the addition of nickel to iron and steel, creates an interest in the influence of larger percentages.

The older opinion was that copper was deleterious; that its chief effect was analogous to that of sulphur in that it rendered iron red short and destroyed its welding power. This view was taken by many eminent metallurgists, some even contending that 0.5 per cent. makes steel worthless. Others claimed that the influence was greatly exaggerated, and instances were cited where rolled sections of 0.50 to 0.75 per cent. of copper did not display red shortness.

Within recent years more systematic investigations have been made to determine the effect of additions of varying percentages of copper to iron and steel.

Ball and Wingham[1] tested four steels with from 0.85 to 7.17 per cent. copper and a carbon content varying from 0.10 per cent. in the former to 0.71 per cent. in the latter, and noted an increase of tensile strength and a decrease of ductility with the increase of copper. The bar with 7.17 per cent. copper was red short. Their conclusions were that the principal effect of copper was to make

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[1] Ir. & St. Inst., 1889, No. 1.

steel hard and that copper within reasonable limits did not materially affect the mechanical properties.

A. L. Colby[2] says that small percentages of copper have no deleterious effect upon the physical properties of steel. He cites various steels of about 0.5 per cent. copper in shafts and gun tubes, which met the requirements of the U. S. Navy. It was also used in ship plates, passing the usual tests required of carbon steels. These steels welded successfully and flanged cold and there was no red shortness in bars or rails with a copper content of 0.39 to 0.49 per cent.

W. Lipin[3] states that iron with a copper content up to 3 per cent. is readily worked but that there is red shortness at 4.7 per cent. copper. Between 7 to 10 per cent. Cu the material cracked badly, and fell to pieces under the hammer. With an increase of copper up to 3 per cent., the tensile strength increased from 26 tons per square inch to 46 tons per square inch, with a decrease of elongation from 27.8 per cent. to 13.3 per cent. He also noted that with an increase of carbon in the steel the maximum percentages of copper must be decreased; also that copper does not affect the welding.

Stead[4] made a very thorough investigation of the influence of copper in steel rails and plates, since, he claimed, the general belief that copper was deleterious was an unjustified prejudice. His article goes fully into the previous work and impressions. He finds that copper between 0.5 and 1.5 per cent. is not detrimental either hot or cold; that 2 per cent. copper makes steel more liable to show the effects of overheating; that small quantities raise the tenacity and the elastic limit and reduce the elongation, but not greatly, however, for small percentages of copper; also that there is no great liability to fracture by shock.

Papers of Stead and Wigham,[5] and of Wigham,[6] deal with the effect of copper in cold wire drawing, and come to the conclusion that copper up to 0.25 per cent. is no disadvantage in the manufacture of the best classes of steel wire.

Wigham, in the last article mentioned above, brings out the

[2] Iron Age, Nov. 30, 1899.

[3] Stahl u. Eisen, Vol. 20.

[4] Ir. & St. Inst., 1901, No. 1.

[5] Ir. & St. Inst., 1909, No. 2.

[6] Ir. & St. Inst., 1906, No. 1.

important point that Professor Turner, in the discussion of the former article of Stead and Wigham, says that where copper is present in ores it is found in association with sulphur. Consequently discrepancies in the earlier tests may be due to this sulphur and not to the direct effect of the copper. This fact, together with that of the increase of red shortness with an increase of carbon, may explain the differences of opinion resulting from the earlier observations.

All of the above research was to excuse the presence of the copper; to break down a seeming prejudice. An investigation with a different object is that of Pierre Breuil, the results of which were given in a paper before the Iron and Steel Institute.[7] His object was to see if there was a beneficial effect due to the addition of copper, and was suggested by the favorable influence of copper on steels for railway axles, which was noticed on some of the French railroads. It is a very extended research, and, as the author says, is a supplement (very much elaborated) to Stead's work, in that the results agree. Being the most exhaustive and latest contribution to our knowledge of copper steels, we shall have occasion to refer to the results frequently throughout this discussion.

Breuil's work was carried out on four series of steels, mild steel (C 0.10—0.17 per cent.); semi-mild steel (C 0.28—0.41 per cent.), and hard steel (C 0.56—0.79 per cent.), and a final series with about 1 per cent. of carbon.

In view of the evidence that the influence of copper varies with the amounts of carbon and of sulphur present in the steel, and very likely also with the other impurities met with in commercial materials, it is of interest to record the results of tests where these elements are a minimum. This study is a part of an extended investigation carried on in the Chemical Engineering Laboratories of the University of Wisconsin under a grant of the Carnegie Institution of Washington, on electrolytic iron and its alloys. Much of the data and results here enumerated were obtained by Messrs. Watts, Kowalke and Thickens.

The primary element in the production of these alloys is iron of high purity, obtained by double electro-deposition. The nature of the material is given in the following table:

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[7] Ir. & St. Inst., 1907, No. 2.

Per cent.	Anode	Double Refined	Electro Fused and Forged
C	0.260	0.012	0.047
S	0.007	None	0.005
Si	0.019	0.013	0.062
P	0.007	0.004	0.016
Mn	0.021	None	None
Iron	(difference)	99.971	

As will be seen from this table, the iron content is 99.97 per cent. The copper used is also of high purity, being obtained by electrodeposition.

The charges were made up in dense electrically shrunk magnesia crucibles; each enclosed in a graphite container. The crucible was covered with a magnesia lid and was buried in an electric resistor furnace. The charges in the crucible were brought to fusion from the cold mixture, held at a high temperature for some time and allowed to cool in the furnace. There was no agitation of the charge and the resultant alloy was due entirely to diffusion. The ingots weighing about 500 grams (1 lb.) were forged into rods about ⅝" in diameter by 18" long, under the steam hammer, and were then turned or ground into the finished test bars.

In spite of precautions to prevent contamination of the charge, some carbon was absorbed. Evidence is that it was set free by the equilibrium reaction, $Fe + CO = FeO + C$. The amount is small, however, and numerous analyses show that it may be taken as well under 0.10 per cent. The other impurities, such as manganese, silicon and sulphur, are negligible. In the tests here enumerated therefore, the effect may be considered as due to the added element only.

FORGING.

A wide range of alloys of varying copper content was made. The observations made in the forging are as follows: Alloys up to 2 per cent. of copper forge well at low heats. Those from 2 per cent. to 7 per cent. will not forge at a low heat, and rather poorly at white heat, the ease of workability varying inversely as the percentage of copper. From 7 per cent. to 75-80 per cent. the alloys may be classed as non-forgeable. Between 80 and 100 per cent. they will forge at a fair red heat but not at a normal forging heat for iron.

In the earlier work alloys above 5 per cent. could not be forged. However, in later tests, in the trial of many alloys of 5 to 10 per cent. of copper at all heats, it was found that with care and a high heat (welding) a 7 per cent. bar could be forged, or even rarely, an 8 per cent.

The lower percentages (below 5) will weld easily in forging, and some bars of 7 per cent. copper were welded while forging. All alloys up to 7 per cent. copper could be welded in an electric welder.

SEGREGATION.

The forgeable samples between 0 and 8 per cent. of copper and a few of the alloys of high copper and low iron were made into test bars for investigation of the tensile strength. Analyses were not made upon all bars; rather, random samples of the entire range of composition were sent to Booth, Garrett & Blair, of Philadelphia, whose valued assistance in this investigation is acknowledged. Their report is given below:

ANALYSES.

Bar	Cu Added	Analysis
147B	0.1	0.089
158A	0.2	0.202
158B	0.4	0.422
158C	0.6	0.592
158D	0.8	0.804
147H	1.0	1.006
147J	1.5	1.510
158G	2.0	2.005
158I	4.0	3.990
158J	5.0	5.070
158K	6.0	6.160
147U	7.0	7.050
86F	95.0	94.340

As will be seen from the tables, the agreement between the added and the actual copper content is exceedingly close. The analytical samples were taken from the turnings obtained in the machining of the test bars after the forging of the ingots. This close agreement after such a method of selection would indicate an entire absence of segregation; also that the materials alloy very well up to a copper content of 7 per cent. This is in accord with the work of the earlier investigators. In view of this close agreement it may be assumed that the actual copper content of the alloys is the same as the added amount.

HARDNESS.

The hardness tests are merely qualitative, being observations made in the machining, sawing and filing. In machining, the alloys with low percentages of copper worked very easily. The hardness increased with the increase of copper until at 5 to 7 per cent., while it was still possible to turn in the lathe, it was with some difficulty. There were the same evidences in the sawing and filing tests, the high copper being classed as extremely hard to saw.

Breuil's investigations show that the hardness does not result through a lowering of the points of transition, thus leaving the steels in a martensitic state, as might be supposed. The structure is a fine pearlite, with a fibrous cementite which is liberated with increasing copper, and this explains the increasing hardness.

Wedding[8] says that copper and sulphide of copper prevent the formation of pearlite and promote the formation of crystals of cementite. It is due to this fact that there is greater hardness of iron when copper and sulphur are present. These explanations seem hardly sufficient to account for the hardening which we have observed without the presence of either copper or sulphur and we expect to make a metallographic study with the hope of throwing a little light upon the subject.

TENSILE STRENGTH TESTS.

Of the bars cut from each rod for the tensile tests, an equal number were reserved for tests as forged and after annealing. In annealing, the samples were packed in a magnesia lined graphite box and were heated in an electric resistor furnace. The temperature was brought up to 900° C and held at this point for several hours, and several hours more were needed for the slow cooling in the furnace. The test samples were approximately

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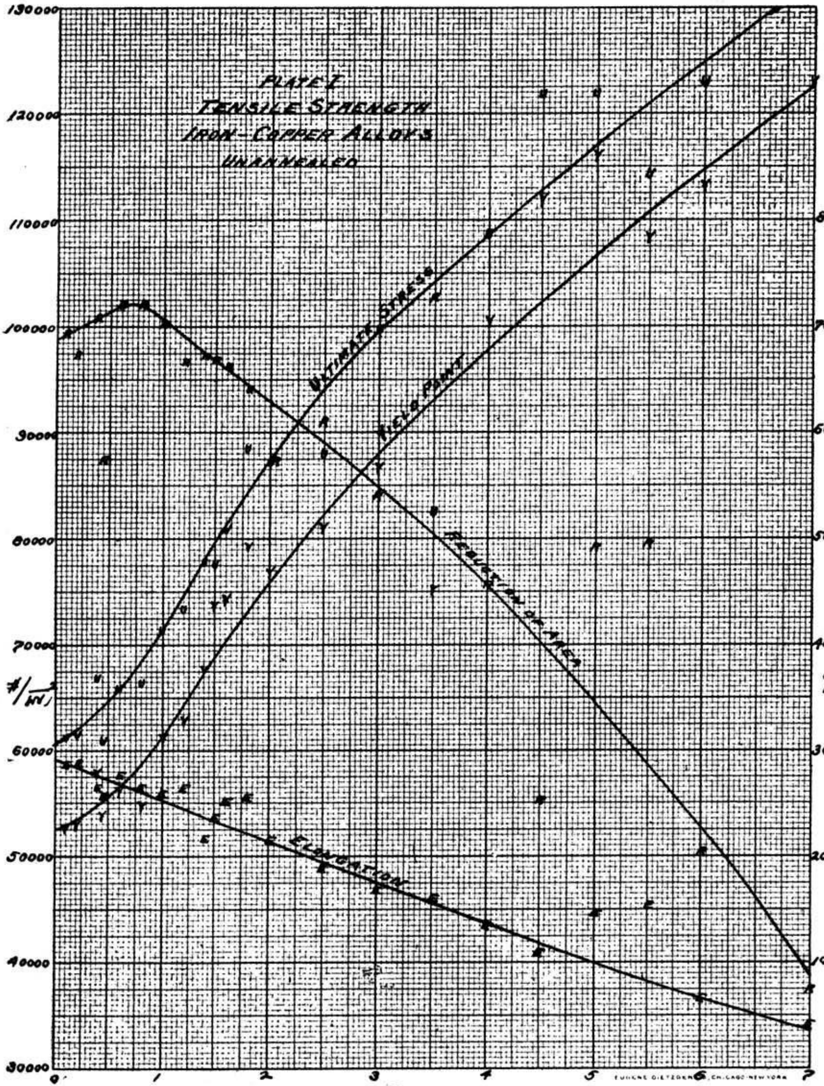
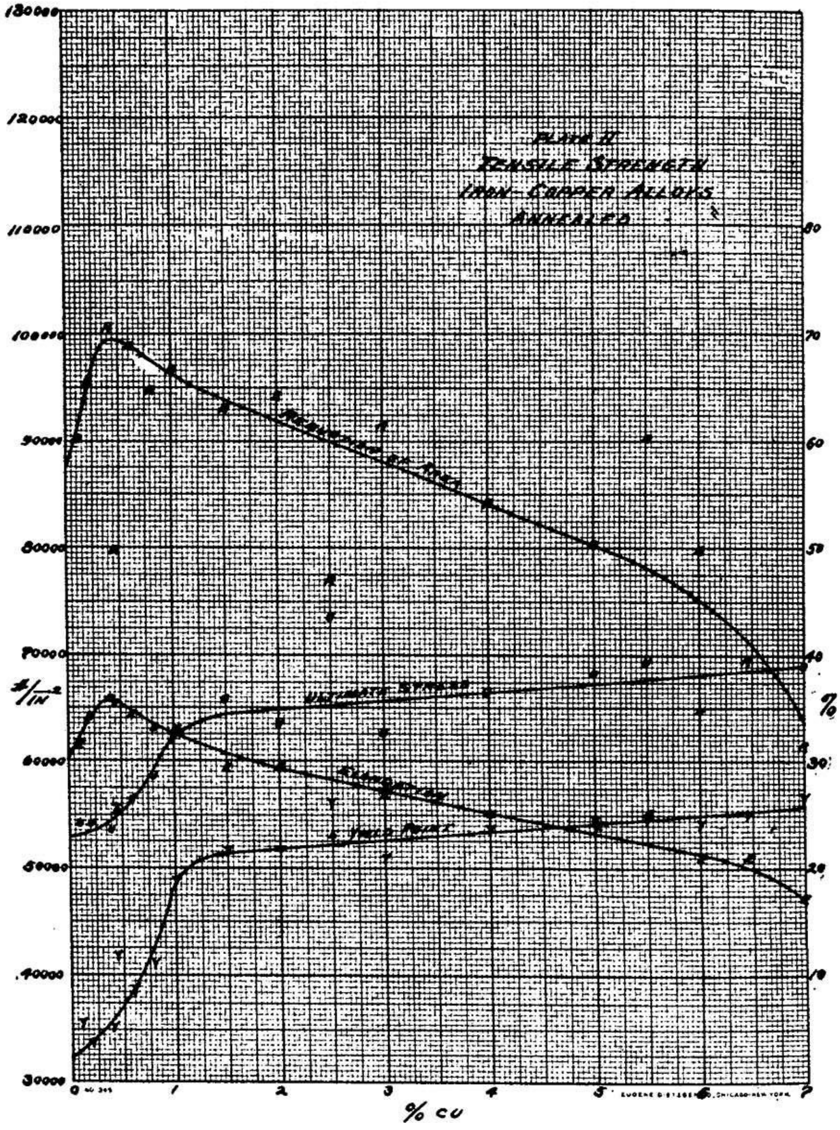
[8] Stahl u. Eisen, December, 1906.



from 0.3 to 0.4 inches in diameter, with a free length of 2 inches. The diameter used in the calculations is the mean of several readings with micrometer calipers. The tests were made on a Riehle 100,000-lb. power-driven machine. The load was applied very slowly and the beam kept in balance. The yield point was obtained with dividers, and was taken as that point at which a



perceptible permanent stretch had taken place. This was checked by the drop of the beam.

The summary of the results of these tests is given in the Tables I and II and in Plates I and II. The detailed data are not given, also no account is taken of bars which showed abnormal results, due to flaws, etc.

TABLE I.

Tensile Strength—Iron-Copper Alloys—Unannealed.

Per. Cent. Cu.	No. of Samples	Yield Point Lbs./in^2			Ultimate Stress Lbs./in^2.			Elongation %/2″			Reduction of Area Per Cent.		
		Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
0.1	3	56,600	45,400	52.580	64.000	60 300	61,180	30.0	27.5	28 5	70.9	66.7	69.2
0.2	5	55.600	50,700	52 930	63.750	60,000	61 470	36.5	24 5	28.7	73 2	56.9	67.2
0.4	2	59,700	56,100	57.900	67 250	66.400	66.825	29.5	23.0	26.2	72 1	69.4	70.7
0.45	2	54,800	53,100	53 950	62 700	58.800	60,750	27.0	24 0	25.5	67 7	47.2	57.4
0.6	2	57,750	54,600	56.170	67,000	64,750	65 875	27.5	27.5	27.5	72.8	71.5	72.1
0.8	2	55,500	53,800	54.650	67 500	65,100	66.300	27.0	25.5	26 2	72.5	71.7	72.1
1.0	5	63,300	56,800	61,250	70 800	68 300	71,380	28.0	21.0	25.8	72.0	66.8	70.3
1.2	2	66,300	59 500	62,900	74.600	72.300	73.400	28.0	24.5	26 2	68.8	64.5	66.6
1.4	2	68,100	67,300	67 700	78.600	76.600	77 600	25.0	18.0	21.5	70.0	64.5	67.2
1.5	3	77,250	70,000	73.920	78,800	76.200	77,300	26.5	20.5	23.5	68.6	64.5	66.9
1.6	2	75,100	73,300	74.200	82.750	79.100	80,925	25.0	25 0	25.0	66.6	66.2	66.4
1.8	2	81,100	77,600	79 350	91.000	86,000	88.500	27.0	24.0	25 5	66.3	61.8	64.0
2.0	3	78,800	73,400	76.930	89 500	82.250	87.010	23.5	17.5	21.2	59.5	54.5	57.0
2.5	2	81,100	81,000	81.050	89 400	86.400	87,900	19.0	18.5	18.7	62.8	59.1	61.0
3.0	6	95,100	73,750	86,810	105.000	83,750	99.640	24.0	12.5	16.7	65.6	36.1	53.8
3.5	1			75.400			82 300			16.0			72.7
4.0	5	111,100	92,700	100 560	120.700	99.200	108.640	17.5	8 0	13.5	52.3	24.8	45.6
4.5	2	117,800	106,400	112,100	127 900	115.500	121,700	17 0	4.5	10.8	47.2	3.9	25.1
5.0	2	119,700	113.000	116,350	123 800	120.000	121,900	15.0	14 0	14.5	50.1	48.3	49.2
5.5	2	114,700	102.300	108,500	122 800	105,200	114,000	15.5	15.0	15.2	53.8	46.6	49.7
6.0	3	124,200	103 000	113.400	136.700	107,500	122,900	9.0	4.5	6.5	36.5	4.1	20.3
7.0	2	128.800	117.000	122,900	133 800	131,000	132.400	6.0	2.0	4.0	12.9	1.7	7.3
8.0	2	146,800	133.500	135.100	160,000	137 500	148.750			0			0

TABLE II.

Tensile Strength—Iron-Copper Alloys—Annealed.

Per Cent. Cu.	No. of Samples	Yield Point Lbs. / in^2			Ultimate Stress Lbs. / in^2			Elongation Per Cent. / 2″			Reduction of Area Per Cent.		
		Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
0.1	2	40,750	34,400	35,570	56,500	51,600	54,050	35.0	28.0	31.5	62.2	58.3	60.2
0.2	4	36,850	31,800	33,660	56,000	52,700	54,020	36.0	29.5	34.1	67.7	62.7	65.6
0.4	2	35,700	35,100	35,400	53,700	53,100	53,400	37.5	34.0	35.7	72.1	69.3	70.7
0.45	2	42,250	41,250	41,750	66,300	64,600	65,400	26.0	25.0	25.5	53.6	46.0	49.8
0.6	2	38,400	38 300	38,850	56,600	56,500	56,550	36.5	32.0	34.2	69.0	68.8	68.9
0.8	2	41,300	40,700	41,000	59,750	57,400	58,570	34.0	32.0	33.0	65.1	64.7	64.9
1.0	4	54,800	46,400	48,920	63,900	61,100	62,350	34.0	30.0	32.6	68.3	66.1	66.8
1.5	6	58,100	48,100	51,570	70,500	62,100	65 720	33.5	22.0	29.2	65.1	59.3	63.1
2.0	6	54,300	49,400	51,620	65,100	60,500	63,200	31.5	27.5	29.5	68.1	62.0	64.4
2.5	1			56,200			73,500			23.0			47.3
3.0	7	53,800	48,700	50,890	67,600	59,000	62,360	33.5	10.5	26.9	69.1	46.3	61.7
4.0	5	57,100	49,600	53,570	70,900	62,700	66.540	28.0	22.0	24.8	65.3	39.3	54.2
4.0	4	57,600	50,700	54,460	74,700	62,400	68,250	29.0	20.5	24.2	62.9	29.1	50.3
5.5	1			54,800			69,300			25.0			60.4
6.0	3	55 500	52,750	54,420	65,600	62,500	64,530	24.5	18.0	20.8	59.0	39.2	49.9
6.45	2	55,750	54,600	55 170	69,700	69,200	69,450	25.5	16.5	21.0	48.1	30.5	39.3
7.0	2	57,150	56,750	56,950	70,900	67,900	69,400	20.0	14.0	17.0	40.8	21.7	31.2
7.5	1			60,200			79,000			16.5			34.2

The results enumerated are the yield point, the ultimate strength, the percentage of elongation in 2 inches and the percentage of reduction of area at fracture. In order to show the consistency of the data there is also given the maximum and minimum values for each of the above items, together with the average of these items for the number of samples enumerated in a separate column. The plates are plotted from the averages of the tables and it is not to be expected, considering the many variables which might arise, in tensile strength tests, that any series will give a simple curve. It is merely hoped to show the tendency of the increasing percentages of copper. The values of the yield point, ultimate strength, elongation and reduction of area are designed as points used in plotting the curves by the appropriate letters Y, U, E and R.

Unannealed.

From the curves of Table I, it will be noted that the rise in the ultimate strength and the elastic limit is almost a linear function of the percentage of copper. The ultimate strength increases from 61,180 lbs. per sq. in. at 0.1 per cent. copper to 132,400 lbs. at 7 per cent. The yield point rises from 52,580 to 122,900. There is a corresponding fall in the elongation from 28.5 per cent. at 0.1 per cent. copper to 4 per cent. at 7 per cent. copper. The reduction of area increases slightly from 69.2 per cent. at 0.1 Cu to 72.1 per cent. at 0.6 and 0.8 per cent. Cu; from this point it falls to 7.3 per cent. at 7 per cent. of copper.

From Table I it will be noted that the ratio of maximum and minimum values to the average is good, except in certain instances which are no doubt somewhat abnormal, but not so much so as to be rejected from the tables. Also, where there are a sufficient number of samples for a good average, the results fall well in line. The greatest variation is at 3.5 per cent. of copper, but here there is only one bar, which is clearly abnormal, with its low ultimate strength and elastic limit and its high reduction of area. The greatest variations from the curve lie above 4 per cent. of copper, and this is to be expected, especially in the unannealed samples, since here we are almost beyond the limit of satisfactory workability.

The results of these tests indicate a high tensile strength which increases with the percentage of copper. The alloys are rather brittle as indicated by the elongation, and the reduction of area. Also, the elastic ratio (ratio of the elastic limit to the ultimate strength) is large, varying from 0.86 at 0.1 per cent. copper to 0.93 at 7 per cent. Cu.

Annealed.

The results of annealing are given in Table II, and Plate II, and the effect is very marked, especially for the higher percentages of copper. There is greater consistency in the results, as is to be expected, and the points fall fairly well in line on the curves.

The greatest deviation from the curves is at 2.5 per cent. and 5.5 per cent. of copper, where there was only one bar of each for the test. The maximum and minimum figures of the table are not widely different.

Up to 1 per cent. copper there is a marked increase of the elastic limit and the ultimate strength with the additions of copper and no falling off in the elongation or reduction. In fact, the latter increase to a maximum at 0.4 per cent. of copper. Beyond one per cent. the curves bend sharply and become more nearly horizontal, being a linear function of the percentage of copper. The elongation and reduction of area fall off in accordance.

Between 1.5 per cent. and 7 per cent. of copper the elastic limit increases from 51,570 to 56,950 pounds, the ultimate from 65,720 to 67,900 pounds, while there is a decrease in the elongation and the reduction of area. Between 0.1 and 1.5 per cent. of copper the elastic limit rises from 35,570 to 51,570 pounds; the ultimate strength from 54,050 to 65,720 pounds; while the elongation and the reduction of area remain about the same. Breuil mentions the 4 per cent. alloy as worthy of further study, and this is no doubt true, since he observes very high values, as indicated by the following table, where the results are given for his mild steel series (C = 0.10 to 0.17 per cent), as rolled, and as annealed at 900° C.:

TENSILE STRENGTH—BREUIL.

UNANNEALED

Per Cent. Cu.	Yield Point Lbs. /sq. in.	Ultimate Stress Lbs. /sq. in.	Elongation Per Cent.	Reduction Area Per Cent.
0	....	..	...	..
0.5	55,000	66,800	25.5	66
1	58,900	70,200	26.5	60
2	67,300	88,700	16.0	58
4	97,600	109,500	13.0	46

ANNEALED

Per Cent. Cu.	Yield Point Lbs. /sq. in.	Ultimate Stress Lbs. /sq. in.	Elongation Per Cent.	Reduction Area Per Cent.
0	35,800	54,900	30.3	63
0.5	38,200	59,000	28.0	60
1	54,800	69,500	26.0	57
2	58,700	70,300	25.0	58
4	65,000	71,500	22.0	63

A comparison of these figures with the results of our researches shows a great similarity, and in plotting the figures there is a very close agreement. In his 4 per cent. alloy as unannealed, to which Breuil calls particular attention, there is an elastic limit of 97,600, an ultimate strength of 109,500, an elongation of 13 per cent. and a reduction of area of 46 per cent. In our tests the results for corresponding material are—elastic limit, 100,560; ultimate strength, 108,640; elongation, 13.5 per cent. and reduction of area 45.6 per cent. For the annealed sample, Breuil gives the elastic limit, 65,000 pounds; ultimate strength, 71,500; elongation, 22 per cent; reduction of area, 63 per cent. Our results are: Elastic limit, 53,750 pounds; ultimate strength, 66,540 pounds; elongation, 24.8 per cent.; reduction of area, 54.2 per cent. In our tests the annealing shows a greater effect, resulting in less strength with greater ductility; and the same is true in the comparison for all percentages of copper.

While Breuil lays particular stress on the 4 per cent. alloy, our results would seem to indicate the greatest value between 1 and 2 per cent., for the annealed samples. The very sharp rise of the elastic limit and the ultimate strength at this percentage gives values but very little less than those for higher copper content; also there is a removal from the region where the forging and welding properties are poorer with consequent uncertainties of result. Likewise, between 1 and 2 per cent. the elastic limit and the reduction of area are very high.

It would hardly be advisable to work with 1 per cent. of copper, since this is on the edge of the limit, where there is liable to be a fall to the lower values obtained with lower percentages of copper. At 1.5 per cent. we are far enough removed so that the slight differences of composition to be met in practice would not bring the material into a dangerous region. Also, the elastic ratio of 0.78 is slightly lower than for the 4 per cent. alloy, where it is 0.81.

We would have considerable hesitation in bringing forward this point without a vast number of tests for confirmation, but for the fact that an observation of Breuil's results indicates the same condition. He has perhaps noticed this fact, but makes no mention of it in his article. As will be seen from the table of his results which is given above, there is a sharp increase between 0.5 per cent. and 1 per cent. of copper, where the elastic limits are 38,200 and 54,800, respectively, and the ultimate strengths 59,000 and 69,500. Again, we note but little change in the elongation and reduction of area. Between 0 and 0.5 per cent., and between 1 per cent. and 2 per cent., the change is not marked. The fact that two independent investigations give this result, seems fairly conclusive of the effect.

Another fact to be noted in our tests is the marked difference between the unannealed and the annealed samples. It would indicate that there is a possible intermediate heat treatment which, not being so drastic in its effect as our long annealing, would give intermediate values, and thus approximate the nickel steels. This condition might be reached in commercial rolling, where heavier masses of metal leave the material in a condition analogous to that resulting from a partial anneal.

To compare the copper-iron wth the nickel alloys we may quote Waddell's extensive investigations.[9] In considering the use of nickel steel for bridge building, he mentions a steel with about 3.5 per cent. nickel, carbon 0.38 per cent., the values for which may be taken as—elastic limit, 60,000 lbs. per sq. in.; ultimate, 105,000 lbs. per sq. in.; elastic ratio from 0.55 to 0.60. These

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[9] Proc. Am. Inst. Civ. Engrs., Sept., 1908.

values are for sections as rolled without heat treatment and working at a somewhat low ductility, as shown by the figures 15 per cent. for nickel steel, 27 per cent. for carbon steel (in 8 inches) and a reduction of area of 41 per cent. for nickel, compared to 55 per cent. for the carbon steels. With the carbon reduced to 0.15, the values become— elastic limit, 45,000; ultimate, 70,000; elongation, 25; and for (C= 0.45) the elastic limit is 65,000, the ultimate 115,000 and the elongation 12 per cent.

These values are higher than ours for the copper iron alloys but are not in direct comparison. Our own figures for a nickel-iron alloy made under the same conditions as the copper-iron series are given in the following table, where the 4 per cent. nickel is compared with the 1.5 per cent. and 4 per cent. copper alloys. There is also given Hadfield's test of an alloy of 3.82 per cent. nickel and carbon = 0.19 per cent.[10]

UNANNEALED

	Elastic Limit	Ultimate Strength	Elastic Ratio	Elongation Per Cent.	Reduction Area Per Cent.
4.00 Ni.	67,000	76,000	0.88	28.5	68 6
1.50 Cu.	73,920	77,300	0.95	23.5	66.9
4.00 Cu.	105,560	108,640	0.97	13.5	45.6
3.82 Ni.	62,720	82,800	0.76	30.0	54.0

ANNEALED

	Elastic Limit	Ultimate Strength	Elastic Ratio	Elongation Per Cent.	Reduction Area Per Cent.
4.00 Ni.	57,000	69,000	0.83	26.5	64.8
1.50 Cu.	51,570	65,720	0.79	29.2	63.1
4.00 Cu.	53,570	66,540	0.81	24.8	54.2
3.82 Ni.	56,000	73,920	0.76	35.0	55.0

The above values for the nickel alloys are less than are commonly assigned to commercial materials where the carbon is a factor. The results are very comparable to those of the copper-iron series made under identical conditions.

Waddell, in his paper, shows that there is an economic advantage in the use of the nickel steels in comparison with the carbon steels ordinarily used, since their increased cost is more than

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[10] Inst. Civ. Engrs., March 28, 1899.

offset by the less weight required, due to their increased strength. Our results and comparisons would indicate that the copper-iron alloys are also worthy of consideration and might be comparable to the nickel steels in use, even if the strength should not reach such high values as those of the nickel. A 1.5 per cent. copper alloy is of promise, since the smaller percentage required and the lessened cost per pound of copper as compared with nickel would result in a lessened cost of construction, even if there is some increase in tonnage required because of the slight decreased strength per equal weight.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

MR. CARL HERING: This paper is of great interest, and we are fortunate in having such papers at our meetings. In looking over the results of others, as well as those in this paper, it appears that there sometimes is a decided discrepancy between the chemical analyses and the physical properties, and it therefore occurred to me that the copper might perhaps act differently, depending upon the physical treatment which the iron received prior to the testing of the sample; for instance, the chilling, hammering, annealing, etc If so, it would explain why the chemical analysis is not a criterion of what the physical properties would be.

PROF. J. W. RICHARDS: I would like to say, speaking from the metallurgical side, that this paper will be received with great interest by the manufacturers of steel in the United States. I was told privately some years ago by the metallurgist of one of the large steel works, for my own private information, that a great deal of their steel had from 0.5 to 0.7 copper in it, and passed all the requirements of the United States Government, proving that it was not injurious to the steel, but rather beneficial. That was then private information. Prof. Burgess' paper makes it public information, and even goes further than the information that was then known. I think it is one of the most important papers, in its commercial aspect, that has been brought before the Society.

DR. ARTHUR H. ELLIOTT: The addition of these metals to iron for certain purposes is extremely interesting, and the one that strikes me as most interesting is its effect on the corrosion of the metal, especially in the making of pipes. This question came up last year at our meeting, and there was a great deal of work done on it. I wonder if there has been anything done with these iron-copper alloys in that direction. It is extremely important, the corrosion of these alloys, because of the small quantities of metals in them.

MR. ROGER C. ALDRICH: I should like to ask whether any experiments were made on the addition of copper to steel. I notice it was stated that the irons had practically no carbon in them, and if any such experiments were made, I would ask if they had the same effect of raising the ultimate strength and elastic limits on the steels as on the iron?

PROF. BURGESS: We did not make a series of copper alloys with steel. We made enough accidentally to find that in the presence of carbon the copper acts in a way entirely different from that described in the paper. It makes it brittle and red-short, and it does not appear desirable to add copper to high carbon steel.

We are studying corrodibility of several hundred alloys which are exposed to various corrosive conditions, and it is too early to make reports; but I am inclined to think that copper-iron is going to be a rather corrodible metal. Unfortunately this is a factor which cannot be determined definitely until after several years have elapsed.

As to Mr. Hering's comment, I entirely agree with him that the physical working of the material, forging as well as the heat treatment of these alloys, has much to do with the strength, and I think that is shown by the relative positions of the curves shown on pages 247 and 248.

DR. ELLIOTT: I think that is very interesting, with regard to the corrosion of the metal, but I did not intend to draw Prof. Burgess's fire. I think that is a good program for another paper.

A paper presented at the Sixteenth General Meeting of the American Electrochemical Society, in New York City, October 30, 1909; President L. H. Baekeland in the Chair.

CERTAIN CHARACTERISTICS OF DRY CELLS.

By Charles F. Burgess and Carl Hambuechen.

A dry cell, like any other electrical apparatus, must possess certain characteristics to enable it to perform the service demanded of it. It is impossible to determine or define in simple terms the desirable characteristics of a dry cell, since this depends upon the service with which it is to be associated.

The greatest usefulness of the dry cell at the present time is probably in the telephone field. The service next in importance is ignition as effected through spark coils; electric bell and annunciator work furnishes the next largest field for dry cells, and the operation of telegraph and alarm circuits, electric clocks, phonographs and other small electrically driven machinery are some of the other uses in which this electrical generator is extensively employed. New uses are continually being evolved, and the demand for dry cells appears to be continually increasing, and this in spite of the fact that the central energy systems for telephone exchanges are displacing large numbers of dry cells, and magneto and other forms of electrical ignition are competing with the dry cell for the ignition business.

A great majority of the uses of dry cells involve relatively low rates of delivery of energy. The cells are called upon intermittently, and the primary requisite of a dry cell appears to be its ability to live over a long period of time. The attainment of this characteristic is shown in marked degree in certain cells on the market, and in this respect marked improvement has been effected during recent years.

Low internal resistance is another important qualification for a satisfactory dry cell, since this enables the cell to deliver its energy to the external circuit with high efficiency. Where very small quantities of energy are required, at a low voltage, low resistance may not be requisite; in other uses where the instantaneous demands upon the battery may be great, low resistance is a most important characteristic. Low internal resistance is usually indicated by high amperage, *i. e.*, the ability of a cell to deliver a large amount of current when short-circuited through an ammeter.

"Minimum polarization" and "rapid recovery" are other factors to which attention is called by manufacturers in advertising their dry cells.

It is impossible to point out which is the most important of these qualities, since the relative importance depends upon the character of service required. Among the minor characteristics which are sought to be attained in dry cell construction are: Absence of the leakage of the liquid, minimum increase of resistance with low temperature, convenience for connecting into circuit, and the general appearance of the cell.

The factors which govern the above characteristics include these: Materials employed in construction, the proportions of materials, the chemical and physical qualities of these materials, methods of assembling.

In spite of the fact that 40,000,000 or thereabout represents the number of dry cells manufactured each year in this country, little scientific work has been done in the way of making a detailed study of the various individual factors which influence the quality of the cell, if we may judge by the meager publications. On the other hand, much scientific work has undoubtedly been done, if we may judge by the marked improvements which have been effected in the product. It appears that dry cell manufacturers who are doing the larger part of this work do not feel inclined to discuss analytically dry cell construction.

Perhaps 80 per cent. of the dry cells made and used are of the so-called No. 6 size, being in cylindrical form, the zinc container 6 inches high and 2½ inches in diameter. As far as the cylindrical zinc container is concerned, there is striking uniformity in dimensions and costruction, the principal difference being in the thickness of the zinc, which may be found to vary from No. 7 to No. 11 sheet zinc gauge.

All cells employ a carbon rod for the cathode plate. In some forms of cells this rests on the bottom layer of paper, and in others it is raised a half inch from the bottom. It extends up through a pitch seal, and a brass cap or brass screw attached to the top constitutes the positive terminal of the cell. Some of the carbons used are of smooth cylindrical shape, while others are corrugated or fluted to give greater contact surface to the filling material.

Another striking similarity in most of the dry cells is the list of materials which are introduced into the zinc container. Similarity then ceases, and we encounter variations in the quality of the materials, the proportions, and in the methods in which the materials are introduced into the container.

The writers are unable to refer to published formulæ which are descriptive of the better type of cells at present in use. The following list and proportion of materials may be taken as fairly representing the filling mixture in well-known types of cells:

10 lbs. of manganese dioxide.
10 lbs. of carbon or graphite, or both.
2 lbs. of sal ammoniac.
1 lb. of zinc chloride.

Sufficient water is added to give proper amount of electrolyte to the cell, and the most suitable quantity depends upon the dryness of original materials, fineness, quality of paper lining, etc.

While these are the essential elements, other materials are frequently added—such as starch or other forms of paste, to improve contact of electrolyte to zinc and promote distribution of action throughout the charge. Mercury is occasionally added to effect amalgamations and prolong life of the zinc.

With the materials as above listed and in the proportions named the resulting cells may be good or they may be practically worthless, depending upon various factors. It is generally believed that purity of materials is the pre-eminent requisite. Commercial conditions, however, prohibit the use of chemically pure materials. The customary specifications for manganese dioxide call for a granulated or powdered material having about 85 per cent. of MnO_2 and less than 1 per cent. of iron. This is a specification which can readily be complied with, and by careful selection and concentration it is possible to get as high as 92 per cent.

Physical qualities, porosity and size are grains are likewise important. The amount of available MnO_2 differs according to the chemical test employed, and "available MnO_2" by test may not be the available MnO_2 under the conditions existing in the cell. In storage batteries PbO_2 is an active material only when in suitable contact or proximity to grid or framework of the positive plate; and MnO_2 in a dry cell is active to a degree, depending upon its contact with the conductive carbon constituting the negative electrode. It is evident that penetration into the interior of a piece of MnO_2 is necessary if the entire mass is to be active; and porosity seems therefore to be important.

It is perhaps superfluous to point out that the purpose of the manganese is to effect depolarization, and thereby to maintain the voltage of the cell during discharge. The qualities designated "minimum polarization" and "great recuperative power" are dependent largely upon the amount and availability of the MnO_2 employed.

Carbon in a powdered or granulated form is employed to give conductivity to the mass of MnO_2 and to furnish a large amount of cathode surface. Retort carbon, coke, petroleum coke and ground carbon rods and electrodes are the various grades of carbon commonly employed for this purpose, and much of the variation found in dry cells is due to varying qualities of this carbon. Graphite is another form of carbon extensively employed in dry cells, and the more recent improvement in dry cells is undoubtedly due largely to the liberal use of this highly conductive though more costly form of carbon.

Sal ammoniac of a very pure grade is generally employed, and in addition to purity, the physical qualities of dryness and freedom from lumps are requisite to ensure proper mixing with the carbon and manganese.

The zinc chloride is also required to be of high purity and to be free from iron.

Sheet zinc constitutes the anode and serves at the same time as a container. Purity is naturally of importance. The purchaser does not have, however, a variety of grades of zinc to choose from.

This anode makes contact with the electrolyte in the form of paper saturated with solutions of zinc and ammonium chlorides.

Ideal conditions call for a corrosion of zinc only in amount equivalent to the current delivered to the external current. Excess of corrosion above this amount is caused by local action, and one of the principal problems in dry cell manufacture is to reduce such local action to a minimum.

There are numerous possible causes of local action. A particle of metal other than zinc, making contact with the zinc electrode surface produces a galvanic couple. Since solder is employed on the side seams and bottoms, some of which frequently finds its way inside the cell, it might be natural to assume this as a most frequent cause of local action. This appears, however, not to be the cause, for while solder is decidedly electronegative to the zinc, it is composed of two metals, lead and tin, both of which have high "over-voltages" which almost entirely prevent current flowing to these metals at the expense of and under the electromotive force set up by the zinc.

Some experimental cells made from sheet zinc streaked with solder on the inner surface showed little if any abnormal deterioration due to local action even after standing for several months.

On the other hand, if the couple be made of copper, or iron in contact with the zinc, the "over-voltage" is not sufficient to prevent the flow of current, and destructive local action occurs.

Copper occasionally finds its way into the dry cell from the brass terminals through corrosion and the diffusion of the copper chloride into the cell. Upon reaching the zinc the copper is deposited and establishes a couple. A small amount of copper placed in a freshly made cell may cause it to run down completely in less than one day, the entire zinc being corroded much as though the cell had been used to its limit.

Iron is less harmful than is copper, and it is something of a question as to just how far it is economical to go in excluding iron from the cell. This seems to be the principal substance which specification of materials seems to exclude. The manganese oxide and carbon are considered the more valuable the lower the percentage of iron contained. This iron cannot be excluded, being present to the extent of perhaps 1 per cent. But this iron cannot be harmful unless it goes into solution, though diffusing to the zinc. The electrolyte is such that dissolving of iron is improbable, since the liberation of ammonia in zinc and ammonium chloride solutions tends to throw out iron.

It occasionally happens that some of the filling material, the manganese oxide and carbon, gets between the paper lining and the zinc. This naturally gives rise to damaging galvanic couples. Each of such particles produces a zone in which corrosion of zinc takes place, and if such contact of carbon and manganese oxide be perforated the effect on the cell is the same as though it were short-circuited.

Inequalities in the zinc itself may cause certain differences in potential, and therefore give rise to galvanic couples. The inequalities of temperature due to soldering give rise to small differences; the solder applied to the surface penetrates into the metal and possibly alters the contact potential in the other side. What appears to be a most frequent cause of local action, and most difficult of control, is the access of air to the active surface.

Some measurements on these potentials have been made by placing between two pieces of sheet zinc a paper soaked in battery electrolyte, the paper having been previously painted around the edges to exclude the influence of the air. The pieces of zinc were then pressed tightly together and differences of potential measured on a potentiometer. Two pieces of zinc cut from different portions of a sheet give slight differences of potential, the maximum value among a number of tests being 0.002 volt, and usually less. Upon heating and slowly cooling one of the pieces of zinc, to duplicate the influence of the soldering temperature, potential differences varying between plus and minus 0.012 volt were observed. Heating and rapidly cooling by quenching had a much smaller influence on the potential. Solder on the reverse side of one of the test electrodes had an influence amounting to 0.004 to 0.007 volt. The influence of air getting to the electrode surface was tested by first perforating one of the test electrodes and pressing it against another piece of unperforated metal with the saturated paper interposed. The first measurement showed a potential of 0.0026 volt, which gradually increased until after two days it had risen to 0.0224, the perforated plate being plus. This is a potential difference sufficiently high to cause somewhat rapid cell deterioration, and points to desirability of excluding as far as possible the access of air to the interior of the cell.

If we were to assume all inequalities of the zinc electrodes to be removed, we still have opportunities for local action due to inequalities in the electrode on the other side of the soaked paper. Non-uniformity in the mixture is detrimental. Some manufacturers place the carbon rod in direct contact with the saturated paper resting on the bottom of the cell, the mixture surrounding it. This must necessarily give rise to some difference of potential, and a measurement of this gave a value of 0.176 volt, in such direction that current tends to flow from the carbon through paper to zinc, thence through the paper to the manganese mixture and back to the carbon. To prevent this source of local action is probably the reason for the majority of cells now being made with the mixture interposed between all portions of the carbon surface and the paper.

It is evident, when we consider the numerous possible sources of trouble leading to faulty cells, that the making of a good dry cell requires care. Amalgamation of the zinc is occasionally resorted to, but it is doubtful whether material advantage accrues through the use of mercury in the dry cell.

It is customary to consider the carbon rod as the cathodic electrode, and in this we have arguments favoring the large corrugated and fluted shapes over the smaller cylindrical shapes, in that greater active electrode surface is thereby attained. It is doubtful, however, whether the surface of this rod is to an appreciable extent an active electrode surface. It makes contact with and is surrounded by a mass of material—carbon, graphite and manganese—possessing metallic conductivity even though moistened by electrolyte. It would therefore be more accurate to consider the active cathode surface as that portion of the mixture just within the paper. While this may be the main cathode surface, it is not exclusively so, and the active surface progresses inward as the action of the cell goes on.

The cathode is a compound one, consisting of an intimate mixture of conductive carbon and graphite in contact with manganese oxide, and the electromotive force of the cell is the summation of the electrode potentials, 0.56 volt for the zinc and about 1 volt for the carbon-manganese oxide mixture, or a combined voltage of 1.56.

While the cell delivers current to the external circuit this voltage decreases, the rapidity depending upon the amount of current drawn. If it were not for the manganese dioxide the drop in the voltage would be very rapid, and the value of the cell is therefore dependent largely upon the active manganese oxide or depolarizer. This manganese oxide is consumed. As commonly stated, it is reduced to Mn_2O_3, and in undergoing this change it becomes inactive both as a depolarizer and as a conductor. It is probable that the MnO_2 possesses sufficient metallic conductivity to contribute something to the conductivity of the cell, and when changed to the lower oxide it loses this conductivity. It thus becomes inert and occupies valuable space. It is natural to assume that the MnO_2 in the outer portions near the paper is the first to become reduced, the action progressing inward to a certain depth, this depending upon various factors, such as the intimacy of contact between the carbon and MnO_2, the purity, fineness and porosity of the latter, etc.

If the MnO_2 possesses metallic conductivity and makes contact with conductive carbon and both are moistened with electrolyte, there is a possibility that a certain amount of chemical action occurs owing to the voltaic couple thus produced.

A study of what actually takes place, chemically and electrically, inside of the dry cell while in action, and while standing in storage, offers an excellent subject for analytical research. While the chemical reactions which take place in the dry cell or other cells of the Leclanché type are frequently explained in a simple manner in text-books, a careful study will show that simplicity does not exist.

The electrical energy output of a dry cell is equal to the ampere-hours multiplied by the voltage. The current which a typical cell will deliver when short-circuited and "run down" in one hour is in the neighborhood of ten ampere-hours. It may go as high as thirty ampere-hours or more as the rate at which the current is drawn is diminished.

The open-circuit voltage is almost universally 1.5 to 1.6 volts.

The useful or effective voltage is less than 1.5 volts, and an average of 1 volt is a fair figure to assume at the cell terminals during a discharge at a rate such that thirty ampere-hours may be drawn. With an electromotive force of 1 volt and a current output of thirty ampere-hours, a fair energy rating for a dry cell is thirty watt-hours.

The voltage at the cell terminals while delivering current naturally depends upon a number of factors, the principal of which are the activity of the depolarizing material and the internal resistance of the cell. The activity of the depolarizer increases as the cell is used, and even more markd is the increase in resistance with the number of ampere-hours delivered.

It is very commonly believed that the increase in resistance is due to the drying out of the cell, but the drying is of very minor importance as compared with other factors. One of these is the increase in resistance due to the partial reduction of the MnO_2. Another is the accumulation, on the surface between the paper and the zinc, of non-soluble impurities of the zinc and the various basic salts and double salts resulting from the electrolytic corrosion.

When a cell is first made up the paper is saturated with a solution of zinc and ammonium chlorides. More zinc chloride is added as a result of the corrosion of the zinc. The increasing concentration of the $ZnCl_2$ in the presence of the ammonium chloride gives just the conditions which are needed for the production of various double chlorides, some of which are much less soluble than the single chlorides.

These insoluble double chlorides occupy the pores and spaces in the paper, crowding out the electrolyte and increasing the resistance. If ammonia is liberated, it may react with the $ZnCl_2$ to form a precipitate of ZnOH, which likewise clogs the cell, unless suffiicent ammonia be present to re-dissolve this precipitate. That this clogging action occurs at the paper and proceeds inward toward the carbon rod is evident, since in taking apart a run-down cell there is usually found a hard crust of an eighth of an inch or more in thickness just inside the paper.

It is no doubt true that improvement in dry cell construction must come through reducing this accumulation of insoluble non-conductive materials. It may be suggested that this precipitation due to double chlorides might be delayed by using only NH_4Cl in the electrolyte to begin with, and, in fact, a somewhat greater ampere-hour output can be obtained in this way. But it involves the more serious disadvantage of shortening the life of the cell on open circuit. The presence of $ZnCl_2$ in the electrolyte decreases in marked degree the local action.

There is no doubt that marked improvement has been made in dry cells during the past few years, and there is no reason to believe that perfection has yet been approached. The field for research in the study of this important device has by no means been fully occupied.

From the technical point of view the need for and possibility of improvement are equally great. The common and grossly inadequate methods of rating dry cells in terms of the number of miles they will run the ignition device on automobiles, or the number of months they will stand up on telephone service, or the number of sparks that they will produce, all of which are dependent upon the kind of device and the nature of the same in connection with which they are used, should give way to rating by energy output.

This can only be done after determining and generally adopting the standard methods for conducting tests.

Chemical Engineering Laboratories,
University of Wisconsin.

DISCUSSION.

Mr. Carl Hering: I have been very much interested in this paper, and I am glad to see that we are at last getting some able contributions on this subject.

The paper states that the electromotive force of the cell is the sum of the two electrode potentials, 0.56 volt for the zinc and about minus one volt for the carbon-manganese oxide mixture, giving the combined voltage at 1.56. It seems to me that there must be something wrong in this. It credits the greater part of the energy to the reduction of the manganese oxide, whereas it seems to me the energy comes chiefly from the oxidation of the zinc. I would like to ask, therefore, how it was determined; if it was determined by measurement, was not the method faulty? It seems that no one has yet been able to measure the absolute single potential of an electrode by a method which is really beyond question. If Prof. Burgess has found a method I would be very glad to know what it is. Calculation would, I think, show that the zinc gives the greater part and the manganese oxide the lesser part of the energy. Generally, the energy contributed by the depolarizer is very small.

The paper also says it would seem better to reduce the formation of the insoluble compounds, that is, that it would seem better to have them soluble. The question arises whether that is really desirable. There is only a very small amount of water in the battery, and that small amount has to do a great deal of work; it seems to me that if the products were soluble rather than insoluble, the water would be used up more rapidly, by having to hold in suspension the products that are formed; it would, therefore, not be available any longer as water. If this is correct, it seems to me that it is rather a desirable thing to arrange to have the chemical products formed insoluble, so that they will deposit out and leave the water there to keep the cell wet. The latter reminds me of an old definition, namely that the dry cell is so called because it always remains wet, in order to distinguish it from a wet cell which may run dry.

MR. CHARLES L. PARSONS: I would ask Prof. Burgess if in his experiments with dry cells he made any experiments in the use of bromates as depolarizing and oxidizing agents. In some work we have done during the last year bromates certainly showed wonderful oxidizing power at low temperature. I am interested to know whether these bromates have been worked with to any extent in dry cell construction. They are getting so that they can be obtained quite cheaply.

MR. J. A. SEEDE: Will Prof. Burgess tell us, approximately, the purity of the zinc in each cell and the weight of the zinc in each cell, also what does he mean by the statement towards the bottom of page 100 that the purchaser does not have a variety of grades of zinc to choose from.

PROF. BURGESS: At the bottom of page 103, where the potential of the zinc is given as 0.56, it is an oversight not to state that that is based upon the use of the so-called normal electrode. If Mr. Hering will look up the Ostwald series of potentials, for the potentials of metals, he will see that that is the value given for zinc. It is simply an arbitrary designation, based on a somewhat arbitrarily chosen zero point.

As to the use of water, this is needed between the zinc and mixture, and if the space which should be occupied by that water is taken up by insoluble materials, crowding the water further back into the mass, the electrolyte is not where it is needed.

As to the bromates, chlorates and many other oxidizing compounds, the use of these in most instances will increase the voltage of the cell and increase the amount of current output, but in general my experience has been that the soluble oxidizing agents are detrimental to the life of the cell, that is, they increase the local action.

My statement about the purity of the zinc is based upon statements which have been made to me by dealers. There appears to be practically one grade of zinc obtainable, it is only a high quality of zinc which can be satisfactorily rolled. The users do not appear to be able to dictate how pure a grade of zinc shall be furnished to them, and they take the best that can be obtained. An analysis of the sheet zinc can, of course, be made—it is some time since I paid any attention to it, and I cannot give the figures for the purity of the zinc which is being used.

MR. S. P. SHARPLES: There are many grades of zinc on the market, and we have been in the habit for years of testing zinc for the ordinary wet batteries. The requirements are now that it shall contain only traces of lead and no iron, and such zinc is readily obtainable on the market. I will mention one brand on the market which we have used, and that is zinc from the Bertha mine, in Virginia, and it is well adapted to use in batteries.

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The Magnetic and Electrical Properties of the Iron-Nickel Alloys.

BY CHARLES F. BURGESS AND JAMES ASTON.

In iron and nickel we have the two most magnetic elements. The fact that a mixture of certain percentages of these two metals results in a non-magnetic alloy makes an investigation of the magnetic qualities of an entire series of these alloys of interest.

There is much literature embodying the results of the research on the irreversibility of certain properties of the nickel-iron alloys and most of the published data of magnetic investigations is concerned with the temperatures of this appearance and disappearance of the magnetic susceptibility for different percentages of nickel.

In the investigation of Barrett, Brown and Hadfield (Jour. Inst. Elec. Engrs., Vol. XXXI, page 674) there is included complete hysteresis loops for a number of nickel-iron alloys in which the carbon runs from 0.13 to 0.23 per cent and the manganese from 0.65 to 1.08 per cent. Also, the magnetization curves of a series was determined by Carpenter, Hadfield and Longmuir (7th Report of the Alloys Research Committee, Inst. Mech. Engrs., Vol. 2, 1905, page 857). In this series the carbon was that of a medium steel (0.41 to 0.52 per cent) and the manganese content varied from 0.79 to 1.03 per cent. These steels, except for the increase of carbon, were almost identical with those of Hadfield, mentioned above; in fact, the work was intended as supplementary to this previous research.

This present paper deals with an investigation of a complete series of iron-nickel alloys in which the endeavor has been to keep down the impurities to the lowest possible point in order that the effects observed may be ascribed entirely to the alloying element. The work is part of an extended investigation of electrolytic iron and its alloys carried out during the past several years at the chemical engineering laboratories of the University of Wisconsin, under a grant of the Carnegie Institution of Washington.

The iron used is of a high degree of purity obtained by a process of double electrodeposition. The electrolytic material has a purity represented by an iron content of 99.97 per cent, the total content of sulphur, phosphorus, manganese and silicon being thus 0.03 per cent. The alloys were prepared by melting this iron with the desired quantity of nickel, also electrolytic material of a high purity, in magnesia crucibles supported by a graphite jacket. The crucibles were covered with a magnesia and a graphite lid and buried in an electric resistor furnace in which the melting was done. The resulting ingots of about 500 grams (1 lb.) in weight, were heated in a forge fire and drawn down under a steam hammer into rods about ⅝ in. in diameter and 18 in. long.

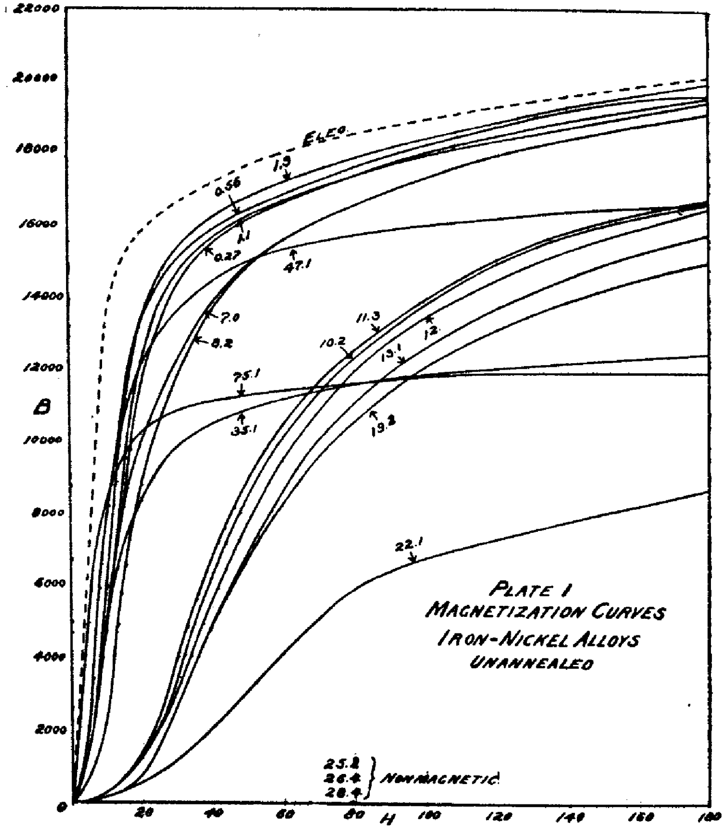

FIG. I.—MAGNETIZATION CURVES. IRON-NICKEL ALLOYS UNANNEALED.

Experience has shown that, in spite of every precaution, there is a slight carbon absorption, unquestionably due to the reaction of the iron upon the carbon monoxide atmosphere of the furnace. The amount, however, is small, and may be assumed in most cases to be well under 0.10 per cent. The other impurities, such as silicon, sulphur, phosphorus and manganese, are entirely negligible. In the present discussion the materials may be considered as binary alloys of iron and nickel and the effects to be due to these two elements alone.

Analysis.

The following series was subjected to magnetic tests.

Bar.	% Nickel Added.	 Analysis.	% Carbon.
144C	0.25	0.27	
144D	0.50	0.56	
144E	1.0	1.07	
144F	2.0	1.93	
144J	7.0	7.05	
157A	8.0	8.17	
157D	10.0	10.20	
157E	11.0	11.29	
157H	12.0	12.07	
144M	13.0	13.11	0.088
144P	19.0	19.21	
166G	22.0	22.11	
154S	25.0	25.20	
166I	26.0	26.40	
166C	28.0	28.42	
166L	35.0	35.09	
166O	50.0	47.08	
166Q	75.0	75.06	

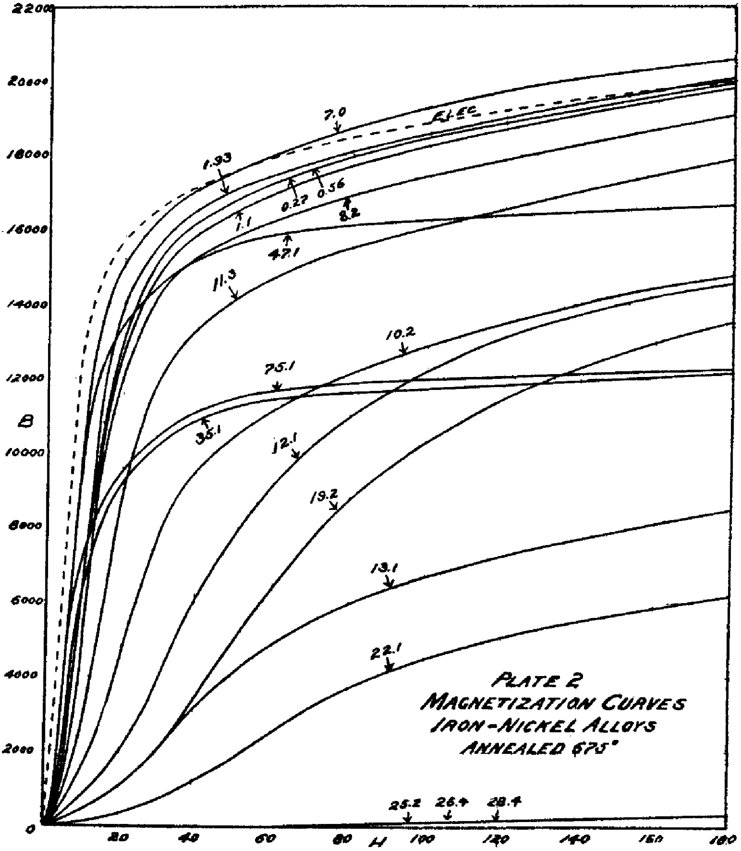

FIG. 2.—MAGNETIZATION CURVES. IRON-NICKEL ALLOYS ANNEALED 675°.

As will be seen, iron and nickel alloy readily and without segregation, since the agreement is strikingly close between the added percentage and that found upon analysis. This evidence is more conclusive when it is remembered that the analyses were made from turnings during the machining of test bars and after the forging of the ingot.

From the rods forged from the ingots, bars were reserved for tensile strength and one was taken for the magnetic tests. The latter was finished to a diameter of 1 cm with a length of about 20 cm. No sample of pure nickel was tested, since it was impossible to forge the ingot into a bar. It was possible to turn all bars in the lathe, although there was considerable difficulty in the range from 10 per cent to 20 per cent of nickel because of the hardness.

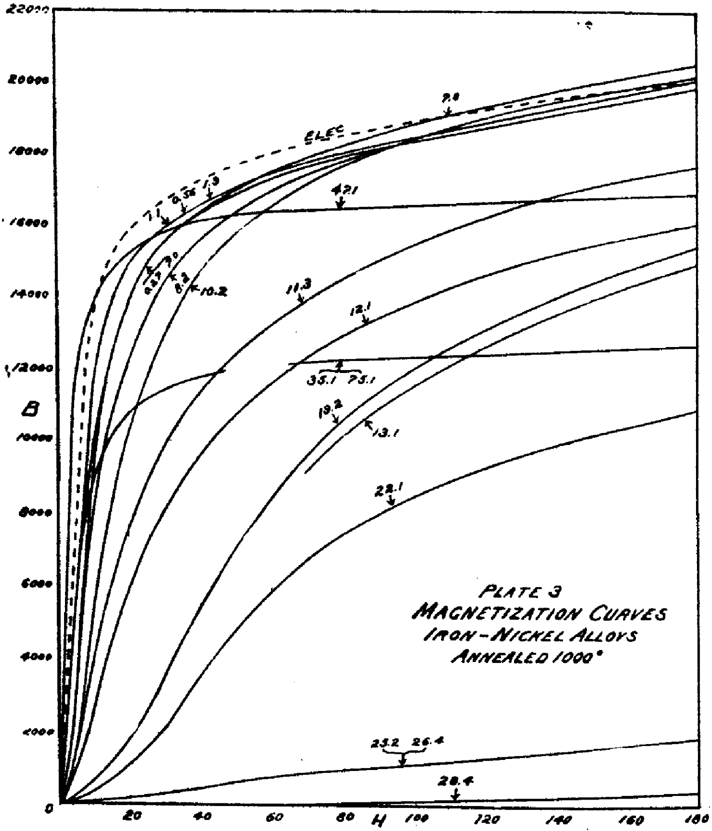

FIG. 3.—MAGNETIZATION CURVES. IRON-NICKEL ALLOYS ANNEALED 1000°.

Table I. Data of Magnetic Tests.

		H = 50				H = 20				H = 10				H = 100			
Bar	% Nickel	Unann	Ann. 675°	Ann. 1,000°	Quench 900°	Unann	Ann. 675°	Ann. 1,000°	Quench 900°	Unann	Ann. 675°	Ann. 1,000°	Quench 900°	Unann	Ann. 675°	Ann. 1,000°	Quench 900°
144C	0.27	2,600	6,000	9,100	10,450	11,400	13,200	13,650	13,900	16,150	16,850	16,800	16,750	17,900	18,400	18,300	18,100
144D	0.56	5,900	5,100	11,950	12,000	13,250	13,250	14,800	15,000	16,400	16,750	17,000	18,050	18,200	18,500	18,400	18,400
144E	1.07	3,500	5,100	11,500	7,600	12,050	12,800	14,650	11,200	16,250	16,500	17,000	15,600	17,800	18,250	18,400	18,400
144F	1.93	4,850	6,600	10,600	9,700	13,250	13,950	14,800	14,200	16,750	17,050	17,000	16,950	18,300	18,550	18,400	18,400
144J	7.05	4,850	10,000	9,500	9,300	9,950	15,050	13,800	13,250	14,750	17,550	17,000	16,750	17,250	19,250	18,750	18,500
157A	8.17	2,600	5,100	8,000	8,350	8,750	12,050	12,150	13,000	14,800	15,800	16,250	16,750	17,250	17,350	18,300	18,500
157D	10.20	50	1,450	5,300	7,950	900	4,650	10,150	12,350	8,550	10,500	15,650	16,450	13,800	12,850	18,350	18,600
157E	11.29	150	2,800	4,100	5,600	1,300	8,800	7,650	10,100	8,900	14,150	12,400	15,450	13,950	16,000	15,400	18,050
157H	12.07	350	750	2,700	4,600	1,300	2,000	5,900	10,100	7,700	7,750	10,700	15,250	13,450	12,200	13,850	17,700
144M	13.11	100	450	700	2,450	800	1,150	1,850	8,150	6,850	4,100	6,800	14,600	12,600	6,650	11,550	16,650
144P	19.21	400	400	650	2,200	1,150	1,050	1,700	7,000	6,750	5,000	7,050	12,950	12,050	10,350	12,050	17,200
166G	22.11	100	100	400	300	500	350	1,100	800	3,100	1,800	4,800	4,150	6,800	4,500	8,500	8,050
154S	25.20	0	0	50	50	0	0	150	100	0	0	500	350	0	100	1,050	850
166J	26.40	0	0	100	0	0	0	200	50	0	0	650	350	0	0	1,200	850
166C	28.42	0	0	0	0	0	0	0	0	0	0	0	0	0	100	100	100
166L	35.09	4,850	6,400	8,800	6,500	8,350	9,250	10,750	8,400	10,850	11,300	12,000	10,650	11,850	11,700	12,300	11,800
166O	47.08	7,850	10,600	13,650	10,300	12,100	13,450	15,150	12,400	14,950	15,550	16,250	14,800	16,000	16,200	16,500	16,000
166Q	75.06	8,300	7,200	8,450	8,700	10,200	9,550	10,650	11,200	11,250	11,450	11,850	11,800	11,800	11,950	12,300	12,100

Magnetic Tests.

The magnetic tests were made upon an Esterline permeameter. This instrument is essentially a small generator, the armature of which is driven at a predetermined constant speed. The voltage generated is proportional to the magnetic flux through the armature, since all factors are constant except this flux. The total number of lines of force is equal to that in the bar under test, since this bar forms part of the magnetic circuit. The necessary rheostats and switches are provided for regulation and reversal of the magnetizing current, for compensation, etc. But one recording instrument is used—a Weston millivoltmeter, calibrated to read directly, without calculation, the flux density B and the magnetizing force H in C.G.S. units.

This instrument was selected because of its adaptability to the work on the several hundred bars on hand and in prospect. It has given good satisfaction in its present form, both as regards rapidity and consistency. The results are not based upon an absolute measurement and the instrument must be calibrated against a standard determined by ballistic test. In our tests, magnetization curves were taken by the method of reversals and hysteresis loops by the step-by-step process. Complete magnetization curves and readings of the retentivity and the coercive force were taken under four different heat treatments, first, as forged; second, after heating to 675 deg. C and slowly cooling; third, after heating to 1000 deg. and slowly cooling, and fourth, after heating to 900 deg. and quenching in water.

The results of the magnetic tests are given in Tables I and II and in the curves of Plates 1, 2, 3 and 4. For purposes of comparison, there is given in each plate a dotted curve, plotted from the data of a test on a bar of electrolytic iron in the unannealed state, and which is of very high magnetic quality. The effect of the increase in the percentage of nickel is very apparent. In the unannealed state the alloys fall into several groups. Bars 144C, 144D, 144E and 144F, with 0.27, 0.56, 1.07 and 1.93 per cent of nickel, are very close together, and but little inferior to the standard. Increase of the nickel to 7.05 and 8.17 in bars 144J and 157A, has resulted in a falling off in quality. This is still greater for 157D (10.20 per cent), 157E (11.29 per cent), 157A (12.07 per cent), 144M (13.11 per cent) and 144P (19.21 per cent), which have a low permeability, and the curves of which take positions in the order of the nickel content. The quality of bar 166G, with 22.11 per cent, has become very poor, and finally bars 154S (25.20 per cent), 166I (26.40 per cent) and 166C (28.42 per cent), have become non-magnetic. Further increase of nickel content in 166L, 166O and 166Q, with 35.09, 49.08 and 75.06, has restored the magnetic quality very markedly, the maximum values being reached with 166O (47.08 Ni). Below the saturation bend of the curves (at about H = 40) these three bars have a very high permeability, but beyond this point the permeability becomes practically unity, with the flux density increasing but little more than the increase in the value of the magnetizing force. This latter feature is even more marked after the subsequent annealings at 675 deg. and 1000 deg.

Annealing at 675 deg. has resulted in general in an improvement of magnetic quality throughout the entire range. This is most marked for 144J, with 7.05 per cent Ni, and 157E, with 11.29 per cent Ni. On the contrary, there has been a deterioration in bars 144M (13.11 per cent), 144P (19.21 per cent) and 166G (22.11 per cent); this is very pronounced in the case of the first of these. A very slight amount of magnetism has been induced in the three non-magnetic bars 154S, 166I and 166C.

The second annealing at 1000 deg. has for those bars with smaller nickel content resulted in an increase of permeability for the lower magnetizing forces, with but little change in the upper ranges. Very pronounced changes have taken place in bar 157D, with 10.20 per cent Ni, which is better throughout, as are bars 157H (12.0 per cent), 144M (13.11 per cent) 144P (19.21 per cent) and 166G (22.11 per cent). The permeability of bar 166O, with 47.08 Ni, has become very high at the lower values of H; in fact, it is about the highest of any of the materials tested in this work. Bars 154S (25.20 per cent) and 166O (26.40 per cent) have become appreciably magnetic.

Quenching at 900 deg. has not resulted in much change, except for the alloys with 11.29 per cent, 12.07 per cent, 13.11 per cent and 19.21 per cent of nickel (157E, 157H, 144M and 144P) where the permeability has greatly increased.

Referring to Table II, the retentivities tend to decrease as we increase the nickel to the compositions of the non-magnetic alloys; and the values of coercive force increase. Beyond this composition the retentivities are again evident, and the coercive forces are small. This is in line with the deductions drawn from the curves and data. In general the coercive forces become smaller with each succeeding heat treatment. For the smaller nickel percentages of 0.27 and 0.56, in bars 144C and 144D, the values 4.3 and 4.2 are about those of electrolytic iron; and the values of coercive force for the three bars with the maximum content of 35.08, 47.08 and 75.06 per cent are markedly low.

The alloys with medium percentages of nickel (10 per cent to 20 per cent) seem to be very susceptible to heat treatment, and are at their best after quenching. This might be explained from the fact that nickel has a tendency to lower the temperature of transition in the iron from the hard γ to the soft α form. Consequently, while slow cooling would result in γ state, with its hardness and low permeability, the quenching, with cooling at lower temperatures, might have a tendency toward transition to the α form, with a resultant softness and better magnetic quality.

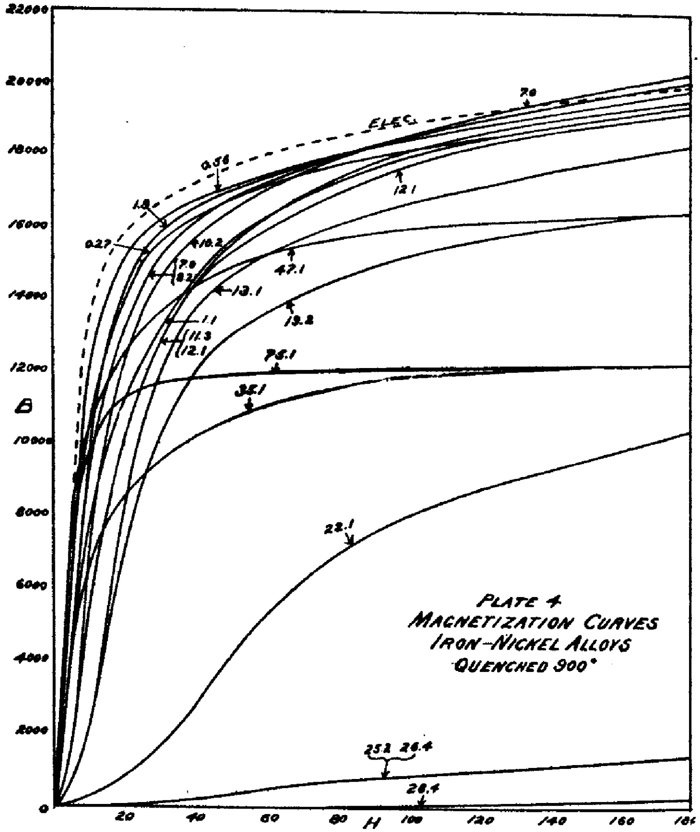

FIG. 4.—MAGNETIZATION CURVES. IRON-NICKEL ALLOYS QUENCHED 900°.

The strange feature of this nickel-iron series is that with two highly magnetic materials we can obtain all degrees of magnetization, even to a non-magnetic range. Equally striking is the fact (not here investigated) that these alloys in the non-magnetic range at normal temperatures become strongly magnetic at lower temperatures which are dependent upon the composition. They remain magnetic upon a rise of temperature of several hundred degrees, when they again become non-magnetic. Many attempts have been made to explain this anomaly, the reasons being based largely upon allotropy in the two elements.

The behavior is such that one might almost suppose that in the molecular arrangement of the alloys the iron and nickel become so oriented as to be of opposing polarity; this opposition becoming more pronounced with increase of the nickel content until finally a balance is reached with the resulting non-magnetic alloy. A further increase of nickel upsets this balance in favor of the nickel with its polarity preponderating.

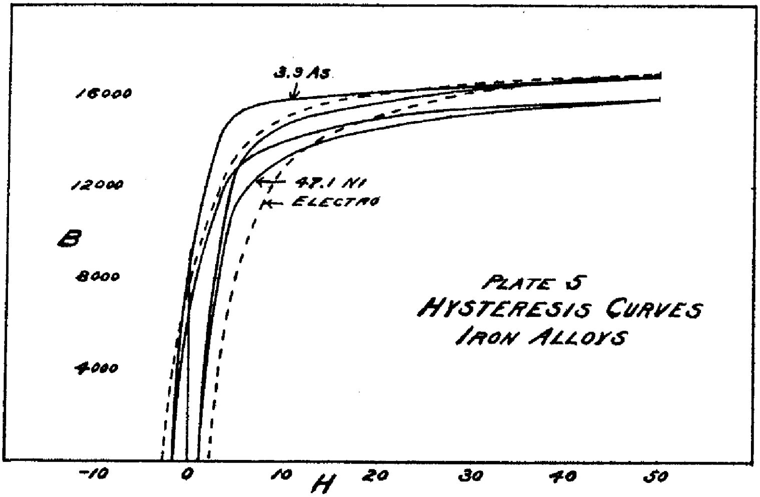

FIG. 5.—HYSTERESIS CURVES. IRON-ALLOYS.

In the range of commercial usage with 2 to 4 per cent of nickel the magnetic properties of the alloys have not fallen off to such an extent as to obviate against the use of the nickel in case the resulting mechanical qualities required are of sufficient importance to warrant its selection.

Hysteresis.

In connection with the magnetic tests, hysteresis curves were taken on such alloys as showed high permeability, especially such as had low magnetizing forces, and in consequence seemed particularly adapted to transformer working.

In the tests the cycle was carried to a maximum magnetizing force of H = 50. Typical bars with low hysteresis losses are noted in the following table; all were annealed at 1000 deg C.

Bar.	Per Cent Composition.	Relative Area of Loops.
117A	Electroforged	1.00
NSW	Swedish anode	1.08
55D	0.067 Al.	1.10
113D	3.862 As.	0.58
123C	1.035 Co.	1.20
166O	47.080 Ni.	0.53
96H	4.655 Si.	0.76
121J	2.059 Sn.	1.01

The results of the measurements upon bar 166O (47.08 per cent Ni) are plotted in Plate 5, together with those on electrolytic iron bar 117A, which was used as the standard of comparison, and 113D with 3.86 arsenic, which latter material showed the highest magnetic quality of any sample tested. The half-loops only are given.

In the above table is noted the relative area of the loops compared to the standard 117A as unity. These figures are indicative of the relative hysteresis losses per cycle of the materials in question. In our tests, therefore, the 50 per cent nickel alloy had the lowest loss, but 53 per cent of the standard and exceeded even the arsenic bar where the loss was 58 per cent of the standard. However, the great cost of this large quantity of nickel would eliminate its extensive use in general practice; also it is in reality not so good a material as some of the other alloys which have but sightly higher loss per cycle and which reach values of flux density considerably higher than the nickel bar for the same magnetizing forces.

Electrical Resistance.

As a study concomitant with that of the magnetic properties the electrical resistance of the bars of the nickel-iron series was determined. The measurements were taken by the fall of potential method by recording the drop across a measured

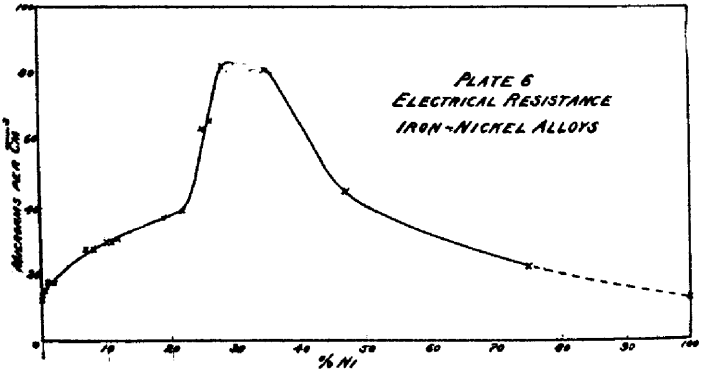

FIG. 6.—ELECTRICAL RESISTANCE. IRON-NICKEL ALLOYS.

Table II. Coercive Force and Retentivity.

Bar	% Nickel	H (Max.) = 200				H (Max.) = 200			
		Coercive force				Retentivity			
		Unann	Ann. 675°	Ann. 1,000°	Quench 900°	Unann	Ann. 675°	Ann. 1,000°	Quench 900°
144C	0.27	13.4	9.0	6.0	4.3	12,400	12,500	10,600	10,900
144D	0.56	11.0	9.1	4.0	4.2	11,400	12,300	10,100	10,700
144E	1.07	11.4	9.3	4.9	6.0	12,600	12,800	11,300	8,900
144F	1.93	10.2	9.0	5.0	6.0	12,800	14,400	11,300	11,700
144J	7.05	11.0	7.5	5.8	5.5	9,100	14,200	10,100	10,700
157A	8.17	12.5	10.0	6.3	6.0	8,000	12,500	9,600	9,500
157D	10.20	44.0	18.0	8.7	7.2	8,700	9,500	8,600	10,300
157E	11.29	32.5	13.5	9.2	8.8	9,200	11,800	7,000	9,500
157H	12.07	35.0	35.5	10.7	9.5	8,800	9,800	5,900	9,500
144M	13.11	34.8	32.5	31.5	14.9	8,500	4,500	7,700	11,900
144P	19.21	38.5	40.5	34.2	15.5	8,400	8,300	8,500	9,300
166G	22.11	44.5	51.8	37.0	42.7	5,000	3,900	6,300	6,100
154S	25.20	Non.	200+	50.3	64.5	Non.	200	1,000	1,000
161I	26.40	Non.	200+	45.5	66.3	Non.	200	1,100	900
166C	28.42	Non.	200+	200+	200+	Non.	2,000	400	400
166L	35.09	7.9	6.5	1.9	2.7	4,800	6,200	4,000	4,500
166O	47.08	6.7	5.5	1.6	1.9	7,700	9,000	8,700	5,200
166Q	75.06	3.1	3.5	1.9	1.5	6,000	4,600	3,600	4,200

length of the bar when a large current of about 50 amp was flowing. In the following table the results are given in microhms per cubic centimeter. There is also noted the relative resistance in terms of the same standard bar of the electrolytic iron which was used in the magnetic tests. (See also Fig. 6.)

Electrical Resistance.

Bar.	% Ni.	Microhms per cu. cm.	Relative resistance.
117A	0	12.1	1.00
144C	0.27	13.1	1.08
144D	0.56	15.4	1.27
144E	1.07	16.9	1.40
144F	1.93	16.4	1.36
144J	7.05	26.9	2.22
157A	8.17	26.7	2.20
157D	10.20	28.6	2.36
157E	11.29	29.4	2.43
157H	12.07	30.3	2.50
144M	13.11	34.8	2.62
144P	19.21	36.2	2.99
166G	22.11	38.7	3.20
154S	25.20	63.2	5.22
166I	26.40	65.5	5.41
166C	28.42	82.0	6.77
166L	35.09	81.1	6.70
166O	47.08	44.7	3.69
166Q	75.06	22.1	1.83
——	100.00	12.4	1.02

There is a gradual increase of resistance with the increase of nickel up to a percentage of 22.11, where there is a sudden rise in the curve at compositions corresponding to those of the non-magnetic alloys. However, the curve continues to rise, reaching a maximum in the range between 28.42 per cent and 35.09 per cent. At these two points the resistances are respectively 82.0 and 81.1 microhms per c.cm, or 6.77 and 6.70 times the resistance of the standard. Beyond this range the two determinations made indicate a fall of resistance with increase of nickel in a curve very similar to that on the other side of the maximum range. The final point of the curve at a nickel content of 100 per cent is taken from a standard handbook. Might not the maximum point in this curve of resistance be at 34 per cent of nickel, corresponding to the compound Fe_2Ni? Measurements of other kinds, such as dilatation, indicate a change of properties at this composition and tend to support the above view.

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February, 1910.

The Magnetic and Electrical Properties of the Iron Copper Alloys.

BY CHARLES F. BURGESS AND JAMES ASTON.

In connection with an extended investigation of iron alloys, carried out at the Chemical Engineering Laboratories of the University of Wisconsin, under a grant of the Carnegie Institution of Washington, a series of tests were made upon the iron-copper group. The results of various physical tests, including hardness, forgeability, and tensile strength, were described at the October, 1909, meeting of the American Electrochemical Society,[1] and were reprinted in the *Electrochemical and Metallurgical Industry*, of December, 1909.

This paper has to deal with the magnetic and electrical properties of the same iron-copper series and is, therefore, supplementary to the one mentioned above.

The details of the preparation of the alloys and of the test samples were given in the previous article, and need not be dwelt upon to any extent here. Electrolytic iron formed the basis of the alloys, together with alloying materials of a corresponding degree of purity; therefore, any properties noted in the tests may be considered as due to the effect of the added elements alone.

Tests were made upon 24 binary alloys of iron and copper, and upon 21 alloys with copper-silicon, copper-aluminium, copper-tin and copper-arsenic.

Of the binary alloys the following have been analyzed, and form the basis of the discussion of this series.

	Per Cent Copper.	
Bar.	Added.	Analysis.
147B	0.1	0.089
158A	0.2	0.202
158B	0.4	0.422
158D	0.8	0.804
147H	1.0	1.006
147J	1.5	1.510
158G	2.0	2.005
158I	4.0	3.990
158J	5.0	5.070
158K	6.0	6.160
147U	7.0	7.050
86F	95.0	94.340

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[1] Physical Properties of Iron-Copper Alloys, by C. F. Burgess and James Aston. Trans. Am. Elec. Soc. Vol. XVI, 1909.

The metals mixed in precisely the added proportions. Ingots with all percentages of copper between 7 and 95 per cent were made, but it was impossible to forge this intermediate series until the copper content reached 90 per cent.

Magnetic Tests.

The magnetic tests were made upon an Esterline permeameter under four different heat treatments—first, as forged; second, after heating to 675° C. and slowly cooling; third, after heating to 1000° C. and slowly cooling; fourth, after heating to 900° C. and quenching in water. The results are noted in Tables I and II and in Plates I, II, III and IV. All tests are compared to standard bar of electrolytic iron of high quality; the curve for this bar is indicated in the plates by a dotted line. In the unannealed condition the materials fall into two groups, with those of 1.5 per cent and less irregularly mixed and of the higher magnetic quality; above 2 per cent the permeability falls off rather quickly as the copper content is increased. This is in line with the hardness tests noted in the previous paper. None of the entire series, however, is of a quality worthy of mention; on the other hand, only bars of 4 per cent and up-

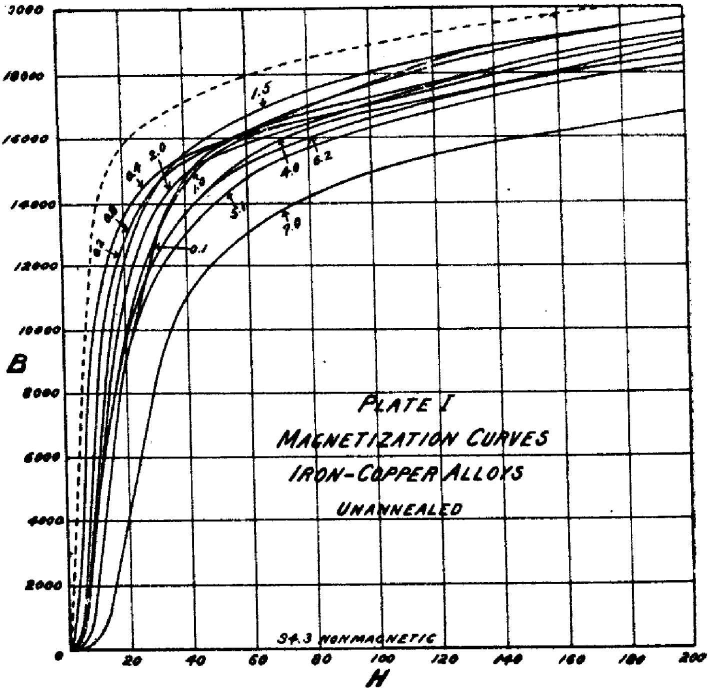

FIG. I.—MAGNETIZATION CURVES, UNANNEALED.

wards of copper are conspicuously poor. Bar 86F, with 94.34 per cent of copper, is non-magnetic.

Annealing at 675° has greatly improved the quality of all of the bars, and the curves now fall with considerable regularity into positions indicating a decrease of permeability with increase of copper content. The two best materials are bars 158B with 0.422 per cent Cu, and 158D, with 0.804 per cent copper; the former is but little inferior to the standard electrolytic curve.

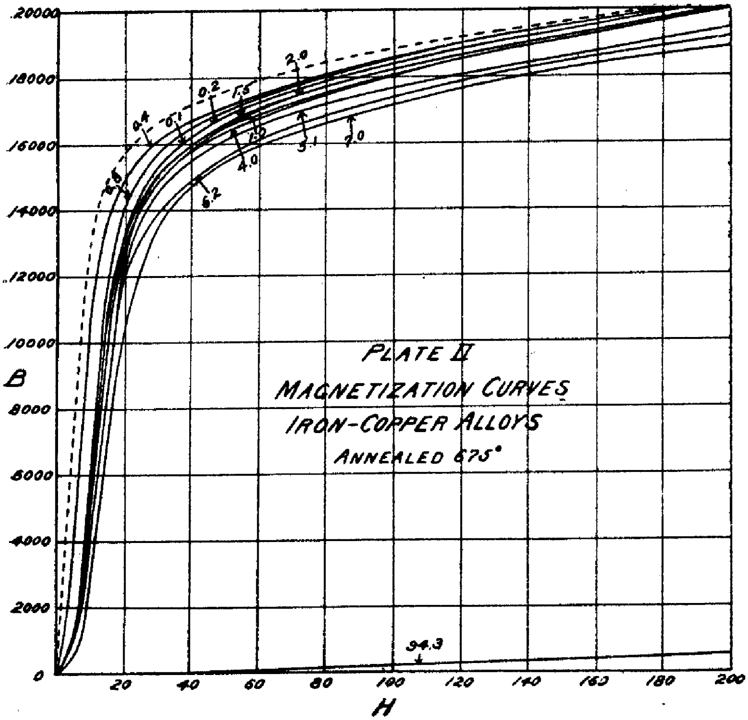

FIG. 2.—MAGNETIZATION CURVES, ANNEALED 675°.

Annealing at 1000° has not changed the relative positions of the curves, but has had the effect very generally observed in all of our work of decreasing the densities reached in the upper ranges. For the lower values of *H* (below 10) there has been an increase of permeability for those alloys of a copper content of less than 1 per cent, but for a percentage of one and upwards there is a deterioration for all values of *H*.

Quenching at 900° shows practically no change in quality from that of the previous treatment, the annealing at 1000°.

In all conditions subsequent to the unannealed state it has been possible to induce a small magnetic flux in bar 86F, with 94.34 per cent Cu; but the amount is too slight to warrant one in classing this material as other than non-magnetic.

No specific deductions can be drawn from the retentivity values of Table II. The values of coercive force follow a general tendency to diminish with the successive treatments, although in a few minutes the reverse is conspicuously evident. The values are at no time low, except for those alloys of less than 1 per cent copper after heating to the higher temperatures.

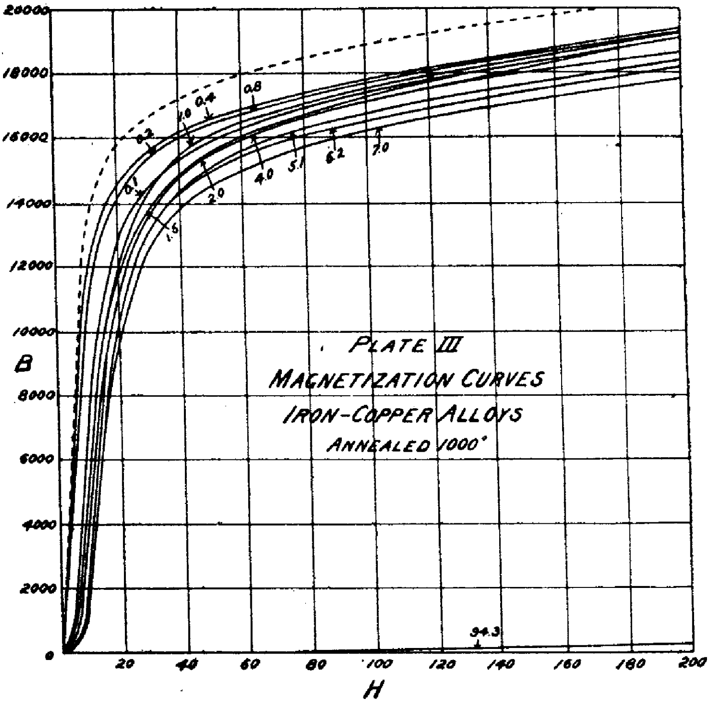

FIG. 3.—MAGNETIZATION CURVES, ANNEALED 1000°.

The results of the later tests on the 12 binary copper bars which were not analyzed give figures somewhat at variance with the results discussed above, in that three of the bars were of very high magnetic permeability.

Among the Cu-Si, Cu-Al, Cu-Sn and Cu-As alloys nothing of high quality was indicated, except for four bars where the percentage of added elements is low.

In the light of previous deductions, and because of the absence of accurate analyses, no conclusions will be drawn regarding these high values. They may be the result of high purity of the electrolytic iron and the absence of the intended content of the alloying elements.

Table I.—DATA OF MAGNETIC TESTS.

Bar	Per Cent Copper	H = 10				H = 20				H = 50				H = 100			
		Unann.	Ann. 675°	Ann. 1000°	Quench 900°	Unann.	Ann. 675°	Ann. 1000°	Quench 900°	Unann.	Ann. 675°	Ann. 1000°	Quench 900°	Unann.	Ann. 675°	Ann. 1000°	Quench 900°
117A	C	13,100	10,000	13,350	11,800	15,700	15,950	15,450	14,600	17,600	17,700	17,050	16,950	18,850	18,850	18,200	18,150
147B	0.09	2,900	5,700	7,600	9,200	8,400	13,250	12,800	12,600	15,650	16,800	15,850	16,200	17,600	18,350	17,400	17,600
158A	0.20	7,700	5,700	10,700	10,300	12,800	13,250	14,050	13,650	16,150	16,800	16,350	16,350	18,100	18,350	17,650	17,700
158B	0.42	10,150	10,950	11,700	11,500	13,500	14,950	14,550	14,300	15,800	17,100	16,550	16,650	17,100	18,500	17,700	17,800
158D	0.80	7,700	6,300	10,700	11,000	12,800	14,000	14,150	14,400	15,700	16,950	16,400	16,550	17,100	18,550	17,550	17,800
147H	1.01	2,900	6,300	5,500	9,200	9,600	13,250	11,950	13,450	15,450	16,500	16,000	16,350	17,100	18,050	17,450	17,650
147J	1.51	5,600	4,300	3,500	8,200	12,100	12,650	11,050	13,850	16,150	16,600	15,550	16,200	18,100	18,200	17,250	17,400
158G	2.00	4,500	5,000	5,500	5,600	10,900	12,650	11,600	10,750	15,400	16,450	15,450	15,250	17,050	18,250	17,100	17,200
158I	3.99	4,500	5,700	4,900	4,100	9,600	12,900	11,050	10,750	14,550	16,350	15,450	15,650	16,800	18,050	17,050	17,400
158J	5.07	2,900	4,300	3,000	2,950	8,900	12,350	10,150	10,300	14,000	16,100	15,050	15,300	16,250	17,650	16,700	17,000
158K	6.16	4,500	4,300	2,200	2,400	9,600	12,000	9,600	9,000	14,550	15,550	14,550	14,600	16,550	17,400	16,200	16,350
147U	7.05	400	3,000	2,400	2,950	4,200	10,400	10,150	8,400	12,150	15,450	14,950	14,200	14,900	17,200	16,500	16,150
86F	94.34	0	0	0	0	0	0	0	0	0	200	100	100	0	50	0	0

Summarizing, it may be said there is no advantage to be gained in adding copper to iron if a good magnetic permeability is wanted. The quality deteriorates almost in proportion to the added copper content. On the other hand, it may be said that there is nothing to be feared from the effect upon the magnetic quality of the small percentages of copper ordinarily found in commercial materials.

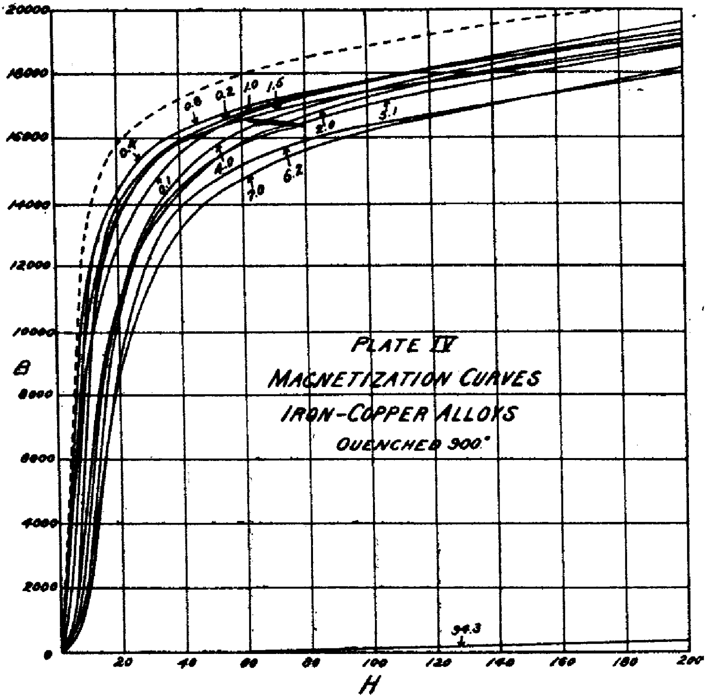

FIG. 4.—MAGNETIZATION CURVES, QUENCHED 900°.

In our previous discussions of the physical properties of the iron-copper alloys, stress was laid upon the fact that the alloys with copper content of from 1 to 2 per cent were entirely comparable with the iron-nickel alloys with percentages of nickel from three to four, which is the range ordinarily adopted in commercial practice. Direct comparison of the magnetic properties of the above-mentioned ranges is not possible, since we do not have the necessary data for the nickel series. However, it is worthy of mention that the magnetic data of the iron-copper alloys of the above-noted percentages is very similar to that for iron-nickel alloys of 1.93 and 7.05 per cent nickel, and they may, therefore, be taken as equal in magnetic quality to the nickel steels. Again, inspection of the magnetization curves, particularly after annealing at 675° C., shows permeabilities for the alloys of 1 to 2 per cent copper sufficiently high for commercial purposes, should their use be desired because of the increased tensile strength.

Electrical Conductivity.

Results of measurements of electrical resistance are given in the following table and in Plate V. The data are given in microhms per cubic centimeter; also in terms of the relative resistance compared to the same standard bar of electrolytic iron used in the magnetic tests. The bars had all been quenched at 900° C.:

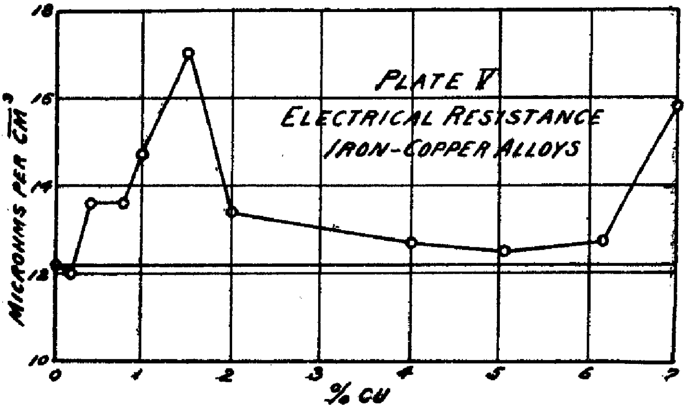

FIG. 5.—ELECTRICAL RESISTANCE.

ELECTRICAL RESISTANCE.

Bar.	Per Cent Cu.	Microhms Per Cu. CM.	Relative Resistance.
147B	0.09	12.2	1.01
158A	0.20	12.0	0.99
158B	0.42	13.6	1.12
158D	0.80	13.6	1.12
147H	1.01	14.7	1.22
147J	1.51	17.0	1.41
158G	2.01	13.4	1.11
158I	3.99	12.7	1.05
158J	5.07	12.5	1.03
158K	6.16	12.7	1.05
147U	7.05	15.8	1.31
86F	94.34	3.9	0.24

The conductivity is in no case above that of the standard iron bar, except for bar 86F, with 94.34 per cent Cu. Here the resistance is only one-fourth that of the iron; however, this alloy really belongs at the copper end of the series.

Table II.—COERCIVE FORCE AND RETENTIVITY.

		Coercive Force H (Max.) = 200				Retentivity H (Max.) = 200			
Bar	Per Cent Copper	Unann.	Ann. 675°	Ann. 1000°	Quench 900°	Unann.	Ann. 675°	Ann. 1000°	Quench 900°
117A	...	5.5	6.2	3.1	2.5	12,300	13,800	10,000	8,000
147B	0.09	13.0	8.7	12.1	4.3	12,700	12,000	10,100	8,400
158A	0.20	7.0	9.3	4.0	3.5	11,100	13,300	8,400	8,400
158B	0.42	7.0	6.0	3.7	3.6	9,900	13,300	8,600	9,300
158D	0.80	9.5	9.5	4.1	4.3	11,500	14,900	8,700	9,100
147H	1.01	14.0	9.5	8.8	5.4	11,100	14,500	10,400	8,700
147J	1.51	12.8	10.5	11.3	7.3	11,100	14,300	12,400	12,500
158G	2.00	10.7	10.0	9.0	8.3	10,200	12,800	10,200	9,900
158 I	3.99	6.0	9.8	9.3	9.7	9,200	13,200	11,100	11,300
158J	5.07	5.7	10.9	11.5	11.2	8,300	13,200	11,500	11,700
158K	6.16	12.5	10.5	11.8	11.8	9,300	11,600	11,800	12,100
147U	7.05	12.5	13.2	12.5	12.6	7,700	12,500	13,100	11,200
86F	94.34	Non.	200+	200+	200 +	Non. Mag.	500	300	400

The resistance rises rapidly to a maximum of 17 microhms per cubic centimeter, at a copper content of 1.51 per cent. Between 2 and 6 per cent copper the conductivity is but little inferior to that of the iron, while at 7 per cent the resistance has again risen to 1.31 times that of the standard.

Later measurements upon numerous unanalyzed iron-copper alloys give results so irregularly scattered in relation to those here given that they should be accepted with caution.

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The Magnetic and Electrical Properties of Iron-Silicon Alloys.

BY CHARLES F. BURGESS AND JAMES ASTON.

The belief was held for a long time that, as far as magnetic properties were concerned, purification was the method to be looked to for improvement of iron; that the highest permeabilities were to be reached the nearer our material approached an analysis of Fe 100 per cent.

That this is not true is now, of course, common knowledge. The work of Barrett and Brown, in 1901,[1] on alloy steels, made by Hadfield, gave for irons with additions of 2¼ per cent of aluminium or 2½ per cent of silicon permeabilities excelling those of pure iron; investigations of the author have shown this same effect by additions of about 2 per cent of tin or about 4 per cent of arsenic.

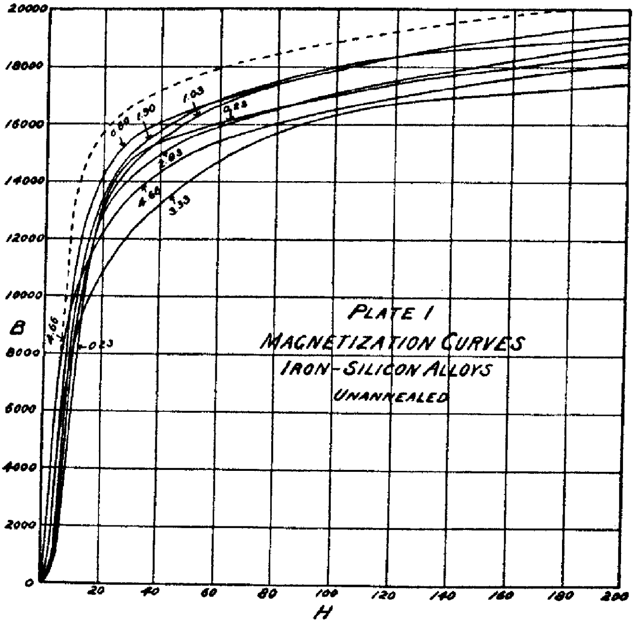

FIG. I.—MAGNETIZATION CURVES, ALLOYS. UNANNEALED.

It is not probable that the influence of these elements, all non-magnetic, is directly, or in a strict chemical sense, the cause of the marked improvement of magnetic quality. It is more likely that the effect is due indirectly through some change in the physical structure of the iron itself. This supposition is seemingly confirmed by the influence of the heat treat-

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[1] "The Conductivity and Magnetic Properties of Alloys of Iron," W. F. Barrett and W. Brown, Jour. Inst. Elec. Engrs., Vol. 31, p. 675.

ment of high-purity iron. Annealing at lower temperatures (about 700° C.) results in improvement of quality throughout the entire magnetization curve, due to the removal of all cooling and forging strains; while annealing at the higher temperature of 100° C. results in a deterioration of quality in the upper ranges, and a higher permeability at low magnetizing forces. And, of course, we have the concomitent increase in the grain size of the iron.

From the investigations of Hadfield, Barrett and Brown has resulted the present-day materials so largely used in transformer work, in which the percentage of silicon varies from about 3 per cent to 6 per cent. In these silicon steels the heat treatment is of importance comparable with that of the silicon content, and the practice seems to be annealing at high temperatures. The result is a material of very high permeability for the lower magnetizing forces; the saturation limit is reached at comparatively low densities, however, and beyond this point the quality is not exceptional. This characteristic makes the steel particularly suited to alternating-current working, where low working densities are the rule. The low hysteresis losses, together with the added benefits of high electrical resistance and slight deterioration due to ageing, are the special features of the silicon steels.

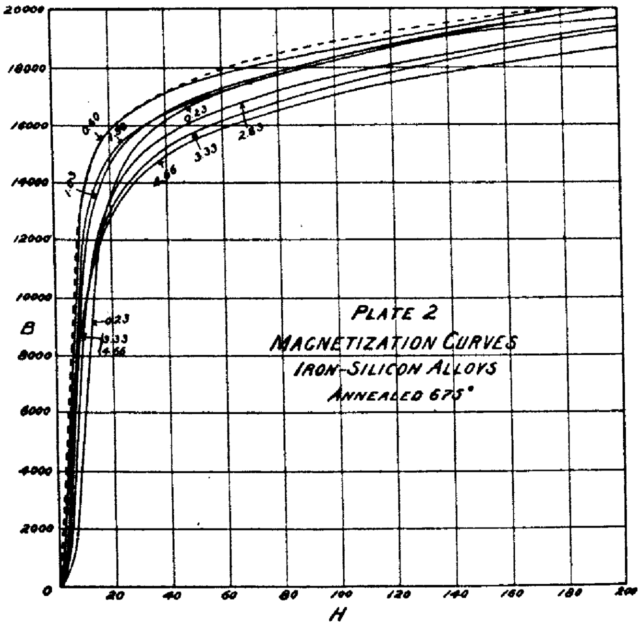

FIG. 2.—MAGNETIZATION CURVES, IRON-SILICON ALLOYS. ANNEALED 675°.

Our investigations[2] covered tests of 15 iron-silicon alloys, of which the following seven bars were analyzed and form the basis for discussion.

PER CENT SILICON.

Bar.	Added.	Analysis.
96F	0.25	0.233
96A	0.50	0.603
96B	1.0	1.033
96C	2.0	1,897
109A	3.0	2,826
113V	7.0	3.334
96H	5.0	4.655

The agreement between added and actual silicon content is close, except for bar 113V.

As mentioned in articles which have appeared previously in this journal, electrolytic iron of high purity (99.9+) formed the basis of the alloys. All effects noted, therefore, may be ascribed, as far as due to chemical composition, to the added element alone. These alloying materials were melted into ingots, which were forged and turned into bars for testing.

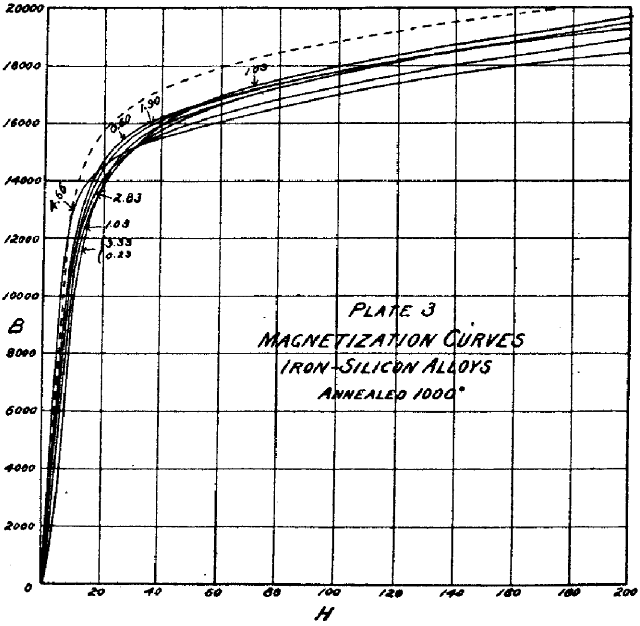

FIG. 3.—MAGNETIZATION CURVES, IRON-SILICON ALLOYS. ANNEALED 1000°

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[2] A research on "Electrolytic Iron and Alloys" at the University of Wisconsin, under grant of the Carnegie Institution of Washington.

The results of the tests are noted in Tables I and II and in Plates 1, 2, 3, and 4. Four heat treatments were adopted—as forged, annealed at 675° C., annealed at 1000° C., and quenched at 900° C. Comparison is made with a standard bar of electrolytic iron of high magnetic quality; this is indicated in the plates by a dotted curve.

In the unannealed condition all the curves fall considerably below the standard, particularly in the upper ranges; the best results are obtained with bars of lower silicon content, and the lowest with those of highest silicon, viz., 113V, with 3.33 per cent Si, and 96H, with 4.66 per cent. However, it will be noted that for the very low values of H these two bars, and particularly 96H, cross the other curves and have the highest permeability of the series.

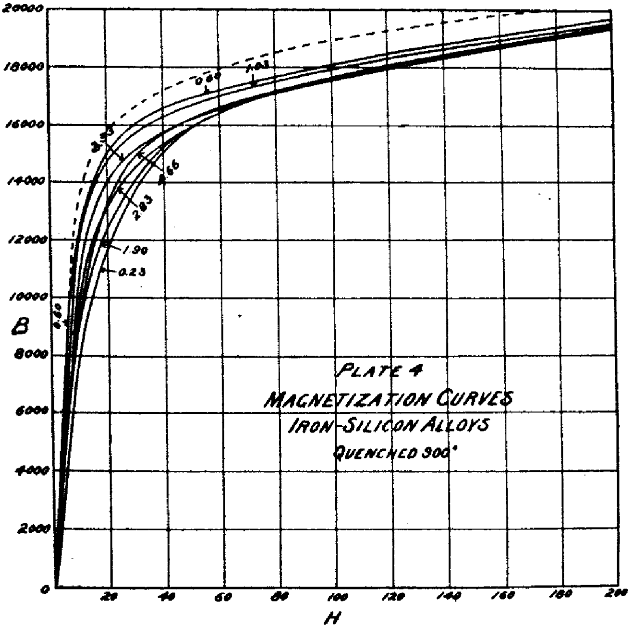

FIG. 4—MAGNETIZATION CURVES, IRON-SILICON ALLOYS. QUENCHED 900°.

Annealing at 675° has raised the maxima of all curves, but the comparative order is about as in the previous condition. Bar 96A, with a low silicon percentage of 0.603, lies very close to the standard throughout the entire length.

Second annealing at the higher temperature of 1000° has resulted in a falling off of the permeability for these bars of lowest silicon content. But for three bars of highest percentage of silicon, viz., 109A (2.83 per cent, 113V (3.33 per cent) and 96H (4.66 per cent), there has been a considerable improvement of quality at the lower magnetizing forces, with but little change

TABLE I.—DATA OF MAGNETIC TESTS.

		H = 10				H = 20				H = 50				H = 100			
Bar.	Per cent Silicon.	Unann.	Ann. 675°.	Ann. 1000°.	Quench 900°.	Unann.	Ann. 675°.	Ann. 1000°.	Quench 900°.	Unann.	Ann. 675°.	Ann. 1000°.	Quench 900°.	Unann.	Ann. 675°.	Ann. 1000°.	Quench 900°.
117A	0	13100	10000	13350	11800	15750	15950	15450	14600	17600	17700	17050	16950	18850	18850	18200	18150
96F	0.23	6500	6000	9750	7850	13100	13250	13700	11550	15750	16700	16250	15850	17000	18350	17700	17700
96A	0.60	10700	13100	11750	12150	14150	15800	14700	14950	16450	17500	16550	16900	17850	18600	17800	18100
96B	1.03	8100	10700	10700	11800	13100	14450	13650	14650	16150	16850	16550	16650	17850	18200	17950	17950
96C	1.90	9200	11600	11200	9150	13450	14850	14450	12250	16350	16800	16500	15850	17950	18200	17750	17600
109A	2.83	8200	8900	11200	10000	12800	13250	14050	13050	15500	16150	16000	15950	17050	17700	17300	17550
113V	3.33	8000	9100	9750	10700	10800	12950	13850	14000	14050	15750	16350	16150	16350	17350	17750	17600
96H	4.66	9750	9300	12950	9100	12200	12700	14550	13200	14950	15400	15750	16250	16500	17100	17000	17600
M E	Com.			12300				14400				16100				17700	
S E	Com.			10100				13100				16300				18000	
252	Com.			10700				13500				16400				17900	
182	Com.			11550				13850				15800				17550	

for the upper ranges. Here the curves fall below those of lower silicon, and all are well below the standard. The effect is most striking for bar 96H, with the highest silicon of the series (4.66 per cent); its permeability is very high below H = 10. At this point the curve has a very sharp bend, and thereafter falls below the others. Quenching at 900° has resulted in a deterioration of quality, particularly in the lower ranges, with but little change at higher magnetizing forces.

The values of retentivity given in Table II reflect the conditions indicated by the magnetization curves, and vary with the maxima reached by the curves. In general, the coercive forces become less with annealing, and reach a minimum after heating to 1000°. Quenching has had a slight tendency toward increase. The very low value of 2.7 is reached by bar 96H (Si 4.66 per cent) after annealing at 1000°, confirming the previous deductions of high permeability for this alloy at low magnetizing forces.

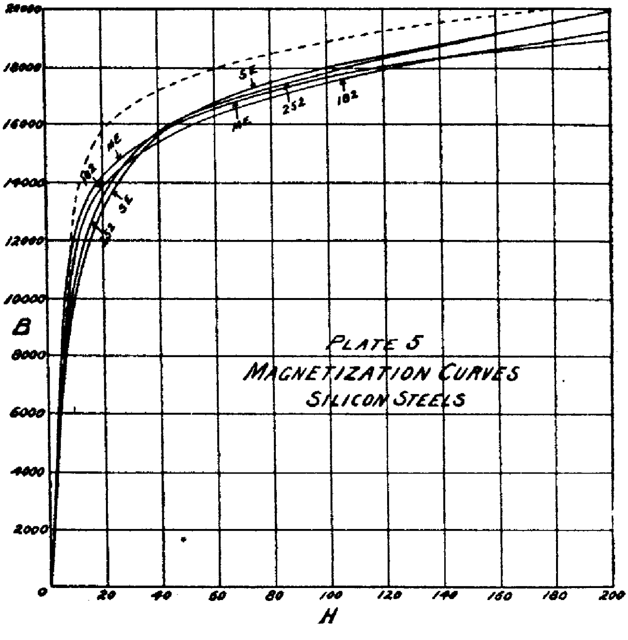

FIG. 5.—MAGNETIZATION CURVES, SILICON STEELS.

Summarizing, the results of these tests do not show a general improvement of permeability due to the presence of silicon in electrolytic iron, but the experience of practice is confirmed in that a high-silicon alloy after annealing at high temperature is of high permeability for very low magnetizing forces and

TABLE II.—COERCIVE FORCE AND RETENTIVITY.

		H (Max.) = 200 Coercive force.				H (Max.) = 200 Retentivity.			
Bar.	Per cent Si..	Unann.	Ann. 675°.	Ann. 1000°.	Quench 900°.	Unann.	Ann. 675°.	Ann. 1000°.	Quench 900°.
117A	0	5.5	6.2	3.1	2.5	12300	13800	10000	8000
96F	0.23	8.6	9.4	5.2	4.3	11700	13800	9200	8000
96A	0.60	5.2	4.5	3.5	3.5	11500	13200	9000	10100
96B	1.03	7.5	6.8	4.1	4.0	12400	14200	9400	10000
96C	1.90	7.7	6.5	4.0	4.3	11800	14100	9300	9100
109A	2.83	8.5	8.2	4.7	5.1	12900	14300	10000	9900
113V	3.33	5.5	5.5	4.5	4.3	8700	11300	8500	9100
96H	4.66	4.5	4.9	2.7	3.3	12000	12800	8000	5600
M E	Com.			2.3				9700	
S E	Com.			2.5				6100	
252	Com.			3.0				8700	
182	Com.			3.5				10600	

densities such as are used in transformer design. The improvement is not so great in our tests as it is in commercial materials; it may be that the effect of the silicon is more pronounced in the presence of certain impurities or after special heat treatment.

Commercial Steels.

For the purpose of comparison there is appended in Tables I and II, and plotted in Plate 5, results of tests on commercial silicon steels, the samples being obtained from steel and electrical manufacturers. The tests were made upon the same apparatus as those discussed above, and the results are thus strictly comparable. The dotted curve of Plate 5 is that of the electrolytic iron standard.

The general character of the silicon steel is well shown and needs no special comment. Curves SE and 252 are of the same brand of material from a large sheet-steel manufacturer, but from samples obtained from different electrical concerns at different periods of time. The uniformity of the material is very striking; this is brought out with great clearness below, where the hysteresis tests data are tabulated.

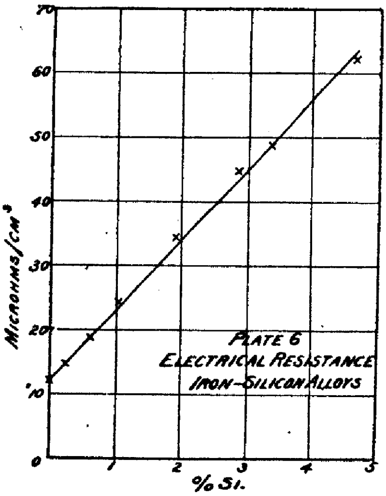

FIG. 6.—ELECTRICAL RESISTANCE IRON-SILICON ALLOYS.

All inductions have been carried to a maximum of $B = 12{,}000$.

Bar.	Per cent Si.	Loop area.	Relative area.	H (Max.)
117A	0	8.65	1.	8.2
96F	0.23	12.58	1.45	30.0
96A	0.60	7.05	0.81	12.5
96B	1.03	8.72	1.01	13.3
96C	1.90	9.53	1.10	1.80
109A	2.83	10.96	1.27	18.0
113V	3.33	8.77	1.02	13.4
96H	4.65	4.39	0.51	7.5
M E	Coml.	5.20	0.60	8.7
SE	Coml.	5.77	0.67	14.7
252	Coml.	6.10	0.71	14.1

These results are hardly a fair criterion of the quality of the electrolytic samples, since all were tested after quenching at 900°.

Electrical Resistance.

A feature of steels for transformer working, second only to the magnetic quality, is a high electrical resistance, to reduce the eddy-current loss. In this respect the silicon steels are an additional advantage.

Measurements of the series discussed in this paper are given in the following table:

Bar.	percent Si.	Microhms per cm^3.	Relative resistance.
117A	0	12.1	1.0
96F	0.233	14.7	1.22
96A	0.603	18.7	1.55
96B	1.033	24.3	2.01
96C	1.897	34.4	2.84
109A	2.826	44.6	3.68
113V	3.334	48.6	4.02
96H	4.655	62.2	5.13
182	Coml. silicon	59.5	4.92

The above data are plotted in Plate 6, where the effect of increasing addition of silicon to the iron is indicated as an maximum of 4.65 per cent.

At this content (and this is the alloy with the minimum hysteresis loss) the resistance has risen to upward five times that of the electrolytic iron standard.

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THE STRENGTH OF THE ALLOYS OF NICKEL AND COPPER WITH ELECTROLYTIC IRON

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MADISON, WISCONSIN
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INTRODUCTION

Of the properties of binary alloys of iron with the common metals comparatively little is known. This is attributed to the fact that pure iron with which to alloy copper or nickel, or tin, or others of the metallic elements, has been a rare laboratory product, and interest has been directed, naturally, to alloys made from commercial materials.

Based upon the discovery of a simple method of refining iron electrolytically, an extensive line of laboratory investigation was begun five years ago in the Applied Electrochemistry Laboratory of the University of Wisconsin, and has been carried on almost without interruption since that time. This investigation has consisted in the production and study of the properties of alloys of iron, eliminating as far as possible the common impurities, sulphur, phosphorus, silicon, manganese and carbon.

This work has been conducted through facilities afforded by the College of Engineering of the University of Wisconsin and through grants from the Carnegie Institution of Washington.

From the large amount of data and information derived from this investigation, a small portion, dealing with the alloys of copper and nickel with iron, is presented in this bulletin. This selection of material has been made on account of the interesting and possibly important influence of small percentages of copper and of nickel on the properties of iron.

It is appreciated by no one more than by the authors that laboratory experiments carried out on the small scale which has been necessary here, can by no means embody all the factors attendant upon large scale production, and the conclusions arrived at can be only suggestive when applied to commercial production of alloys.

The study of iron alloys of the degree of purity which we have attained is not alone of scientific interest, since recent improvements in commercial materials make it possible to secure remarkably pure iron at reasonable cost.

The fact which impresses itself most emphatically upon one who undertakes to study the properties of iron alloys, is that he has an unlimited field to deal with and one which has not been cultivated intensively or even superficially.

Not only are there new alloys to be produced, but much of the older work on iron and steel, now considered as on a fairly settled basis, can be repeated with profit in the light of a modern knowledge as to the influence on the properties of material, of variations in heat treatment, and other factors.

In presenting this bulletin, the writer acknowledges indebtedness to numerous of his colleagues who have assisted in this work, and especially, to Mr. Carl Hambuechen, who worked out the details for refining iron electrolytically, to Dr. Oliver P. Watts and Mr. Otto Kowalke, who conducted the laboratory work of this investigation for two years, and to Mr. James Aston who as joint author has done much more than his share in writing this report on the alloys of nickel and copper with iron.

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THE STRENGTH OF THE ALLOYS OF NICKEL AND COPPER WITH ELECTROLYTIC IRON

ELECTROLYTIC IRON

The basis of the alloys dealt with here is iron of a high degree of purity, obtained by double electrodeposition. In the first refining, high grade Swedish bar iron is used as anode material, and the metal is deposited upon both sides of a sheet lead cathode. These cathodes are then used as anodes in a second set of tanks, and a double refined product is obtained upon a sheet aluminum cathode. This electrolytic iron is stripped off in sheets ¼ inch to ⅜ inch in thickness about 10 inches square, and is broken up for use in the crucibles.

The character of deposited material is indicated in the following table. The analyses given in the first three columns are those of Messrs. Booth, Garrett and Blair, of Philadelphia. Also, all of the analytical work on the alloys proper, including those appearing later in this discussion, are the work of the above laboratory, and acknowledgment is due for their liberality and interest in the work. The most recent analysis of the double refined iron is given in the last column, and was reported by Mr. Alvan C. Davis, of Edgeworth, Pa.

	Swedish Anode.	Single Refined.	Double Refined.	Double Refined.
Carbon	0.260	0.013	0.012	0.000
Sulphu	0.007	0.007	None.	0.003
Silicon	0.109	0.003	0.013	0.002 or less.
Phosphorus	0.007	0.020	0.004	0.003
Manganese	0.021	None.	None.	0.020
	0.404	0.043	0.029	0.028
Iron (difference)	95.596	99.957	99.971	99.972

The analyses of the final product differ somewhat in the percentages of the various impurities found. Whether this is due to the difference of the material at the different times of sampling, or to the limiting error of the analytical method in detecting the small percentages actually found, is problematical. However, the initial product used in the preparation of the alloys may be considered of negligible impurity, with an iron content of 99.97 per cent.

PREPARATION OF ALLOYS

In the preparation of the alloys, the brittle electrolytic iron was broken into small pieces, and the pre-determined amounts needed for each charge, together with the addition elements, were weighed out. The charges were placed in specially prepared magnesia crucibles, which were in turn protected by a graphite jacket. The crucibles were buried in an electric furnace of the resistor type; the charge being prevented from contamination by a magnesia lid luted on the crucible, and a graphite cover for the jacket.

The charges were brought to fusion, and held at this temperature for a few hours after which the current was cut off from the furnace and the latter was allowed to cool down. There was no agitation of the charge, the resulting alloy being entirely due to diffusion of the elements. The ingots weighed about 500 grams (1 lb.)

In spite of every precaution, there was some absorption of carbon by the charge. There is every indication that this was due to the interaction between the iron and the carbon monoxide furnace atmosphere, whereby carbon was set free by the reaction $Fe + CO = FeO + C$, and then taken up by the iron by cementation. The amount absorbed varied somewhat with the conditions of the melt, and probably also with the nature of the alloying element. Numerous analyses, however, showed the amount to be well under 0.10 per cent; sulphur, silicon, phosphorus and manganese are negligible. A charge of electrolytic iron melted into an ingot and forged under the same conditions employed in the preparation of the alloys showed by analysis carbon 0.047, sulphur 0.005, silicon 0.062, phosphorus 0.016, manganese 0.0.

In the tests, therefore, the properties observed may be ascribed to the addition elements.

The ingots were heated in a forge fire and drawn out under a steam hammer into rods about ½ inch in diameter and 20 inches long. These rods were cut into appropriate lengths and machined for the tensile strength tests into bars approximating 0.3 to 0.4 inch in diameter over a free length of 2 inches. Qualitative observations were made of forgeability and of hardness in machining.

An equal number of samples were reserved for testing as forged and after annealing at 900°C. The tests were made upon a Riehle 1,000,000 pound power-driven machine. The load was applied very slowly, and the elastic limit, or rather, the yield point, was determined by means of dividers, being taken as that load at which a perceptible stretch occurred in a marked 2-inch length of the bar. This was checked by the drop of the beam. In the later tests, multiple dividers were used, enabling the yield point to be observed very closely, as well as the elongation at this point. The data recorded included the load at the yield point, and the maximum necessary to rupture the bar; also the elongation in two inches and the reduction of area at the fracture.

This particular discussion may be divided into three general parts—(1) the nickel-iron series; (2) the copper-iron series; (3) a series with iron alloyed with both nickel and copper.

NICKEL-IRON ALLOYS

Much has been written regarding certain nickel steels for commercial usage and there has been considerable investigation of these particular alloys. Also, there is much literature on the metallography and the theory of nickel steels, with which phase this paper is not particularly concerned. There is comparatively little published data of research, especially systematic research on the effect of the addition of varying percentages of nickel to steels of otherwise comparable compositions.

Of the latter, to which the present paper is largely supplementary or correlative, may be mentioned the following:

Between 1892 and 1902, the Prussian Society for the Encouragement of Industry published several reports dealing with the mechanical properties of the nickel-iron alloys (Berichte des Sonderausschüsses für Eisen-Nickel Legierungen. 1892–1902).

R. A. Hadfield (Inst. Civ. Engrs., 1898, Volume CXXXVIII, page 1) gives data of a very complete study of a series of nickel-iron alloys, covering the mechanical and physical properties. The nickel varies from 0 to 50 per cent, with other impurities as follows: C, 0.13 to 0.23 per cent; Si, 0.20 to 0.38; S, 0.08 to 0.11; P, 0.05 to 0.09; Mn, 0.65 to 1.08.

L. Guillet (Bul. Soc. d'Encour pour l'Industrie Nationale, May, 1903) publishes the results on three series of steels with nickel from 2 to 30 per cent, manganese low and carbon about 0.12, 0.22 and 0.82 per cent in the several series. The work includes the mechanical tests and the metallographic study with a view of finding the relation between the physical properties and the structure.

Carpenter, Hadfield and Longmuir (7th Report, Alloys Research Committee, Inst. Mech. Engrs., Vol. 2, 1905, page 857) give the data of a thorough investigation of a series of alloys with nickel from 0 per cent to 20 per cent, carbon 0.41 to 0.52; manganese, 0.79 to 1.03. This research was intended as a supplement to Hadfield's work mentioned above, the steels being practically of the same composition, except that there was an increase of the carbon content from a mild steel proportion of about 0.20 per cent to that of a medium steel with 0.45 per cent.

In the present research the effort has been to determine the effect of additions of varying percentages of nickel to iron in the absence of other impurities, especially carbon. As mentioned heretofore, the iron is of such purity that the results observed may be ascribed to the nickel addition alone. The added nickel was electrolytic material of high grade.

ANALYSIS

Ingots were prepared of all compositions from 0 to 100 per cent of nickel, but the mechanical tests here enumerated are confined largely to the range of 0 per cent to 20 per cent of nickel. The analyses given below are of a series of random selection which is representative of the entire range.

ANALYSES.

Mark.	Per cent Ni.		Per cent C.
	Added.	Analysis.	
144C	0.25	0.27	
144D	0.50	0.56	
144E	1.0	1.07	
144F	2.0	1.93	
144J	7.0	7.05	
157A	8.0	8.17	
157D	10.0	10.20	
157E	11.0	11.29	
157H	12.0	12.07	
144M	13.0	13.11	0.088
144P	19.0	19.21	
166G	22.0	22.11	
154S	25.0	25.20	
166I	26.0	26.40	
166C	28.0	28.42	
166L	35.0	35.09	
166O	50.0	47.08	
166Q	75.0	75.06	

As might be expected from the close analogy of the properties of nickel and iron, the agreement of the analytical results with the percentage of nickel added to the charge, is exceedingly close and when it is considered that the samples for analysis were from turnings of test bars after the ingots had been forged into rods, it may be taken as evidence of the perfect alloying of iron and nickel and the entire absence of segregation in the ingot.

FORGING

Ingots were generally sound and the lower percentages forged about the same as iron and at normal temperatures. In fact, there was no trouble in forging any of the alloys within the range of 0 to 20 per cent of nickel. Alloys of 25, 26, 28, 35, 50 and 75 per cent of nickel forged without special difficulty, although in an earlier trial one ingot with 75 per cent smashed. A 100 per cent nickel was not forgeable. In later tests an ingot of 30 per cent nickel smashed and one of 34 per cent was partially destroyed. With extreme care and high welding heats, and with the liberal use of flux a good bar was drawn out of an 85 per cent ingot. A high heat is probably necessary for all of the high nickel alloys.

The discrepancies noted in the forgeability might be due to oxidation such as Hadfield experienced, and which caused such red shortness that he was compelled to use manganese and aluminum as deoxidizers; or there might be a critical range at about 34 per cent of nickel at a composition corresponding to a definite compound of Fe_2Ni. It is at about this composition that the greatest difficulty is experienced in forging, and other measurements of various characters tend to support this supposition of a compound.

WELDING

There was no difficulty in welding low nickel bars during forging. The high nickel alloys, including one of 85 per cent nickel, which tended to crumble at lower heats, welded nicely at very high temperatures of working and with the liberal use of borax to prevent oxidation. Bars of all percentages of nickel were welded in the electric welder, although some failures were noted between 18 per cent and 35 per cent of nickel. These welds were not subjected to tests other than those indicated by grinding the juncture and testing with the hands.

HARDNESS

The hardness tests are such qualitative results as were noted in the machining, sawing and filing necessary in preparing the test bars. In the unannealed condition, working was easy for alloys up to and including 7 per cent of nickel; the alloys were rather stiff from 8 per cent to 10 per cent, inclusive, and hard between 11 per cent and 20 per cent, with the 20 per cent alloy less hard than some of those of intermediate compositions. All alloys were machined in the unannealed state with lathe tools, although this was very difficult in the range between 10 and 20 per cent of nickel. The higher nickel bars were again soft.

After annealing there was a somewhat noticeable hardness, beginning at about 11 to 13 per cent, but it was not extreme in any case, and there was no difficulty in sawing or machining.

BENDING

These tests were again only qualitative, being the observations in breaking bars sawed half through and in the unannealed condition. Alloys from 0 to 2 per cent nickel cracked at a 60° angle; from 3 per cent to 8 per cent, inclusive, at 45°; 9 to 10 per cent, at 30°, and from 11 per cent to 20 per cent, inclusive, the bars broke off short. The fracture changed from a fibrous to a granular at about 10 per cent of nickel.

The above hardness and bending tests are in agreement with the tensile tests noted below.

TENSILE STRENGTH TESTS

The summary of results is included in Tables 1 and 2 and in Plates I and II. The detailed data are not given; also no records are noted of abnormal results due to defective bars, etc.

In the summary are given the yield point and ultimate strength in pounds per square inch, the percentage of elongation in 2 inches, and the percentage of reduction of area at fracture. There are also included the maximum, minimum and average values of each of the above items, together with the number of samples from which such average is calculated. This furnishes an indication of the consistency of the data. In the plates, the yield point, the ultimate strength and the elongation and the reduction of area for varying percentages of nickel are designated by appropriate symbols, and are the values given in the tables in the columns of averages.

With these points as a guide, smooth curves are drawn in each case. With the many factors affecting somewhat the strength of a metal, it is not expected that the points will fall consistently on a curve. It is intended merely that the curve will show the tendency of the effect of increasing the percentage of nickel in the alloy.

UNANNEALED

The results of the tests in the unannealed state are enumerated in Table 1 and the general summary is best noted by referring to the curves on Plate 1. Between 0 and 8 per cent of nickel there is a gradual increase of the ultimate strength and elastic limit which are approximately linear functions of the percentage increase of nickel. At a nickel content of 0.25 per cent the figures are 66,730 for the ultimate strength and 57,180 for the yield point, these values rising to 91,740 lbs. and 70,770 lbs., respectively, for an increase of nickel to 8 per cent. The elongation and reduction of area indicate a decrease of ductility between 0 and 2 per cent. From this point they rise to a maximum at 5 per cent of nickel, above which percentage there is a gradual falling off until the composition of 8 per cent of nickel is reached. At 5 per cent nickel we note values of 64,030 for the elastic limit and 77,150 for the ultimate strength, with the high values of 29.2 for the elongation and 65.2 per cent for the reduction of area. The elastic ratio, however, is high, being 0.83.

Beyond 8 per cent of nickel there is a decided upward bend in the curves for the ultimate strength and elastic limit and a corresponding drop in those for the reduction of area and the elongation, indicating, therefore, a brittle zone. This is most pronounced at 11 per cent of nickel, where the yield point is 148,240 and the ultimate strength 181,230, while the elongation falls off to 7 per cent and the reduction of area to 25.5 per cent. On increasing the nickel above 12 per cent there is a return of ductility indicated by the gradual rise of the elongation and the marked increase of the reduction of area. At 20 per cent nickel we have the very high values of elastic limit 115,500, ultimate strength 186,000, with the accompanying elongation of 16 per cent and reduction of area of 59.5 per cent. The brittle zone may be said to extend from 10 per cent to 15 per cent of nickel.

The data for percentages of nickel above 20, which are not plotted, show a still further increase of ductility; at 50 per cent of nickel we have values of elastic limit of 75,700, ultimate strength 108,500, elongation 26.5 per cent, reduction of area 63.77 per cent.

These facts are in accord with the bending and hardness tests noted heretofore where the maximum brittleness lay between 10 per cent and 20 per cent in bending and the greatest difficulty in machining was in the same range.

ANNEALED

Results of the tests on the annealed bars are given in Table 2 and Plate II. The effect of annealing has been to lower the ultimate strength and the elastic limit throughout the entire range with the accompanying increase of elongation and reduction of area; this, however, without materially altering the general influence of the nickel. We note the same gradual increase of maximum stress and yield point over a range which is now extended to 10 per cent of nickel instead of 8 per cent. At this point the same sharp increase takes place and the elongation and reduction of area fall off in accordance. The point of minimum ductility is now at 13 per cent, where the elongation has fallen off to 11.6 per cent and the reduction of area to 34.6 per cent. The pronounced maximum of strength is now not present, the elastic limit of 97,730 and the ultimate strength of 121,810 being below the maximum values of the tests. At 11 per cent of nickel, the composition of the former alloy of least ductility, the deviations of maximum and minimum values are large, lying between extremes of 23 per cent and 0 per cent for the elongation and between 65.2 per cent and 0 per cent for the reduction of area.

The brittle zone is quite as pronounced as it was in the unannealed condition, but is now more limited in extent and may be said to cover the range from 12 per cent to 15 per cent of nickel. Above 15 per cent there is the same gradual increase of elongation and marked rise in the reduction of area, but we do not note the marked ductility at the 20 per cent nickel alloy which was observed for the unannealed bar.

COMPARISONS

The safe values to be assumed for nickel steels of the compositions used in commercial practice may be taken from Waddell's elaborate paper before the American Society of Civil Engineers in September, 1908. For bridge structures he recommends a composition of 3½ per cent of nickel and 0.38 per cent of carbon, with values of elastic limit of 60,000 lbs. per square inch, and ultimate strength of 105,000 lbs. per square inch.

These figures are for sections as rolled, and with a ductility somewhat lower than for ordinary steels, as is evidenced by the elongation of 15 per cent for nickel against 27 per cent for carbon steel (in 8 inches) and a reduction of area of 41 per cent and 55 per cent, respectively. For a lower carbon content with the same nickel the values become—elastic limit 45,000, ultimate strength 70,000, elongation 25 per cent; and for the increase of carbon to 0.45 per cent the elastic limit is taken as 65,000, maximum stress 115,000 and the elongation 12 per cent.

Values noted from our research for an alloy of 3 per cent of nickel are—yield point 62,920, ultimate strength 74,860, elongation (in 2″) 24.5 per cent, reduction of area 63.9 per cent; and for nickel = 4 per cent, the elastic limit is 65,000, maximum stress 75,670, elongation 27.8 per cent and the reduction of area 66.5 per cent. These values become, after annealing—yield point 55,400, ultimate strength 70,670, elongation 27.5 per cent, reduction of area 67.6 per cent for the alloy of 3 per cent nickel; and for the nickel content of 4 per cent the elastic limit is 52,100, maximum stress 70,070, elongation 28.4 and reduction of area 66.7. The ultimate strengths are well in accord with Waddell's assumptions for low carbon steels, with the elastic limit approaching that of his higher carbon materials.

Of the other tests recorded it is possible to make direct comparisons with Hadfield's results (Inst. Civ. Engrs. 1888–9). His alloys had a carbon content from 0.13 per cent to 0.23 per cent and manganese in the appreciable amounts of 0.65 per cent to 1.08 per cent. For the alloy of 3.82 per cent of nickel the results were as follows: as unannealed, elastic limit 62,700; maximum stress 82,900; elongation 35.8; reduction of area 55.6. These figures are in very close agreement with the 4 per cent alloy of our tests.

In Guillet's tests, for his low carbon series ($C = 0.12$) and for bars in the unannealed state, the maximum stresses and elastic limits are lower throughout than ours for like percentages of nickel. For his 5 per cent alloy the elastic limit is 43,200, maximum stress 52,800, elongation 25 per cent; our values are, respectively, 64,030, 77,150 and 29.2 per cent. However, the same general influences of the addition of nickel are observed.

A most interesting comparison is that of the effect of increasing percentages of nickel. The references are to articles mentioned at the beginning of this section of the paper.

In Hadfield's tests there was a gradual increase of strength and a decrease of ductility with the smaller additions of nickel. The maximum breaking stresses were at 11 to 16 per cent of nickel in the unannealed state with a minimum ductility at 15.5 per cent of nickel. After annealing the maximum strength is at 11.4 per cent of nickel with the lowest ductility at a composition of 9.5 per cent. There is a fair return of ductility at about 24 per cent of nickel after passing through the brittle zone.

Guillet's tests were on three series of alloys, each of a different percentage of carbon, and all with low manganese. He found in each series a brittle zone. For the alloys of lowest carbon = 0.12 per cent, the lowest minimum ductility was at 15 per cent of nickel; for carbon = 0.22 it was at 10 per cent nickel; and for carbon = 0.82 per cent it was at a nickel content of 7 per cent.

In the Report of the Alloys Research Committee, where the carbon was that of a medium steel, being from 0.41 to 0.52, and the manganese was high (0.79 to 1.03), there was a distinctly brittle zone at 4.95 per cent of nickel and extending to 16 per cent. From this point there was a recovery of the ductility.

The results of the present research which are most nearly representative of the effect of nickel alone, indicate the same brittle zone with the least ductility at 11 per cent of nickel in the unannealed state and at 13 per cent after annealing.

This agrees fairly well with the observations of Hadfield and Guillet, to whose materials our compositions are most nearly similar. The location of this brittle area can hardly be definitely fixed, since differences in impurities and heat treatment no doubt affect the composition and the range.

CONCLUSIONS

As a result of this research, taken in conjunction with the other tests enumerated, and of which it is largely confirmatory, it may be said that the effect of the addition of nickel to iron is as follows:

1. To increase the strength with a slight decrease of ductility in the range of lower nickel content.

2. Beyond this range the addition of nickel causes a sudden increase of strength with a marked decrease of ductility over a zone of decided brittleness.

3. The position of the brittle zone varies with the carbon content and probably with a variation in the other impurities, such as manganese, if present in appreciable amounts. For a pure alloy, where the effect is due to nickel alone, the area may be set between 10 per cent and 16 per cent of nickel. The addition of carbon places the zone at lower percentages of nickel, beginning in the neighborhood of about 10 per cent for carbon = 0.22 per cent and at about 7 per cent nickel for carbon = 0.82 per cent, where the other impurities are small. It may commence as low as 5 per cent nickel in medium carbon steels (C = 0.44) where the manganese rises to 1 per cent. Accompanying this brittleness there is a marked hardening in the material.

4. Annealing while not greatly affecting the region of the brittle zone or the extent of the brittleness, has a tendency to confine the range to more narrow limits.

5. For percentages of nickel above those of the zone of brittleness there is a restoration of the ductility and softness.

IRON-COPPER ALLOYS

The influence of copper on iron and steel has for long been a subject of controversy and contradiction. It is only comparatively recently that the effect has been investigated systematically and some of the doubt eliminated.

The prevalence of appreciable quantities of copper in the ores of certain districts makes of value a knowledge of its effect, detrimental or otherwise, when present in small amounts. Also, the intimate relation of copper, nickel and iron, and the beneficial effect of the addition of nickel to iron and steel, creates an interest in the influence of larger percentages.

The older opinion was that copper is deleterious; that its chief effect was analogous to that of sulphur in that it rendered iron red short and destroyed its welding power. This view was taken by many eminent metallurgists, some even contending that 0.5 per cent makes steel worthless. Others claimed that the influence was greatly exaggerated and instances were cited where rolled sections of 0.50 per cent to 0.75 per cent of copper did not display red shortness.

Within recent years more systematic investigations have been made to determine the effect of additions of varying percentages of copper to iron and steel.

Ball and Wigham (Ir. & St. Inst., 1889, No. 1) tested four steels with from 0.85 per cent to 7.17 per cent copper and a carbon content varying from 0.10 per cent in the former to 0.71 per cent in the latter, and noted an increase of tensile strength and a decrease of ductility with the increase of copper. The bar with 7.17 per cent copper was red short. Their conclusions were that the principal effect of copper was to make steel hard and that copper within reasonable limits did not materially affect the mechanical properties.

A. L. Colby (Iron Age, Nov. 30, '99) says that small percentages of copper have no deleterious effect upon the physical properties of steel. He cites various steels of about 0.5 per cent copper in shafts and gun tubes, which meet the requirements of the United States Navy. It was also used in ship plates, passing the usual tests required of carbon steels. These steels welded successfully and flanged cold, and there was no red shortness in bars or rails with a copper content of 0.39 per cent to 0.49 per cent.

W. Lipin (Stahl u. Eisen, Vol. XX) states that iron with copper content up to 3 per cent is readily worked but that there is red shortness at 4.7 per cent copper. Between 7 per cent to 10 per cent copper the material cracked badly, and fell to pieces under the hammer. With an increase of copper up to 3 per cent the tensile strength increased from 26 tons per square inch to 46 tons per square inch, with a decrease of elongation from 27.8 per cent to 13.3 per cent. He also notes that with an increase of carbon in the steel the maximum percentages of copper must be decreased; also that copper does not affect the welding.

Stead (Ir. & St. Inst., '01, Vol. I.) made a very thorough investigation of the influence of copper in steel rails and plates, since, he claimed, the general belief that copper was deleterious, was an unjustified prejudice. His article goes fully into the previous work and impressions. He finds that copper between 0.5 per cent and 1.5 per cent is not detrimental either hot or cold; that 2 per cent copper makes steel more liable to be overheated; that small quantities raise the tenacity and the elastic limit and reduce the elongation, but not greatly, however, for small percentages of copper; also that there is no great liability to fracture by shock.

Papers of Stead and Wigham (Ir. & St. Inst., '09, Vol. II) and of Wigham (Ir. & St. Inst., '06, Vol. I) deal with the effect of copper in cold wire drawing and come to the conclusion that copper up to 0.25 per cent is no detriment in the manufacture of the best classes of wire.

Wigham, in the last article mentioned above, brings out the important point that Professor Turner, in the discussion of the former article of Stead and Wigham, says that where copper is present in ores it is found in association with sulphur. Consequently discrepancies in the earlier tests may be due to this sulphur and not to the direct effect of the copper. This fact, together with that of the increase of red shortness with an increase of carbon, may explain the differences of opinion resulting from the earlier observations.

All of the above research was to excuse the presence of the copper; to break down a seeming prejudice. An investigation with a different object is that of Pierre Breuil, the results of which were given in a paper before the Iron and Steel Institute (Ir. & St. Inst. '07, No. 2). His effort was to see if there was a beneficial effect due to the addition of copper and was suggested by the favorable influence of copper on steels for railway axles, which was noted on some of the French railroads. It is a very extended research, and as the author says, is a supplement (very much elaborated) to Stead's work, in that the results agree. Being the most exhaustive and latest contribution to our knowledge of copper steels, we shall have occasion to refer to the results frequently throughout this discussion.

Breuil's work was carried out on four series of steels,—mild steel ($C = 0.10$ per cent — 0.17 per cent), semi-mild steel ($C = 0.28$ per cent — 0.41 per cent), and hard steel ($C = 0.56$ per cent

— 0.75 per cent) and a final series with about 1 per cent of carbon.

In view of the evidence that the influence of copper varies with the amounts of carbon and of sulphur present in the steel, and very likely also with the other impurities met with in commercial materials, it is of interest to record the results of tests where these elements are a minimum. The following discussion is of a series of iron-copper alloys made with electrolytic iron and copper as a basis. The preparation of the test samples is described in the introductory chapter of this paper.

FORGING

A wide range of alloys of varying copper content was made. The observations made in the forging are as follows: Alloys up to 2 per cent of copper forge well at low heats. Those from 2 per cent to 7 per cent will not forge at a low heat, and rather poorly at white heat, the ease of workability varying inversely as the percentage of copper. From 7 per cent to 75 per cent—80 per cent the alloys may be classed as non-forgeable. Between 80 per cent and 100 per cent they will forge at a fair red heat but not at a normal forging heat for iron.

In the earlier work alloys above 5 per cent could not be forged. However, in later tests, in the trial of many alloys of 5 per cent to 10 per cent of copper at all heats, it was found that with care and a high heat (welding) a 7 per cent bar could be forged, or even rarely, an 8 per cent.

The lower percentages (below 5) will weld easily in forging, and some bars of 7 per cent copper were welded while forging. All alloys up to 7 per cent copper could be welded in an electric welder.

SEGREGATION

The forgeable samples between 0 per cent and 8 per cent of copper and a few of the alloys of high copper and low iron were made into test bars for investigation of the tensile strength. Analyses were not made upon all bars; rather, random samples of the entire range of composition were tested, with the following results:

ANALYSES.

Mark.	Cu. added.	Analysis.
147B	0.1	0.099
158A	0.2	0.202
158B	0.4	0.422
158C	0.6	0.592
158D	0.8	0.804
147H	1.0	1.006
147J	1.5	1.510
158G	2.0	2.005
158I	4.0	3.990
158J	5.0	5.070
158K	6.0	6.160
147U	7.0	7.050
86F	95.0	94.340

As will be seen from the tables, the agreement between the added and the actual copper content is exceedingly close. The analytical samples were taken from turnings obtained in the machining of the test bars after the forging of the ingots. This close agreement after such a method of selection would indicate an entire lack of segregation; also that the materials alloy very well up to a copper content of 7 per cent. This is in accord with the work of earlier investigators. In view of this close agreemént it may be assumed that the actual copper content of the alloys is the same as the added amount.

HARDNESS

The hardness tests are merely qualitative, being observations made in the machining, sawing and filing. In machining, the alloys with low percentages of copper worked very easily. The hardness increased with the increase of copper until at 5 per cent to 7 per cent, while it was still possible to turn in the lathe, this was done with some difficulty. There were the same evidences in the sawing and filing tests, the high copper being classed as extremely hard to saw.

Breuil's investigations show that the hardness does not result through a lowering of the points of transition, thus leaving the steels in a martensitic state, as might be supposed. The structure is a fine pearlite, with a fibrous cementite which is liberated with increasing copper, and this explains the increasing hardness.

Wedding (Stahl u. Eisen, December, '06) says that copper and sulphide of copper prevent the formation of pearlite and promote the formation of crystals of cementite. It is due to this fact that there is greater hardness of iron when copper and sulphur are present. These explanations seem hardly sufficient to account for the hardening which we have observed without the presence of either carbon or sulphur and we expect to make a metallographic study with the hope of throwing a little light upon the subject.

The summary of the results of these tests is given in Tables 3 and 4, and in Plates III and IV. The detailed data are not given; also no account is taken of bars which showed abnormal results, due to flaws, etc.

In conformity with those of the nickel-iron series, the results enumerated are the yield point, the ultimate strength, the percentage of elongation in 2 inches and the percentage of reduction of area at fracture. Again, in order to show the consistency of the data there is also given the maximum and minimum values for each of the above items, together with the average of these items for the number of samples enumerated in a separate column. The plates are plotted from the averages of the tables and smooth curves drawn to indicate as nearly as possible the tendency of the increasing additions of copper. The values of the yield point, ultimate strength, elongation and reduction of area are designated as points used in plotting the curves by the same symbols used for the nickel alloys.

UNANNEALED

From the curves of Plate III, it will be noted that the rise in the ultimate strength and the elastic limit is almost a linear function of the percentage of copper. The ultimate strength increases from 61,180 lbs. per sq. in. at 0.1 per cent copper to 132,400 lbs. at 7 per cent. The yield point rises from 52,580 to 122,900. There is a corresponding fall in the elongation from 28½ per cent at 0.1 per cent copper to 4 per cent at 7 per cent copper. The reduction of area increases slightly from 69.2 per cent at 0.1 per cent copper to 72.1 per cent at 0.6 per cent and 0.8 per cent copper; from this point it falls off to 7.3 per cent at 7 per cent of copper.

From Table III it will be noted that the ratio of maximum and minimum values to the average is good, except in certain instances which are no doubt somewhat abnormal, but not so much so as to be rejected from the tables. Also, where there are a sufficient number of samples for a good average, the results fall well in line. The greatest variation is at 3½ per cent of copper, but here there is only one bar, which is clearly abnormal, with its low ultimate strength and elastic limit and its high reduction of area. The greatest variations from the curve lie above 4 per cent of copper, and this is to be expected, especially in the unannealed samples, since here we are almost beyond the limit of satisfactory workability.

The results of these tests indicate a high tensile strength which increases with the percentage of copper. The alloys are rather brittle as indicated by the elongation, and the reduction of area. Also the elastic ratio (ratio of the elastic limit to the ultimate strength) is large, varying from 0.86 per cent at 0.1 per cent copper to 0.93 at 7 per cent copper.

ANNEALED

The results of annealing are given in Table 4 and Plate IV, and the effect is very marked, especially for the higher percentages of copper. There is greater consistency in the results, as is to be expected, and the points fall fairly well in line on the curves.

The greatest deviation from the curves is at 2½ per cent and 5½ per cent of copper, where there was only one bar of each for the test. The maximum and minimum figures of the table are not widely different.

Up to 1 per cent copper there is a marked increase of the elastic limit and the ultimate strength with the additions of copper and no falling off in the elongation or reduction. In fact, the latter increases to a maximum at 0.4 per cent of copper. Beyond one per cent the curves bend sharply and become more nearly horizontal, being a linear function of the percentage of copper. The elongation and reduction of area fall off in accordance.

Between 1½ and 7 per cent of copper the elastic limit increases from 51,570 to 56,950 lbs., the ultimate from 65,720 lbs. to 67,900, while there is a decrease in the elongation and the reduction of area. Between 0.1 per cent and 1.5 per cent of copper the elastic limit rises from 35,570 lbs. to 51,570 lbs; the ultimate strength from 54,050 lbs. to 65,720 lbs; while the elongation and the reduction of area remain about the same. Breuil mentions the 4 per cent alloy as worthy of further study, and this is no doubt true, since he observes very high values, as indicated by the following table, where the results are given for his mild steel series (C = 0.10 per cent to 0.17 per cent), as rolled, and as annealed at 900° C.

TENSILE STRENGTH—BREUIL.

Per cent Cu.	Yield point No. 1 per in.²	Ultimate stress No. 1 per in.²	Elongation Per cent.	Reduction area per cent.
UNANNEALED:				
0	....	....	....	....
0.5	55.000	66,800	25.5	66
1.0	58.900	70,200	26.5	60
2.0	67,300	88,700	16.0	58
4.0	97.600	109,500	13.0	46
ANNEALED:				
0	35,800	54,900	30.3	63
0.5	38,200	59,000	28.0	60
1.0	54.800	69,500	26.0	57
2.0	58,700	70,300	25.0	58
4.0	65.000	71,500	22.0	63

A comparison of these figures with the results of our researches shows a great similarity, and in plotting the figures there is a very close agreement. In his 4 per cent alloy as unannealed, to which Breuil calls particular attention, there is an elastic limit of 97,600, an ultimate strength of 109,500, and an elongation of 13 per cent and a reduction of area of 46 per cent. In our tests the results for corresponding materials are—elastic limit, 100,560; ultimate strength, 108,640; elongation, 13½ per cent; reduction of area 45.6 per cent. For the annealed sample, Breuil gives elastic limit 65,000 lbs; ultimate strength 71,500, elongation 22 per cent, reduction of area 63 per cent. Our results are; elastic limit 53,570 lbs., ultimate strength 66,540, elongation 24.8, reduction of area 54.2. In our tests the annealing shows a greater effect, resulting in less strength with greater ductility; and the same is true in the comparison for all percentages of copper.

While Breuil lays particular stress on the 4 per cent alloy, our results would seem to indicate the greatest value between 1 per cent and 2 per cent for the annealed samples. The very sharp rise of the elastic limit and the ultimate strength at this percentage gives values but very little less than those for higher copper content, with a lessened cost for the addition element; also there is a removal from the region where the forging and welding properties are poorer with consequent uncertainties of result. Likewise, between 1 per cent and 2 per cent the elastic limit and the reduction of area are very high.

It would hardly be advisable to work with 1 per cent of copper, since this is on the edge of the incline, where there is liable to be a fall to the lower values obtained with lower percentages of copper. At 1½ per cent we are far enough removed so that the slight differences of composition to be met in practice would not bring the material into a dangerous region. Also, the elastic ratio of 0.78 is slightly lower than for the 4 per cent alloy, where it is 0.81.

We would have considerable hesitation in bringing forward this point without a vast number of tests for confirmation, but for the fact that an observation of Breuil's results indicate the same condition. He has perhaps noticed this fact, but makes no mention of it in his article. As will be seen from the table of his results which is given above, there is a sharp increase between 0.5 per cent and 1 per cent of copper, where the elastic limits are 38,200 and 54,800, respectively, and the ultimate strengths 59,000 and 69,500. Again, we note but little change in the elongation and reduction of area. Between 0 per cent and 0.5 per cent, and between 1 per cent and 2 per cent, the change is not marked. The fact that two independent investigations give this result, seems fairly conclusive of the effect.

Another fact to be noted in our tests is the marked difference between the unannealed and the annealed samples. It would indicate that there is an intermediate heat treatment which, not being so drastic in its effect as our long annealing, would give intermediate values, and thus approximate the nickel steels. This condition might be reached in commercial rolling, where heavier masses of metal leave the material in a condition analogous to that resulting from a partial anneal.

To compare the copper-iron with the nickel alloys we may again quote Waddell's extensive investigations mentioned previously under the nickel-iron series. Repeating this data, we note a steel with about 3½ per cent nickel, carbon 0.38 per cent, the values for which may be taken as: elastic limit 60,000 lbs. per sq. in., ultimate strength 105,000 lbs. per sq. in., elastic ratio from 0.55 to 0.60. These values are for sections as rolled without heat treatment and working at a somewhat low ductility, as shown by the figures 15 per cent for nickel steel, 27 per cent for carbon steel (in 8 inches) and a reduction of area of 41 per cent for nickel, compared to 55 per cent for the carbon steels. With the carbon reduced to 0.15, the values become: elastic limit 45,000, ultimate 70,000, elongation 25 per cent; and for ($C = 0.45$) the elastic limit is 65,000, the ultimate 115,000 and the elongation 12 per cent.

These values are higher than ours for the copper-iron alloys but are not in direct comparison. Our own figures for a nickel-iron alloy made under the same conditions as the copper-iron series, are given in the following table, where the 4 per cent nickel is compared with the 1.5 per cent and 4 per cent copper alloys. There is also given Hadfield's test of an alloy of 3.82 per cent nickel and carbon = 0.19 per cent (Inst. Civ. Engrs., March 28, '99).

	Elastic limit.	Ultimate strength.	Elastic ratio.	Elongation per cent.	Reduction of area per cent.
UNANNEALED:					
4.00 Ni..............	67,000	76,000	0.88	28.5	68.6
1.50 Cu..............	73.920	77,300	0.95	23.5	66.9
4.00 Cu..............	105,560	108,640	0.97	13.5	45.6
3.82 Ni..............	62,720	82,800	0.76	30.0	54.0
ANNEALED:					
4.00 Ni..............	57,000	69.000	0.83	26.5	64.8
1.50 Cu..............	51,570	65.720	0.79	29.2	63.1
4.00 Cu..............	53,570	66,540	0.81	24.8	54.2
3.82 Ni..............	56,000	73,920	0.76	35.0	55.0

The above values for the nickel alloys are less than are commonly given to commercial materials where the carbon is a factor. The results are very comparable to those of the copper-iron series made under identical conditions.

Waddell, in his paper, shows that there is an economic advantage in the use of the nickel steels in comparison with the carbon steels ordinarily used, since their increased cost is more than offset by the less weight required, due to their increased strength. Our results and comparisons would indicate that the copper-iron alloys are also worthy of consideration and might be comparable to the nickel steels in use, even if the strength should not reach such high values as those of the nickel. A 1½ per cent copper alloy is of promise, since the smaller percentage required and the lessened cost per pound of copper as compared with nickel would result in a lessened cost of construction, even if there is some increase in tonnage required because of the slightly decreased strength per equal weight.

NICKEL-COPPER-IRON ALLOYS

In view of the well known beneficial effect of the addition of nickel to iron, and because of the very great and rather unexpected increase of tensile strength observed in our tests of the copper-iron alloys, due to the increasing percentage of copper, it was thought advisable in order to round out this research, to carry out tests on a series of alloys in which both nickel and copper were added to the electrolytic iron.

The advisability of the investigation was prompted by several considerations—first, the benefits observed by the separate additions of nickel and copper might be coupled in their joint use; second, the close relationship of copper, nickel and iron in chemical and physical properties might lead to interesting results in a ternary alloy; third, and this was the reason of greatest weight—there is on the market a nickel-copper alloy which would make a very desirable addition agent, in case the simultaneous presence of both copper and nickel give a tensile strength no less than that observed for the two separate alloys.

We refer to Monel metal, resulting from the reduction of certain ores from which, by smelting alone, this alloy is formed. The main constituents are nickel and copper, in the proportions of about three to one, respectively. The material is, for the present at least, obtainable at a price about equal to that of copper, and very much below the cost of nickel. Here, then, is a means of getting nickel additions for steel, provided the copper carried does not neutralize the effect of the nickel.

Some particulars regarding Monel metal are given below.

ANALYSIS.

Nickel	66.90	67.96
Copper	24.35	26.00
Iron	5.00	2.80
Manganese	2.18	1.62

Mechanical tests gave for cast samples ultimate strengths of 30,400 and 35,000 lbs. per sq. in. For rolled samples the figures were—elastic limit 74,400 and 79,000 lbs. per sq. in., ultimate strength 100,000 and 104,000 lbs. per sq. in.

Thus we see that the alloy has very good inherent mechanical properties, and the analyses indicate, besides the nickel and copper, only iron and manganese, and the latter is no detriment to steels.

Examining the above table of analyses, we note a nickel-copper ratio of about 2½ or 3 to 1. The desirable addition of nickel to steels is from 3 per cent to 4 per cent. Our tests give as a desirable amount in the iron-copper series about 1½ per cent of copper. Comparing these, we see here a ratio of about 2½ or 3 per cent to 1, the Monel proportions. This striking analogy prompted the following series, in which the nickel was varied from 2 per cent to 6 per cent, with the copper in each case in a 3 to 1 ratio. Unfortunately, at the time the alloys were made, no Monel metal was on hand, and they were made by adding the proper amounts of copper and nickel. The preparation of the alloys and test samples was in all respects in conformity with the methods described previously in this paper.

The series prepared was as follows—

Bar.	Per cent Nickel.	Per cent Copper.
174M	2	0.7
174N	3	1.0
174O	4	1.3
174P	5	1.6
174R	6	2.0

Analyses have not been made to confirm these percentages. However, in view of the close agreement in both the nickel and the copper series, the actual amounts are probably very close to those indicated above.

The whole series forged without difficulty at normal heats, and could be worked at low temperatures also, without indications of red shortness in any instance.

For the tests, three samples were cut from each forged rod, of which two were annealed at 900° C, and one left unannealed. Before annealing, the bars were machined to a diameter of about ⅜ inch over a free length of 2 inches. This work was done without difficulty in the lathe, except for Bars 174P. One of these samples was finished in the lathe, showing no material hardness; the other two, however, had a hard seam which made it necessary to grind them to size. Subsequently, both bars showed flaws in the tests.

TENSILE STRENGTH TESTS

The results of the tests are indicated in Table 5 and in Plates V and VI. In the plates the yield point, maximum stress, elongation and reduction of area are plotted for each composition, the same designating symbols being used as noted in the previous tests. No effort has been made to draw a smooth curve following the points; instead, they have been connected by straight lines. This was done because of the small number of tests of each alloy.

UNANNEALED

But one bar of each composition was available for test in the unannealed condition. The results, however, are fairly consistent, and reference to Plate V shows an increase of ultimate stress and elastic limit with increase of the alloying elements, from 79,200 to 99,700 and from 62,100 to 81,700, respectively, for the limiting alloys of 2Ni 0.7Cu and 6Ni 2Cu. The elongation and reduction of area fall off in accordance, but the extreme values of 22 per cent to 28 per cent, and 39.3 per cent to 58.8 per cent, respectively, are very good, and indicate an absence of any brittleness. Even the minimum addition of 2Ni 0.7Cu gives the very high values of elastic limit 62,100, ultimate stress 79,200, elastic ratio 0.78, elongation in 2 inches 26 per cent and reduction of area 56.7 per cent.

ANNEALED

Two bars of each composition were annealed at 900° C for several hours. The tabulated results show very great consistency, not only for the two bars of each alloy, but also in the tendency of the increasing additions, best shown in Plate VI.

Annealing has had but little effect on the bars, except at the lower end of the series, where it has decreased the elastic limit and ultimate strength, with a corresponding increase of elongation and reduction of area. The values for the composition 2Ni 0.7Cu are, however, still good, averaging in ultimate stress 68,700, yield point 48,600, elongation 30 per cent, reduction of area 61.5 per cent. For the higher percentage additions the strengths have been increased by annealing and, as is shown most clearly by the curves of Plate VI, the increase of strength has been uniform with increase of nickel and copper, and rises to the extremely high values of elastic limit 83,200 and maximum stress 103,700, for the highest percentage of 6Ni 2Cu. Elongation and reduction fall off with the increase, but here again we have values denoting good ductility, with no sign of brittleness.

COMPARISONS

In order to make direct comparison of the effects of the addition of nickel and copper to iron in the ternary alloys, with those of the separate additions of the two elements in the binary series, Table 6 has been prepared. In this table the average yield points, ultimate stresses, elongations and reductions of area are noted in columns for the nickel-copper-iron, nickel-iron and copper-iron groups. The percentage compositions are given in the order of the ternary series; for the binary series the values are those from Tables 1, 2, 3 and 4, corresponding to the percentages of the separate elements in the two columns of compositions of Table 6.

The comparability of the copper-iron and nickel-iron groups is clearly shown, indicating the facts noted in the previous discussion of the separate groups. The values, line for line, are not markedly different, even though we are comparing directly proportions of nickel to copper in the ratio of 3 to 1.

The effect of the double addition of nickel and copper is most striking. In all but one or two instances the values for the ternary alloy exceed those for either binary series, at both the elastic limit and the ultimate stress. And the effect is even more marked after the annealing of the bars. In fact, one might almost treat the copper as so much added nickel, and compare bars on the basis of a certain nickel content on the one hand, against an equal quantity of nickel plus copper in the ternary alloy. And even this will not do for the higher percentages of the nickel-copper-iron alloys, since, especially for the annealed bars, the strength of the ternary alloys is very markedly greater than any of the binary series. These high strength values are reached with practically no diminution of ductility, as is indicated by comparison of the figures for elongation and reduction of area.

For those annealed bars corresponding to a composition of 4 per cent nickel plus 1.3 per cent copper, which in the discussion of the binary series we mentioned as the percentages in each case of greatest utility, we find the same relation holding as in the rest of the alloys. The values for the ternary alloy are: elastic limit 67,600, maximum stress 84,700, elongation 28 per cent and reduction of area 55.6 per cent. For a binary 4 per cent nickel alloy the figures are: elastic limit 52,100, ultimate stress 70,100, elongation 28 per cent and reduction of area 66.7 per cent; and for a 1½ copper alloy: yield point 51,600, ultimate 65,700, elongation 29 per cent, reduction of area 63.1 per cent.

These tests, therefore, while not as extensive as would be desirable to draw absolute conclusions, are sufficiently consistent to warrant the statement that for carbon-free materials, at least, the simultaneous presence in iron of nickel and copper does not destroy the good effects of the separate percentages of each element in a binary series. On the contrary, there is apparently an increase of tensile strength without loss of ductility, and no evidence of a brittle zone throughout the series.

How far the percentages may be increased before there is evidence of brittleness or red shortness, is problematical.

While all of our alloys have been made of iron practically free from carbon, the combined influence of nickel and copper has appeared so marked as to warrant further investigation. It also appears highly important that similar study be made of the effect of these alloying agents upon commercial steels with their customary percentages of impurity.

TABLE 1.

TENSILE STRENGTH—IRON NICKEL ALLOYS—UNANNEALED

		YIELD POINT lbs/sq. in.			ULTIMATE STRESS lbs/sq. in.			ELONGATION PER CT 2″			REDUCTION OF AREA PER CT.		
% Ni	No.	Max.	Min.	Av.	Max.	Min.	Av.	Max	Min.	Av.	Max	Min.	Av.
0.25	3	66,600	48,250	57,180	75.600	55.600	66,730	28.5	22.0	25.2	65.7	50.0	57.6
0.50	2	58,200	55,400	56,800	70,700	67.700	69,200	21.5	19.0	20.2	62.8	58.8	60.8
1.00	4	58,200	51.300	56,820	72.300	66,200	68,320	32.5	18.5	25.2	68.5	53.0	60.9
2.00	4	63,000	55,000	58,520	74.700	67.300	70,350	33.5	17.0	26.0	65.5	43.7	60.7
3.00	5	67,500	56,700	62,920	79.500	67,900	74,860	29.0	17.5	24.5	65.0	62.4	63.9
4.00	3	68,900	61,000	65,000	75,500	75,200	75,670	29.5	26.5	27.8	68.8	62.2	66.5
5.00	4	71,800	59,700	64,030	78,700	73,800	77,150	32.0	26.5	29.2	69.7	59.7	65.3
6.00	1	....	....	67,300	....	....	77.300	.....	.....	29.0	.....	.....	68.5
7.00	4	82,750	63,200	70,080	93,100	79,800	85,500	28.0	18.5	25.2	66.1	57.3	61.0
8.00	4	78,300	65,700	70,770	98,000	83,900	91,740	31.0	14.5	22.6	64.8	49.1	56.1
9.00	5	113,800	69,800	80,760	136,000	97,700	112,700	24.0	8.0	18.4	63.4	45.4	57.7
10.0	5	141,400	89,400	118,960	172,900	120,500	153,360	15.5	2.0	9.1	53.7	2.9	29.0
10.5	3	150,000	104,900	134,470	188,800	123,600	166,200	10.0	4.0	6.2	48.5	3.5	24.9
11.0	7	166,800	123,400	148,240	205,000	165,200	181,230	9.5	2.0	7.0	55.7	1.4	25.5
12.0	5	168,800	116,700	141,140	195.800	150,000	178,420	13.0	2.5	7.1	43.5	2.2	23.8
13.0	4	152,000	116,500	130,620	203,500	129,500	171,500	10.5	3.0	6.9	70.5	9.8	43.4
15.0	2	133,500	116,500	125,800	211,000	167,000	184,730	14.5	4.5	8.2	58.7	12.1	34.1
18.0	3	148,800	126,800	138,170	183,500	176,000	178,500	13.5	10.5	12.3	60.0	38.5	49.3
19.0	3	149,000	126,200	134,730	189,500	175,800	183,270	15.0	13.5	14.2	59.6	46.8	53.1
20.0	1	....	....	115,500	....	....	186,100	.....	.....	16.0	.....	.....	59.5
21.0	2	143,700	131.700	137.700	181,700	180.000	180,850	14.0	8.0	11.0	48.9	25.1	37.0
25.0	1	....	....	56,400	....	....	104,200	.....	.....	45.0	.....	.....	68.3
45.0	1	....	....	54,600	....	....	82,000	.....	.....	32.5	.....	.....	65.0
50.0	1	....	....	75,700	....	....	108,500	.....	.....	26.5	.....	.....	63.7

TABLE 2.

TENSILE STRENGTH—IRON NICKEL ALLOYS—UNANNEALED

		YIELD POINT lbs/sq. in.			ULTIMATE STRESS lbs/sq. in.			ELONGATION PER CT 2".			REDUCTION OF AREA PER CT.		
%Ni.	No.	Max.	Min.	Av.	Max.	Min.	Av.	Max	Min.	Av.	Max	Min.	Av.
0.25	2	40,200	35,900	38,050	51,100	49,600	50,350	36.5	33.5	35.0	74.4	65.0	69.7
0.50	2	43,300	37,700	40,500	59,200	51,700	55,450	37.5	35.5	36.5	70.3	70.1	70.2
1.00	3	44,400	43,300	43,830	63,500	57,200	59.830	36.0	29.5	33.7	73.5	66.5	68.8
2.00	3	51,200	46,400	48,770	66,600	63,100	64,400	39.0	31.0	34.2	69.1	58.6	65.4
3.00	3	61,100	44,400	55,400	74,900	65.700	70,670	30.5	23.5	27.5	73.3	62.8	67.6
4.00	3	57,800	47.400	52,100	73,300	67,900	70,070	32.0	22.5	28.4	70.3	63.4	66.7
5.00	4	62,800	52,800	58,320	77,100	70,750	73,230	32.5	29.0	31.4	70.3	64.5	68.1
6.00	1	....	....	56,400	....	....	75,300	.....	.....	29.5	.....	.....	64.2
7.00	3	58,600	57,300	58,130	79,100	74.000	72,970	31.0	19.0	26.7	67.5	43.2	58.5
8.00	3	67,250	61,300	63.320	82,600	73,400	78,470	33.0	27.0	30.2	68.8	58.3	64.4
9.00	3	74.700	70,750	72,180	96,300	84,300	89,970	29.0	21.0	25.1	65.4	50.3	60.2
10.0	3	81,200	66,400	71,800	98,400	80,700	89,300	24.0	20.5	22.3	61.5	54.7	59.1
10.5	3	71,900	67.500	69,100	92,750	86,200	89,450	25.5	22.0	24.2	61.0	50.5	57.2
11.0	5	127,200	69,800	99,160	167,500	95,750	121,810	23.0	0.0	11.6	65.2	0.0	34.6
12.0	3	111,300	80.000	97,730	142,400	118,200	121,800	16.5	11.0	14.5	47.2	8.3	35.8
13.0	4	140,700	114,800	128,050	177,000	148,500	161,370	14.0	2.0	6.8	51.6	1.4	18.2
15.0	2	142,000	110,600	126,300	180,500	126,100	153,300	16.5	4.5	10.5	66.5	4.8	35.8
18.0	2	146,900	128,500	137,700	182,100	181,000	181,550	15.0	5.0	10.0	58.9	9.9	34.4
19.0	2	120.800	111,500	116,150	185,200	176,200	180,700	11.5	10.0	10.7	45.6	31.9	38.7
20.0	1	....	....	111,000	....	....	124,900	.....	.....	21.5	.....	.....	62.5
21.0	1	....	....	122,600	....	....	193,700	.....	.....	4.0	.....	.....	4.2

TABLE 3.

TENSILE STRENGTH—IRON COPPER ALLOYS—UNANNEALED

Per cent Cu.	No. of samples.	YIELD POINT lbs/sq. in.			ULTIMATE STRESS lbs/sq. in.			ELONGATION PER CT., 2"			REDUCTION OF AREA PER CT.		
		Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
0.1	3	56,600	45,400	52,580	64,000	60.300	61,180	30.0	27.5	28.5	70.9	66.7	69.2
0.2	5	55,600	50,700	52,930	63,750	60,000	61,470	36.5	24.5	28.7	73.2	56.9	67.2
0.4	2	59,700	56,100	57,900	67,250	66,400	66.825	29.5	23.0	26.2	72.1	69.4	70.7
0.45	2	54,800	53,100	53,950	62,700	58,800	60,750	27.0	24.0	25.5	67.7	47.2	57.4
0.6	2	57,750	51,600	56,170	67,000	64,750	65,875	27.5	27.5	27.5	72.8	71.5	72.1
0.8	2	55,500	53,800	54,650	67.500	65,100	66,300	27.0	25.5	26.2	72.5	71.7	72.1
1.0	5	63,300	56,800	61,290	70,800	68,300	71,380	28.0	21.0	25.8	72.0	66.8	70.3
1.2	2	66,300	59,500	62,900	74,600	72.300	73,400	28.0	24.5	26.2	68.8	64.5	66.6
1.4	2	68,100	67,300	67,700	78.600	76.600	77.600	25.0	18.0	21.5	70.0	64.5	67.2
1.5	3	77,250	70,000	73,920	78,800	76,200	77,300	26.5	20.5	23.5	68.6	64.5	66.9
1.6	2	75,100	73,300	74,200	82,750	79,100	80,925	25.0	25.0	25.0	66.6	66.2	66.4
1.8	2	81,100	77,600	79,350	91.000	86,000	88,500	27.0	24.0	25.5	66.3	61.8	64.0
2.0	3	78,800	73,400	76,930	89,500	82,250	87,010	23.5	17.5	21.2	59.5	54.5	57.0
2.5	2	81,100	81,000	81,050	89,400	86,400	87,900	19.0	18.5	18.7	62.8	59.1	61.0
3.0	6	95,100	73,750	86,810	105,000	83,750	99.640	24.0	12.5	16.7	65.6	36.1	53.8
3.5	1	....	....	75,400	....	....	82,300	.....	.....	16.0	.....	.....	72.7
4.0	5	111,100	92,700	100,560	120,700	99,200	108,640	17.5	8.0	13.5	52.3	24.8	45.6
4.5	2	117,800	106,400	112,100	127,900	115,500	121,700	17.0	4.5	10.8	47.2	3.9	25.1
5.0	2	119,700	113,000	116,350	123,800	120,000	121,900	15.0	14.0	14.5	50.1	48.3	49.2
5.5	2	114,700	102,300	108,500	122,800	105,200	114,000	15.5	15.0	15.2	53.8	46.6	49.7
6.0	3	124,200	103,000	113,400	136,700	107,500	122,900	9.0	4.5	6.5	36.5	4.1	20.3
7.0	2	128,800	117,000	122,900	133,800	131,000	132,400	6.0	2.0	4.0	12.9	1.7	7.3
8.0	2	146,800	133,500	135,100	160,000	137,500	148,750	.....	.....	0	.....	.....	0

TABLE 4.

TENSILE STRENGTH—IRON COPPER ALLOYS—ANNEALED

Percent cu.	No. of samples.	Yield Point lbs/sq. in.			Ultimate Stress lbs/sq. in.			Elongation Per Ct/2"			Reduction of Area Per Ct		
		Max.	Min.	Av.	Max.	Min.	Av.	Max	Min.	Av.	Max	Min.	Av.
0.1	2	40,750	34.400	35.570	56,500	51,600	54,050	35.0	28.0	31.5	62.2	58.3	60.2
0.2	4	36,850	31,800	33,660	56,000	52,700	54,020	36.0	29.5	34.1	67.7	62.7	65.6
0.4	2	35,700	35,100	35,400	53,700	53,100	53,400	37.5	34.0	35.7	72.1	69.3	70.7
0.45	2	42,250	41,250	41.750	66,300	64.600	65,400	26.0	25.0	25.5	53.6	46.0	49.8
0.6	2	38,400	38,300	38,850	56,600	56,500	56,550	36.5	32.0	34.2	69.0	68.8	68.9
0.8	2	.41,300	40,700	41,000	59,750	57,400	58,570	34.0	32.0	33.0	65.1	64.7	64.9
1.0	4	54.800	46,400	48,920	63,900	61,100	62,350	34.0	30.0	32.6	68.3	66.1	66.8
1.5	6	58,100	48,100	51,570	70,500	62.100	65,720	33.5	22.0	29.2	65.1	59.3	63.1
2.0	6	54,300	49,400	51.620	65,100	60,500	63,200	31.5	27.5	29.5	68.1	62.0	64.4
2.5	1	....	....	56,200	....	....	73,500	.....	.....	23.0	.....	.....	47.3
3.0	7	53,800	48,700	50.890	67,600	59,000	62,360	33.5	10.5	26.9	69.1	46.3	61.7
4.0	5	57,100	49,600	53,570	70,900	62,700	66,540	28.0	22.0	24.8	65.3	39,3	54.2
5.0	4	57,600	50,700	54.460	74.700	62,400	68,250	29.0	20.5	24.2	62.9	29.1	50.3
5.5	1	....	....	54,800	....	....	69,300	.....	.....	25.0	.....	.....	60.4
6.0	3	55,500	52.750	54,420	65,600	62,500	64,530	24.5	18.0	20.8	59.0	39.2	49.9
6.45	2	55,750	54,600	55.170	69,700	69,200	69.450	25.5	16.5	21.0	48.1	30.5	39.3
7.0	2	57,150	56,750	56,950	70,900	67,900	69,400	20.0	14.0	17.0	40.8	21.7	31.2
7.5	1	....	....	60,200	....	....	79,000	.....	.....	16.5	.....	.....	34.2

TABLE 5.

NICKEL-COPPER-IRON ALLOYS—TENSILE STRENGTH

Bar.	% Ni.	% Cu.	Diam.	Area.	STRESS/in².		Elong. %/2"	Reduced Area.	Reduction of Area %	Remarks.
					Yield point.	Maximum.				
UNANNEALED.										
174M	2	0.7	0.372	0.1087	62,100	79,200	0.26	0.0471	56.7	
N	3	1.0	0.374	0.1099	67,400	80,100	0.28	0.0452	58.8	
O	4	1.3	0.373	0.1093	63,300	85,700	0.23	0.0594	45.7	
P	5	1.6	0.375	0.1104	66,500	89,400	0.22	0.0670	39.3	
R	6	2.0	0.374	0.1099	81,700	99,700	0.25	0.0511	53.5	
ANNEALED.										
174M	2	0.7	0.371	0.1081	48,400	68,200	0.30	0.0391	63.8	
			0.373	0.1093	48,900	69,200	0.30	0.0445	59.3	
N	3	1.0	0.375	0.1104	56,400	73,600	0.35	0.0337	69.5	
			0.375	0.1104	57,100	71,400	0.28	0.0456	58.7	Slight flaw.
O	4	1.3	0.373	0.1093	68,600	84,700	0.28	0.0437	59.9	
			0.373	0.1093	66,600	84,700	0.27	0.0531	51.3	
P	5	1.6	0.375	0.1104	73,100	83,400				(Machined hard.) Broke at flaw } Split.
			0.200	0.0314	75,200	89,500				Broke at flaw
R	6	2.0	0.374	0.1099	83,900	104,800	0.22	0.0452	58.8	
			0.375	0.1104	82,500	102,700	0.21	0.0511	53.7	Short longitudinal split.

TABLE 6.

COMPARISON—IRON-NICKEL-COPPER ALLOYS

% Ni.	% Cu.	YIELD POINT.			MAX. STRESS.			% ELONG.			% RED.		
		Ni-Cu	Ni.	Cu.	Ni-Cu.	Ni.	Cu.	Ni-Cu.	Ni.	Cu.	Ni-Cu.	Ni.	Cu.
UNANNEALED.													
2	0.7	62,100	58,500	54,700	79,200	70,300	66,300	26	26	26	56.7	60.7	72.1
3	1.0	67,400	62,900	61,300	80,100	74,800	71,400	28	24	26	58.8	63.9	70.3
4	1.3	63,300	65,000	67,700	85,700	75,670	77,600	23	28	21	45.7	66.5	67.2
5	1.6	66,500	64,000	74,200	89,400	77,150	80,900	22	29	25	39.3	65.3	66.4
6	2.0	81,700	67,300	76,900	99,700	77,300	87,000	25	29	21	53.5	68.5	57.0
ANNEALED.													
2	0.7	48,600	48,800	41,000	68,700	64,400	58,600	30	34	33	61.5	65.4	64.9
3	1.0	56,800	55,400	48,900	72,500	70,670	62.300	31	27	33	59.1	67.6	66.8
4	1.3	67,600	52,100	51,600	84,700	70,100	65,700	28	28	29	55.6	66.7	63.1
5	1.6	74,200	58,300	....	86,400	73,200	....	.....	31	.....	.....	68.1	.....
6	2.0	83,200	56,400	51,600	103,700	75,300	63,200	22	29	29	56.2	64.2	64.4

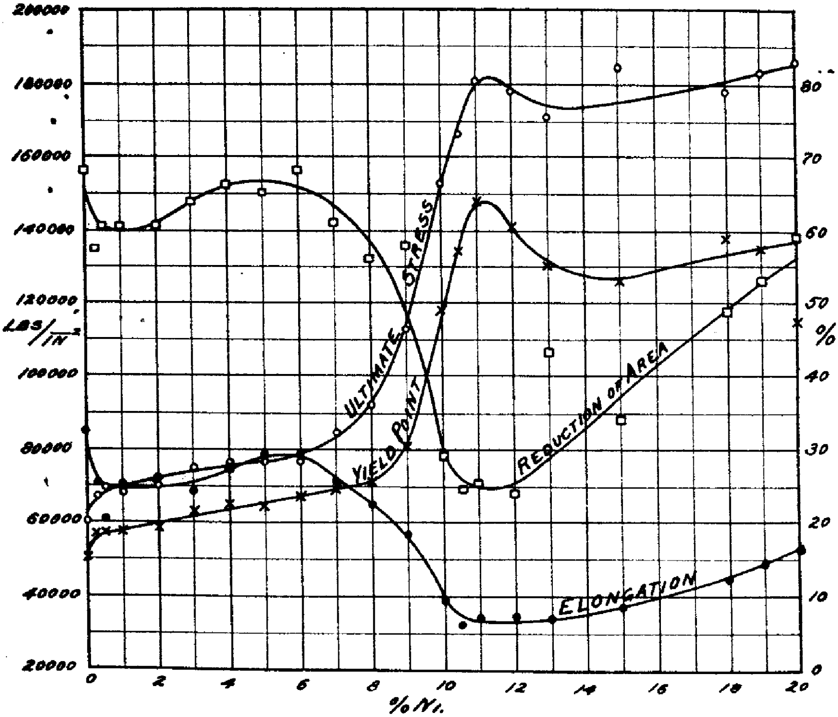

PLATE I

TENSILE STRENGTH IRON-NICKEL ALLOYS UNANNEALED

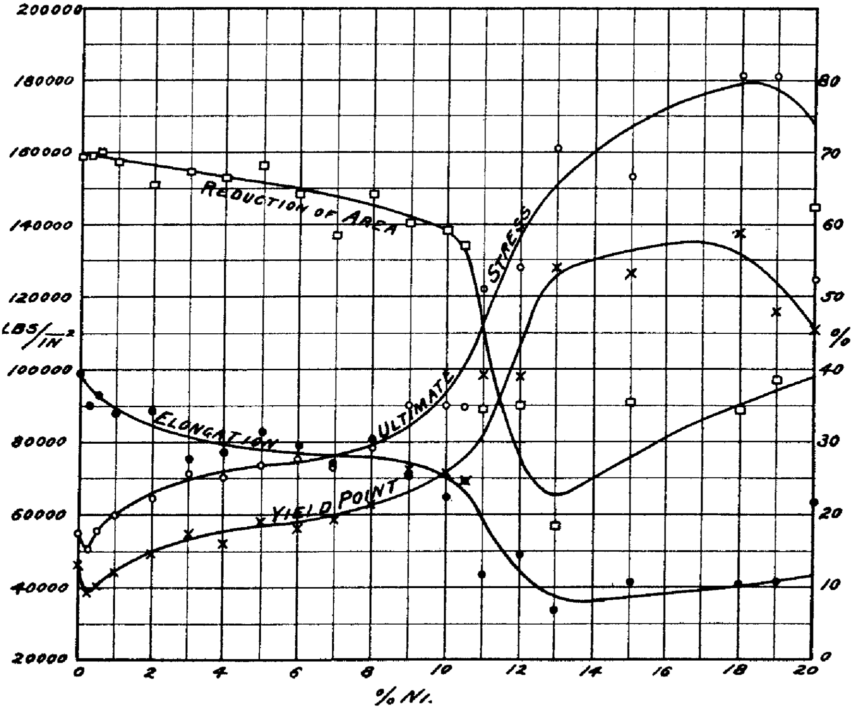

PLATE II

TENSILE STRENGTH IRON-NICKEL ALLOYS ANNEALED

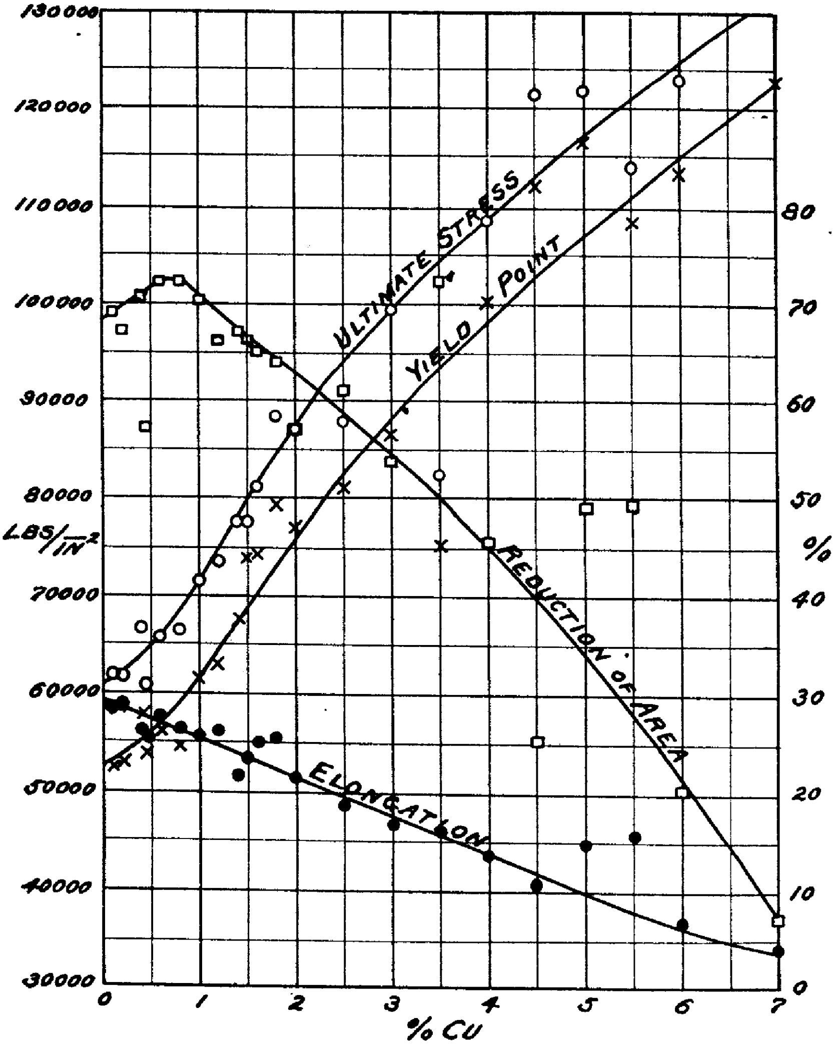

PLATE III

TENSILE STRENGTH IRON-COPPER ALLOYS UNANNEALED

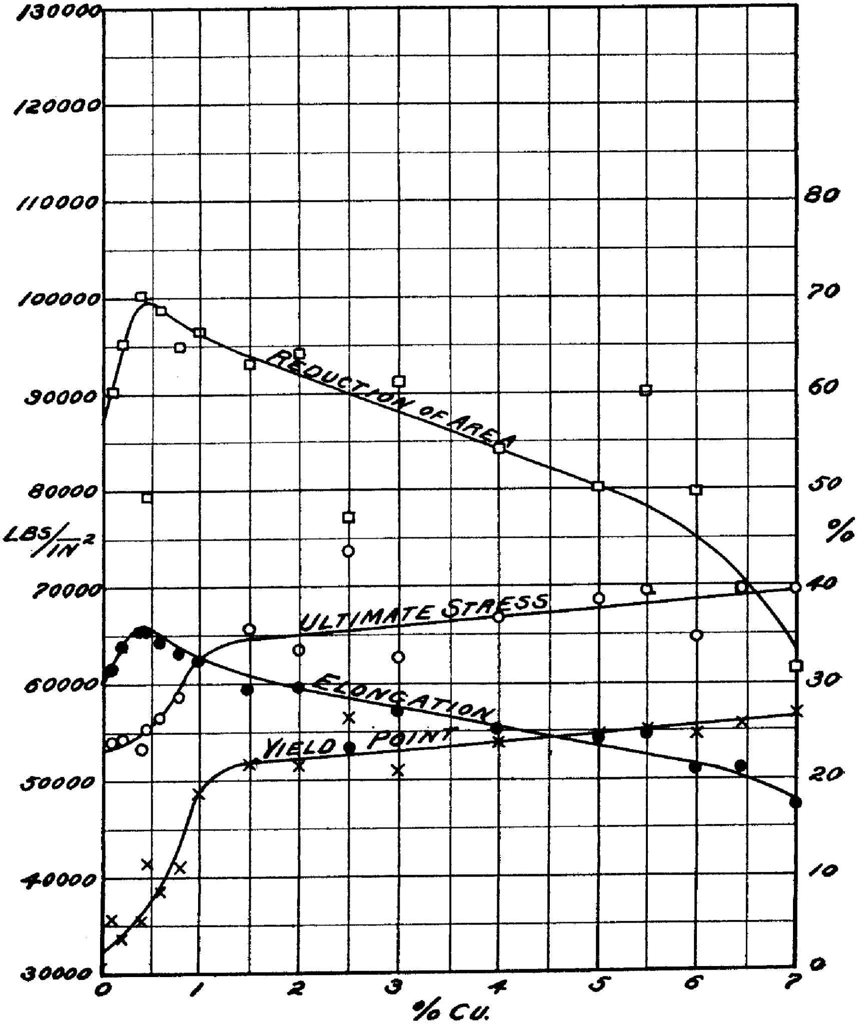

PLATE IV

TENSILE STRENGTH IRON-COPPER ALLOYS ANNEALED

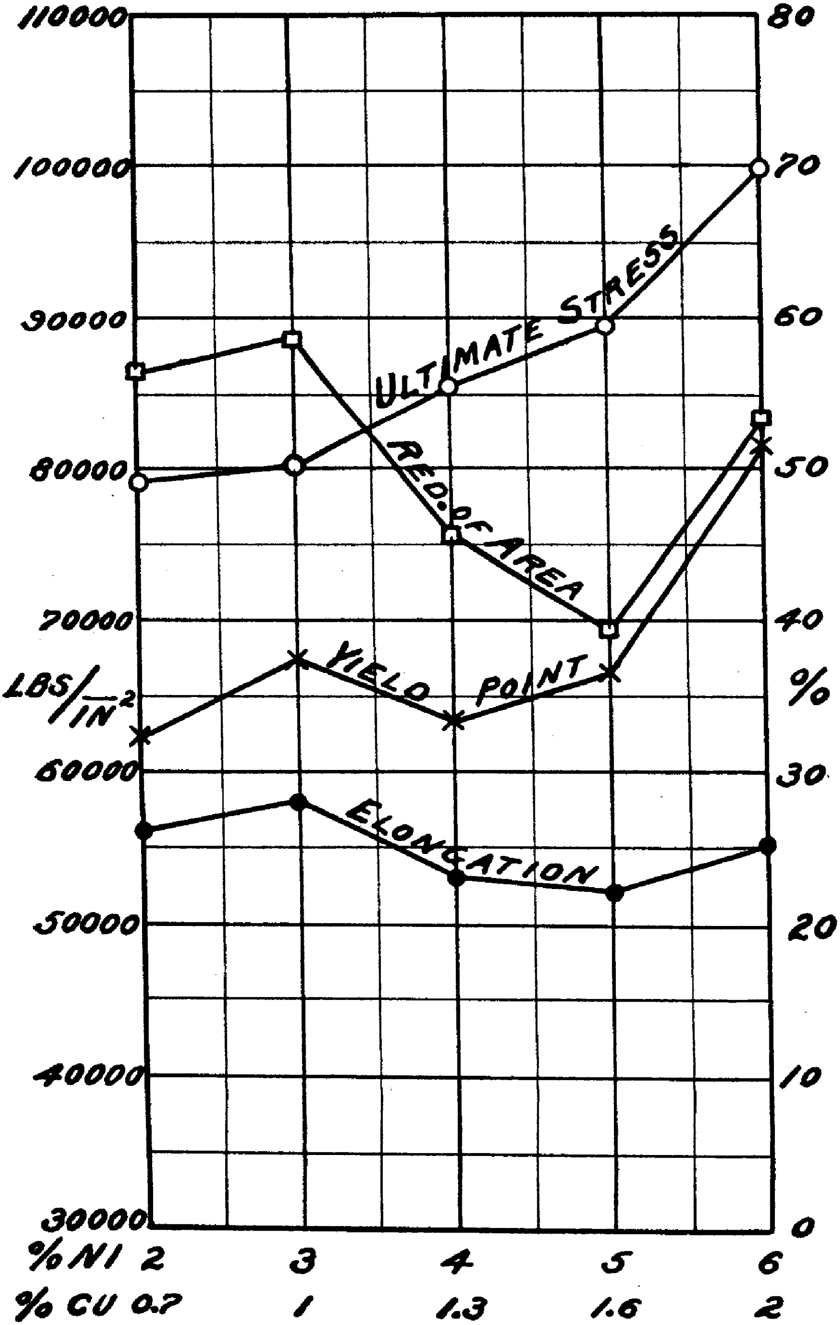

PLATE V

TENSILE STRENGTH IRON-NICKEL-COPPER ALLOYS UNANNEALED

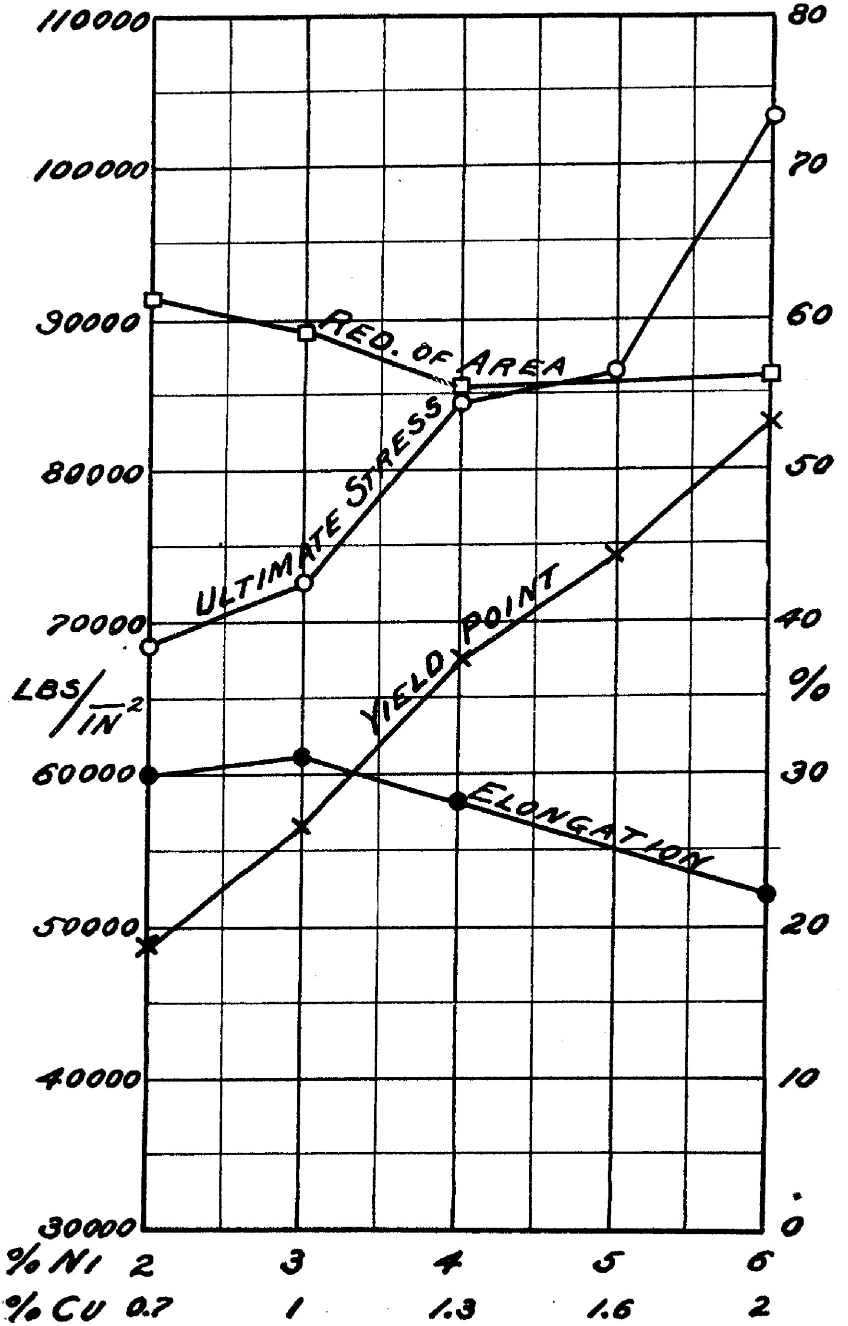

PLATE VI

TENSILE STRENGTH IRON-NICKEL-COPPER ALLOYS ANNEALED

REPRINTED FROM METALLURGICAL AND CHEMICAL ENGINEERING, April, 1910

The Magnetic Properties of Electrolytic Iron and Some Commercial Steels.

BY CHARLES F. BURGESS AND JAMES ASTON.

In connection with tests of the various properties of iron alloys made from electrolytic iron,* measurements were made of the magnetic quality. The results on certain of the binary series have been presented in several articles in previous issues of METALLURGICAL AND CHEMICAL ENGINEERING. In these discussions it was pointed out that the primary material in the preparation of the alloys was electrolytic iron of high purity (99.9 + iron); and a common standard of comparison throughout all the tests was a bar forged from an ingot of electrolytic iron.

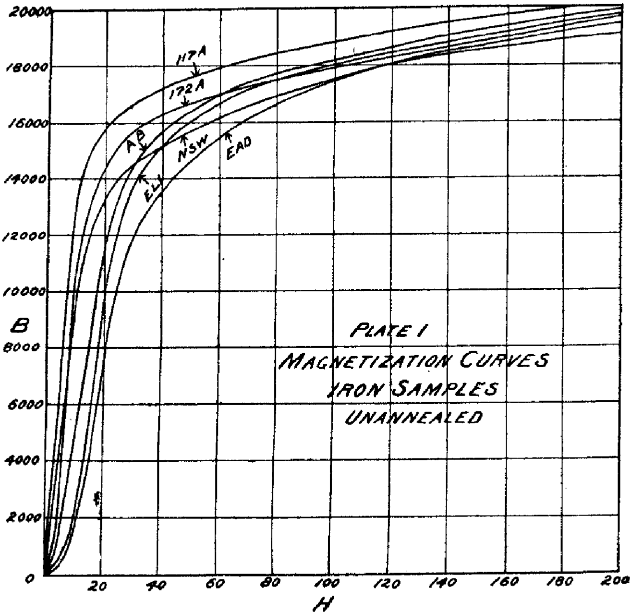

FIG. I.—MAGNETIZATION CURVES. IRON SAMPLES. UNANNEALED.

In this paper we are presenting data of tests made upon various samples of electrolytic iron, together with those upon the original anode material, indicating thus the effect of refining upon the magnetic quality. We have also embodied for comparison the results upon commercial samples of different degrees of purity.

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* Investigation of electrolytic iron and iron alloys made in the Chemical Engineering Laboratories of the University of Wisconsin under a grant from the Carnegie Institution of Washington.

Magnetic testing is not on such a basis at present that data of different investigators, at different periods of time and by different methods of testing, are strictly comparable. Even in the absolute ballistic method results are often markedly inconsistent; and comparisons of heterogeneous collections of data are likely to be misleading. All of our data, while open to the common objection to intercomparison, were obtained by the same operator upon the same apparatus, with every precaution taken, before any series of tests were made, to have consistent checking to a standard; the results, therefore, may be considered strictly comparable among themselves.

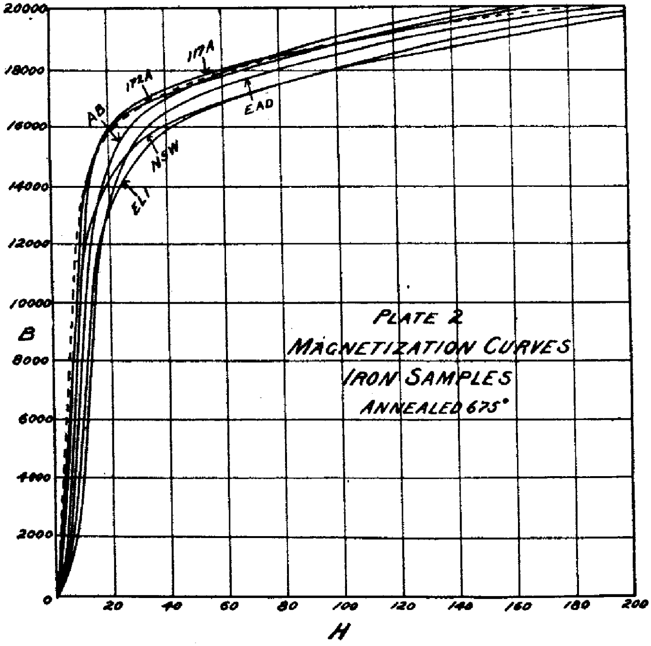

FIG. 2.—MAGNETIZATION CURVES. IRON SAMPLES. ANNEALED 675°.

Electrolytic Iron Tests.

Tests under four different heat treatments have been made upon the sample noted in the following table:

Bar.	Character.	C.	P.	Si.	S.	Mn.	Fe.
NSW	—Swedish anode, forged..	0.260	0.007	0.109	0.007	0.021	99.596
EAD	—Single refined as deposited, not forged......	0.019	0.013	0.002	0.006	0	99.960
117A	—Electrolytic, melted and forged	0.047	0.016	0.062	0.005	0	99.870
AB	—Electrolytic, melted and forged	0.120	0.014	0.001	0.009	0	99.856
ELI	—Electrolytic, melted and forged	0.012	0.041	0.008	0.019	Tr.	99.920
172A	—Electrolytic, melted and forged	....	....	....	....	....	.....

NSW is forged from one of the anode bars as used in the single refining tanks, and was bought for high-grade Swedish iron. The analysis indicates a somewhat high carbon content, but the material has the desirable quality of being very low in phosphorus, which is a troublesome element in the refining operation, as will be seen by examination of the phosphorus content of the refined bars. The indications are that all of the phosphorus had been carried over to the cathode, and the percentage content in the product increased because of the loss of iron in the slimes. However, it must be noted here that analyses of the double refined iron showed a phosphorus content of only 0.003 per cent. The analyses above show also the difficulty of preventing the absorption of carbon by the charges, due to the reducing action of the iron upon the carbon monoxide furnace atmosphere.

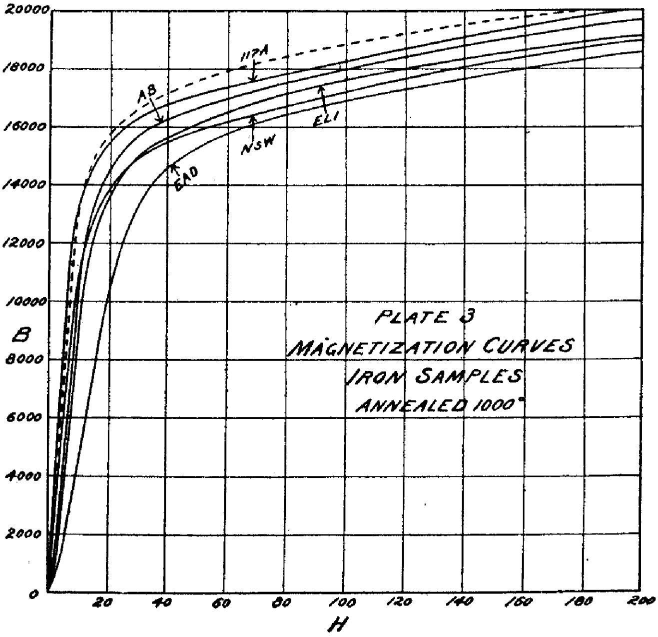

FIG. 3.—MAGNETIZATION CURVES. IRON SAMPLES. ANNEALED 1000°.

Bar EAD was cut from a heavy single refined cathode sheet without melting or forging (in fact, without any heating whatever) and is thus representative of the electrodeposited material. Bars 117A, AB, ELI, and 172A are made of electrolytic iron melted into ingots and forged into rods. For 172A, double refined material was used.

The results of the tests are indicated in Tables I and II and in the curves plotted in Plates 1, 2, 3 and 4. In the unannealed condition, the forged electrolytic iron bars (117A, AB, ELI, and 172A) represent a considerable variation in relative quality. This cannot be ascribed to the difference in purity, as will be noted on comparison of the analyses. The differences are very likely due largely to the molecular condition of the samples, as a result of lack of uniformity in the forging temperature and to strains set up in working. Bars 117A and 172A are especially good, the former in particular being so uniformly good in the unannealed state and throughout the entire length of the curve that it was chosen as the standard comparison curve for all our tests.

The effect of successive heat treatments is seen by inspection of the curves and tables. For comparison, the curve for 117A as unannealed is indicated by a dotted line. A marked improvement throughout the entire range of the curves is the result of heating to 675° and slowly cooling, due no doubt to the removal of all forging strains and the opportunity afforded for the grain size of the material to become normal. The improvement is most pronounced in the poorer samples of the unannealed tests (AB and ELI) and it is very slight in bar 117A, indicating, perhaps, that the forging treatment left it in practically its best molecular condition.

A second heating has been accompanied by an improvement of the quality in the lower ranges of the magnetizing force, but except for these ranges, the densities fall below those for the lower annealing temperature.

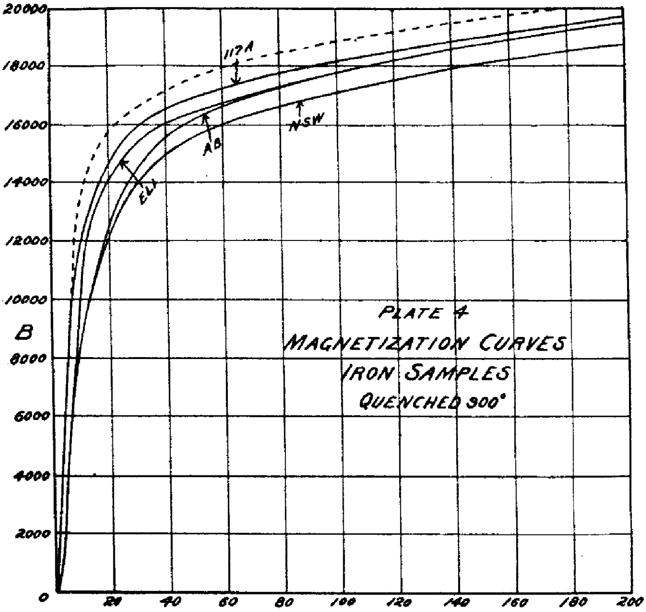

FIG. 4.—MAGNETIZATION CURVES. IRON SAMPLES. QUENCHED 900°.

Quenching from a temperature of 900° C. has been accompanied by a deterioration of the quality for all magnetizing forces. This effect is most marked for the lower valves of H,

TABLE I.—DATA OF MAGNETIC TESTS.

Bar. Composition.	H = 10				H = 20				H = 50				H = 100			
	Unannealed,	Annealed, 675°.	Annealed, 1000°.	Quenched, 900°.	Unannealed.	Annealed, 675°	Annealed, 1000°	Quenched, 900°.	Unannealed,	Annealed, 675°.	Annealed, 1000°.	Quenched, 900°.	Unannealed.	Annealed, 675°.	Annealed, 1000°.	Quenched, 900°.
NSW—Anode	9,500	10,000	10,850	8,400	13,200	14,200	13,900	12,050	15,700	16,500	15,850	15,550	17,450	18,000	17,200	17,100
EAD—As deposited	1,650	4,000	4,700	....	7,300	13,250	10,300	....	14,550	17,050	15,300	....	17,450	18,500	16,900	....
117A—Electro-forged	13,100	10,000	13,350	11,800	15,750	15,950	15,450	14,600	17,600	17,700	17,050	16,950	18,850	18,850	18,200	18,150
AB—Electro-forged	4,900	7,700	10,900	8,400	11,450	14,650	14,600	12,400	16,400	17,500	16,650	16,200	18,150	19,050	17,600	17,750
ELI—Electro-forged	2,000	6,000	9 300	10,000	9,550	13,050	13,600	14,050	16,000	16,400	16,100	16,450	18,000	18,050	17,600	17,750
172A—Electro-forged	10,400	12,500	8,000	....	14,300	15,900	12,700	....	16,700	17,450	16,100	....	17,900	18,850	17,600	....
AI—High purity	10,800	....	....	....	14,500	....	....	....	17,200	....	....	....	18,800	....	....	....
277—Commerc'y pure.	11,100	....	....	....	14,500	....	....	....	17,100	....	....	....	18,600	....	....	....
258—Norway	11,700	....	....	....	14,800	....	....	....	16,500	....	....	....	18,100	....	....	....
131—Bessemer	7,900	....	....	....	13,100	....	....	....	16,400	....	....	....	18,200	....	....	....
FB—Sheet	....	11,900	....	....	....	15,200	....	....	....	17,500	....	....	....	18,800	....	....
390,389—Sheet	4,200	8,200	....	....	9,800	12,700	....	....	15,100	16,300	....	....	17,400	17,800	....	....
392—Cast steel	....	11,700	....	....	....	14,900	....	....	....	16,800	....	....	....	18,300	....	....
OH—Open hearth	7,800	....	....	....	12,200	....	....	....	15,700	....	....	....	17,700	....	....	....
CRU—Crucible	3,600	....	....	....	8,100	....	....	....	13,700	....	....	....	16,600	....	....	....
248—Tool	400	....	....	....	1,600	....	....	....	10,100	....	....	....	14,900	....	....	....
391—Cast iron	1,300	....	....	....	3,200	....	....	....	6,200	....	....	....	8,200	....	....	....

but, all in all, it is very slight, indicating in a way the purity of the material, since, although the temperature was sufficiently high, the absence of carbon had prevented any hardening. This is more clearly brought out in Table II, where the coercive force and retentivity are indicated for the various treatments. The coercive force, indicative of the magnetic hardness, which in turn varies with the physical hardness, has become less under the successive heatings.

The effect of the refining is indicated by comparison of the curves for bar NSW, the anode material, with those discussed above. Unannealed, and at lower magnetizing forces, it is very good magnetically; in fact, it excels two (AB and ELI) of the four refined bars. 117A and 172A are better, however, throughout the whole range of tests. After the first heat treatment the superiority of this Swedish anode is less marked, even at low values of H; and in all cases, at higher values of the magnetizing forces (H above 20) the electrolytic curves reach higher maxima of density. Further annealing at 1000° C. has only served to increase the general effect just mentioned.

The influence of the carbon is most interestingly evident in the following table, where the coercive forces are given after annealing at 1000° C. and again after quenching at 900°.

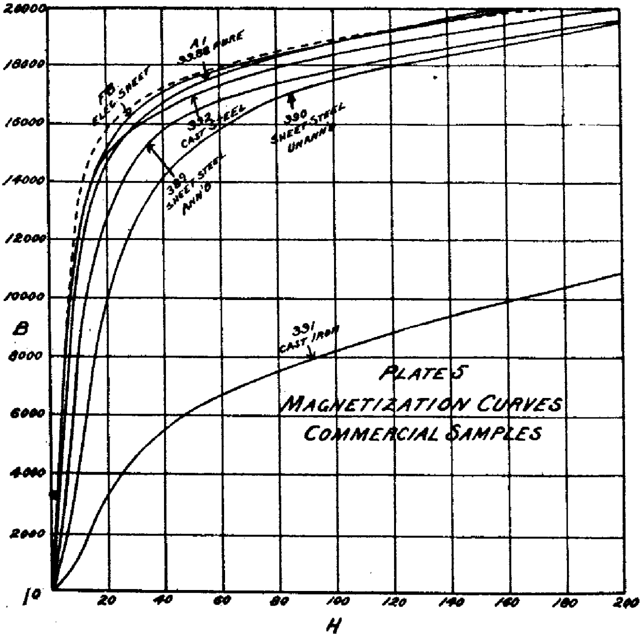

FIG. 5.—MAGNETIZATION CURVES. COMMERCIAL SAMPLES.

Bar.	Per cent, C.	Coercive Force Annealed, 1000°.	Coercive Force Quenched, 900°.
ELI	0.012	6.0	5.5
117A	0.047	3.1	2.5
AB	0.120	5.5	5.5
NSW	0.260	3.9	5.0

In this group of curves, one of the most interesting is EAD, made, as mentioned previously, from electrolytic iron as deposited, without melting or forging. In the original condition it may be classed as rather poor material, falling well below the other curves in the lower ranges of magnetizing force, and having the high coercive force of 18.5. After the first annealing, however, it has become very good material, taking a place in the midst of the others. The coercive force has fallen off to 9.3, or one-half of its former value, and the value of B for $H=20$ has almost doubled, from 7300 to 13,250. The effect may be ascribed to the driving off of the hydrogen occluded in the electrodeposition, and perhaps the allied alteration in crystalline structure.

Commercial Samples.

Included in Tables I and II and plotted in Plates 5 and 6 are the results of tests on commercial samples of types representing varying degrees of purity. The descriptions of the materials are as follows:

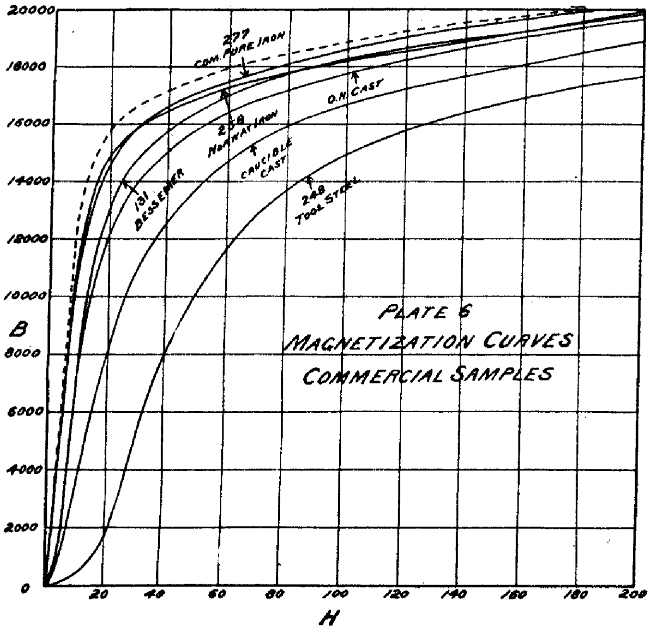

FIG. 6.—MAGNETIZATION CURVES. COMMERCIAL SAMPLES.

Bar.	Character.
A. I.	High purity commercial iron, made by basic open-hearth process. Purity, 99.884; C, 0.030. Sample cut from rolled bar and tested without heat treatment.

277. Commercially pure iron—composition and heat treatment unknown.
258. Norway iron—composition and heat treatment unknown.
131. Bessemer steel—composition and heat treatment unknown.
F. B. Sheet steel—made and treated especially for electrical purposes.
390. Second quality sheet steel from large electrical manufacturer—not annealed.
389. Same as 390, but annealed.
392. Cast steel used by large electrical manufacturer.
O. H. Open-hearth cast steel for electrical work.
CRU. Crucible cast steel from same source as O. H.
248. Tool steel.
391. Cast iron.

The direct comparison of these materials with the electrolytic samples can be made through the medium of standard 117A, which is shown on Plates 5 and 6 by a dotted curve.

TABLE II.—COERCIVE FORCE AND RETENTIVITY.

	H (MAX) = 200 Coercive Force.				H (MAX) = 200 Retentivity.			
Bar. Composition.	Unannealed.	Annealed, 675°.	Annealed, 1000°.	Quenched, 900°.	Unannealed.	Annealed, 675°.	Annealed, 1000°.	Quenched, 900°.
NSW—Anode	5.5	4.8	3.9	5.0	11,400	12,700	9,000	8,500
EAD—As deposited	18.5	9.3	6.2	..	11,200	12,900	4,900	....
117A—Electro-forged	5.5	6.2	3.1	2.5	12,300	13,800	10,000	8,000
AB—Electro-forged	10.0	8.1	5.5	5.5	12,000	13,800	10,700	8,500
ELI—Electro-forged	7.9	9.5	6.0	5.5	13,900	12,000	10,900	13,400
172A—Electro-forged	7.0	5.0	5.8	..	12,400	12,300	9,400	....
AI—High purity	4.0	..	..	..	9,600	....	....	....
277—Com. pure	3.8	..	..	..	10,100	....	....	....
258—Norway	4.2	..	..	..	11,350	....	....	....
131—Bessemer	7.1	..	..	..	12,250	....	....	....
F.B.—Sheet	..	3.0	..	..	....	9,800	....	....
390, 389—Sheet	9.3	5.2	..	..	9,650	8 900	....	....
392—Cast steel	..	3.6	..	..	....	9,700	....	....
OH—Open hearth	7.1	..	..	..	11,400	....	....	....
CRU—Crucible	11.5	..	..	..	9,200	....	....	....
248—Tool	29.1	..	..	..	10,450	....	....	....
391—Cast iron	12.3	..	..	..	4,800	....	....	....

But little comment is necessary in this comparison. The effect of chemical purity of the material is indicated by the high quality of those materials of higher purity. The result of judicious annealing is shown in curves 389 and 390, a low-grade material markedly improved by the heat treatment.

Hysteresis tests on several of these materials are given below, all being carried to a uniform maximum flux density of B = 12,000 per square centimeter.

Bar.	Loop Area.	Relative Area.	H (Max.).
117A	8.65	1.	8.2
NSW	8.14	0.94	13.0
389	11.36	1.31	16.1
390	20.56	2.38	28.0
FB	7.25	0.84	10.3
AI	9.18	1.06	12.0

Bars 117A and NSW were tested after quenching, and this should be borne in mind in making comparisons.

A few general conclusions may be pointed out as a result of the tests.

The refining of commercial steels results in improvement of the magnetic qualities.

The amounts of impurities met with in commercial practice do not result in a serious deterioration of the quality.

Judicious heat and mechanical treatment has an importance equal to that of chemical composition, and proper annealing undoubtedly results in marked improvement in the magnetic quality.

CHEMICAL ENGINEERING LABORATORIES,
UNIVERSITY OF WISCONSIN.

Reprinted from Metallurgical and Chemical Engineering, August, 1910.

The Strength of the Alloys of Electrolytic Iron and Monel Metal.

By Charles F. Burgess and James Aston.

For several years past there has been conducted at the Chemical Engineering Laboratories of the University of Wisconsin, under grant of the Carnegie Institution of Washington, an extensive series of tests on the properties resulting from the addition of various alloying elements to electrolytic iron. As part of the tests, a study was carried out upon the strength of the alloys of this iron with varying proportions of nickel and of copper.

The results of the nickel series were published in Bulletin No. 346 of the University of Wisconsin,[1] and those of the copper series were presented before the American Electrochemical Society in October, 1909,[2] and reprinted in the abovementioned university bulletin. While this work may in large measure be classed as supplementary or correlative to the work of other investigators,[3] it was considered well worth undertaking in view of the high degree of purity of the electrolytic iron, and the consequent opportunity of ascribing any observed effects solely to the alloying element, and the elimination thereby of one question of doubt arising in most investigations of the alloy steels.

The results of these earlier tests were largely confirmatory of the work of the other investigators mentioned, the chief differences noted in our tests being a shifting of the regions of certain physical properties because of variations of carbon content. The general conclusions may be stated as follows:

Iron-Nickel Alloys.

1. With increase of nickel there is an increase of strength with a slight decrease of ductility in the range of lower nickel content.

2. Beyond this range the addition of nickel causes a sudden increase of strength with a marked decrease of ductility over a zone of decided brittleness.

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[1] The Strength of the Alloys of Nickel and Copper with Electrolytic Iron. C. F. Burgess and James Aston. *Bulletin* Univ. of Wis., Eng. Series, Vol. 6, No. 2, March, 1910. (See Book Reviews in this issue.—Editor.)

[2] Physical Properties of Iron Copper Alloys. C. F. Burgess and J. Aston. *Trans.* Am. Elec. Chem. Soc., Vol. XVI, 1909.

[3] Nickel Steels: R. A. Hadfield, Inst. Civ. Engrs., 1898, Vol. CXXXVIII; R. Guillet, *Bul.* Soc. d'Encour, May, 1903; 7th Report Alloys Research Committee, Inst. Mech. Engrs., Vol. 2, 1905. Copper Steels: P. Breuil, *Jour.* Ir. & St. Inst., No. 2, 1907.

3. The position of the brittle zone varies with the carbon content and probably with a variation of other impurities, such as manganese, if present in appreciable amounts. For a pure alloy where the effect is due to nickel alone, the area may be set between 10 per cent and 16 per cent of nickel. The addition of carbon places the zone at lower percentages of nickel, as low as 7 per cent nickel for carbon = 0.82 per cent, or even as low as 5 per cent if the manganese rises to 1 per cent.

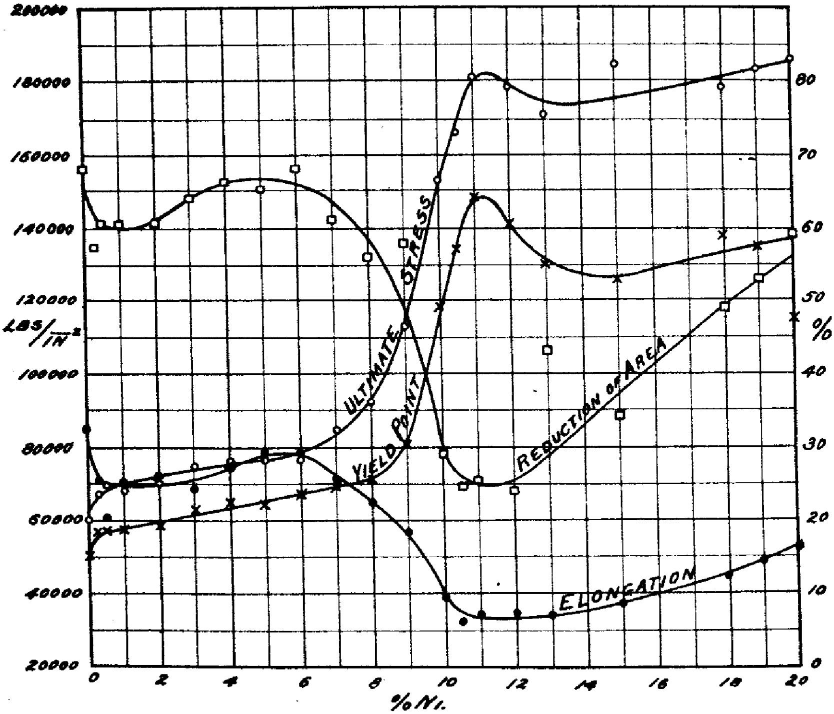

FIG. I.—TENSILE STRENGTH IRON-NICKEL ALLOYS UNANNEALED.

4. Accompanying this brittleness there is a marked hardening in the material.

5. Annealing, while not greatly affecting the region of the brittle zone or the extent of the brittleness, has a tendency to confine the range to more narrow limits.

6. For percentages of nickel above those of the zone of brittleness there is a restoration of the ductility and softness.

The data of this series are given briefly in Tables 2 and 3, and plotted in Figs. 1 and 2.

Iron-Copper Alloys.

The results are tabulated in Tables 2 and 3 and plotted in Figs. 3 and 4. They are in disagreement with the generally accepted opinion that copper is a very deleterious impurity in steels. It seems evident that the detrimental effect commonly noted is due rather to the combined influence of the copper and some of the elements met with in commercial steels, notably carbon and sulphur. In the absence of carbon, unannealed samples showed a successive increase of tensile strength up to the maximum copper addition of 7 per cent (the limit of forgeability). The yield point was close to the ultimate strength, and the elongation fell off with regularity. Brittleness, therefore, was the accompaniment of the copper additions, and increased with the percentage present.

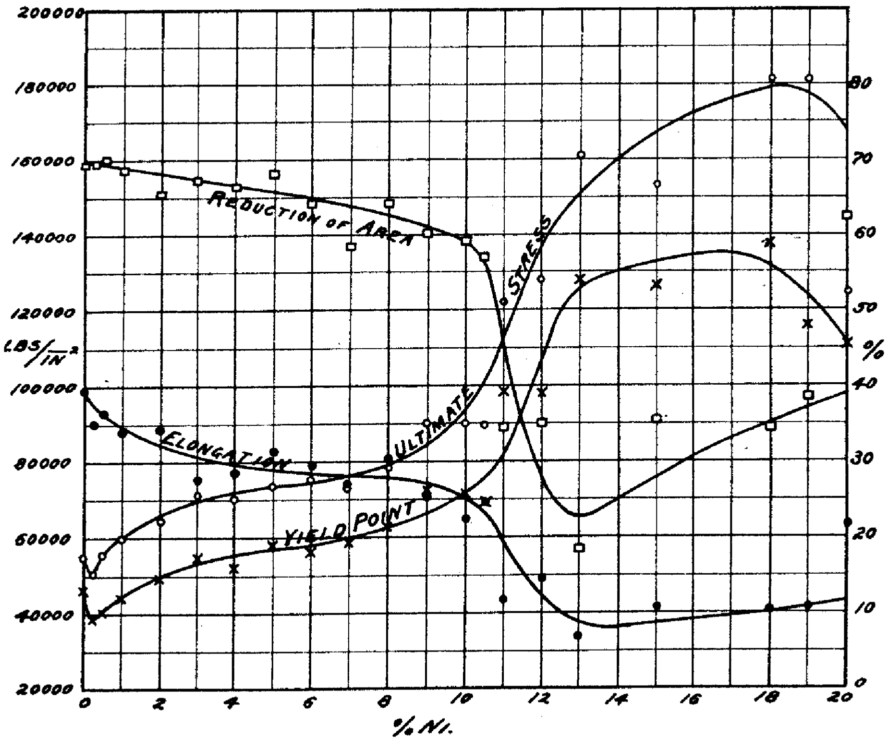

FIG. 2.—TENSILE STRENGTH IRON-NICKEL ALLOYS ANNEALED.

Annealing had a most marked effect, lowering the ultimate strength and elastic limit throughout, but especially for copper percentages above 1. The elongation became very good throughout the entire range. The result was, therefore, an alloy of very good properties, and this fact was brought out in the paper previously referred to. We mentioned particularly the addition of 1½ per cent of copper as being advantageous, because this small amount of addition agent resulted in properties almost as good as those obtained with larger quantities of copper, and approached the results reached with the customary nickel content.

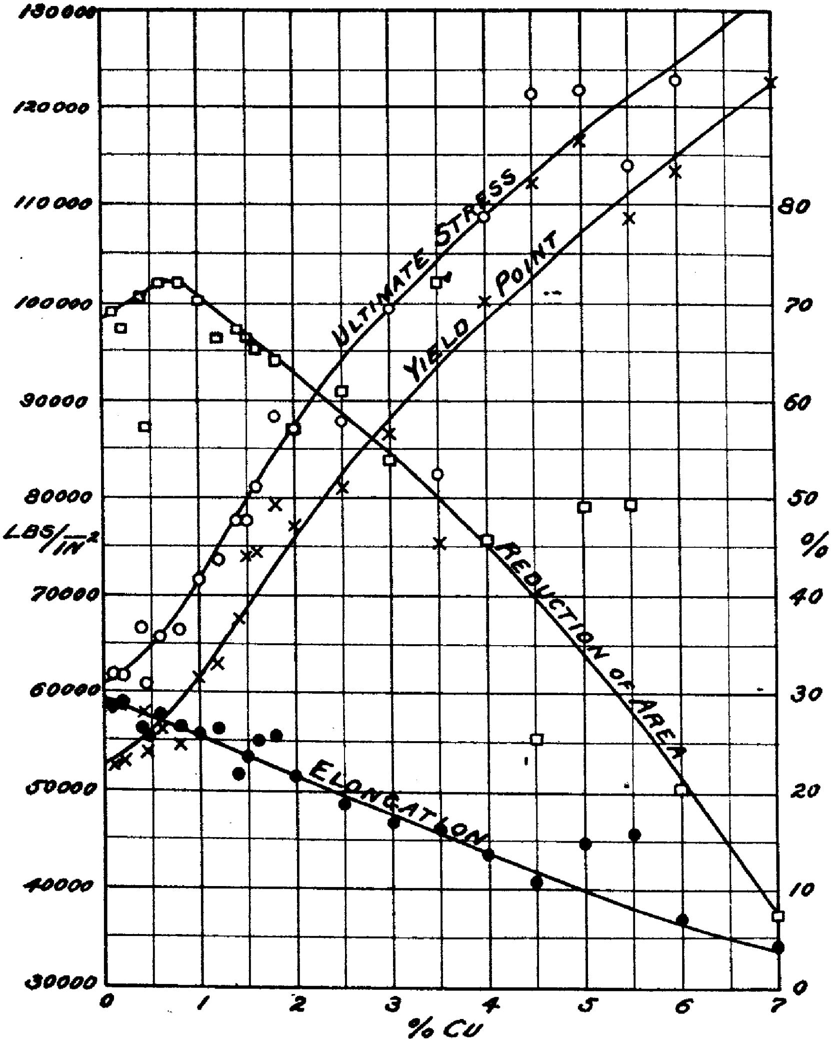

FIG. 3.—TENSILE STRENGTH IRON-COPPER ALLOYS UNANNEALED..

Iron-Nickel-Copper Alloys.

The present paper is the direct outcome of the observations noted in the two binary series of alloys just discussed; its inception was due to reasons expressed in the above-mentioned university *Bulletin,* in which some preliminary work was reported and which reasons may be quoted verbatim here.

"In view of the well-known beneficial effect of the addition of nickel to iron, and because of the very great and rather unexpected increase of tensile strength observed, in our tests of the copper-iron alloys, due to increasing percentage of copper, it was thought advisable in order to round out this research to carry out tests on a series of alloys in which both nickel and copper were added to the electrolytic iron.

"The advisability of the investigation was prompted by several considerations—first, the benefits observed by the separate additions of nickel and copper might be coupled in their joint use; second, the close relationship of copper, nickel and iron in chemical and physical properties might lead to interesting results in a ternary alloy; third, (and this was the reason of greatest weight), there is on the market a nickel-copper alloy which would make a very desirable addition agent, in case the simultaneous presence of both copper and nickel gave a tensile strength no less than that observed for the two separate alloys.

"We refer to Monel metal, resulting from the reduction of certain ores from which, by smelting alone ,this alloy is formed. The main constituents are nickel and copper, in the proportions of about three to one, respectively. The material is, for the present at least, obtainable at a price about equal to that of copper, and very much below the cost of nickel. Here, then, is a means of getting nickel additions, provided the copper carried does not neutralize the effect of the nickel."

In the preliminary study no Monel metal was available for use. The alloys were made up by additions of nickel and copper up to a total combined content of 8 per cent. The Monel ratio of three nickel to one copper was adhered to, and, strange to say, the proportion of 1½ per cent of copper to 4½ per cent of nickel gives the values approximately the best observed in the separate alloys. The results of this work, given in Tables 2 and 3, and in the dotted curve of Plates 5 and 6, were sufficiently encouraging to warrant carrying the investigation to higher total addition content, and with Monel metal as the alloying agent.

Some particulars regarding Monel metal are given below:

Analyses.

Nickel	66.90	67.96
Copper	24.35	26.00
Iron	5.00	2.80
Manganese	2.18	1.62

Mechanical tests gave for cast samples ultimate strengths of 30,400 lb. and 35,000 lb. per square inch. For rolled samples the figures were: elastic limit, 74,400 lb. and 79,000 lb. per square inch; ultimate strength, 100,000 lb. and 104,000 lb. per square inch.

Thus we see that the alloy has very good inherent mechanical properties, and the analyses indicate, besides the nickel and copper, only iron and manganese, and the latter is no detriment to steels.

The iron used was of a high degree of purity, obtained by a double electrolytic refining of Swedish iron. The electrolytic iron may be considered 99.97 pure. In the preparation of the alloys the brittle iron was broken into small pieces and melted in an electric furnace of the resistor type with the predetermined amounts of Monel metal. Specially prepared magnesia crucibles were used, these in turn being protected by a graphite jacket; and contamination of the charge was prevented by a magnesia lid luted on the crucible and a graphite cover for the jacket.

During the melt there was no agitation of the charge, the resulting alloy being entirely due to diffusion of the elements. This was facilitated by holding the charges above the melting temperature for a few hours, and by slow cooling in the furnace. The ingots weighed about 500 grams (1 lb.), and after forging, each furnished enough material for three test bars approximating 0.4 in. finished diameter over a free length of 2 in. Ingots were made up with the Monel metal increasing by gradations of 2 per cent to a maximum addition of 20 per cent. Samples were tested as forged and after annealing at 900° C.

The tests were made upon a Riehle 50,000-lb. power-driven machine. The load was applied very slowly, and the yield point was determined by means of multiple dividers. This was checked by the drop of the beam.

From 2 to 12 per cent of alloying addition, the ingots forged readily over a wide range of heats; from 12 to 18 per cent high temperatures were necessary and the bars did not forge well below bright red heat, while for those ingots with 18 and 20 per cent of Monel metal a white scintillating heat was necessary. Up to and inclusive of the 12 per cent addition, the test bars were machined in the lathe; above this grinding was resorted to, the material being too hard for efficient working with lathe tools.

Tensile Strength Tests.

The summary of results is included in Table 1 and in Figs. 5 and 6. There is noted the yield point and ultimate strength in pounds per square inch, the percentage of elongation in 2 in., and the percentage of reduction of area at fracture. There are

TENSILE STRENGTH TABLE I.

ELECTROLYTIC IRON-MONEL METAL ALLOYS.

Per cent Monel.	No. Sample	Yield Point lbs. / sq. in			Max. Stress lbs. / sq. in			Elongation % / 2″			Reduction Area %		
		Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.	Max.	Min.	Av.
UNANNEALED													
2	1			49300			71000			22.5			62.5
4	3	67400	57000	61070	88700	77000	81000	30.0	30.0	30.0	69.0	61.5	64.3
6	1			72500			84000			25.0			54.0
8	3	92500	91400	91830	118300	117200	107670	20.0	20.0	20.0	55.2	51.8	53.2
10	3	150500	132000	139830	170000	158000	163000	15.0	10.0	12.8	42.6	28.6	37.1
12	3	161000	153500	157500	189000	180500	185400	13.5	12.5	13.0	44.5	36.1	40.4
14	4	152000	130000	144370	182000	157300	166820	10.0	5.0	6.9	30.0	8.5	16.4
16	3	171000	154000	162500	191500	179000	184330	12.5	5.0	9.8	37.3	12.2	27.2
18	2	172000	168200	170100	215000	196000	205500	10.0	5.0	7.5	27.6	7.2	17.4
20	2	191000	183200	187100	205000	202000	203500	7.5	4.5	6.0	8.8	5.8	7.3
ANNEALED 900°C.													
2	2	40500	40000	40250	64500	61500	63000	30.0	30.0	30.0	70.0	58.0	64.0
4	2	71600	71000	71300	91000	84600	87800	25.0	22.5	23.7	61.0	59.5	60.2
6	2	94000	88000	91000	109000	105600	107300	20.0	17.5	18.7	51.7	47.3	49.5
8	3	98500	75800	88100	115200	90700	102970	21.0	18.5	19.8	64.6	59.0	62.5
10	3	158000	126200	144400	165000	131000	150000	17.0	15.0	15.7	59.8	45.0	51.9
12	3	160800	120000	145930	167200	126000	151400	15.5	10.0	12.2	50.5	31.6	39.0
14	2	150000	143600	146800	156000	147000	151500	10.0	10.0	10.0	40.7	36.0	38.3
16	3	152000	120000	138000	166500	142000	153000	11.5	10.0	10.8	41.6	39.5	40.5
18	2	157000	103000	130000	166500	158000	162250	13.5	7.5	10.5	29.4	11.9	15.7
20	2	130000	123400	126700	170000	139900	154950	5.0	2.5	3.8	1.1	1.0	1.1

included also the maximum, minimum and average values of each of the above items, together with the number of samples from which such average is calculated. In the plates the yield point, ultimate strength, elongation and reduction of area for

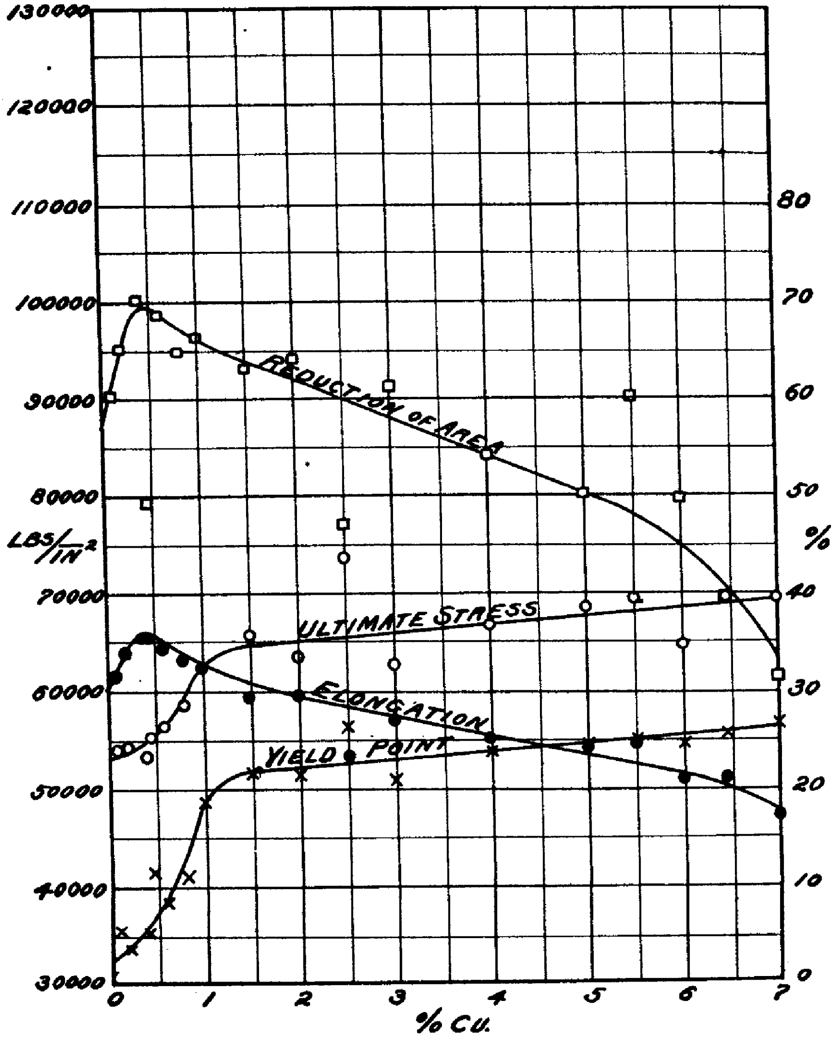

FIG. 4.—TENSILE STRENGTH IRON-COPPER ALLOYS ANNEALED.

varying percentages of alloying additions are designated by appropriate symbols, and are the values given in the tables in the columns of averages.

With these points as a guide, smooth curves are drawn in each case. With the many factors affecting somewhat the strength of a metal, it is not expected that the points will fall consistently on a curve. It is intended merely that the curve will show the tendency of the effect of increasing the percentage of Monel metal in the alloy.

Unannealed.—The results of the tests in the unannealed state are enumerated in Table 1, and the general summary is best noted by referring to the curves in Fig. 5. Between 0 and 8 per cent there is a rather rapid rise in the ultimate strength and the elastic limit; the latter rises more rapidly, however, and at 8 per cent the elastic ratio is 0.85, indicating brittleness. This is confirmed by the falling off in the values of elongation and reduction of area. Up to 4 per cent of Monel addition there is an increase of ductility, and at this point we note the very fair values of ultimate stress 81,000, yield point 61,070, elongation 30 per cent, and reduction of area 64.3 per cent.

From 8 per cent upward there is a rapid increase in the maximum strength and elastic limit, but with ever-increasing brittleness, as is indicated by the steady falling off of the curves for elongation and reduction of area. The highest values reached for the series were for one of the bars with 18 per cent of alloying addition, the figures being: ultimate, 215,000; yield point, 172,000; elongation, 10 per cent, and reduction of area, 27.6 per cent.

Annealed.—These data are noted in Table 1 and Fig. 6. In the alloys of lower Monel additions annealing has had but little effect on the properties. In fact, and this was noted in the preliminary iron-nickel-copper series, the tendency has been to increase the ultimate strength and elastic limit without material falling off in the ductility. For those alloys with 4, 6 and 8 per cent of addition (the probable useful range) the strength is higher. We now note an increase of ultimate stress and yield point in almost a linear function of the amount of alloying material until at 10 per cent the values are: ultimate, 150,000; yield point, 144,400; elongation, 15.7 per cent; reduction of area, 51.9 per cent. The elongation and reduction of area are in accordance with the stress values.

Between 10 and 20 per cent of Monel metal the ultimate strength undergoes but little variation, while the elastic limit becomes less with increasing additions. Strangly enough, the elongation and reduction becomes steadily less, the latter in particular falling off very abruptly at the higher percentages.

Comparisons.

Direct comparisons of the general tendencies in the iron-Monel metal alloys is best made by means of the curves of Plates 1, 2, 5 and 6. In the unannealed condition (Figs. 1 and

5) there is a marked similarity, considering equal percentages of total additions. In each case there is a maximum of strength and elasticity at about 12 per cent. Up to this quantity there is a continual rise, more abrupt, however, in the case of the Monel alloys; and beyond 12 per cent there is the same dip in the curves with subsequent rise. On the other hand the nickel alloys show a brittle zone at about 12 per cent, with a recovery of ductility with further additions; with the Monel metal alloys the brittleness becomes more pronounced with increasing additions.

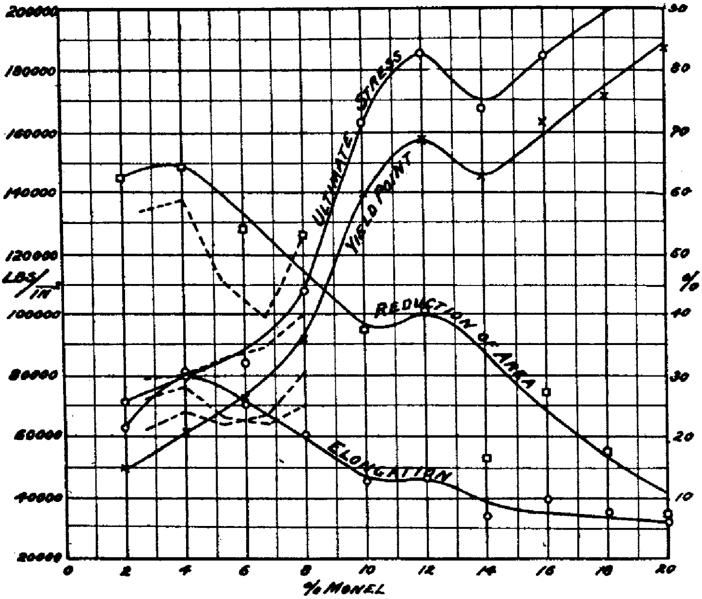

FIG. 5.—TENSILE STRENGTH IRON-MONEL METAL ALLOYS, UNANNEALED.

The relations in the annealed samples (Figs. 2 and 6) are similar to those commented upon above. The same brittle zone with subsequent recovery is noted in the nickel series, but in the Monel metal alloys the brittleness increases continuously. Up to 10 per cent of total additions the increase of ultimate strength and elastic limit is much more pronounced with Monel metal than with nickel alone, but the ductility is greater in the latter case. In both cases the pronounced maximum of strength and elasticity is now not noticed. On the other hand, while annealing of the nickel alloys has lowered the ultimate strength and the elastic limit throughout the entire range, with an accompanying increase of elongation and reduction, the effect

TABLE 2

COMPARISON IRON-NICKEL-COPPER ALLOYS — UNANNEALED

Per cent Addition	Yield Point				Max. Stress				Per cent Elong.				Per cent Red.			
	Ni	Monel	Ni Cu	Cu	Ni	Monel	Ni Cu	Cu	Ni	Monel	Ni Cu	Cu	Ni	Monel	Ni-Cu	Cu
1.5				73920				77300				23.5				66.9
2.0	58520	49300		76930	70350	71000		87010	26.0	22.5		21.2	60.7	62.5		57.0
2.7			62100				79200				26.0				56.7	
3.0	62920			86810	74860			99640	24.5			16.7	63.9			53.8
4.0	65000	61070	67400	100560	75670	81000	80100	108640	27.8	30.0	28.0	13.5	66.5	64.3	58.8	45.6
5.0	64030			116350	77150			121900	29.2			14.5	65.3			49.2
5.3			63300				85700				23.0				45.7	
6.0	67300	72500		113400	77300	84000		122900	29.0	25.0		6.5	68.5	54.0		20.3
6.6			66500				89400				22.0				39.3	
8.0	70770	91830	81700	135100	91740	107670	99700	148750	22.6	20.0	25.0	0	56.1	53.2	53.5	0
10.0	118960	139830			153360	163000			9.1	12.8			29.0	37.1		
12.0	141140	157500			178420	185400			7.1	13.0			23.8	40.4		
14.0		144370				166820				6.9				16.4		
15.0	125800				184730				8.2				34.1			
16.0		162500				184330				9.8				27.2		
18.0	138170	170100			178500	205500			12.3	7.5			49.3	17.4		
19.0	134730				183270				14.2				53.1			
20.0	115500	187100			186100	203500			16.0	6.0			59.5	7.3		

of heating of the Monel metal series has been pronounced only for percentages above 10, below this range the result is to increase the strength somewhat with little alteration of ductility.

In Tables 2 and 3 are collected the data of all of the series in order to make direct comparisons of the effects of the addition of Monel metal and of nickel and copper to iron in the ternary alloys, with those of the separate additions of the two elements in the binary series. The several items are noted in columns for each group; the compositions are given as the total percentage of alloying addition; the separate proportions of nickel and copper in the ternary series can be calculated from an assumed ratio of three nickel to one copper.

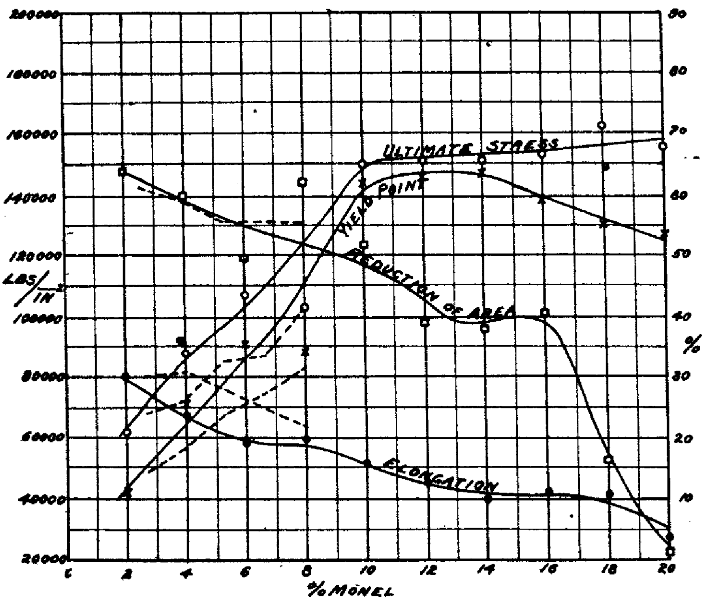

FIG. 6.—TENSILE STRENGTH IRON-MONEL METAL ALLOYS, ANNEALED.

In the preliminary work the object was to see whether the properties ordinarily accompanying the addition of nickel to iron were detrimentally affected by the copper carried in Monel metal and the comparison was made on the basis of equal nickel content and regarding the copper as so much superfluous addition. However, it was found that the copper had a beneficial effect, and a more rational comparison, therefore, can be made by tabulating on the basis of total addition material.

But little discussion of the figures is necessary. It will be noted that the ternary alloys (both Monel and nickel-copper)

TABLE 3

COMPARISON IRON-NICKEL-COPPER ALLOYS

ANNEALED

Per cent Addi. tion	Yield Point				Max. Stress				Per cent Elong.				Per cent Red.			
	Ni	Monel	Ni Cu	Cu	Ni	Monel	Ni Cu	Cu	Ni	Monel	Ni Cu	Cu	Ni	Monel	Ni-Cu	Cu
1.5				51750				65720				29.2				63.1
2.0	48770	40250		51620	64400	63000		63200	34.2	30.0		29.5	65.4	64.0		64.4
2.7			48600				68700				30.0				61.5	
3.0	55400			50890	70670			62360	27.5			26.9	67.6			61.7
4.0	52100	71300	56800	53570	70070	87800	72500	66540	28.4	23.7	31.0	24.8	66.7	60.2	59.1	54.2
5.0	58320			54460	73230			68250	31.4			24.2	68.1			50.3
5.3			67600				84700				28.0				55.6	
6.0	56400	91000		54420	75300	107300		64530	29.5	18.7		20.8	64.2	49.5		49.9
6.6			74200				86400									
8.0	63320	88100	83200		78470	102970	103700		30.2	19.8	22.0		64.4	62.5	56.2	
10.0	71800	144400			89300	150000			22.3	15.7			59.1	51.9		
12.0	97730	145930			121800	151400			14.5	12.2			35.8	39.0		
14.0		146800				151500				10.0				38.3		
15.0	126300				153300				10.5				35.8			
16.0		138000				153000				10.8				40.5		
18.0	137700	130000			181550	162250			10.0	10.5			34.4	15.7		
19.0	116150				180700				10.7				38.7			
20.0	111000	126700			124900	154950			21.5	3.8			62.5	1.1		

hold their own with either of the binary alloys through the entire range. And this is especially true in the annealed samples, particularly below 10 per cent of total additions, the range of probable greatest utility. At 4 per cent, for example, we note the following figures: ultimate strength, 87,800 and 70,070 yield point, 71,300 and 52,100; elongation, 23.7 and 28.4, and reduction 60.2 and 66.7, these figures being, respectively, for total Monel metal and nickel additions. The ductility of the Monel samples is entirely comparable to that of the nickel series in the unannealed condition; after annealing it is somewhat lower. But this may be due to the necessity of different annealing temperatures since in the ternary nickel-copper-iron series higher values for elongation are the rule.

These results seem to warrant the conclusion that for the carbon-free alloys, at least, the combined addition of nickel and copper in the proportions found in the commercial Monel metal does not result in any deterioration of the good qualities conferred by the nickel alone; in fact, the copper has good inherent qualities of its own. The general effect is the same for both series for equal total alloying additions. Whether these same good features will result from like additions to commercial steels, with their customary amounts of impurities, is a problem now under consideration.

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Über die Eigenschaften der Trockenelemente.[1]

Von **Charles F. Burgess** und **Carl Hambuechen.**

Die erforderlichen Eigenschaften eines Trockenelementes allgemein auseinanderzusetzen, ist unmöglich, da sie von dem jeweiligen Zweck, dem das Element dienen soll, abhängig sind. Die größte Verwendung findet das Trockenelement wohl augenblicklich im Telephonwesen; dann folgt als nächstgrößtes Gebiet die Verwendung zur Widerstandszündung. Elektrische Klingeln und Meldewerke bilden ein weiteres Feld für Trockenelemente, und Telegraphen, Wecker, Phonographen und zahlreiche kleine elektrisch betriebene Maschinen der verschiedensten Art sind auch noch Gebiete, auf denen das Trockenelement ausgedehnte Verwendung findet. Fortwährend tauchen andere neue Verwendungsarten auf, und die Nachfrage nimmt stetig zu, trotz des Umstandes, daß große elektrische Kraftzentralen für die Stadtfernsprechvermittlungsämter große Mengen von Trockenelementen überflüssig machen, während magnetische und andere Arten elektrischer Zündung mit der durch Trockenelemente auf dem Gebiete der Zündung im Wettbewerb stehen.

Wohl bei den meisten Anwendungsarten des Trockenelementes ist nur eine verhältnismäßig geringe Energieabgabe erforderlich. Die Elemente werden nur zeitweise gebraucht, und das erste Erfordernis eines Elementes scheint in einer möglichst langen Lebensdauer zu bestehen. Daß diese charakteristische Eigenschaft in hohem Maße erreicht wird, zeigt sich an gewissen im Handel befindlichen Trockenelementen, und in dieser Hinsicht sind in den letzten Jahren große Verbesserungen erzielt worden. Ein geringer innerer Widerstand ist eine weitere wichtige Eigenschaft guter brauchbarer Trockenelemente, da dadurch das Element in den Stand gesetzt wird, seine Energie an den äußeren Stromkreis mit hohem Wirkungsgrad abzugeben. Wo nur sehr kleine Energiemengen erforderlich sind, bei geringer Spannung, ist ein geringer Widerstand nicht so nötig, bei anderen Verwendungsarten mit großen augenblicklichen Anforderungen an die Batterie ist er dagegen sehr wichtig. Geringer innerer Widerstand wird gewöhnlich durch eine große Stromstärke angezeigt, d. h. die Fähigkeit eines Elementes, einen starken Strom bei Kurzschluß durch ein Ampèremeter zu liefern. Möglichst geringe Polarisation und die Fähigkeit, sich wieder zu erholen, sind ferner zwei weitere Faktoren, auf welche die Fabrikanten beim Anpreisen ihrer Trockenelemente besonders hinweisen.

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[1] Vortrag, gehalten auf der 16. Generalversammlung der American Electrochemical Society in New York City, 28.—30. Oktober 1909.

Es ist nicht zu sagen, welche von diesen Eigenschaften die wertvollste ist, da die relative Wichtigkeit von dem Zweck, dem das Trockenelement dienen soll, abhängt. Zu den weniger wichtigen Eigenschaften, die man bei der Herstellung zu erstreben sucht, gehören: vollständige Undurchlässigkeit für die Flüssigkeit, möglichst geringe Zunahme des Widerstandes bei niedriger Temperatur, möglichst leichtes Einschalten in den Stromkreis und ein gutes Aussehen des Elementes.

Die Faktoren, von welchen diese genannten Eigenschaften abhängen, sind folgende: Das zur Herstellung verwendete Material, die Mengenverhältnisse der Materialien, die chemischen und physikalischen Eigenschaften dieser Materialien, sowie die Art des Aufbaues. Trotzdem 40 Millionen oder noch mehr Trockenelemente jährlich in den Vereinigten Staaten von Amerika hergestellt werden, sind nur wenig wissenschaftliche Untersuchungen zum genaueren Studium der verschiedenen Einzelfaktoren, welche die Qualität eines Elementes beeinflussen, unternommen worden, wenn man von wertlosen Veröffentlichungen absieht. Anderseits ist unzweifelhaft wissenschaftlich auch in dieser Hinsicht viel geleistet worden, wenn man die augenfälligen Verbesserungen in Betracht zieht, die an den Elementen geschaffen worden sind. Es scheint, als ob die Trockenelementfabrikanten, denen das größte Verdienst hierbei zufällt, nicht geneigt sind, über die Konstruktion des Trockenelementes bis ins Kleinste hinein zu diskutieren. Etwa 80 % der hergestellten und benutzten Trockenelemente haben die sogen. Größennummer 6, sind von zylindrischer Form und besitzen einen Zinkbehälter von 6 Zoll Höhe und $2^1/_2$ Zoll Durchmesser. Was den zylindrischen Zinkbehälter anbelangt, so besteht in den Maßen und der Konstruktion eine auffallende Gleichmäßigkeit, der Hauptunterschied liegt in der Dicke des Zinks, die zwischen der Zinkplattenstärke Nr. 7 bis Nr. 11 schwankt. Bei allen Elementen wird ein Kohlestab als Kathode verwendet. Bei einzelnen Formen der Elemente ruht dieser Kohlestab auf der papiernen Bodenschicht, bei anderen bleibt er einen halben Zoll vom Boden entfernt. Oben wird der Kohlestab durch eine Pechdichtung geführt und trägt an seinem Ende eine Messingkappe oder -schraube, die den positiven Pol des Elementes darstellt. Bisweilen sind die verwendeten Kohlen glatt, von zylindrischer Form, während andere zur Erzielung einer größeren Oberfläche gerippt oder geriffelt sind. Eine weitere auffallende Ähnlichkeit der meisten Trockenelemente besteht hinsichtlich der Stoffe, mit denen der Zinkbehälter angefüllt wird. Dagegen erstreckt sich diese Ähnlichkeit nicht mehr auf das Verhältnis der Mengen dieser Stoffe zueinander und auf die Art der Füllung der Behälter. Es ist unmöglich, hie über alle die Vorschriften zu berichten, die für die besseren Arten der im Gebrauch befindlichen Elemente bestehen. Nachstehende Stoffe nebsr Angabe ihrer Mengenverhältnisse geben ein Bild der Durchschnittst mischung der bekanntesten Arten der Trockenelemente: 5 kg Mangandioxyd, 5 kg Retortenkohle oder Graphit, oder auch beide zusammen- 1 kg Salmiak oder 0,5 kg Chlorzink. Dazu kommt eine genügende, Menge Wasser, die von der Trockenheit obiger Stoffe, ihrer Feinheit und der Qualität der Papierauskleidung usw. abhängig ist. Während dies die wesentlichsten Bestandteile sind, gibt man außerdem häufig noch weitere Stoffe zu, wie z. B. Stärke oder andere teigartige Massen, um den Kontakt des Elektrolyten mit dem Zink inniger zu gestalten und um eine bessere Gleichmäßigkeit innerhalb der Füllung hervorzurufen. Manchmal findet sich ein Zusatz von Quecksilber, um das Zink durch Amalgamation länger haltbar zu machen.

Bei Verwendung der obengenannten Stoffe und der angegebenen Mengenverhältnisse können die Elemente brauchbar oder aber auch praktisch wertlos sein, was von mehreren Faktoren abhängig ist. Allgemein betrachtet man die Reinheit der verwendeten Körper als besonders erforderlich; aber kaufmännische Erwägungen schließen die Verwendung chemisch reiner Stoffe aus. Die üblichen Anforderungen setzen für das Mangandioxyd eine granulierte oder gepulverte Sorte mit über 85 % MnO_2 und unter 1 % Eisen fest. Diese Sorte ist leicht erhältlich und läßt sich bei geeigneter Auswahl und Konzentration auf 92 % bringen. Die physikalischen Eigenschaften, Porosität und Größe der Körner sind ebenfalls von Wichtigkeit. Die Menge des wirksamen MnO_2 ist je nach der verwendeten chemischen Prüfung eine verschiedene, und die durch Untersuchung ermittelte Menge ist durchaus nicht gleich der unter den in dem Element herrschenden Bedingungen tatsächlich zur Wirkung gelangenden. Bei Akkumulatoren ist Bleisuperoxyd nur dann ein wirksamer Stoff, wenn es sich in direkter Berührung oder ganz in der Nähe des Gitterwerkes der positiven Platte befindet, und auch die Wirksamkeit des MnO_2 ist bis zu einem gewissen Grade abhängig von dem Kontakt mit dem leitenden Kohlestab, der die negative Elektrode darstellt. Ferner ist klar, daß eine möglichst vollständige Durchdringung der MnO_2-Teilchen mit dem Elektrolyten nötig ist, um die gesamte Masse wirksam zu machen, weshalb die Porosität von großer Wichtigkeit ist. Es ist vielleicht überflüssig, darauf hinzuweisen, daß der Zweck des Mangans darin besteht, die Depolarisation zu bewirken und dadurch die Spannung des Elementes während der Entladung aufrecht zu erhalten; die als möglichst geringe Polarisation und schnelle Regenerierungsfähigkeit bezeichneten Eigenschaften richten sich nach der Menge und der Ausnutzbarkeit des verwendeten MnO_2. Um die MnO_2-Masse leitend zu machen und die Kathodenoberfläche zu vergrößern, wird die Kohle in gepulverter oder granulierter Form verwendet. Retortenkohle, Koks, Petrolkoks und gemahlene Bogenlampenkohlen und Elektroden sind die gewöhnlich dazu verwendeten Arten; die größten Abweichungen der Trockenzellen untereinander werden durch die verschiedenen Eigenschaften dieser Kohlensorten hervorgerufen. Salmiak wird allgemein in sehr reinem Zustande verwendet und muß trocken und fein gemahlen sein, um eine gute Mischung mit der Kohle und dem Mangansuperoxyd zu erzielen. Auch das Zinkchlorid muß sehr rein und frei von Eisen sein. Gewöhnlich wird Zinkblech zur Herstellung der Anode verwendet und bildet gleichzeitig den Behälter; auch hier ist reines Material von Wichtigkeit. Die Anode steht mit dem Elektrolyten in Berührung durch eine mit Lösungen von Zink- und Ammoniumchlorid getränkte Papierschicht. Der Idealzustand wäre der, daß die

Korrosion des Zinks nur im Verhältnis steht zu der nach außen abgegebenen Strommenge. Es wird aber eine dieses Mengenverhältnis übersteigende Korrosion durch Lokalströme hervorgerufen, und eins der Hauptprobleme der Trockenelementindustrie besteht darin, diese lokalen Ströme auf das Mindestmaß herabzusetzen. Die Lokalströme haben nun zahlreiche mögliche Ursachen. Irgend ein anderes neben dem Zink vorhandenes Metallteilchen, das mit der Oberfläche der Zinkelektrode in Berührung kommt, erzeugt ein galvanisches Element für sich. Wenn zum Befestigen der Wände und des Bodens Lötmittel verwendet worden sind, so gelangt häufig etwas davon in das Element, und dies wird sehr oft als ein Grund des lokalen Angriffes auf das Zink betrachtet. In Wirklichkeit aber ist das Lötmittel zwar elektronegativ gegen Zink, aber es besteht aus zwei Metallen, Blei und Zinn, die in der Spannungsreihe dem Zink so nahe stehen, daß ein Strom auf Kosten des Zinks fast völlig unterbleibt. Einige Versuchselemente aus auf der Innenseite verlötetem Zinkblech zeigten, wenn überhaupt, nur geringe Verschlechterung infolge lokaler Ströme selbst nach monatelangem Stehen. Anderseits ist aber, wenn das galvanische Element aus Kupfer oder Eisen mit Zink besteht, die Überspannung nicht groß genug, um die Strombildung zu verhindern.

Kupfer findet gewöhnlich Eingang in das Trockenelement durch Korrosion der Messingteile der Pole und Diffusion des Kupferchlorids in das Element. Beim Zusammentreffen mit dem Zink schlägt sich das Kupfer nieder, und es bildet sich eine galvanische Kette. Wird eine kleine Menge Kupfer in ein noch neues Trockenelement gebracht, so verdirbt es dieses in weniger als 24 Stunden, und das gesamte Zink wird dabei so völlig zerstört, als ob das Element bis zur äußersten Erschöpfung gebraucht worden wäre. Eisen ist weniger schädlich als Kupfer, und es ist sogar eine Frage, wie weit es sich praktisch empfiehlt, es vollständig aus dem Element fernzuhalten. Mangandioxyd und Kohle sollen der allgemeinen Ansicht nach um so brauchbarer sein, je geringer ihr Eisengehalt ist. Aber es kann eigentlich gar nicht schädlich wirken, solange es nicht in Lösung geht, und dies kann kaum eintreten, da durch Freiwerden des Ammoniaks in der Zink- und Ammoniumchloridlösung ein Ausfällen des Eisens bewirkt wird. Bisweilen kommt es vor, daß etwas von den Füllstoffen, Mangandioxyd und Kohle, zwischen die Papierschicht und das Zink gerät. Dies bewirkt natürlich die Entstehung schädlicher galvanischer Ketten; jedes solcher Partikelchen ruft eine Zerstörung des Zinks in gewissem Umkreise hervor. Ungleichmäßigkeiten im Zink selbst bewirken Unterschiede im Potential und veranlassen die Bildung galvanischer Ketten.

Sehr oft besteht die Ursache von Lokalströmen, die sehr schwer zu kontrollieren ist, in dem Zutritt der Luft zur wirksamen Oberfläche. Einige Messungen der alsdann auftretenden Potentiale wurden vorgenommen, durch Zwischenlegen eines mit dem Elektrolyten getränkten Papieres zwischen zwei Zinkblechstücke, dessen Ränder vorher zwecks Abhaltung der Luft mit Ölfarbe bestrichen worden waren. Darauf wurden die Zinkbleche fest aufeinandergepreßt und die Potentialdifferenzen an einem Elektrometer gemessen. Zwei

Stücke aus verschiedenen Stellen eines Bleches gaben nur geringe Potentialdifferenzen, und zwar betrug der Höchstwert einer Reihe von Versuchen 0,002 V. und gewöhnlich noch darunter. Beim Erhitzen und langsamen Abkühlen eines der Zinkstücke zwecks Erhöhung des Einflusses der Löttemperatur wurden Potentialdifferenzen zwischen + 0,012 und — 0,012 beobachtet. Erhitzen und sehr schnelles Abkühlen durch Abschrecken ergab einen viel geringeren Einfluß auf das Potential. Lot auf der Innenseite einer der Versuchselektroden rief eine Beeinflussung hervor, die sich auf 0,004 bis 0,007 V. belief. Der Einfluß der an die Elektrodenoberfläche gelangenden Luft wurde geprüft durch Durchlöchern einer der Versuchselektroden. Die ersten Messungen zeigten ein Potential von 0,0026 V., das allmählich zunahm und nach zwei Tagen 0,024 V. betrug, wobei die durchlöcherte Platte positiv war. Diese Potentialdifferenz ist hoch genug, um eine schnelle Abnutzung des Elementes zu bewirken. Es ergibt sich hieraus deutlich die Notwendigkeit, das Eindringen der Luft ins Innere des Elementes möglichst zu verhindern. Selbst wenn wir annehmen, daß alle Ungleichheiten der Zinkelektroden beseitigt sind, so ist dennoch die Möglichkeit lokaler Ströme vorhanden infolge von Ungleichheiten in der Elektrode auf der anderen Seite des getränkten Papieres. So sind Ungleichmäßigkeiten in der Mischung von Nachteil. Einige Fabrikanten bringen ferner den Kohlestab in direkte Berührung mit dem getränkten Papier am Boden des Elementes. Dies muß notwendigerweise Potentialdifferenzen hervorrufen, und eine Messung ergab dabei den Wert von nicht weniger als 0,176 V., und zwar in der Weise, daß der Strom von der Kohle durch das Papier zum Zink geht, dann durch das Papier zum Mangangemisch und zurück zur Kohle. Zur Vermeidung dieser Quelle lokaler Ströme muß die depolarisierende Mischung zwischen alle Teile der Kohlenoberfläche und des Papiers sorgfältig zwischengestampft werden, was ja auch meistens geschieht.

Gewöhnlich nimmt man seine Zuflucht zur Amalgamation des Zinks, doch ist es durchaus fraglich, ob ein wesentlicher Vorteil durch Einführung des Quecksilbers in die Zelle erreicht wird. Gewohnheitsgemäß wird der Kohlestab als Kathode angesehen, und man zieht deswegen die größere geriefelte Form der kleinen zylindrischen Oberfläche vor. Der Kohlestab steht nun aber im Kontakt mit der ihn umgebenden Masse — Kohle, Graphit und Braunstein —, die selbst beim Anfeuchten durch den Elektrolyten ein Leiter erster Klasse ist. Wichtiger ist es daher, als aktive Kathodenoberfläche denjenigen Teil der Mischung anzusehen, der unmittelbar am Papier liegt. Die Kathode ist eine Verbindung aus dem innigen Gemisch von leitender Kohle und Graphit mit Manganoxyd, und die elektromotorische Kraft des Elementes ist die Summe der Elektrodenpotentiale, 0,56 V. für das Zink und über 1 V. für das Kohle-Mangan-Gemisch, zusammen also 1,56 V.

Während das Element an den äußeren Stromkreis Strom abgibt, nimmt diese Spannung ab, und zwar hängt die Geschwindigkeit der Abnahme von dem Betrag des entnommenen Stromes ab. Wenn das Mangandioxyd nicht wäre, würde die Spannung sehr schnell sinken, und der Wert des Elementes hängt demnach in erster Linie von dem aktiven Mangandioxyd oder dem Depolarisator ab. Dieses Mangandioxyd wird verbraucht, wie man gewöhnlich annimmt, und dabei zu Mn_2O_3 reduziert; es wird bei dieser Umwandlung unwirksam sowohl als Depolarisator wie als Leiter. Wahrscheinlich besitzt das MnO_2 genügend metallische Leitfähigkeit, um seinen Teil zu der Leitfähigkeit des Elementes beizusteuern; wenn es aber in das niedere Oxyd übergeführt ist, verliert es diese. Es wird auf diese Weise unwirksam und nimmt nur wertvollen Platz fort. Natürlich ist anzunehmen, daß das MnO_2 in seinem äußeren, dem Papier am nächsten gelegenen Teile zuerst reduziert wird; die Wirkung setzt sich dann nach innen bis zu einer gewissen Tiefe weiter fort, die von verschiedenen Faktoren abhängig ist, wie z. B. von der innigen Berührung zwischen Kohle und MnO_2, von der Reinheit, Feinheit nnd Porosität des letzteren usw. Wenn das MnO_2 metallische Leitfähigkeit besitzt und in Berührung steht mit der leitenden Kohle, so ist, befeuchtet man beide mit dem Elektrolyten, die Möglichkeit vorhanden, daß auch eine chemische Wirkung eintritt infolge der Bildung einer galvanischen Kette.

Eine Untersuchung darüber, was sowohl chemisch wie elektrisch innerhalb des Trockenelementes vor sich geht, während es arbeitet und während es unbenutzt steht, würde ein ausgezeichnetes Thema zu einer analytischen Arbeit bilden. Während die chemischen Reaktionen im Trockenelement oder in Elementen vom Leclanché-Typ in den Lehrbüchern meistens recht einfach erklärt werden, dürfte eine sorgfältige Untersuchung ergeben, daß diese Einfachheit durchaus nicht besteht. Die Ausbeute eines Trockenelementes ist gleich den Ampère-Stunden multipliziert mit der Spannung. Die Strommenge, die ein typisches Element liefert, das durch Kurzschluß während einer Stunde erschöpft wird, beträgt etwa 10 Ampère-Stunden. Sie kann aber bis auf 30 Ampère-Stunden oder mehr steigen, wenn der Strom ihm langsamer entnommen wird. Die Spannung des offenen Stromkreises ist immer gleichmäßig 1,5–1,6 Volt. Die nutzbare oder effektive Spannung ist kleiner als 1,5 Volt, und der Durchschnitt von 1 Volt an den Polen ist der richtigste Wert während einer Entladung, die etwa 30 Ampèrestunden liefern soll. Mit einer elektromotorischen Kraft von 1 Volt und einer Stromabgabe von 30 Ampèrestunden beträgt der Energiewert eines Trockenelementes 30 Watt-Stunden.

Die Spannung zwischen den Polklemmen während der Stromabgabe hängt natürlich von einer Anzahl Faktoren ab, deren wichtigste die Aktivität der Depolarisationsmasse und der innere Widerstand des Elementes sind. Die erstere wächst beim Gebrauch des Elementes, und noch ausgeprägter ist das Anwachsen des Widerstandes mit der Anzahl der abgegebenen Ampèrestunden. Es wird allgemein angenommen, daß die Widerstandszunahme durch das Austrocknen des Elementes bewirkt wird, jedoch ist das von weit geringerer Wichtigkeit im Vergleich zu anderen Faktoren. Dazu gehört, wie wir gesehen haben, die teilweise Reduktion des MnO_2, ferner die Anhäufung unlöslicher Verunreinigungen des Zinks und der verschiedenen basischen Salze und

Doppelsalze (die durch elektrolytische Korrosion enstanden sind) auf der Oberfläche zwischen dem Papier und dem Zink. Bei der Herstellung des Elementes wird das Papier mit einer Lösung von Zink- und Ammoniumchlorid gesättigt. Infolge der Korrosion des Zinks kommt nunmehr Zinkchlorid hinzu. Die zunehmende Konzentration des $ZnCl_2$ in Gegenwart des Ammoniumchlorids bietet gerade die erforderlichen Bedingungen zur Bildung verschiedener Doppelchloride, von denen einzelne weniger leicht löslich sind als die einfachen Chloride. Diese unlöslichen Doppelchloride dringen in die Poren und Zwischenräume des Papiers, verdrängen den Elektrolyten und erhöhen den Widerstand. Wenn Ammoniak frei wird, so kann dieses mit dem $ZnCl_2$ reagieren unter Bildung eines Niederschlages von $Zn(OH)_2$, der für das Element schädlich ist, falls nicht genügend Ammoniak zu seiner Wiederauflösung vorhanden ist. Daß diese schädliche Wirkung bei dem Papier auftritt und nach innen hin zur Kohle fortschreitet, ist erwiesen, da man bei der Untersuchung eines verbrauchten Elementes gewöhnlich eine harte Kruste von $^1/_8$ Zoll oder noch stärker gerade an der Innenseite des Papiers findet.

Zweifellos lassen sich Verbesserungen an Trockenelementen erzielen durch Herabsetzung einer derartigen Anhäufung unlöslicher Nichtleiter. Es ist anzunehmen, daß dieser durch Doppelchlorid hervorgerufene Niederschlag vermieden werden kann durch Verwendung von NH_4Cl in Elektrolyten allein, und tatsächlich ließ sich in solchem Falle eine etwas größere Ampère-Stunden-Angabe erzielen. Anderseits hat das aber den Nachteil einer Verkürzung der Lebensdauer des Elementes bei offenem Stromkreis im Gefolge, und die Anwesenheit von $ZnCl_2$ im Elektrolyten vermindert in merklichem Grade die Lokalströme. Zweifellos sind während der beiden letzten Jahre auffällige Verbesserungen an den Trockenzellen erzielt worden, und es ist kein Grund zu der Annahme vorhanden, daß nicht noch weitere Vervollkommnungen erzielt werden. Vom technischen Standpunkt aus ist die Notwendigkeit von Verbesserungen ebenso groß wie deren Möglichkeit. Die gewöhnlichen und völlig unzulänglichen Methoden, die Trockenzellen nach der Meilenzahl zu schätzen, wenn sie zur Zündung bei Automobilen gebraucht werden, oder nach der Anzahl Monate, während der sie im Telephondienst benutzt wurden, oder auch nach der Funkenzahl, also alles Methoden, die abhängig von der Art des Apparates sind, in dem sie gebraucht werden, sollten sämtlich einer Beurteilung auf Grund ihrer Leistung Platz machen, was aber nur erreicht werden kann, wenn vorher Normalmethoden dafür festgelegt und allgemein angenommen werden.

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Hardness Tests on Alloys of Nickel and Copper with Electrolytic Iron—I.

By G. A. Roush.

While hardness as a *prime* factor is limited mainly to tool steels, it is still of sufficiently great importance in so many other materials that any investigation of this property is of interest. The relative hardness of any material varies with the kind of stress to which it is subjected. Hence different methods of measuring hardness, employing different methods of applying the testing stress will give results which are not strictly comparable. A series of samples arranged according to increasing hardness as measured by machining in a lathe will not necessarily remain in the same order when tested by a compression method. For this reason it is desirable that in any particular test the stress applied may be as nearly as possible similar to the stress to which the material will be subjected in use. In this investigation, however, no one particular use of the materials in hand was under consideration, so any method by which a series of comparative results could be obtained was sufficient.

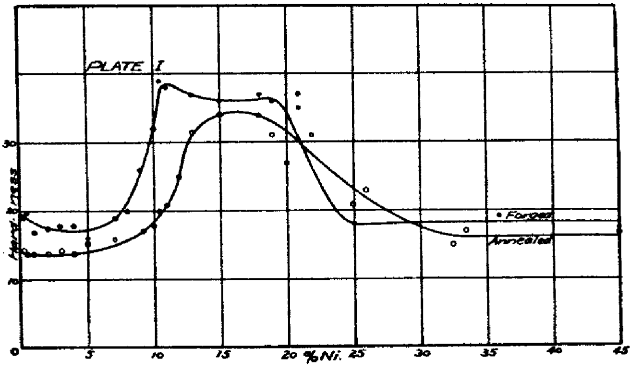

FIG. I.—HARDNESS OF FORGED AND ANNEALED NICKEL ALLOYS.

The method used for determining the hardness was the scleroscope method devised by Albert F. Shore in 1906. The scleroscope was first put on the market in 1907, and is now used quite extensively in the commercial field as a means of determining hardness. The instrument consists of a vertical glass tube provided with a graduated scale suspended over a steel anvil, on which the sample to be tested is placed; a small steel plunger with a diamond point, suspended in the top of the tube, is allowed to drop on the sample clamped on the anvil, the rebound of the plunger being read off on the scale at the back of the tube. When the plunger reaches the surface of the metal under test it carries a certain amount of potential energy, and the weight of the plunger, the height of the fall and the area of striking surface are so proportioned that in all cases this energy is sufficient to exceed the elastic limit of any material which may be under test. This being the case, the material on receiving the impact of the plunger is stressed beyond its elastic limit and given a permanent deformation. If the elastic limit of the material under test is high, the excess energy of the plunger is small, and only a small dent is made on its surface. That portion of the material immediately adjoining the deformed portion has then been stressed only up to its elastic limit, and in regaining its original form causes the plunger to rebound a certain distance. If the metal under test has a low elastic limit a smaller portion of the energy of the falling plunger is used in overcoming the elasticity, and a greater portion is used in displacing metal. The stress of the adjoining metal is then only sufficient to give the plunger a small rebound. This rebound is then taken to represent the hardness of the material under test.

Basing his conclusions on this line of reasoning, Shore makes the statement[1] that the curve for hardness, as determined by the scleroscope, is very nearly parallel to the curve of elasticity, but since the value obtained in any test for hardness depends to a certain extent on the method used to obtain the result, there is liability for considerable variation.

Preparation of the Materials.

This investigation covers a series of alloys of nickel and iron up to a nickel content of 50 per cent, and of copper and iron up to a copper content of 8 per cent, being a part of the extended study of electrolytic iron and iron alloys that is being carried on in the Chemical Engineering Laboratories of the University of Wisconsin, under grant from the Carnegie Institute. The results are of particular value in that they are obtained from materials the history of which is completely known, and which have been subjected to a number of other tests.[2]

The preparation of the electrolytic iron is sufficiently familiar that it does not require particular notice here. The iron used in the preparation of the alloys, according to several analyses,

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[1] *Amer. Mach.*, Nov. 14, 1907.

[2] See a, Physical Properties of Iron-Copper Alloys, Burgess and Aston, Trans. Amer. Electrochem. Soc., 16, 241-256. 1909.
b, The Magnetic and Electrical Properties of Iron-Nickel Alloys, Burgess and Aston, Met. and Chem. Eng., 8, 23-26, 1910.
c, The Magnetic and Electrical Properties of Iron-Copper Alloys, Burgess and Aston. Met. and Chem. Eng., 8, 79-81, 1910.
d, The Strength of the Alloys of Nickel and Copper with Electrolytic Iron, Burgess and Aston, Bull. of Univ. of Wis., Eng. Series, Vol. 6, No. 2.

showed a purity of about 99.97 per cent, the latest analysis being as follows:

Carbon	0.000
Sulphur	0.003
Phosphorus	0.003
Silicon	0.002 or less.
Manganese	0.020
Iron, by difference	99.972 per cent.

The alloys were prepared by melting the iron with the calculated mounts of the added substance in magnesia crucibles in an electric resistance furnace, as described in the papers mentioned above. The amount of carbon absorbed in the melting has been shown by several different analyses to be less than 0.10 per cent, so that the hardening observed can be accounted as due to the addition elements.

The number of bars tested of each composition varies from 1 or 2 up to 12 or 15, and in each case 10 or more readings were taken on each bar, and averaged for the final result. Considerable variation was noticed in the various bars and in different parts of the same bar, due to irregularities in forging and annealing, but the general averages show a fair degree of uniformity.

Not all of the finished alloys were subjected to analysis, but a sufficiently large number of both the nickel and the copper series was analyzed to make one safe in making the assertion that all were sufficiently close to the calculated composition for the requirements of an investigation of this kind. A few analyses typical of the series are given below.

Nickel Alloys.

Mark.	Calculated.	Found.
144C	0.25	0.27
144F	2.0	1.93
144J	7.0	7.05
157H	12.0	12.07
166G	22.0	22.11
166L	35.0	35.09

Copper Alloys.

Mark.	Calculated.	Found.
158A	0.2	0.202
147H	1.0	1.006
158I	4.0	3.990
147U	7.0	7.050

All samples were tested in the forged condition and after annealing at 900° C.

Nickel-Iron Alloys.

There are no investigations described in the literature which are strictly comparable to the results given here, since in other investigations there have been present considerable quantities of impurities which had to be taken into account while in this case these impurities are kept down to a point where the variations observed may be ascribed to the nickel alone.

The hardness tests, as shown, bear out the general qualitative observations made by Burgess and Aston in their work on the same alloys.[3] In the forged condition up to 7 per cent Ni the curve is concave and lies slightly below the value found for pure iron. From 7 per cent to 11 per cent there is a rapid rise to a maximum, dropping off slightly to 19 per cent, and then a rapid drop up to 25 per cent to about the value for pure iron, where it remains practically constant. In the annealed condition the curve starts at about the value for pure iron, rising gradually to 10 per cent, then abruptly to a maximum at 16 per cent, followed by a sharp decline up to 32 per cent, and then remains practically constant at a value slightly higher than that of pure iron. As a rule, the variations noted are not large. From 21 per cent to 30 per cent the curve for the annealed samples lies above that for the forged samples. Aside from this, the values found for the annealed samples were about what would naturally be expected as deduced from the curve for the forged samples.

Results on the forged nickel are given in Table I, and on the annealed nickel in Table II, both being plotted together in Plate I.

TABLE I.

Hardness of forged nickel samples.

Per cent Ni.	Number.	Maximum.	Minimum.	Average.
0.25	3	20	15	18
0.5	3	21	17	20
1.0	3	19	15	17
2.0	4	18	17	17½
3.0	5	20	16	18
4.0	5	21	16	18
5.0	5	17	15	16
7.0	5	21	18	19
8.0	5	21	19	20
9.0	6	28	21	26
10.0	5	34	26	32
10.5	3	44	34	39
11.0	8	41	32	38
12.0	5	36	34	35
13.0	6	39	35	37
15.0	3	37	35	36
18.0	3	45	38	37
19.0	2	36	35	35½
20.0	1	..	27	27
21.0	3	40	33	37
25.0	2	20	16	18
36.0	3	20	19	19
45.0	3	20	15	17

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[3] See reference above, 2d. p. 10.

Copper-Iron Alloys.

As in the nickel-iron series, quantitative measurements confirm the qualitative observations made on these materials.[4] In the forged condition up to 1½ per cent the hardness curve is concave and lower than that of pure iron. From 1½ to 2½ per cent it proceeds in a straight line, a trifle above that for pure iron, and from 2½ per cent on there is a continued rise. In the annealed condition the hardness increases in a straight line with only a very slow rise throughout the series. In the copper series the variations of the individual readings from the mean were much larger than in the nickel series.

The results from the forged samples are given in Table III and from the annealed samples in Table IV. Both series of results are plotted together in Plate II.

TABLE II.

Hardness of annealed nickel samples.

Per cent Ni.	Number.	Maximum.	Minimum.	Average.
0.25	5	15	14	14½
0.5	5	15	13	14
1.0	4	16	12	14
2.0	4	15	13	14
3.0	5	15	13	14½
4.0	6	15	12	14
5.0	7	17	14	15½
7.0	6	17	15	16
8.0	6	18	15	16
9.0	8	19	15	17
10.0	5	19	17	18
10.5	7	22	18	20
11.0	6	24	18	21
12.0	5	26	23	25
13.0	10	36	26	31½
15.0	3	35	32	34
18.0	6	36	31	34
19.0	5	35	28	31
21.0	2	35	34	34½
22.0	1	..	31	31
25.0	1	..	21	21
26.0	1	..	23	23
35.0	1	..	15	15
36.0	1	..	17	17
45.0	2	19	16	17

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[4] See reference above, 2d. p. 20.

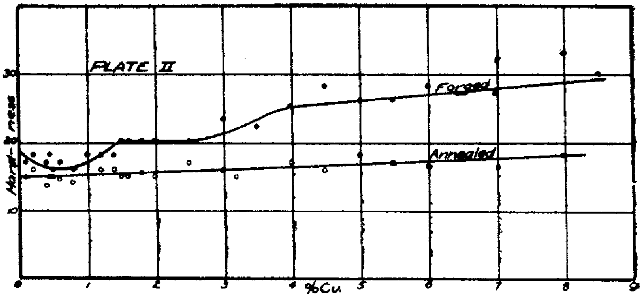

FIG. 2.—HARDNESS OF FORGED AND ANNEALED COPPER ALLOYS.

TABLE III.

Hardness of forged copper samples.

Per cent Cu.	Number.	Maximum.	Minimum.	Average.
0.1	6	20	17	18
0.2	6	20	16	18
0.4	3	18	17	17
0.45	4	20	17	18
0.5	1	..	16	16
0.6	3	18	16	17
0.8	4	18	15	16
1.0	10	24	16	18
1.2	2	20	16	18
1.4	3	21	17	18
1.5	3	21	19	20
1.6	4	22	18	20
1.8	6	21	19	20
2.0	6	21	17	20
2.5	3	21	19	20
3.0	7	25	21	23
3.5	1	..	22	22
4.0	7	28	22	25
4.5	2	30	26	28
5.0	4	30	23	26
5.5	2	28	25	26
6.0	3	30	25	28
6.45	4	36	25	27
7.0	4	29	24	27
7.5	4	27	24	26
8.0	2	37	29	33
8.5	1	..	30	30

TABLE IV.

Hardness of annealed copper samples.

Per cent Cu.	Number.	Maximum.	Minimum.	Average.
0.1	8	17	14	15
0.2	8	17	13	16
0.4	3	15	12	13½
0.45	7	16	13	15
0.5	2	17	13	15
0.6	3	15	14	14½
0.8	5	15	11	14
1.0	15	22	12	15
1.2	1	..	16	16
1.4	1	..	16	16
1.5	10	16	13	15
1.6	2	15	15	15
1.8	2	16	15	15½
2.0	13	16	13	15
2.5	4	19	16	17
3.0	14	18	14	16
3.2	1	..	15	15
4.0	11	18	15	17
4.5	3	18	15	16
5.0	8	20	15	18
5.5	3	20	16	17
6.0	6	23	14	16½
6.45	6	21	16	18½
7.0	7	19	14	16½
7.5	9	18	11	15½
8.0	2	19	17	18

General Discussion.

Kuranow and Zemezuzny[5] have attempted to correlate the hardness of alloys with the metallographic condition of the material. Their conclusions are that when two metals form a solid solution the hardness increases and the curve passes through a maximum which generally coincides with the maximum electrical resistance; when the two metals form a mechanical mixture of two components the hardness curve will be a straight line; a definite compound may have a hardness either higher or lower than either of the constituent metals. These conditions are fulfilled, however, in neither the copper nor the nickel series of alloys. In Plates III and IV are plotted the hardness and the electrical resistance for comparison.[6] Curve I shows the resistance in microhms per cubic centimeter, Curve II the hardness of the annealed samples, and Curve III the hardness

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(5) *Jour. Russ. Phys. Chem. Ges.*, 40, 1067, 1908; *Zeit. Anorg. Chem.*, Oct., 1908; *Jour. Soc. Chem. Ind.*, 93, 1909.

(6) Values for electrical resistance are those measured by Burgess and Aston for these same samples; see reference 2b.

of the forged samples. In the iron-nickel series a solid solution is formed throughout the series, and a rise in hardness is to be expected. So far the rule holds good, but the maximum hardness is between 10 per cent and 20 per cent, while the maximum in the resistance curve is above 30 per cent.

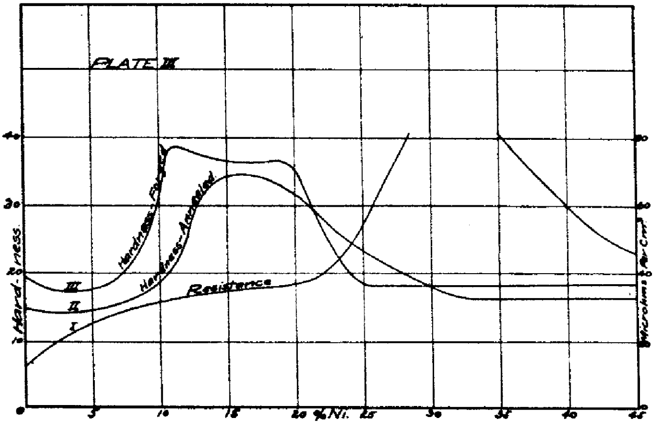

FIG. 3.—HARDNESS AND RESISTANCE OF NICKEL ALLOYS.

In the iron-copper series a solid solution is formed up to 3.5 per cent Cu; above that point the two metals are present as a mechanical mixture of two components. According to this a rise of hardness is to be expected up to 3.5 per cent, the curve bearing a maximum at 1.5 per cent, followed by a straight line beyond 3.5 per cent. The hardness, however, in the forged sample lies below that of pure iron, rather than above, the curve bears no definite maximum, and is not a straight line beyond the range of the solid solution. In the annealed samples the straight line curve persists throughout the series.

Portevin[7] refers to the above conditions in his investigation of the electrical resistance of various ternary steels, and after comparing his results with the hardness obtained by Guillet[8] on similar steels, reports a greater variation from this law for the nickel steels than for any of the other materials that he examined.

Conclusions.

From the facts here presented the following conclusions may then be drawn:

1. The addition of nickel to iron gives a maximum range of hardness between 10 per cent and 20 per cent.

2. The addition of copper to iron, up to 8 per cent, gives a gradual, but irregular, increase in hardness.

3. The nickel and copper alloys in the range studied are ex-

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[7] Rev. de Metall., 6, 1304, 1909.

[8] Les Aciers Speciaux, Dunod, Paris, 1904.

ceptions to the law of hardness formulated by Kuranow and Zemezuzny.

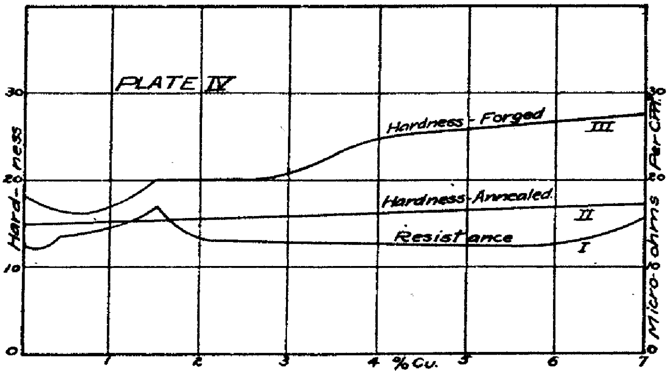

FIG. 4—HARDNESS AND RESISTANCE OF COPPER ALLOYS.

The results of a similar investigation on the effect of the addition of nickel and copper together to iron are in the course of preparation and will be ready for presentation shortly.

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Hardness Tests on Alloys of Nickel and Copper with Electrolytic Iron.—II.

BY G. A. ROUSH.

In a previous paper[1] the writer has discussed the effects of the addition of nickel and of copper to electrolytic iron, and the present paper is a continuation of this investigation, giving the effects of the addition of these elements together to iron, it being a part of the extended study of electrolytic iron alloys that is being carried out in the Chemical Engineering Laboratories of the University of Wisconsin, under grant from the Carnegie Institution.

In view of the results obtained from the nickel and copper series of alloys with electrolytic iron, it is of interest to note the results of combining both metals in one alloy. This particular part of the investigation is of interest in two ways: first, in view of the possibility of the hardening properties of the two metals being more or less additive so that the copper will increase the already high values obtained with the nickel alloys, and, second, if the copper does not actually detract too much from the value of the nickel additions, the probability of being able to substitute the new commercial alloy, Monel metal, in place of the more expensive nickel as the addition agent.

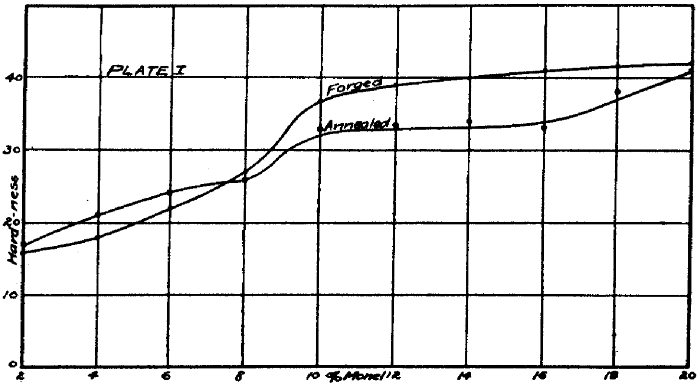

FIG. I.—HARDNESS OF FORGED AND ANNEALED MONEL ALLOYS.

With this in view, alloys were made, in the same way as before, with from 2 per cent to 20 per cent of Monel metal and tested for hardness by means of the scleroscope. On account of the close agreement that was noted between the added quantities and the actual analysis in the previous series and the fact that Monel, being a commercial alloy, is subject to slight variation, it was not thought necessary to make any analyses of

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[1] This journal, August, 1910.

these alloys, but to simply record them according to the proportions of Monel that had been added to the melt. In the calculation of the ultimate composition of the alloys the average analysis of the Monel was taken as showing two-thirds nickel and one-fourth copper, the impurities not being taken into consideration since they could not be controlled.

The hardness curve for the forged samples rises rather rapidly up to 10 per cent, and then more gradually to the end of the series. In the annealed samples the rise up to 10 per cent is not quite so abrupt, and from 10 per cent to 16 per cent is practically a straight line; from 16 per cent to the end of the series the rise is about the same as that below 10 per cent. The variation of the readings from the mean is less in this series than in either the nickel or copper series. Up to 7½ per cent the curve for the annealed samples lies above that for the forged samples, and the indications are that the curves would cross again slightly above 20 per cent.

The results are given in Tables I and II, both being plotted together in Fig. 1.

TABLE I.—HARDNESS OF FORGED MONEL ALLOYS

Per cent Monel.	Number,	Maximum.	Minimum.	Average.
2	1			16
4	3	18	18	18
6	1			22
8	3	28	26	27
10	3	42	34	37
12	3	40	37	39
14	1			40
16	3	42	40	41
18	2	43	40	41½
20	2	43	41	42

TABLE II.—HARDNESS OF ANNEALED MONEL ALLOYS.

Per cent Monel.	Number,	Maximum.	Minimum.	Average.
2	2	17	17	17
4	3	21	21	21
6	2	25	23	24
8	3	28	24	26
10	2	34	32	33
12	2	34	33	33½
14	3	40	31	34
16	3	41	31	33
18	3	42	35	38
20	3	41	40	41

In Figs. 2 and 3 are given the comparisons between the single additions of nickel and copper, and their addition together. First (I) the base line for iron is given in the forged condition at 18 and in the annealed condition at 14. Along with this are plotted the variations from the iron value caused by the addition of different amounts of nickel and copper (II and III). These values are then combined to form a fourth curve (IV), which is the result that might be expected if the hardening properties of the two metals when added together are strictly additive. The fifth curve (V) is the result actually obtained from the additions as stated, in comparison with what is to be expected from curve IV.

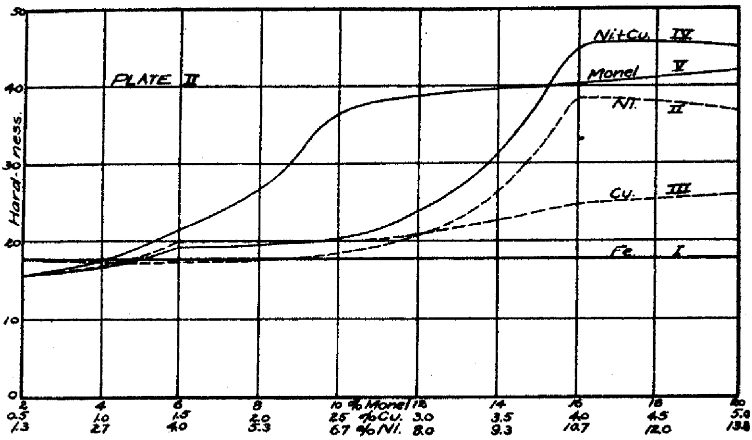

FIG. 2.—COMPARISON CURVES FOR FORGED ALLOYS.

In the forged condition the hardness does not reach quite such a high value as might be expected, if the hardening powers of the two metals were additive, but the maximum value is reached at a much lower percentage, so that the small difference in hardness is more than balanced by the economy of the smaller addition. In the annealed samples the hardness is much above anything that could be predicted from the results obtained from the single metals, the difference being particularly pronounced between 8 per cent and 16 per cent.

The comparison of the nickel and Monel curves shows several points in favor of the Monel. The maximum available hardness in both the forged and annealed condition, without the addition of excessive quantities of Monel, is at about 11 per cent or 12 per cent against 16 per cent for the pure nickel, the maximum values in both cases being practically the same. This leaves a large margin in favor of the Monel, a smaller quantity of a cheaper material giving the same results as a larger quantity of a more expensive material.

As can be seen from Curves I and II, in Figs. 2 and 3, the addition of pure nickel to iron gives no appreciable increase in hardness below 6 per cent, while the addition of the same quantity of Monel gives a marked increase in the hardness, and it is within this range that most of the nickel-steels for construction work are found.

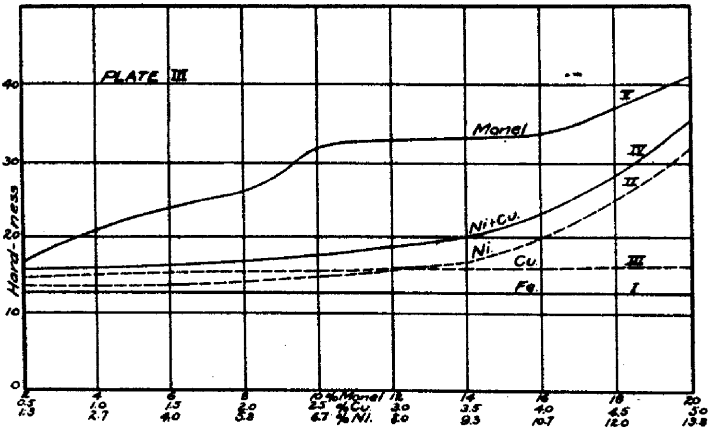

FIG. 3.—COMPARISON CURVES FOR ANNEALED ALLOYS.

It is possible that some commercial use may be made of the fact that at about 7½ per cent Monel the hardness of the material is the same in both the forged and the annealed condition. With the pure nickel it is necessary to go to 21 per cent to obtain similar conditions.

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October 1910

Hardness and Its Measurement.

BY G. A. ROUSH.

The physical property termed *hardness* has been defined in several different ways, and many different methods have been devised to measure it. Owing to the fact that hardness is in itself not a definite property, but the result of a combination of several different properties, this has given rise to results that are comparative only in a small degree, since the operation of one of the methods may depend on the measurement of an entirely different property or set of properties from some other method.

For example, it is evident that the elasticity and ductility of a material form a larger factor in the test where hardness is defined as the resistance of a body to permanent deformation than where hardness is defined as the resistance to penetration by another body. Hence the desirability of analyzing the exact components of any hardness tests that may be applied, and establishing such relations between these components that definite conclusions can be drawn from the results obtained. This is, however, a matter of considerable difficulty, and has not yet been accomplished.

Recent investigations have shown results pointing to a definite relation of this kind, but just exactly what it is cannot yet be stated. The object of this paper is the comparison of the hardness data[1] and the other physical tests[2] on the alloys of nickel,

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[1] *Met. and Chem. Eng.*, (a) p. 468, Aug., 1910; (b) p. 522, Sept., 1910.

[2] (a), Physical Properties of Iron-Copper Alloys, Burgess and Aston, *Trans. Amer. Electrochem. Soc.*, 16, 241-256, 1909; (b), The Magnetic and Electrical Properties of Iron-Nickel Alloys, Burgess and Aston, *Met. and Chem. Eng.*, 8, 23-26, 1910; (c), The Magnetic and Electrical Properties of Iron-Copper Alloys, Burgess and Aston, *Met. and Chem. Eng.*, 8, 79-81, 1910; (d), The Strength of the Alloys of Nickel and Copper with Electrolytic Iron, Burgess and Aston, *Bull. Univ. of Wis.*, Eng. Series, Vol. 6, No. 2; (e), The Strength of the Alloys of Electrolytic Iron and Monel Metal, Burgess and Aston, *Met. and Chem. Eng.*, 8, 452, 456, 1910.

copper and Monel metal with electrolytic iron that have been made in the Chemical Engineering Laboratories of the University of Wisconsin, working under grant from the Carnegie Institution.

As has been said, the relative hardness of any material varies with the kind of stress to which it is subjected. The different properties which apparently may enter into and influence the results obtained by the different methods of testing are density, elasticity, ductility and tenacity. The degree in which these properties, taken in combination, are affected by the stress applied determines the hardness of the material under these conditions. One and the same metal may show an entirely different degree of comparative hardness, depending on which of these components predominates in the final result, and a metal that is shown harder than another by one method may be softer when tested by a different method.

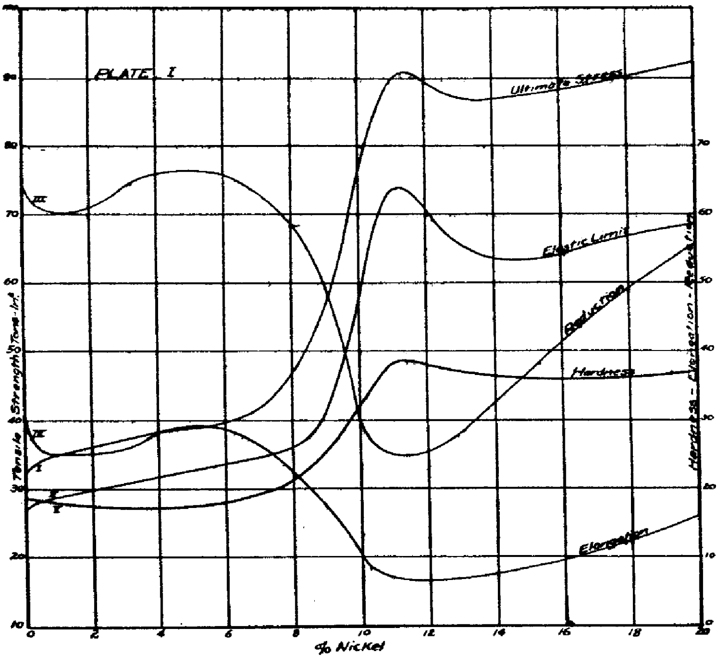

FIG. I.—TENSILE STRENGTH AND HARDNESS OF FORGED NICKEL ALLOYS.

A series of samples arranged according to increasing hardness as measured by machining in a lathe will not necessarily remain in the same order when tested by a compression method. On this basis Turner[3] divides hardness into four different classes—tensile hardness, cutting hardness, abrasion hardness, and elastic hardness.

The method used for determining the hardness in the investigations cited was the scleroscope method devised by Albert F. Shore in 1906, and is described as follows: "The instrument consists of a vertical glass tube provided with a graduated scale, suspended over a steel anvil on which the sample to be tested is placed; a small steel plunger with a diamond point, suspended in the top of the tube, is allowed to drop on the sample clamped on the anvil, the rebound of the plunger being read off on the scale at the back of the tube. When the plunger reaches the surface of the metal under test it carries a certain amount of potential energy, and the weight of the plunger, the height of the fall and the area of the striking surface are so proportioned that in all cases this energy is sufficient to exceed the elastic limit of any material which may be under test.

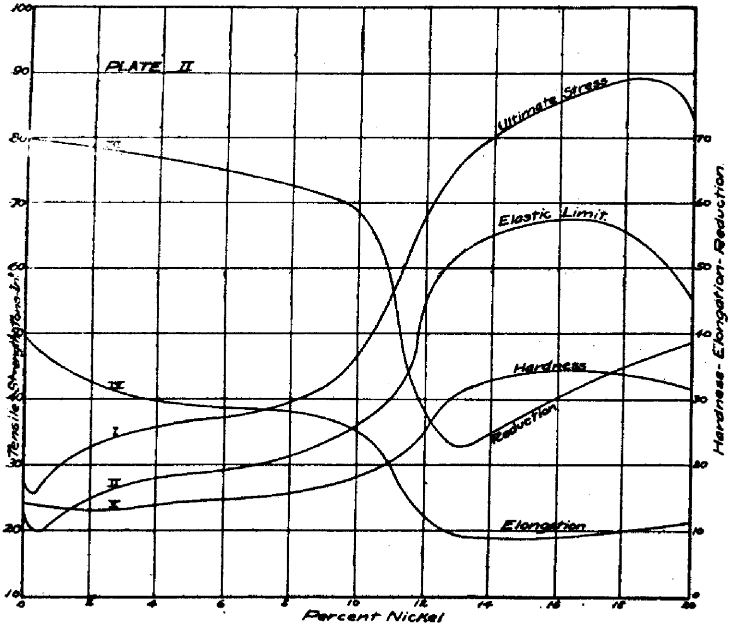

FIG. 2.—TENSILE STRENGTH AND HARDNESS OF ANNEALED NICKEL ALLOYS.

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[3] *Jour. Iron and St. Inst.*, 1909, (1), p. 426.

"This being the case, the material on receiving the impact of the plunger is stressed beyond its elastic limit and given a permanent deformation. If the elastic limit of the material under test is high, the excess energy of the plunger is small and only a small dent is made on the surface. That portion of the material immediately adjoining the deformed portion has then been stressed only up to its elastic limit, and in regaining its original form causes the plunger to rebound a certain distance. If the metal under test has a low elastic limit a smaller portion of the energy of the falling plunger is used in overcoming the elasticity, and a greater portion is used in displacing metal. The stress of the adjoining metal is then only sufficient to give the plunger a small rebound. This rebound is then taken to represent the hardness of the material under test."

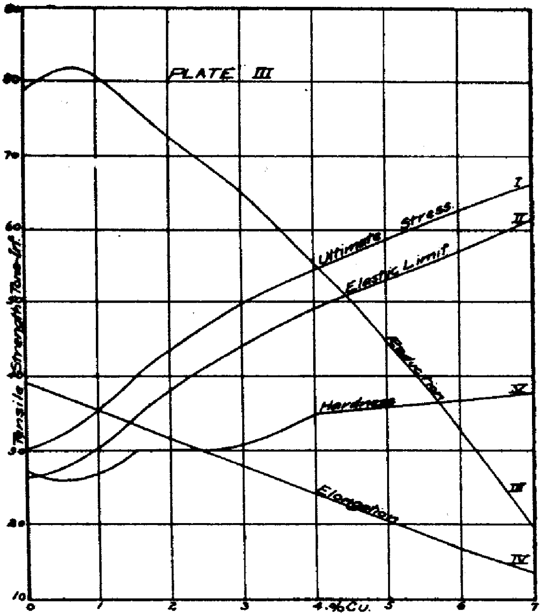

FIG. 3.—TENSILE STRENGTH AND HARDNESS OF FORGED COPPER ALLOYS.

Basing his conclusions on this line of reasoning, Shore makes the statement[4] that the curve of hardness as determined by the scleroscope is very nearly parallel to the curve of elasticity, but since the value obtained in any test for hardness is the resultant

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[4] *Amer. Mach.*, Nov. 14, 1907.

of the different factors mentioned above it can be seen that this will be true only when those factors other than elasticity enter into the result to a very small extent, and that frequently the variation will be large.

Reference may also be made here to the statement made in the first paragraph of this paper in relation to the different properties affecting a hardness test, and the interpretation of the results for different purposes. In the article by Burgess and Aston referred to above[5] the iron-nickel alloys between 11 and 20 per cent are classed simply as "hard," no reference being made to any particular difficulty in machining, while the copper alloys above 5 per cent are said to have been machined with difficulty. The comparative hardness of the copper alloys, however, as measured by the scleroscope, is some 25 per cent lower than the nickel alloys.[6]

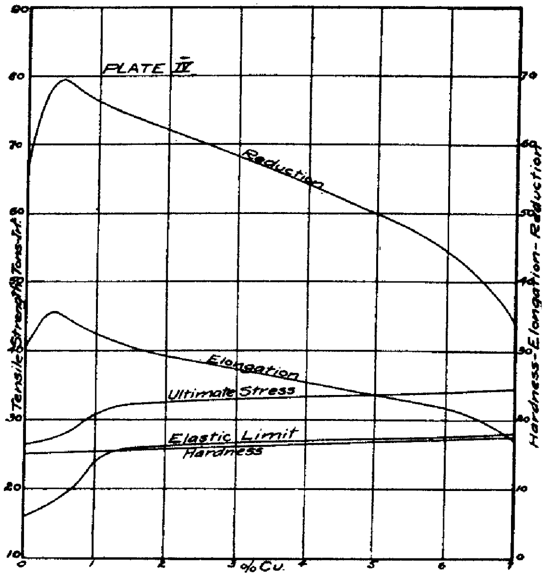

FIG. 4.—TENSILE STRENGTH AND HARDNESS OF ANNEALED COPPER ALLOYS.

The comparison of the hardness curves with other tests that

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[5] See reference above, 2d, pp. 10 and 20.

[6] See reference above, 1a, Tables I and III.

have been made on the same materials is a matter of considerable interest. In Figs. 1 to 6 are reproduced the hardness curves for the nickel, copper and Monel alloys referred to,[7] along with the tensile tests on the same bars taken from the articles by Burgess and Aston cited above.[8] In each of these plates curve number I is the ultimate stress, II is the elastic limit, III is the reduction of area, IV is the elongation and V is the hardness.

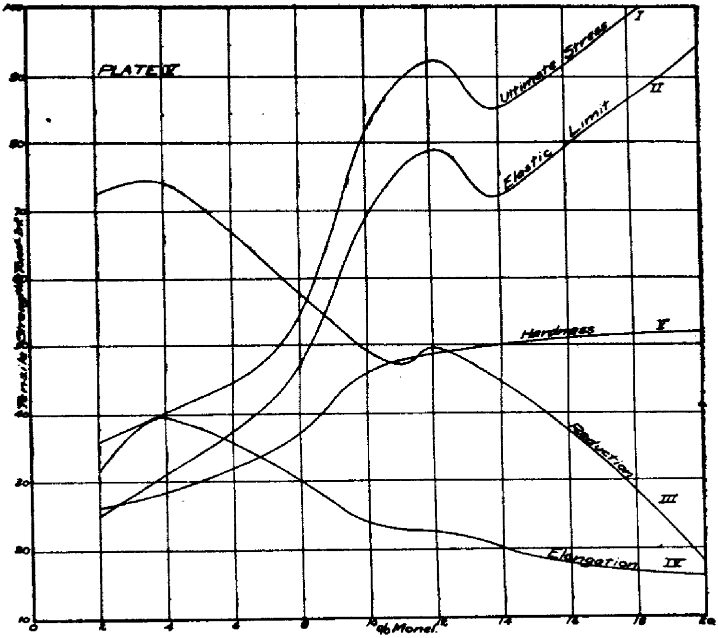

FIG. 5.—TENSILE STRENGTH AND HARDNESS OF FORGED MONEL ALLOYS.

As has been said, the hardness curve roughly approximates the general direction of the curve for the elastic limit, but in many points there is a wide difference. If the two curves followed each other exactly, it would be a simple matter to plot a curve showing the relationship between the two, which could be used to convert hardness tests directly into tests on elastic limit.

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[7] See reference above, 1a and b.

[8] See reference above, 2d and e.

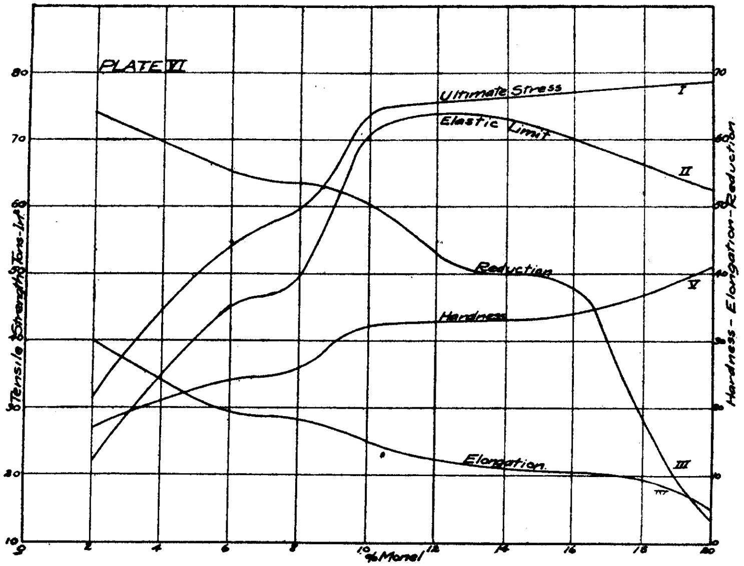

FIG. 6.—TENSILE STRENGTH AND HARDNESS OF ANNEALED MONEL ALLOYS.

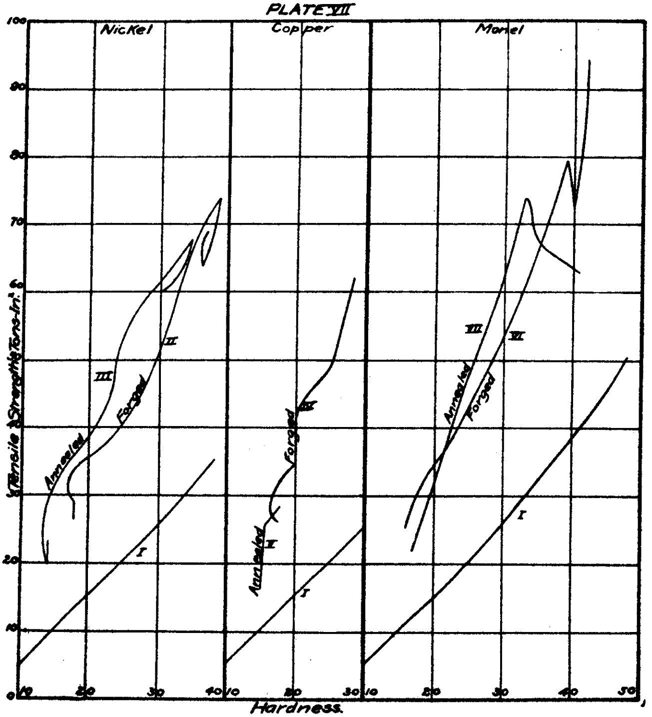

FIG. 7.—STRENGTH-HARDNESS CURVES.

Among the data sent out with the scleroscope by the manufacturers is a table for converting hardness into elastic limit. This table is said to serve as a means of obtaining the strength tests on all metals below a hardness of 60, except cast iron and brittle alloys such as those of antimony. The data in this table are plotted in graphical form in curve I, Fig. 7. This shows a simple relationship between the hardness and the elastic limit varying only slightly from a straight line function. This curve is obtained by plotting hardness as abscissæ and elastic limit as ordinates.

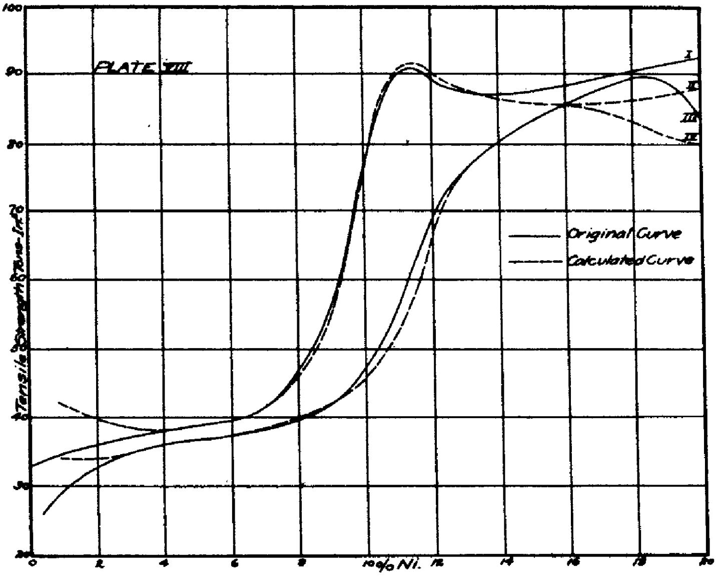

FIG. 8.—ULTIMATE STRENGTH OF NICKEL ALLOYS.

The relations between the hardness and the elastic limit as shown by the curves in Fig. 1 to 6 fail, however, to follow any such simple relation as this, nor are the values obtained at all close to those obtained by Shore. Furthermore, each one of the six series tried out here gives a different relation, and not one simple relation for all.

Curves II and III of Fig. 7 show respectively the results obtained by plotting in this same way the hardness and elastic limit of the forged and annealed nickel alloys; curves IV and V are from the forged and annealed copper alloys, and curves VI and VII from the forged and annealed Monel alloys.

In the nickel and Monel series the shape of the curves for the forged and annealed samples is not radically different, showing that the existing relations between the hardness and elastic limit are not materially changed by annealing the material, but in the copper series the change is quite marked.

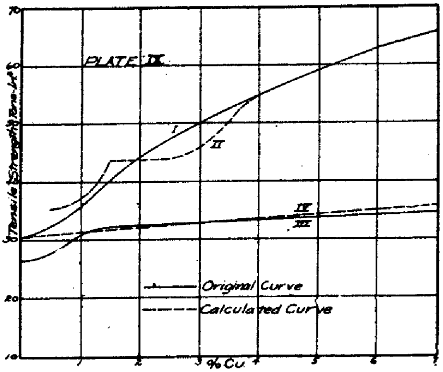

FIG. 9.—ULTIMATE STRENGTH OF COPPER ALLOYS.

A comparison of the hardness curves with those of elongation and reduction of area shows that it is the ductility of the material that causes the greater part of the variation of the hardness and elastic limit curves. Since the difference between the elastic limit and the ultimate strength depends to a certain extent on the ductility of the material it is probably more nearly correct to compare hardness with ultimate strength rather than with elastic limit. Following out this idea the attempt was made to reproduce the ultimate strength curves from the hardness curves, with the results shown in Figs. 8, 9, 10.

A conversion factor was obtained by dividing the ultimate strength shown at the middle of the curve by the hardness at the corresponding point, and this factor was then used to convert the remaining points on the hardness curve into values for ultimate strength. In each case the original curve for the forged samples is number I and the calculated curve is number II; the original curve for the annealed samples is number III and the calculated curve is number IV. These conversion factors, of course, differ somewhat for the different materials, but the variation is not as large as might be expected. The factors are as follows:

For forged nickel	2.38
For annealed nickel	2.60
For forged copper	2.38
For annealed copper	2.02
For forged Monel	2.25
For annealed Monel	2.30

None of the curves calculated in this way coincide throughout with the original, but they fall close enough to be of value in noting the points where the variations come, and may, in the light of further data, help in the location and evaluation of the factor or factors that are lacking to make the two curves duplicates.

It appears then that the scleroscope gives measures of hardness only approximately proportional to the elastic limit of the material, and will require individual calibration curves for each series of alloys in order that its readings may be resolved into values for strength. Six partial curves are given herewith in Fig. 7.

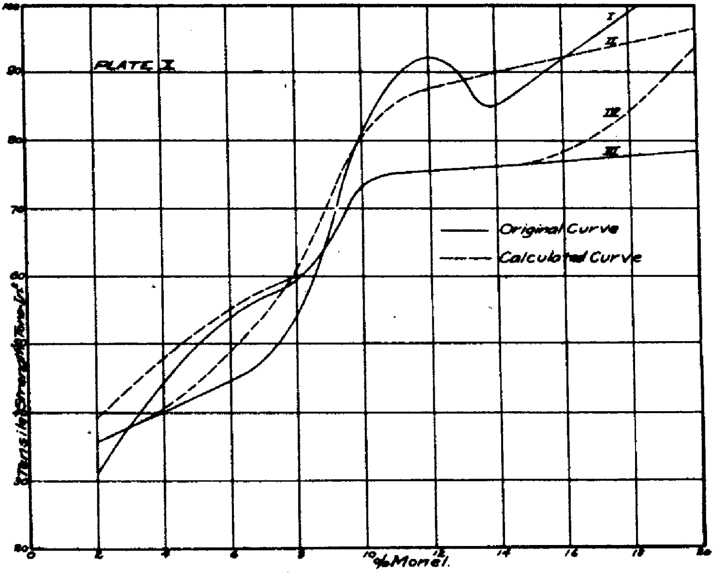

FIG. 10.—ULTIMATE STRENGTH OF MONEL ALLOYS.

While the results shown here point to the existence of a definite relation between hardness and elastic limit or ultimate strength, it appears that this relation is of such a complicated nature as to require further data than are now at hand to determine its exact nature and reduce it to mathematical terms.

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Madison, Wis.

A paper read by title at the Eighteenth General Meeting of the American Electrochemical Society, in Chicago, October 15, 1910, President W. H. Walker in the Chair.

SOME ALLOYS FOR PERMANENT MAGNETS.

By C. F. Burgess and James Aston.

In the investigation of electrolytic iron and its alloys, carried out at the University of Wisconsin, under grant of the Carnegie Institution of Washington, tests were made of the magnetic qualities of all samples. Among these, many showed low permeabilities and high coercive forces suggesting their utility for permanent magnets, rather than as electromagnetic material. Upwards of 100 samples were tested for this feature; all of the bars contained chromium, manganese, molybdenum, nickel and tungsten as binary alloys, or in various combinations together or with other elements.

Much information regarding the best steels and the best treatment for permanent magnets has undoubtedly been accumulated by the manufacturers and users of such material, but is held as a trade secret; and published data along these lines is very meager. Again, such publications deal largely with the study of the critical points of the steels, with the view of determining the proper heat treatment to give them for the best service.

The tests here recorded are for the most part on carbon free alloys. The results are mainly of value, therefore, as indicating the influence of the various elements in inducing the conditions necessary for a good permanent magnet. They were made upon an Esterline permeameter, an apparatus giving directly the flux density in the bar under test for any impressed magnetizing force. It consists of a small dynamo, driven at predetermined constant speed. The test bar forms part of the magnetic circuit of the generator, and can be subjected to magnetizing forces of varying degrees. The flux density in the bar, being directly proportional to the voltage set up, can be read off on a properly calibrated millivoltmeter.

It is not necessary to make a complete magnetization curve in testing material for permanent magnets. The desirable feature is to have as high a residual magnetism as possible, or, better, to have a high retentivity after some disturbing factor has tended to destroy the residual magnetism, together with a high coercive force to resist the tendency towards this loss of the magnetic flux. The method of procedure was as follows: The bar was inserted in the permeameter, the magnetizing force, H, was raised to the maximum of 200 and the density, B (MAX), was recorded, H was decreased to zero, and the retentivity, B (RET), noted; next the coercive force, Hc, necessary to reduce the retentivity to zero, was determined. Similar readings were taken for the reverse magnetizing forces, and the average of these positive and negative readings of B (MAX), B (RET) and Hc for each bar was recorded for comparison. In fact, the whole operation is identical with the taking of a hysteresis loop, in which only the few readings noted above were recorded.

The bars were tested as forged, and after water quenching at 1000° C. To prevent oxidation of the samples while heating them for quenching, a barium chloride bath was used. The quenching at 1000° C. may not have brought out the best qualities of some of the bars; but it was deemed the best general treatment, since with so many bars under test, it was impossible in this research to subject each sample to tests for its critical points and special conditions of heating.

In addition to the general test noted above, all bars which showed a fair retentivity and a coercive force above Hc = 30 were subjected to a test for their stability or their ability to hold residual magnetism after shock. For this test the bar was subjected to the maximum magnetizing force of Hc = 200, and the retentivity noted when this magnetizing force was reduced to zero. The bar was then removed from the machine, subjected to the disturbing factor, and the retentivity again recorded after reinserting the sample in the permeameter. The two means commonly employed in practice for seasoning permanent magnets were used, namely, jarring or rapping the bar, and boiling. For the latter treatment, each bar was inserted in a piece of wrought iron pipe, which served as a shield to prevent the mutual influences of the magnetic fields, and boiled in water for three hours.

A large number of comparative trials of the rapping and boiling treatments showed them to be practically equal in their effect, and because of the simplicity of the former, it has been resorted to in the later tests. However, should the material be very brittle, it would be safer in practice to use the boiling method.

As indicating the efficiency of the rapping treatment, there are noted below the results of successive jarring upon the retentivity or a bar of composition 7Cr 3W 2Mo (7, 3 and 2 being the percentages of the three elements).

H (MAX) = 200
B (MAX) = 11100
B (RET) = 7500
B (RET) = 4900 (removed and rapped 1)
B (RET) = 4700 " " " 2
B (RET) = 4700 " " " 3

As will be seen, but one vigorous rapping is necessary, since this reduces the residual magnetism to a value which is but little changed by further shock.

Only the general summary of the tests are given, since it was not deemed advisable in a paper of this character to include the complete tabulation of the data. In Table I are noted the data of the stability tests which, as mentioned previously, include only those materials best suited for permanent magnets. The alloys are divided into five groups, according to their content of chromium, manganese, molybdenum, nickel and tungsten, either alone with iron, or together with iron and any other elements except the above five; in addition, a sixth miscellaneous group includes materials of various compositions in which more than one of the above five metals are present.

The results as a whole showed a wide variation in the physical and magnetic hardness of the various bars, not only before quenching, but afterwards as well. Also, it appeared that the effect of quenching was varied in its results, with either increase or decrease of coercive force, or with no material alteration. However, it appeared that where marked changes were the result, it was generally with an increase of magnetic hardness.

Chromium. In the chromium group, it appears that this element alone, even in percentages as high as 16.65, does not result in bars of high coercive force suitable for permanent magnets, even after quenching at 900° C. And the coercive force was no higher with large than with small chromium additions.

TABLE I.

Stability of Permanent Magnets.

H(MAX) = 200.

Bar No.	Composition (The figures give the percentage present.)	As Forged			Quenched at 1000° C		
		B(Ret)	After Rapping		B(Ret)	After Rapping	
			B(Ret)	Hc		B(Ret)	Hc
	CHROMIUM STEELS						
133E	4Cr 0.84Si	15050	...	14.9	9000	3500	41.5
133D	5Cr 0.84Si	7500	3300	41.0	9500	4800	41.8
133B	5Cr 1.4Si	15700	...	16.2	8800	3900	46.0
160J	5Cr 0.3V	7400	3400	53.0	9000	2700	42.2
160H	5Cr 0.5V	9000	3600	50.5	9100	4200	45.0
160K	5Cr 1V	8400	4100	48.1	9200	4900	49.0
133L	6Cr 0.4Si	15650	...	14.9	9600	3700	49.0
133K	6Cr 0.84Si	15300	...	13.6	9400	5200	52.3
147Z	6Cr 1.3Si	9200	...	16.2	8800	3400	50.0
133F	6Cr 1.68Si	14300	...	17.9	8300	3800	50.0
133M	8Cr 1Si	12550	..	16.2	8700	2400	48.5
111S	10Cr 2Si	10000	...	19.2	7100	3600	54.0
155K	10Cr 2Si 0.3V 0.6C	11200	2300	30.5	3000	1600	69.0
137L	10Cr 2Si 2Ti	10850	...	16.4	7500	4200	62.0
122E	10Cr 3Si	10800	..	12.3	7400	3500	47.8
160I	10Cr 0.3V	7500	4000	72.5	7800	3500	58.0
155L	10Cr 0.3V 0.65C	4600	3100	84.6	7200	...	91.9
160G	10Cr 0.5V	7000	3600	65.0	...	...	...
163O	10Cr 1V	7600	3500	62.8	8400	4500	54.5
141C	10.3Cr 1V 2Si 0.3C	9500	...	20.9	8000	2600	38.0
133N	13Cr 1.8Si	12750	...	16.7	7100	4000	62.8
136H	17Cr 1½Si	2100	1100	89.3	4900	2700	85.0
	MANGANESE STEELS						
170D	6Mn	8500	4000	50.0	...	...	...
	MOLYBDENUM STEELS						
160E	4Mo 0.6V	12950	...	15.3	10400	2600	33.3
156E	8Mo 0.3V 0.6C	9900	3500	37.8	12000	5000	52.2
160C	10Mo 0.3V 0.4C	13700	...	23.7	10400	4900	55.8
163H	10Mo 1V 0.4C	10850	...	25.1	9400	5000	53.5
141F	10Mo 1.2C	...	...	...	10100	4000	37.0
	NICKEL STEELS						
160M	10Ni 0.6V	9700	3400	30.8	9700	4000	27.2
146P	10Ni 2Si 1C	6700	3200	58.7	1000	900	58.0
	TUNGSTEN STEELS						
160P	4W 0.4V	8250	...	12.4	11300	3300	37.5
163J	4Wo 0.4V 0.5C	11200	3000	34.8	8800	4100	67.5
163D	4W 0.4V 0.6C	10400	2900	33.0	9200	4600	68.2
163K	4W 0.4V 0.8C	8900	2800	32.5	6600	4400	70.6
155X	5W 0.5C	10350	...	24.5	12000	5200	52.5
WIC	6W + C (?)	12500	2700	28.0	...	...	
163E	7W 0.3V 0.6C	10900	3800	38.0	9600	5600	81.0

TABLE I.—*Continued.*

Stability of Permanent Magnets.

H(MAX) = 200.

Bar No.	Composition (The figures give the percentage present.)	As Forged			Quenched at 1000° C		
		B(Ret)	After Rapping		B(Ret)	After Rapping	
			B(Ret)	Hc		B(Ret)	Hc
	MISCELLANEOUS STEELS						
150C	2Cr 10Mo 0.5C 0.3V	6900	3600	58.0	10700	6300	77.2
155S	10Cr 5Mo	8700	4000	59.0	7300	3600	70.5
155U	2Cr 10W	10100	. . .	23.4	9500	3900	49.0
156F	3Cr 8W	9400	. . .	24.1	9900	4700	47.5
163A	5Cr 2W 0.6C	6900	3800	61.0	7300	2500	55.0
163G	5Cr 5W 0.6C	3400	1700	68.5	6400	4200	85.0
163C	10Cr 2W	7400	4200	71.7	7500	4200	62.0
156K	10Cr 2W 2Si	5800	3200	76.6	. . .		
156J	10Cr 2W 0.6C	4900	3000	89.9	7100	4800	95.0
156H	10Cr 2W 0.3V	6900	3700	66.0	6900	3800	61.4
156I	10Cr 2W 0.3V 0.6C	4300	2500	82.7	7000	3900	91.0
155V	10Cr 10W	5800	3300	80.5	6500	3600	72.7
150B	2Cr 10W 10Mo 0.3V 0.4C	6100	3500	66.5	8400	3700	59.0
150D	2Cr 16W 5Mo 0.3V 0.5C	5700	3600	64.0	8600	5000	63.5
163B	7Cr 3W 2Mo	7300	4100	82.5	7400	2500	47.5
156G	10Cr 2Mo 2W	7100	4100	78.5	6600	3800	65.8
156M	10Cr 2W 2Mo 0.6C	4300	2500	82.0			. .
156P	10Cr 2W 2Mo 2Si 0.3V	8500	1900	31.0	6800	2700	60.0
136M	5Cr 3Mn 4Mo 1Si	10800	5300	64.7	5800	2900	72.2
140Q	5Cr 6Mo 10Mn 10Ni 1C	10100	4000	38.2	7000	4400	85.3
144Z	2Cr 10Ni	8100	3200	36.9	8200	3300	29.0
154E	5Cr 10Ni	9100	4000	57.7	5400	2900	47.0
154F	7Cr 10Ni	4700	2500	64.0	2000	1100	55.7
154A	10Cr 8Ni	1600	. . .	80.8	800	300	73.5
136V	10Ni 5Mo	9600	2300	36.0	8600	3600	32.0
146Q	10Ni 10Mo 1C	5500	3000	69.7	5500	2800	70.4
146S	10Ni 10Mo 0.5C	8900	4900	61.0	8400	4000	52.0
152Z	10Ni 5W	8400	3100	36.0	8600	2800	29.7
155Y	10Ni 5W	9050	. . .	17.0	10900	4600	38.0
155AB	15Ni 5W	8300	3000	38.5	8000	2300	37.8
156A	1Mn 2Mo	9450	. . .	27.3	10600	4600	38.5
155P	1Mn 10Mo 0.5C	6900	3600	61.0	11200	5400	57.5
156C	2Mn 5Mo 0.6C	9500	5500	57.2	8400	4700	68.0

A large number of chrome-silicon alloys were tested, and in practically all cases the bars were relatively soft and of low coercive force in the forged condition. The coercive forces in all but two instances were well below 30, and the alloys were thus unsuited in this state for permanent magnets. In these two instances but little change resulted on quenching; but for the other bars, quenching resulted in a marked increase of coercive force; and with the accompanying relatively high retentivities, these materials were well adapted for permanent magnets. The best alloys seemed to have about a medium chromium content (5 or 6 percent), since then the retentivity was high and the coercive force great enough to ensure stability.

The addition of vanadium also seemed to be very beneficial, although in this case the raw forged bars were especially hard, and the coercive forces were high initially, and suffered but little change in quenching. Here again, the best results seem to be gained with medium chromium content, because of the higher retentivities.

In a few instances, carbon was present, together with vanadium and silicon. The materials showed hardening upon quenching, but the magnetic results were no better than where there was no carbon.

Summarizing, it may be said that the addition of chromium alone to carbonless iron will not result in a material suitable for permanent magnets; but that the further addition of 0.75 to 1 percent of silicon or 0.3 to 0.5 percent of carbon to 5 or 6 percent of chromium is highly beneficial, and gives an alloy very suitable for this class of service.

Manganese. According to the classification adopted, the only manganese alloys falling in this group were of a series in which manganese alone in varying amounts had been added to the iron. In the raw forged condition, the coercive force increased, with a corresponding decrease of retentivity, for each increase of manganese content, until at 10.41 percent Mn the alloy was non-magnetic. A bar with 10 percent of manganese had the high coercive force of 90.1, but the retentivity was too low for permanent magnets. The most satisfactory bars were two with 4.51 and 6.0 Mn, where the retentivities were fairly high and the coercive forces great enough to insure stability.

But three bars were tested after quenching, and the result was a decrease of coercive force, a peculiarity corroborated by other tests upon this series.

Molybdenum. Of the entire set of results for this series of alloys, only one was magnetically hard in the forged condition; this was a bar of composition 8Mo 0.3V 0.6C, which had the high retentivity of 9200 and the fair coercive force of 39.0. In the quenched condition, there was practically no change in any of the carbon free alloys. But in four cases where carbon was present, the quenching resulted in physical hardening of the bars, and they became very fine materials for permanent magnets, with exceptionally high retentivities and very good coercive forces. In one case, a bar with 4Mo and 0.6V attained a good coercive force; whether this was due to absorbed carbon is problematical. If the magnetic hardening took place without the aid of carbon, it would indicate that the proper conditions of temperature, etc., might have the same effect on the other molybdenum alloys. This is merely conjecture, however, and the tabulated results showed no hardening effect of vanadium, such as was noted for the chromium alloys.

Nickel. In the binary alloys of nickel and iron, increase of nickel caused a decrease of retentivity and increase of coercive force, until at about 26 percent of nickel the material was non-magnetic. Beyond this percentage, the magnetic properties were restored, the alloys being of rather high permeability and low coercive force. Quenching at 900° C. invariably greatly decreased the coercive forces, so that none of the binary nickel alloys can be considered suitable for permanent magnets in the quenched condition, either because of low coercive force, or because of low retentivity where the coercive force is ample.

The addition of vanadium resulted in increased magnetic hardness, which was again increased by quenching. The most satisfactory bar was one with 10Ni 0.6V, which in the forged condition had a retentivity of 9900 and a coercive force of 32.6; both values were slightly lowered by quenching. One bar with 10Ni 2Si 1C had a fair retentivity of 6800 with a high coercive force of 62.0 in the forged condition; but after quenching it became almost non-magnetic.

The nickel alloys as a whole, therefore, cannot be regarded as satisfactory materials for permanent magnets. In this case, as noted for chromium, the vanadium seems to act as a hardening agent.

Tungsten. Seven binary alloys of tungsten and iron were recorded, with a tungsten content varying from 0.93 to 23.87 percent. In no instance was the coercive force high enough to make them suitable for permanent magnets; and quenching had but little effect, usually resulting in a decrease of coercive force. For the two alloys where there was an addition of vanadium, one bar, with 4W 0.4V, became, after quenching, an exceptionally good permanent magnet, with a retentivity of 11300 and coercive force of 43.8; on the other hand, another sample, with 7W 0.3V, experienced but slight increase of hardness. A bar with 5W 0.5C became noticeably harder after quenching, with increase of retentivity and coercive force to the high values of 11700 and 59.0. Four other bars were very good for permanent magnets as forged, and there was a marked hardening, due to quenching.

Summarizing, the binary alloys of tungsten and iron are not satisfactory for permanent magnets. The addition of vanadium may be beneficial, and the addition of carbon certainly is. There were in this series some highly satisfactory alloys; of those worthy of particular mention, however, all but one contained carbon.

Miscellaneous. This miscellaneous group included such a large number of combinations of these several self-hardening alloys that a systematic discussion of the results is difficult. Of the 51 bars here grouped, almost two-thirds were good materials for permanent magnets. The effect of quenching was somewhat varied; in 13 instances there was a considerable increase of coercive force, in 30 cases but little change, and in 6 instances a marked decrease. In 4 cases bars which were originally poor became of fair quality after quenching; and in numerous instances the quality of fair materials was greatly improved; in no case, however, has quenching resulted in a bar of fair quality becoming poor material for permanent magnets, although at times the quality was better before quenching than after.

One of the most striking features noted was the detrimental effect of the additions of nickel, with its tendency towards non-magnetic alloys. In all cases where the material was classed as non-magnetic, or where it was worthless for permanent magnets because of very low retentivity, there was a considerable amount of nickel present. Of the 17 bars of poor quality for permanent magnets, 12 had nickel; and of the 5 bars without nickel, the quality was poor not because of a tendency towards being non-magnetic, but because the coercive force was too low. Several bars of nickel with chromium, with molybdenum, or with tungsten, had fair retentivities together with high coercive forces.

The various combinations of chromium with molybdenum or tungsten, either alone or with additions of silicon, vanadium and carbon, gave generally satisfactory results. In fact, it is difficult to point out any preferable combinations of these various self-hardening elements beyond the caution to keep nickel out of the alloy.

Of particular quality may be mentioned the following:

Bar	Composition	B (Ret.)	Hc.	
136M	5Cr 3Mn 4Mo 1St	11350	55.8	As forged
136V	10Ni 5Mo	10150	36.7	
150C	2Cr 10Mo 0.5C 0.3V	10500	78.0	Quenched
155Y	10Ni 5W	10300	35.2	
156A	1Mn 2Mo	10500	39.6	
155P	1Mn 10Mo 0.5C	10750	58.4	

Strange to say, two of these alloys have a high nickel content, but they may be put down as exceptions to the general rule. The values given above indicate a very high standard of material for permanent magnets.

Summarizing, it may be deduced from the above tests that chromium, manganese, molybdenum and tungsten are the important additions in the manufacture of steels for permanent magnets; but the presence of some third element is necessary. While carbon is beneficial, it is possible to obtain highly satisfactory materials either by various combinations of the above four elements or by suitable additions of silicon or vanadium, the latter, in particular, being very desirable. Also, suitable materials may be made which will require quenching, although in this case carbon is most beneficial; or, if desired, equally satisfactory results may be obtained without.

Stability. As mentioned previously in the general discussion of the tests for permanent magnets, a better indication of the value of material for this service is obtained by a stability test which gives the residual magnetism after shock. In our tests the rapping method was used, the details being given above. Those bars were tested which showed a coercive force above 30, either before or after quenching, this being considered the minimum value at which permanence might be expected.

The details are tabulated in Table I, in the same order as used in the general discussion. The figures of interest are those for the retentivity, B (RET), after rapping; they show the marked decrease of the residual magnetism due to shock, a decrease averaging about 50 percent, but varying according to the coercive force of the material under test.

For purposes of comparison, and for illustrating the above points, the following tables have been prepared. For Table II the data have been taken from general tests, and there are listed those bars having a retentivity above B (RET) = 10,000, and a coercive force exceeding Hc = 30.0, the order being according to the value of B (RET). In Table III, the selections are taken from stability Table I, and are ranked on the basis of the values of B (RET) after rapping.

TABLE II.

Bar	Composition	B (Ret.)	Hc.	
WIC	(6W + (?) C)	13450	30.0	As forged
156E	8Mo 0.3V 0.6C	11750	53.7	Quenched
155X	5W 0.5C	11700	59.0	Quenched
136M	5Cr 3Mn 4Mo 1Si	11350	55.8	As forged
160P	4W 0.4V	11300	43.8	Quenched
163J	4W 0.4V 0.5C	11050	38.0	As forged
155P	1Mn 10Mo 0.5C	10750	58.4	Quenched
155K	10Cr 2Si 0.3V 0.6C	10700	32.9	As forged
163D	4W 0.4V 0.6C	10650	35.5	As forged
150C	2Cr 10Mo 0.5C 0.3V	10500	78.0	Quenched
156A	1Mn 2Mo	10500	39.6	Quenched
163E	7W 0.3V 0.6C	10450	39.4	As forged
160E	4Mo 0.6V	10400	35.0	Quenched
160C	10Mo 0.3V 0.4C	10350	59.8	Quenched
155Y	10Ni 5W	10300	35.2	Quenched
136V	10Ni 5Mo	10150	36.7	As forged
141F	10Mo 1.2C	10000	37.4	Quenched

TABLE III.

Bar	Composition	B (Ret.) After Rapping	Hc.	
150C	2Cr 10Mo 0.3V 0.5C	6300	77.2	Quenched
163E	7W 0.3V 0.6C	5600	81.0	Quenched
156C	2Mn 5Mo 0.6C	5500	57.2	As forged
155P	1Mn 10Mo 0.5C	5400	57.5	Quenched
136M	5Cr 3Mn 4Mo 1Si	5300	64.7	As forged
155X	5W 0.5C	5200	52.5	Quenched
133K	6Cr 0.84Si	5200	52.3	Quenched
150D	2Cr 16W 5Mo 0.3V 0.5C	5000	63.5	Quenched
163H	10Mo 1V 0.4C	5000	53.5	Quenched
156E	8Mo 0.3V 0.6C	5000	52.2	Quenched

As will be seen by comparison of the two tables, there are bars listed in Table III which do not appear in Table II. Another feature is that the order of rank is not the same for those materials which are noted in both tables. It will be noted, likewise, that some of the alloys which have high rank in Table II are low down in Table III, or do not appear at all, because the coercive forces are not great enough to retain a high residual magnetism after shock. All materials listed in Table III have high coercive forces, about Hc = 50, and it would appear that for permanent magnets to give good service it should reach this value.

As a result of these tests, it appears that for the investigation of materials for permanent magnets, this stability test gives a very satisfactory indication of the quality. In addition, of course, it would be necessary to test the ageing qualities, or the ability to retain this residual magnetism for long periods of time, and under working conditions.

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Some Physical Characteristics of Iron Alloys.

BY CHARLES F. BURGESS AND JAMES ASTON.

In connection with an investigation[1] of the properties of electrolytic iron and its alloys having a carbon content so low as to warrant their being considered as practically carbon free, the forgeability, welding and machining of these metals were tested and the results are summarized herein.

The basis of all the alloys is iron of a high degree of purity, obtained by a double electrolytic refining of commercial Swedish iron. This electrodeposited material has an impurity content of about 0.03 per cent, the iron by difference being 99.97 per cent. The desired amounts of this pure iron are weighed out, together with the proper percentages of the alloying elements, and placed in a covered magnesia-lined graphite crucible, which latter is buried in an electric furnace of the resistor type. After melting, an ingot is obtained of about 500 grams (1 lb.) in weight. Under these conditions of melting there is no agitation of the charge, nor is there any addition of the desired elements to the molten charge, and the resultant alloy is obtained entirely by diffusion of the elements, after being together brought to fusion from the cold state.

The ingots are heated in a forge fire and drawn out under a steam hammer into a rough bar from ½ in. to ⅝ in. in diameter and about 18 in. to 20 in. long, and from this the necessary test samples are obtained by turning or grinding.

The results of the above method of preparing the alloys are indicated by the agreement between the percentages of the alloying elements as added and as obtained by analysis of the turnings after melting and forging. Analyses of about 100 of the binary alloys show that very generally there is but little variation between the added and actual percentages, particularly among those elements which are most commonly used in alloy steels. In the nickel, copper and cobalt series this agreement is strikingly close; with tungsten, molybdenum, chromium, manganese and silicon it is reasonably so. In the last mentioned series, one alloy with an added content of 7 per cent Si showed on analysis only 3.33 per cent, but this variation is exceptional and not to be generally expected. Silver, selenium, aluminum and lead do not alloy at all in the proportions added; for silver this is particularly true, since the maximum percentage as analyzed is 0.697 per cent, while a maximum of 10 per cent was added. The most striking and unexpected instances are noted in the tin and arsenic series. Both of these metals vaporize at temperatures far below the melting point of iron. And yet we find very considerable amounts of the elements remaining in the alloy. For tin, the order of the series does not change, and about half of the added content remains; for arsenic, the agreement is very close up to an actual percentage of about 4, which seems to be the saturation limit, since for the alloys of 6 per cent and 10 per cent of added As the content has fallen to the above percentage.

Random analyses for carbon show small percentages, varying somewhat in the different alloys. Investigation leads us to believe that the greater part is due to the absorption of the carbon set free in the equilibrium reaction of iron upon the carbon monoxide gas of the furnace ($Fe + CO = FeO + C$). The amount of this carbon and other impurities is so small, however, that whatever properties are observed in the alloys may be said to be due to the addition of the various elements.

The notes given in the appended tables are the results of observations during the working of the ingots into test bars, and are qualitative, rather than quantitative. For the forging, we are indebted to Mr. Lottes, instructor in forge practice at the University, who has given a great deal of attention to the working of alloy steels. In case trouble was encountered in working at normal forging temperatures, different heats were tried to determine the best conditions. Upon indications of cracking or crumbling efforts were made to weld the bar, and the result noted. In general the welding tests were made upon a Thomson electric welder. The nature of the weld was determined by grinding the juncture and by testing with the hands. In many cases, no doubt, as Hadfield has aptly said, "the pieces may be stuck together and not truly welded, as a tensile test would soon show."

The machining tests include the nature of the material in the lathe, or its general hardness as noted in sawing and filing. All are in the condition resulting from forging, and without any annealing or other heat treatment.

In the tables the forging, welding and machining characteristics are arranged in three columns, and the various alloys are grouped alphabetically under the head of the predominating element. The observations were usually made and noted on each bar, but the results are given as a summary of the general effect of the alloying additions. The table is sufficiently explanatory to obviate the necessity of much discussion.

The forgeability of the various alloys does not differ greatly from that of similar commercial materials, qualitatively speaking; quantitatively, the effect of the impurities, especially the carbon content, will no doubt change the limiting ranges. Likewise, while carbon is conducive to the hardening by quenching of many of the alloys, and while it has its quantitatve effect upon all, it will be noted that chromium, manganese, molybdenum, nickel and tungsten promote self-hardening properties, even when carbon is absent. In fact, many of these last named alloys make satisfactory lathe tools, either in their air hardened condition or after quenching.

In addition to the materials listed in the tables, a large number of alloys were made up, of which the compositions and the results obtained are too diversified to enable systematic deductions to be drawn. These were very largely combinations of iron with several of the five elements mentioned above, and which are those generally found in self-hardening steels. They were very generally so hard as to require grinding into test bars, and practically all were forgeable with care in selecting the proper temperature, the precautions necessary being those usually taken in the working of high-speed steels.

Physical Characteristics of Iron Alloys.

Forging.	Welding.	Machining.
Electrolytic Iron. Easy. Brittle as deposited. Loses brittleness on heating to redness. Fused material can be worked cold. Forges well at all heats.	Easy in forge and also in electric welder.	Somewhat hard as deposited; can be easily machined, but is brittle. Like soft iron after heating or fusion.
Aluminum. (2-½%) forged well at forging heat.	Did not weld in electric welder.	A1-Fe bars trifle harder than iron but turn easily.
(2.3%) forges at welding heat.	Did not weld in forge. Welds in electric welder. (2%) welds in electric welder.	
Antimony. Alloys up to 10% made, but only that with 1% would forge. Rest crumbled.		No trouble in machining the alloy of 1% added Sb.
Arsenic. Alloys up to 4%. Forge well at normal heats. High As requires higher temperatures and must not be worked at dull heats.	All weld in electric welder.	Soft. Brittle at higher As content. Turns easily.
Odor upon slight heating.		Marked odor even upon grinding bars.

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[1] This investigation is being conducted in the Chemical Engineering Laboratories of the University of Wisconsin largely through a grant of the Carnegie Institution of Washington.

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Forging.	Welding.	Machining.
Bismuth. Forged without difficulty, but Bi present in not more than trace, even though 10% added to charge.		Soft and easily machined. Bi content doubtful.
Cadmium. But one alloy made of 5% added content. Forged easily. Analysis showed no Cd present.	Welded in electric machine.	Soft and turned like steel.
Chromium. Alloys up to 22% added Cr made. Analysis agrees with added %. Forge easily at all heats, and can be worked at low temperatures. At *Cr* content of 10% they forge somewhat more difficultly.	But one Cr bar (1%) tested did not weld in electric machine.	The Cr and CrSi are in general hard, and are not put in soft condition by any annealing process.
Many CrSi alloys made, and in general forge well. Must be treated like self-hardening steels. They forge in all % Cr up to 20 or 30 and Si to several %. Forging becomes more difficult where Si reaches 3 or 4%. Temperatures used, a forging or yellow heat.	Many CrSi alloys did not weld in electric welder, but many others of about the same composition did. Evidently care needed to get right conditions.	
Further addition of Mo, Ni, or Mn to CrSi does not materially affect forgeability.	Cr + W + Si and Cr + Mo + Mn + Si did not weld in electric welder.	
Cr and Ni in all % up to 10 of each work well.	Cr + Ni in all % up to 10 of each will weld in forging.	
Addition of 0.3 to 0.5% V to alloys with up to 10% Cr did not affect forgeability.		Cr V **alloys hard.**
NiCr alloys up to 10% of each in alloy, together with 1 or 2% Si or up to 1% C, or a total of C + V = 1% forged well at normal temperatures.		These alloys were hard.
Most of the failures in forging are among Cr alloys + some other element. But in other cases alloys of like composition forged.		
Cobalt. Alloys up to 6% added and analyzed amounts agreed. Forged without difficulty at normal forging temperatures.	All were welded in electric welder except 6% Co.	Soft, except for 6% Co, which is slightly harder. But all can be machined in lathe.
Copper. Wide range of alloys of all compositions. Analysis agreed with added.	Low percentages (below 5) will weld in forging.	Lower % works easily.
Up to 2% forge well at low heats.	Also some bars of 7% welded in forge heating.	Somewhat harder with these % but work without difficulty. Hardness increases with increase of Cu. At 7% the alloy is very hard.
2 to 7% will not forge at low heat and poorly at white heat.	Up to 7% welded in electric welder.	
7% to 75 — 80% will not forge.	High % not welded.	
80 to 100% forge at fair red heat but not at normal forging heat for iron.		
In earlier work, alloys above 5% could not be worked. In later tests, many alloys of 5 to 10% were tried at all heats. With care and a high heat (welding) a 7% bar can be forged (or even an 8% rarely).		High Cu alloys work like copper. Drag on tool.
80% Cu alloy forges somewhat cold and works well at dull red.		
A 75% Cu smashed at dull red. Alloys of 5 Cu 1 Al 2 Cu ½" forged easily at high heat.	Also welded in forging.	Work easily in lathe.
But a 4½ Cu 4½ Al and a 10 Cu 4 Al smashed in forging. Likewise an 89 Cu 4 Al.	Several bars of 1 to 3% Cu and 0.5 to 1 Al welded in elec. welder.	
Two alloys of 2 As 3 Cu and 4 As 3 Cu forged at normal temperatures. The former checked badly and the latter broke in swage.	All of CuAs bars welded in elec. welder. 3 to 5 Cu and 1 to 4 As.	4 As 3 Cu brittle and hard. Also 2 As 3 Cu hard. Works easily in lathe.
The CuSi alloys worked with difficulty if Cu and Si rise to appreciable amounts. When total of Cu + Si exceeds 7% they forge with difficulty. One reported forged with 6.67 Cu and 6.67 Si, but no analysis to confirm these amounts.	1 bar 0.5 Cu and 0.25 Si did not weld in elec. welder. One of 3 Cu + 0.5 Si did.	CuSi alloys work easily like wrought iron.
At high Cu % (90 and above) the alloys do not forge if Si of 1% is present.		High Cu with Al or Si worked like Cu.
Lead. But one alloy of 3% added, but only 0.06% analysis. Worked at forging and welding heat cracked and finally broke in swage.	This one bar did not weld in electric welder.	
Manganese. Several alloys of manganese content up to 12% made. Analysis checked reasonably well. All forged without difficulty at forging and welding heats.	Bars of 0.50 and 4% Mn welded in electric machine. 12% bar did not weld.	Became hard at about 4%. 1 and 2% alloys machined with air hardening lathe tools. Others ground.
Molybdenum. Alloys up to 15% made. Analysis in agreement. Forges well at all heats. Generally worked at forging and low forging heats.		Hard, becoming very hard at 5% and upward.
Addition of 0.6 to 1.2 C to 8 to 10% Mo will forge with care. Low forging heat. An ingot of 15% Mo 1 C did not forge.		Hard.
An ingot of 10 Mo 2 Si forged at weld heat while one of 10 Mo 4 Si did not.	Also welds.	All hard.
Alloys of 5 to 10 Mo and 10 Cr forged at normal heat. Addition of 0.5C or V to this requires care in heating and working.		
A 10 Mo 2 Ni forged well.		
Various alloys of Mo up to 10% with additions of 1 or 2% Mn or about 0.5 V or about this % V with up to 0.6 C forged well at normal heats.		Hard.
Nickel. All percentages made from 0 to 100 Ni. Analysis checked closely. Lower percentages forge same as iron at normal forging temperature. Ingots sound, but usually beads on top, probably due to extrusion of last fluid material by contraction on cooling. Alloys of 25, 26, 28, 35, 50 and 75% Ni were forged without especial difficulty, although in an earlier instance a 75% smashed at low and high heat. Could not forge a 100% Ni. In	High nickel alloys (one of 85% Ni) which tended to crumble at lower heats, were welded nicely at very high temperatures of working and the liberal use of borax. Bars with all percentages of Ni were welded in elec. welder, but some failures are noted between 18% and 35% Ni.	Soft at lower percentages Ni. Becomes of moderate hardness with 10% Ni, increasing to maximum at 20-30%. Can be machined with lathe tools for all compositions, though in hardest range it is with some difficulty.

Forging.	Welding.	Machining.
later tests an alloy of 30% smashed, and one of 34% partially. With extreme care and high welding heats, with the liberal use of flux and working only at the very highest temperatures, a good bar was drawn out of an 85% Ni ingot. This high heat is probably necessary for all high Nickel. There might be a critical range about 34% Ni (Fe_2Ni?). Magnetic and resistivity tests indicate this (also dilation tests of Guillaume).		
10% Ni with 2 to 10% Cr forges easily with low Cr. Rather hard with high Cr. High forging heat.		
10 Ni with 1 to 2% Si forged with difficulty. Also with 2 Si + 1 C.		
10 to 20% Ni with 10 Mo + 1 C forged with difficulty. Also 10 Ni with 10 Mo + 2 Si.		
Ni-V alloys with 0.3 to 0.6 V and 5 to 10% Ni forged well at normal forging heat.		Ni-V alloys hard. Can be worked with proper tools.
Selenium. Only couple of alloys of low Se content.	Welded in electric machine.	
Silicon. Alloys of Si content up to 7%. Highest reported on analyzed bars 4.65%. Agreement fairly close. Works well, but for higher silicon great care must be used. Bars of 5% and 7% added Si worked at welding heat and light blows with liberal use of borax. A 6% bar smashed when working at 1 lower heats. Bars tend to shell and will not weld together.	All bars welded in electric machine. One failure noted but does not prove lack of weldability for this composition. With care, bars of lower per cent Si can be welded in forge with liberal use of borax.	Below 1% Si can be readily sawed and machined. Hardness noticeable above 1% in sawing, and at higher amounts of 6% to 7% Si the alloys are hard and very brittle. Can be worked with lathe tools, however.
An alloy of 2 Si + 0.8% C was hard to forge.		
Silver. Ingots made up to 10% added silver. Analysis shows maximum of but 0.69% Ag. Forges well at all heats.	All welded in electric welder. One failure noted with highest added Ag of 10%, but analysis shows little Ag, so no proof from this bar of lack of welding properly.	All bars soft, and machined without difficulty.
Tin. Alloys of added tin up to 10% made. Above 5% added were lost in forging, upon being tried at forging and welding heats. Highest % by analysis 2.09 from ingot of 4% added tin.	3% added tin alloy welded in forging. All bars welded in electric machine.	Higher tin alloys brittle. Works well in lathe. Somewhat harder than iron. Works like steel.
These lower percentages work fairly well, but care must be taken in heating and in working, especially near the limiting per cent of forgeability. Will not stand full welding or very low heats.		
Addition of 2% As to 2% Sn makes non-forgeable alloy.		Hard and brittle.
1½ Sn 4 Si smashed in forging and 3 Sn 1 Si cracked at all heats.		
1 Sn 2 Al worked with difficulty and 2 Sn 1 Al and 4 Sn 1 Al could not be forged.	Welded in electric welder.	
3 Sn 1 Cu 1 Al smashed in forging.		
A ½ Sn 1 Cu forged OK at high heat but not at low.		
3 Sn 0.2 P forged.	Also welded.	
Tungsten. Binary alloys up to 20% added W made. Analysis agrees closely.	All % weld in forging at welding heats.	Became hard with increasing % W until at 20% are very hard.
Forge nicely at all heats. Most of bars worked at normal forging temperatures.	All % welded in electric machine.	
5 to 15 W with 0.4 to 0.6 C forge at forging and welding heats.	Also weld in forging.	Hard.
13 W 3 Mo 0.4 C forges at high heat.	Welds.	Hard.
18 W, 6 Cr, 0.6 C, 0.3 V 10 W, 10 Mo. 0.2 C, 0.3 V, 2 Cr, 16 W, 5 Mo, 2 Cr, 0.5 C, 0.3 V hardly forgeable, except with extreme care.		Very hard.
W-Ni alloys with about 5% W and Ni from 2 to 15% forged well at forging heat.		Hard.
W-V alloys of 4 to 7% W and V from 0.3 to 0.4% worked well at forging heat. Also addition of 0.5C did not affect forgeability.		Hard.
Vanadium. 2 bars of 0.2% and 0.3% added V. No analysis. Forge well at normal heat.		Bars a trifle hard. Finish easily.

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Influence of Arsenic and of Tin Upon the Magnetic Properties of Iron.

By CHARLES F. BURGESS and JAMES ASTON.

It is an interesting fact of both scientific and commercial importance that pure iron is not necessarily the best iron for use in electrical machinery or apparatus where it is desirable to keep down the magnetic losses. Indeed, the addition of certain elements to this iron may greatly improve the magnetic properties. The addition of silicon has so greatly improved the materials used in transformer construction as to have given rise to what may be termed a revolution in the transformer industry.

The success in the use of silicon calls attention to what may be accomplished by the use of certain other alloying elements, and the purpose of this paper is to point out the apparent influence of arsenic and of tin, elements which, in the experiments here recorded, show a material reduction in hysteresis losses and an increase in permeability as compared with an approximately pure iron taken as a standard.

The results here given are submitted with due appreciation of the fact that methods of making magnetic tests are not sufficiently accurate or standardized to make the measurements of different observers strictly comparable. Also, that the alloys produced and upon which measurements have been made are not sufficient in number to warrant the assumption that factors other than the alloying agent may not have some influence upon the results which have been obtained.

In a paper presented at the fifteenth meeting of the American Electrochemical Society in May, 1909, the writers gave the results of observations on alloys of electrolytic iron with arsenic and bismuth in which the analyses of the electrolytic iron in the various iron alloys used are given; also the methods of preparing the samples and of conducting the tests. The data here given are an extension of this work, the results of further measurements, and a description of alloys with tin, a metal which is shown to have much the same influence on iron as has arsenic.

The magnetic tests are made with an Esterline permeameter. The alloys were prepared by melting electrolytically refined iron with different proportions of arsenic and of tin in magnesia crucibles placed inside of graphite containers and heated in an electrical resistor furnace. The ingots weighing about one pound were subsequently forged into rods and machined into bars 1 cm in diameter. These bars were tested for their magnetic properties under various heat treatments.

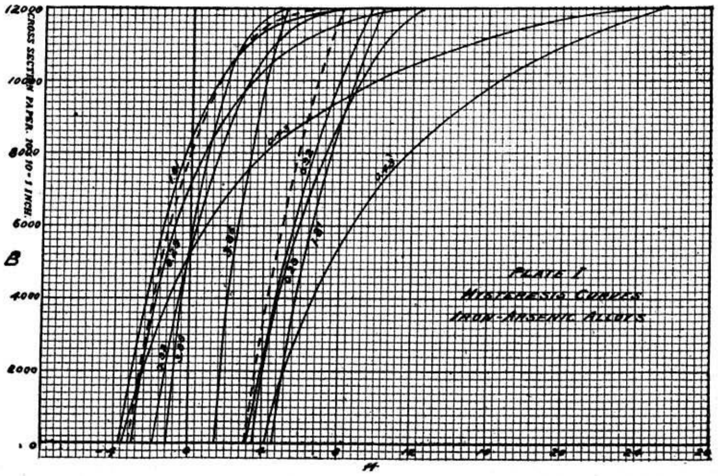

FIG. I.—HYSTERESIS CURVES. IRON-ARSENIC ALLOYS.

Check analyses have been made to determine the actual content of tin and arsenic. In the case of the arsenic the analyses checked closely with the amounts added to the crucible up to about 4 per cent, while in the case of tin there were material discrepancies between the amount added and the amount found in the resultant ingot.

As noted in the above mentioned article, the magnetic tests are all compared with a forged electrolytic iron sample, which is used as a standard. In the following table is given the analysis of this bar, together with the compositions of the original anode stock of Swedish iron and the resultant product after two electrolytic refinings:

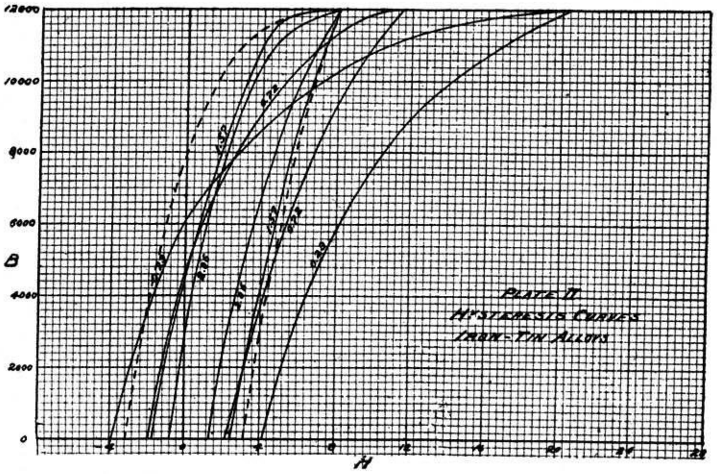

FIG. 2.—HYSTERESIS CURVES. IRON-TIN ALLOYS.

Per Cent.	Anode.	Double Refined.	Electro-forged.
C	0.260	0.012	0.047
S	0.007	None	0.005
Si	0.109	0.013	0.062
P	0.007	0.004	0.016
Mn	0.021	None	None

Iron (difference) 99.971.

As will be seen from this table, the refined material has a purity of 99.97 iron and is representative of the material used in the preparation of the alloys.

The magnetic tests were made upon all samples under four different heat treatments—first, as forged; second, after heating to 675° C. and slowly cooling; third, after heating to 1000° C. and slowly cooling; fourth, after heating to 900° C. and quenching in water. In our general series of tests the quality is indicated by a magnetization or B-H curve and by readings of the retentivity and coercive force. In this paper, since alloys of arsenic and tin are of promise mainly for transformer working, where low hysteresis loss is the governing factor, these results have been determined for a fixed value of flux density (B = 12,000) and are here plotted.

In Table I the quality of the standard is given and can be compared with the Swedish anode material, which anode stock is of a quality comparable to ordinary high grades of wrought iron. The standard reference loop for electrolytic iron is indicated in the plates as a dotted curve. It is not the best pure iron sample which we have tested, but is satisfactory as a standard in showing that if the alloys equal this material they have exceptional magnetic qualities.

Arsenic.

Tests of the iron-arsenic alloys under the four different conditions previously mentioned have been made upon the following:

Bar.	Calculated per cent arsenic.	Actual per cent arsenic.	Carbon Per Cent.
121 I	0.25	0.292	.....
121 H	0.50	0.430	.....
113 A	1.0	0.915	.....
113 B	2.0	1.810	0.042
113 D	4.0	3.862	.....
113 F	6.0	4.141	.....
113 H	10.0	3.563	.....

TABLE I—MAGNETIC TESTS DATA.

Bar	Comp. Per Cent.	H = 10				H = 20				H = 50				H = 100			
		Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900
Iron																	
N S W	Anode	9,500	10,000	10,850	8,400	13,200	14,200	13,900	12,050	15,700	16,500	15,850	15,550	17,450	18,000	17,200	
117 A	Elec forg.	13,100	10,000	13,350	11,800	15,750	15,950	15,450	14,600	17,600	17,700	17,050	16,950	18,850	18,850	18,200	18,150
Arsenic																	
121 I	0.29	10,500	13,200	10,800	11,200	14,750	15,550	14,100	14,750	16,900	17,250	16,500	16,700	18,350	18,550	17,850	17,950
121 H	0.43	7,000	7,800	10,400	8,100	13,000	14,000	13,750	12,750	16,300	16,600	15,950	16,250	17,800	18,100	17,250	17,600
113 A	0.92	6,200	6,250	11,950	12,600	13,200	14,050	14,750	15,300	16,450	17,000	16,650	17,050	17,950	18,550	17,950	18,250
113 B	1.81	8,3[illegible]	11,850	12,600	10,300	13,950	15,750	15,150	13,800	16,700	17,450	16,850	16,650	17,950	18,750	18,150	18,250
113 H	3.56	12,400	14,200	12,300	13,450	15,000	16,100	14,600	15,450	16,700	17,550	16,650	16,900	17,950	18,750	17,950	18,000
113 D	3.86	13,850	15,050	14,850	13,600	15,350	16,300	15,750	15,450	16,450	17,550	16,850	16,900	17,600	18,650	17,850	18,100
113 F	4.14	13,300	14,200	14,650	.....	15,500	15,900	15,750	.....	17,000	17,250	17,050	.....	18,200	18,450	18,150	.....
Tin																	
111 B	0.29	2,150	8,650	9,400	9,000	9,300	13,600	13,150	13,000	16,350	16,650	16,150	16,250	18,250	18,250	17,600	17,900
103 C	0.34	3,900	6,400	9,400	11,000	10,550	13,200	13,300	14,150	16,450	16,700	16,250	16,250	18,600	18,350	17,700	17,900
103 D	0.69	5,800	7,600	11,300	13,750	12,450	13,750	14,800	15,750	16,300	16,950	16,900	17,200	18,100	18,650	18,200	18,400
111 &	0.72	9,400	11,700	11,300	14,150	13,950	15,600	15,200	16,300	17,500	17,900	17,350	17,550	19,250	19,200	18,500	18,700
111 A	1.57	8,700	11,700	14,000	14,350	13,300	15,200	15,750	15,550	16,500	17,100	17,150	16,700	18,050	18,400	18,300	17,600
121 J	2.06	12,900	12,400	13,350	13,750	14,750	15,200	15,000	15,350	16,200	16,750	16,250	16,450	17,250	17,950	17,400	17,500

In addition, later tests have been made upon bars of added arsenic content of 1, 3 and 5 per cent, but analyses have not been made to confirm these percentages. Although the arsenic was supposed to be present up to 10 per cent, analysis shows 4.141 per cent as the maximum, seemingly the saturation point under the conditions of our melt. Below this percentage the arsenic is taken up by the iron in about the added proportions.

The material formed sound ingots and forged easily throughout. The bars were readily machined, but were brittle for the higher arsenic content. The alliaceous odor was very evident upon the slightest heating, being very intense during forging and readily detected even upon slight heating, due to grinding. Data of the magnetic tests are given in Tables I and II and typical curves are plotted in Plate I. The higher densities are in general reached after the annealing at 675°, while the minimum hysteresis losses at low magnetizing forces are obtained by annealing at the higher temperature of 1000°.

The hysteresis curves, however, are plotted for a fixed maximum density of 12,000 lines per square centimeter, after the last heat treatment, the quenching at 900° C. This heat treatment in reality amounts to an additional annealing, since no hardening was observed, due no doubt to the absence of carbon in the alloy. This can be seen by inspection of Table II, where the coercive forces become successively lower, even after quenching.

Nothing of particular interest is brought out in the alloys of low arsenic content. Those with a very low percentage of arsenic lie close to the electrolytic standard; with additional arsenic there is a falling off in quality. The most interesting features are noted with the iron-arsenic content of 3.86 per cent, 4.14 per cent and 3.56 per cent. Very high flux densities are reached for small impressed fields, especially after annealing, where these arsenic alloys are equal to the electrolytic material for values of H above 50 and are considerably superior below, thus ranking with the best material for which records are available.

The value as magnetic material is more clearly brought out in the hysteresis loops plotted in Plate I and the data given in Table III. There is a marked decrease in the area of the loop (which is representative of the hysteresis loss per magnetic cycle for the bar) with a high arsenic percentage of 3.86. Relative areas compared with the electrolytic standard as unity are 1.08 and 1.26, for arsenic 0.29 per cent and 0.43, respectively; this area falling off to 0.56, with arsenic 3.56 per cent, and to 0.39 for the bar with 3.86 per cent arsenic.

In our previous paper we recorded also the effect of the addition of arsenic to ordinary iron. A good grade of transformer sheet steel was melted into ingots alone and with an addition of 5 per cent of arsenic, then forged and turned into test bars. The result was a marked improvement in the magnetic quality, due to the addition of the arsenic. The effect was particularly pronounced for the lower magnetizing forces.

Tin.

A number of alloys of iron and tin were tested, of which the following six were analyzed and form the basis of this discussion:

Bar.	Per Cent Tin. Added.	Per Cent Tin. Analysis.	Per Cent Carbon.
111 B	0.2	0.288	.....
103 C	0.5	0.342	.....
103 D	1.0	0.068	0.095
111 &	2.0	0.717	.....
111 A	3.0	1.568	.....
121 J	4.0	2.059	.....

This series is somewhat analogous to the iron-arsenic series in that the volatilization point of the tin is reached before the fusing point of the iron. The analyses show that a considerable amount of the tin has been lost (about 50 per cent), but that there is still a large percentage remaining and that the bars have a resultant tin content varying in the order of the added amounts.

The data of the magnetic tests are given in Tables I and II, and representative results are plotted in Plate I. The hysteresis loops are again those obtained after quenching at 900° C.

As in the arsenic series, we note nothing of particular interest in the alloys with lower percentages of tin. They are comparable to the electrolytic standard. The real value is indicated in the hysteresis data where there is to be noted a perceptible falling off in the loss with the increase of tin. This loss is especially low in the alloys of highest tin content of 1.57 per cent and 2.06 per cent, where the relative areas are 0.67 and 0.40, respectively, compared with the standard as unity.

Comparisons.

Magnetic testing is not on such a basis that data from various sources can be taken as absolute, and on this account comparisons are apt to be misleading. Recognizing this fact, we have endeavored to make our comparisons more exact by collecting samples of commercial material and testing this upon our own apparatus. In Plate III and Table III are given the results of tests upon representative samples of high-grade materials, including silicon steels from several manufacturers and users. AM is a very pure commercial iron (99.88-Fe). AP and M are silicon sheet steels for transformer service. F is an electrical sheet steel, composition unknown.

At this place it may be well to mention that we have also made alloys of iron and silicon and our results are analogous to those of commercial silicon sheets. Our material, of course, differs essentially in being a binary alloy, practically free from the other elements usually met in practice.

In addition to the column in Table III showing the relative hysteresis losses by means

TABLE II—COERCIVE FORCE AND RETENTIVITY.

Bar	Comp. Per Cent.	H (Max) = 200 Coercive Force Unann'd				H (Max) = 200 Retentivity Unann'd			
		Unann'd	Ann'd 675	Ann'd 1000	Quench 900	Unann'd	Ann'd 675	Ann'd 1000	Quench 900
Iron									
N S W	Anode	5.5	4.8	3.9	5.0	11,400	12,700	9,000	8,500
117 A	Elec forged	5.5	6.2	5.1	2.5	12,300	13,800	10,000	8,000
ARSENIC.									
121 I	0.29	6.5	5.5	4.5	4.0	12,400	14,600	9,900	10,800
121 H	0.43	8.2	8.0	5.5	4.3	12,700	12,700	9,400	8,600
113 A	0.92	9.5	9.2	5.3	3.0	12,700	14,700	12,300	9,500
113 B	1.81	5.9	5.0	3.7	3.0	10,300	12,200	8,900	8,600
113 H	3.56	4.5	4.0	2.7	2.7	11,000	13,400	8,600	8,900
113 D	3.86	4.0	3.5	2.0	2.1	12,100	13,000	6,500	8,600
113 F	4.14	5.0	3.3	2.3	..	10,800	12,300	8,900	.....
TIN.									
111 B	0.29	23.5	7.5	5.3	5.0	12,100	11,700	9,100	8,700
103 C	0.34	12.3	8.9	5.5	3.6	12,300	12,700	9,400	8,600
103 D	0.69	7.5	7.7	4.3	3.7	8,000	12,300	10,400	12,100
111 &	0.72	7.0	5.7	3.9	2.9	11,000	13,200	8,700	8,900
111 A	1.57	6.0	4.0	4.0	3.3	10,000	13,100	11,900	10,800
121 J	2.06	3.0	4.3	3.5	2.5	8,100	11,300	9,300	8,600

of the integrated areas of the loops, we have added a column designed "relative value," and in which we have endeavored to represent the values of the materials for transformer working more consistently than is done by taking into account the hysteresis losses alone. For example, in Table III, in integration of the loops for electrolytic and Swedish iron at the same working density of B = 12,000, the hysteresis loss for the latter is 0.94, compared to electrolytic material as unity. But to reach this density the Swedish iron requires a magnetizing force of 13 and electrolytic iron but 8. Evidently, therefore, the greater number of turns necessary, together with the increased length of magnetic circuit required to give space for this extra winding, makes Swedish material of lower grade.

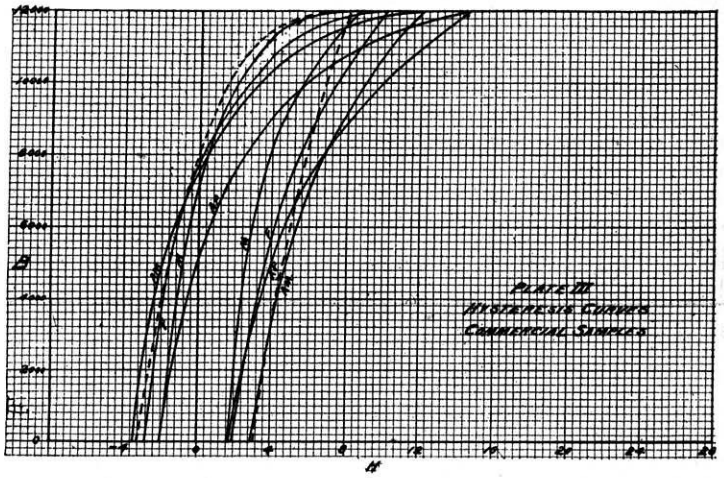

FIG. 3.—HYSTERESIS CURVES. COMMERCIAL SAMPLES.

To take into account these various factors we find that a very fair approximation of the value is obtained by making the comparison on the basis of the relative products of the loop area, times the magnetizing force required to reach the fixed density of B = 12,000 per sq. cm. These figures, compared to the standard electrolytic bar as unity, are plotted in the column "relative value."

TABLE III—RELATIVE HYSTERESIS LOSSES.

Bar.	Comp. %.	Loop Area in².	Relative Area.	B(Max) = 12000 H(Max).	Relative Value.
IRON.					
N S W	Anode	8.14	0.94	13.0	1.49
117 A	Elec forged	8.65	1.0	8.0	1.0
ARSENIC.					
121 I	0.29	9.36	1.08	12.7	1.67
121 H	0.43	10.90	1.26	25.4	3.90
113 A	0.92	7.41	0.86	9.8	1.01
113 B	1.81	11.61	1.34	10.5	1.72
113 H	3.56	4.88	0.56	6.2	0.43
113 D	3.86	3.37	0.39	5.1	0.24
TIN.					
111 B	0.29	11.42	1.32	20.2	3.26
103 C	0.34	9.59	1.11	20.5	2.77
103 D	0.69	8.00	0.93	10.5	1.19
111 &	0.72	6.09	0.70	11.5	0.99
111 A	1.57	5.86	0.67	8.1	0.67
121 J	2.06	3.46	0.40	8.1	0.40
COMMERCIAL.					
F	Sheet steel	7.25	0.84	10.2	1.22
A P	Silicon sheet	5.77	0.67	14.7	1.20
M	Silicon sheet	5.20	0.60	8.7	0.64
A M	High purity iron	9.18	1.06	12.0	1.55

Examination of the above table shows several materials with lower hysteresis losses than the electrolytic standard. Among these are a number of commercial samples; and of the alloys we note those of high arsenic and high tin content. The materials having the very lowest losses are the two bars of highest percentages of arsenic and tin. These comparative figures are better shown in the column of relative values, where, as discussed above, there is taken into account also the magnetizing force required to reach the maximum density of 12,000 lines per sq. cm.

The addition to iron of arsenic and tin has the desirable effect noted with silicon, viz., an increase of the electrical resistance with a consequent reduction of eddy current losses. Should further investigation show ageing qualities comparable to those of the silicon alloys, these iron-arsenic and iron-tin alloys are worthy of attention for transformer working in view of the evident low hysteresis and high permeability.

The above results were obtained as a part of a more extended investigation carried on under a grant of the Carnegie Institution, of Washington.

Chemical Engineering Laboratories,
University of Wisconsin.

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Observations Upon the Alloys of Iron and Manganese

By CHAS. F. BURGESS and JAMES ASTON

With the development of modern steel-making processes manganese may be said to be present in practically all steels. As the universal cure-all, the tonic of the metallurgist, it is added as a deoxidizer and in sufficient excess (up to about 1 per cent) to minimize the effect of the sulphur present. In larger quantities, running to a percentage of 10 or upward, we find it in various alloy steels for the special properties conferred.

As far as the resulting mechanical properties are concerned, we are justified in using considerable amounts of manganese, since the effect is beneficial, rather than otherwise. But how about its use in the large quantities of steel employed for its purely electrical features, in the form of sheet and also as castings?

In connection with our work upon the properties of electrolytic iron and its alloys, carried out under a grant of the Carnegie Institution, of Washington, we have observed certain peculiarities in the magnetic behavior of the iron-manganese alloys which may be of interest. The primary constituent in the preparation of these alloys is iron of high purity, gotten by double electrodeposition from Swedish iron anode bars. The character of this material may be seen in the following table:

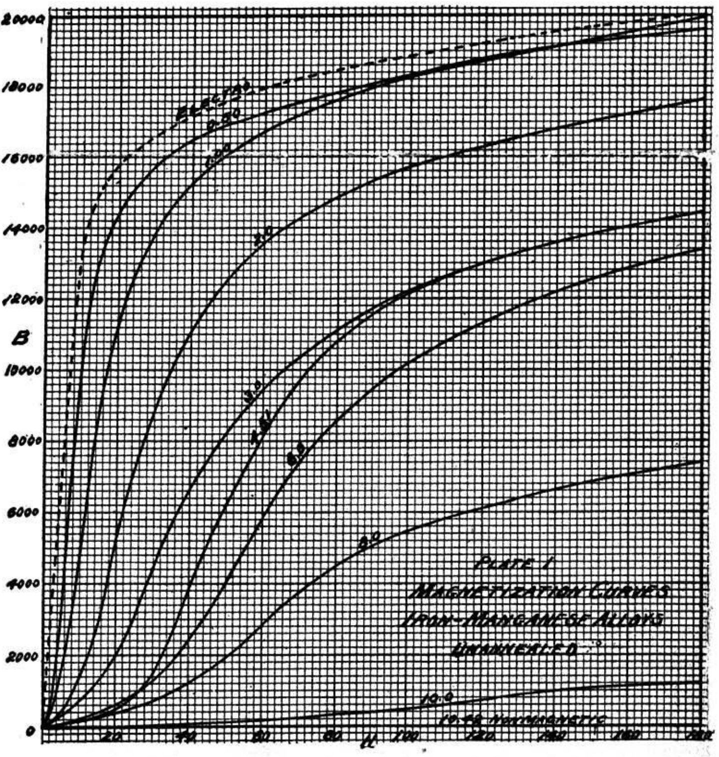

FIG. 1.—MAGNETIZATION CURVES, IRON-MANGANESE, UNANNEALED.

	Swedish Anode	Double refined as deposited	Electrolytic fused and forged
C	0.260	0.012	0.047
S	0.007	None	0.005
Si	0.109	0.013	0.062
P	0.007	0.004	0.016
Mn	0.021	None	None
Iron (by difference 99.971)			

In view of the very small amount of impurities present in the electrolytic iron, the properties of the alloys prepared may be considered to be due solely to the presence of the alloying elements. The alloys were prepared by melting the electrolytic iron, together with the other desired element, in a covered magnesia-lined graphite crucible, bedded in an electric resistor furnace. The ingot, about 1 lb. in weight, was then forged into a rod under a steam hammer. Two bars were obtained for tensile strength tests and one for the magnetic measurements.

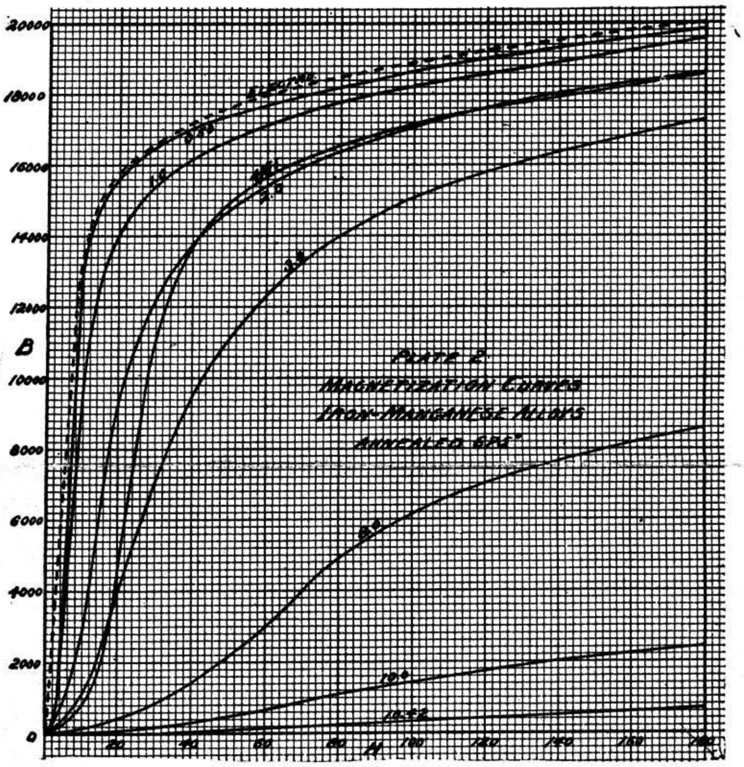

FIG. 2.—MAGNETIZATION CURVES, IRON-MANGANESE, ANNEALED 675°.

The following alloys with manganese were tested:

Bar	% Manganese Added	% Manganese Analysis
123H	0.50	0.505
170A	1.0	
170B	2.0	
170C	3.0	
144V	3.5	
123I	4.0	4.514
170D	6.0	
170E	8.0	
170F	10.0	
123J	11.9	10.419

Analyses have been made upon but three of the samples as indicated above. However, in these three instances, the intended and actual percentages are in reasonably close agreement, and it may be assumed, especially since manganese and iron are closely allied, that the bars not analyzed have a manganese content approximately as indicated by the added percentage.

All of the alloys forged readily at normal heats. Bars with

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0.50 per cent and 1 per cent manganese were soft and machined easily with ordinary lathe tools, but it was somewhat difficult because of their hardness. Above 3 per cent of manganese it was necessary to resort to grinding to work the forged pieces into finished test bars.

Tensile strength tests were made on only three of the bars, the results being as follows:

Bar	%MN	Stress per sq. in. Elas. Limit	Stress per sq. in. Ultimate	Per cent Red. Area	Per cent Elongation
123H	0.505	45200	57300	76.6	31
123I	4.514	196000	196000	0	0
123J	10.419	64500	88800	4.1	6

These figures can hardly be used as a basis for discussion, except that they bear out the general conclusion obtained in tests of commercial materials. Addition of 0.50 per cent of manganese has caused but little variation from the results with pure iron; at 4.51 per cent Mn we are in the region of great strength and brittleness, as is indicated by the high ultimate strength and the negligible elongation. At the highest percentage of manganese (10.42) the material still has high ultimate strength, but a greater toughness, shown by the elongation of 6 per cent.

The magnetic tests were made upon on Esterline permeameter, under four conditions of heat treatment, viz.: as forged, after annealing at 675° C., after annealing at 1000° C., and after quenching at 900° C. All results are compared to a standard bar of forged electrolytic iron in its unannealed state. The curve for this sample is indicated by a dotted line, and material of a quality equal to this standard is of very high grade.

The magnetic tests data are indicated in Tables I and II and Plates 1, 2, 3 and 4. In the unannealed condition the alloys show a successive deterioration in permeability with increasing manganese content, until at the maximum percentage, 10.42 (123J), the bar is non-magnetic. Bars 123H and 170A, with 0.50 per cent and 1 per cent, are not greatly inferior to the standard, this being especially true of 123H, and the discrepancy is still less after the annealing at 675°.

This annealing has resulted in a marked betterment of magnetic quality for all bars, the increase being most striking for bar 123I (4.51 per cent Mn). Bar 123J (10.42 Mn) becomes slightly magnetic and remains so throughout the succeeding tests, but it may be regarded as a non-magnetic alloy.

The second annealing at the higher temperature of 1000° has caused a considerable decrease of permeability of all bars and for all values of the magnetizing force; in fact, the materials are in practically the same condition as when raw forged. This decrease is most striking for the 4.51 per cent Mn bar, as was the previous increase.

But three of the bars have been tested in the quenched condition, and the only important feature is the great improvement in bar 123I (4.51 Mn), which has been restored to its best condition, as obtained after the first annealing at 675°. Whether this is due to any direct effect of quenching or to the reheating at the lower temperature of 900° is problematical.

The values of coercive force and retentivity, as indicated in Table II, follow most closely the fluctuations pointed out in the discussion above. The retentivities increase as a result of annealing at 675°, decrease at the high heating of 1000°, and again increase with the quenching at 900°. For bar 123H (0.50 Mn) the coercive forces become less with each annealing, and there is little change after quenching. But for other bars the values of coercive force decrease with annealing at 675°, increase after heating to 1000°, and again become less after quenching at 900°.

The deductions to be drawn from these tests may have an important bearing upon certain problems in the manufacture of steel for electrical purposes, particularly steel castings. It is well known that there is a decided lack of uniformity in this material, and experience shows that numerous concerns have difficulty in making castings of this class, although for other

TABLE I.—DATA OF MAGNETIC TESTS.

BAR	Comp. %	H=10 Unann.	H=10 Ann. 675°	H=10 Ann. 1000°	H=10 Quench 900°	H=20 Unann.	H=20 Ann. 675°	H=20 Ann. 1000°	H=20 Quench 900°	H=50 Unann.	H=50 Ann. 675°	H=50 Ann. 1000°	H=50 Quench 900°	H=100 Unann.	H=100 Ann. 675°	H=100 Ann. 1000°	H=100 Quench 900°
123H	0.50	9,850	13,000	11,300	10,700	14,300	15,600	14,550	14,400	16,950	17,400	16,600	16,850	18,300	18,400	17,900	18,150
170A	1.0	4,850	9,700	5,400	.....	11,000	14,000	11,200	.....	16,100	16,700	15,800	.....	18,200	18,000	17,800	.....
170B	2.0	1,350	3,100	1,100	.....	5,100	9,200	3,750	.....	12,500	14,700	11,350	.....	15,700	16,700	15,350	.....
170C	3.0	650	1,150	900	.....	1,900	4,000	3,150	.....	8,150	11,050	10,750	.....	12,200	14,550	14,650	.....
144V	3.5	1,100	850	950	.....	3,500	2,700	3,050	.....	10,600	10,150	9,800	.....	13,700	13,600	13,550	.....
123I	4.51	150	800	500	900	500	4,600	1,200	3,350	6,150	14,900	5,250	13,700	12,100	16,800	10,600	16,400
170D	6.0	200	.....	.....	.....	600	.....	.....	.....	3,950	.....	.....	.....	10,150	.....	.....	.....
170E	8.0	150	150	50	.....	350	400	100	.....	1,900	2,100	750	.....	5,450	6,100	1,750	.....
170F	10.0	0	50	150	0	0	100	200	.....	100	450	450	.....	500	1,400	1,300	.....
123J	10.42	0	0	0	0	0	0	0	0	0	50	50	150	0	300	300	500

TABLE II.
COERCIVE FORCE AND RETENTIVITY, H(max.) = 200

BAR	Comp'd%	COERCIVE FORCE Unann.	COERCIVE FORCE Ann. 675°	COERCIVE FORCE Ann. 1000°	COERCIVE FORCE Quench 900°	RETENTIVITY Anann.	RETENTIVITY Ann. 675°	RETENTIVITY Ann. 1000°	RETENTIVITY Quench 900°
123H	0.50	6.5	5.7	4.5	4.8	11,000	12,500	9,700	10,100
170A	1.0	9.6	6.9	7.0	....	10,800	14,700	9,000	....
170B	2.0	19.2	12.5	16.0	....	10,500	11,600	8,800	....
170C	3.0	28.7	23.0	24.0	....	8,500	9,800	9,600	....
144V	3.5	20.8	28.0	24.5	....	7,600	10,600	8,900	....
123I	4.51	41.5	23.0	45.2	23.9	8,600	15,000	8,000	12,900
170D	6.0	50.8	......	......	....	9,200	......	......	....
170E	8.0	58.7	57.5	65.0	....	5,200	6,100	2,000	....
170F	10.0	90.1	70.7	80.0	....	1,100	1,800	1,900	....
123J	10.42	Non.	103.0	121.0	78.5	Non.	400	5,000	800

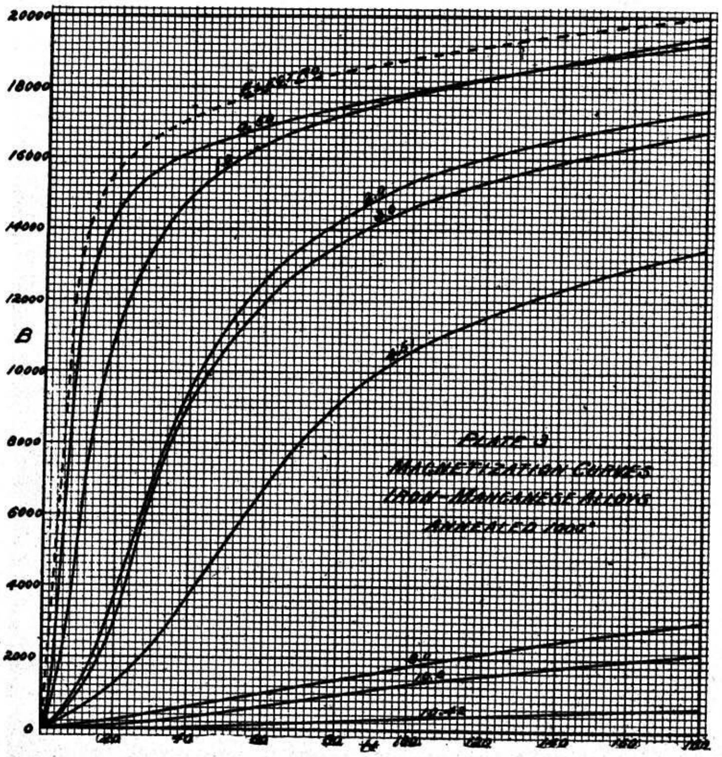

FIG. 3.—MAGNETIZATION CURVES, IRON-MANGANESE, ANNEALED 1000°.

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purposes their product is of high grade. Our results indicate a falling off in the magnetic quality of the alloys with an increase of manganese. For a percentage of 0.50 the permeability is but slightly less than that of the standard electrolytic sample. At 1 per cent Mn the quality has become appreciably less, and on further increase to 2 per cent the alloy is of comparatively low grade.

If this be true in the above series, might it not be that in commercial material where the carbon and other elements are by no means negligible that the limits of manganese content are even more closely drawn than our results indicate, and are thus very often overstepped, particularly in foundry practice? It is beyond question that any addition of manganese is a detriment. Why, therefore, in steels for electrical work, where in general strength is of secondary consideration, adhere to manganese additions? Cannot the sulphur be reduced to the lowest possible limits, and cannot the oxidation be taken care of by addition of an element such as silicon, an excess of which has a beneficial effect? Or will not the electric refining furnace solve the whole problem?

But of greater bearing than the actual manganese content is the marked susceptibility of these alloys to variations in the heat treatment. Judicious annealing at low temperatures may be of greatest benefit to material which would otherwise be condemned, while an overheating may spoil a good material or nullify the effect of heat treatment. This factor may be relevant in commercial work, where very often castings are not annealed at all; and in other cases the annealing is done without skilled supervision or without the check of a pyrometer. Or, even if carefully conducted, the temperatures used, while suitable for general work, may be too high for the electrical steels.

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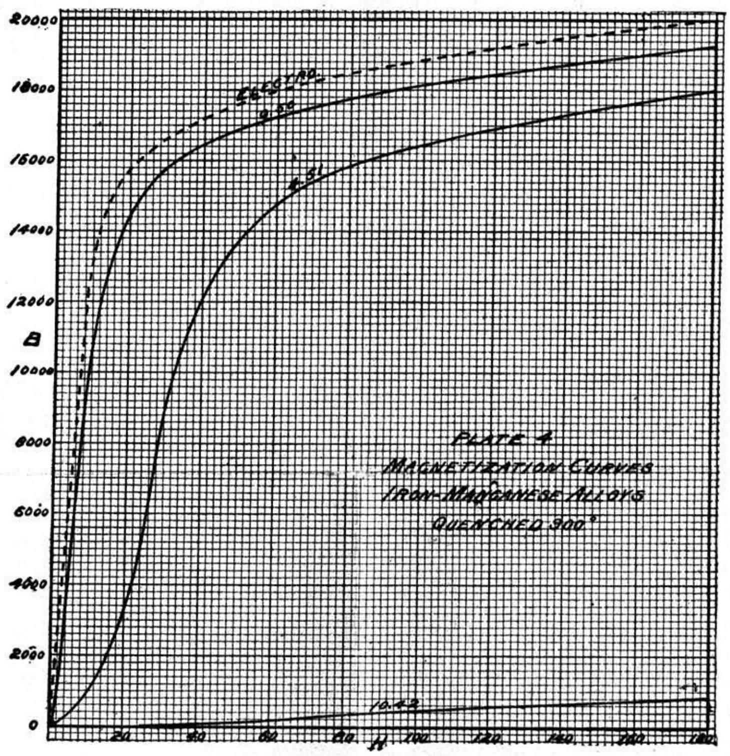

FIG. 4.—MAGNETIZATION CURVES, IRON-MANGANESE, QUENCHED 900°.