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REPRINTS

DEPARTMENT OF CHEMICAL ENGINEERING

UNIVERSITY OF WISCONSIN

Volume 4

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Influence of Silicon Upon the Properties of Ferrosilicon

Pure Commercial Alloys Containing More Than 50 per Cent Silicon Contain the Primary Compound FeSi and a Decomposition Product $FeSi_2$—Very Accurate Estimates of Silicon Content Can Be Made Quickly by Specific Gravity Determinations

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FERROSILICON has repeatedly been studied by different investigators. These investigations have been based chiefly upon ferrosilicon produced in small charges, the alloys being then treated with different solvents and the residues analyzed. Hahn assigned[1] the compounds Fe_2Si, FeSi and $FeSi_2$. De Chalmot[2] described the compound Fe_3Si_2. His determinations, however, checked up so poorly that they were not accepted as full proof of the existence of this compound, and none of the later investigators have encountered it. Gins[3] believed that the compound Fe_3Si was produced in the blast furnace from 10 per cent ferrosilicon. Tick maintained that this compound did not exist in the pure state, but only in combination with manganese such as the compound $(FeMn)_3Si$. Naske[4] believed that he had found the compound $FeSi_3$ in 50 per cent ferrosilicon after treatment of this alloy with hydrofluoric acid. This compound was not encountered by any later investigators and there is little proof of its existence.

In 1905, W. Guertler and G. Tammann[5] published the results of their researches on ferrosilicon, based chiefly upon thermal investigations. They melted Fe (99.77 per cent) and Si (98 per cent Si, 1 per cent Fe) in a porcelain test-tube placed in an electric furnace and observed the cooling and heating curves. Thermoelements were protected by ordinary porcelain tubes in the investigation of alloys containing less than 75 per cent Si. With higher silicon content the porcelain tubes were protected by sheet platinum and magnesia. Melting was performed in an atmosphere of nitrogen. In their investigations, results of which are diagrammed in Fig. 1, they encountered the two compounds Fe_2Si and FeSi, but not the compounds Fe_3Si, Fe_3Si_2, $FeSi_2$ and $FeSi_3$. However, we are not justified in excluding the existence of these last-named compounds on this account. Guertler and Tammann worked with very small charges at an average rate of heating and cooling of 100 deg. per minute. It is easily understood that the manner of crystallization obtained in this way is different from the manner obtained in large commercial charges; for instance, Dr. Pick (1906) found crystals of $FeSi_2$ in large blocks of ferrosilicon which had cooled slowly. On the whole, the following list represents the supposed ferrosilicon compounds, all but the first being relatively definitely proved:

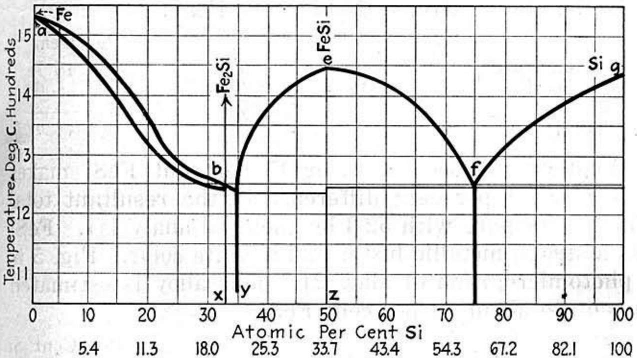


FIG. 1. EQUILIBRIUM DIAGRAM FOR IRON: SILICON ACCORDING TO GUERTLER AND TAMMANN (1905)

	Per Cent Si		Per Cent Si
Fe_3Si	14.289	FeSi	33.33
Fe_2Si	20.00	$FeSi_2$	50.00
Fe_3Si_2	25.00	$FeSi_3$	60.00

MATERIALS FOR THE PRESENT INVESTIGATION

For investigation a series of samples of ferrosilicon containing from 49.1 per cent Si to 77.46 per cent Si were obtained from Borregaard, and a sample containing 93.41 per cent Si from Kopperaaen, Meraker.

The following samples were selected and analyzed:

No.	Per Cent Si		Per Cent Si
1	93.41	12	66.25
2	77.50	13	65.70
3	76.28	14	64.10
4	76.00	15	61.95
5	75.90	16	61.40
6	74.82	17	59.10
7	72.90	18	56.01
8	72.55	19	52.30
9	72.00	20	50.90
10	71.25	21	49.10
11	70.32		

It was necessary to polish the specimens with the greatest care, because there was a tendency for large pieces to break loose from the surface, especially with alloys between 55 and 70 per cent Si. Alloy No. 18 with 56.01 per cent Si was so brittle that it could easily be broken apart with the fingers. The most brittle specimens were bonded with Canada balsam in a bunsen flame whereby they received sufficient mechanical strength for polishing.

Eutectic and separated crystalline aggregates could easily be distinguished under the microscope without etching. An attempt was made to etch the sections with weak hydrofluoric acid and weak NaOH solutions in order to see the structure of the crystalline aggregates. However, this etching gave unfavorable results, the portion of the sections which were broken out became larger and the image in the microscope less distinct. Crystals of $FeSi_2$ etched satisfactorily.

Tidskrift for Kemi, vol. 16, No. 1 (1919). From the Technical High School Laboratories of Technical Inorganic Chemistry, Prof. Thv. Lindeman.

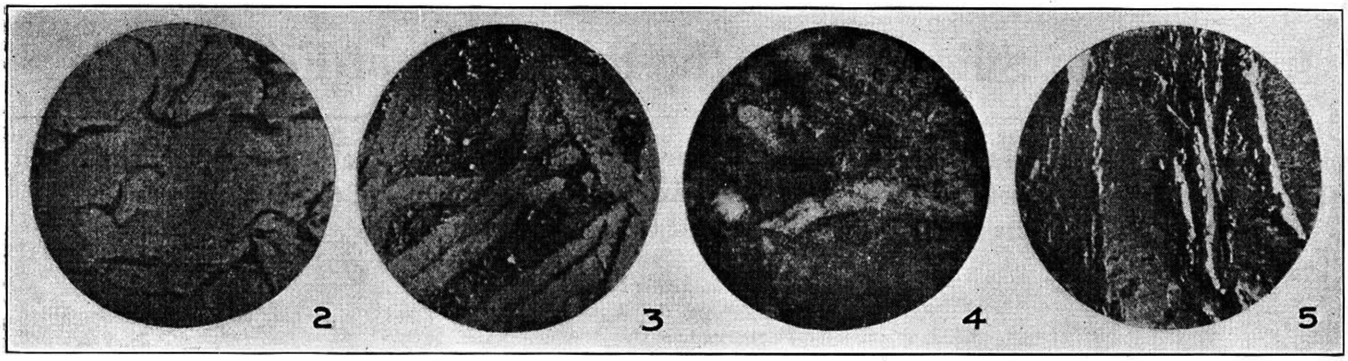
[1] *Lieb. Ann.* vol. 129, p. 57 (1864).

[2] *J. Am. Soc.*, vol. 21, p. 58 (1899).

[3] *Elektrochemie* (1901), vol. 3, p. 38.

[4] *Chem. Zeit.* (1903), vol. 27, p. 48.

[5] *Z. Anorg. Chem.*, 1905, vol. 47, p. 163.



FIGS. 2 TO 5. MICROSTRUCTURE OF FERROSILICON SAMPLES
Fig. 2. 93.4 per cent Si. × 50. Fig. 3. 77.5 per cent Si. × 50. Fig. 4. 56 per cent Si. × 65. Fig. 5. 49.1 per cent Si. × 20.

In silicon-rich melts, according to the diagram (Fig. 1), one would expect to find silicon crystals in a surrounding eutectic having a composition of about 60 per cent Si and 40 per cent Fe. This proved to be the case, except that the eutectic apparently has a composition of about 55 per cent Si and 45 per cent Fe. Crystals of silicon were observed as rather long crystalline aggregates in the midst of the surrounding eutectic; they are gray and have a bright hard surface with only a few small pieces chipped away from the surface. The surrounding eutectic presents a dotted structure with a light gold color. Large portions of the eutectic which were removed during polishing appear as black spots under the microscope.

Silicon in alloy No. 1 (93.41 per cent Si) appears in large smooth surfaces, separated by veins of eutectic (Fig. 2). The relative proportion of Si and eutectic could not be determined with accuracy by the planimetric method on account of the relatively large sizes of the crystals.

In Fig. 3 I have found it possible to obtain more truly representative portions of silicon and eutectic in one microsection. An alloy containing 56.01 per cent Si shown in Fig. 4 is the lowest in the series where crystals of pure silicon are found. This is not a representative picture of the distribution of Si, but it is that part of the section which shows the maximum amount of crystallized silicon; other portions were entirely without crystallized silicon. Intermediate analyses (alloys 2 to 17) show a progressively diminishing silicon content and an increasing eutectic content. As above noted, the eutectic works out to be about 55 per cent Si; 45 per cent Fe.

Besides the sections which are illustrated above, alloys 13, 14, 15 and 16, with 65.70, 64.10, 61.95 and 61.40 per cent Si respectively, were also investigated with the microscope. These samples, together with No. 17, approach the percentage corresponding closely to the compound $FeSi_3$ proposed by Naske. I could, however, find no indication of such a compound. All specimens showed a uniform decrease in Si and increase in eutectic content. In alloy 6, containing 74,82 per cent Si, I estimated that the amounts of crystallized silicon and eutectic present were almost equal. Figuring eutectic to contain 55 per cent Si, we obtain:

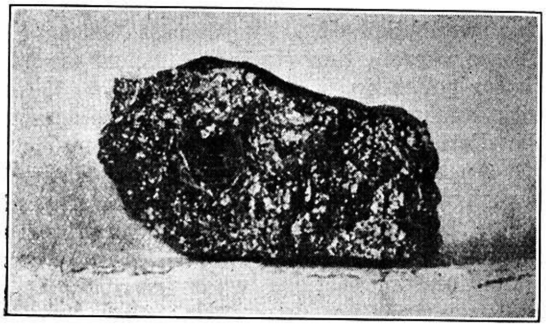


FIG. 6. LARGEST GEODE FOUND. × 2.

	Per Cent Si
50 per cent Si	50
50 per cent eutectic	27.5
Total	77.5

a departure of about 3 per cent from the correct amount as given by chemical analysis.

Alloy 19, containing 52.3 per cent Si, shows the same eutectic mixed with a new crystal form, FeSi. (See Fig. 1). Measurement of various photographs of this alloy show that the crystallized FeSi comprises from 10 to 15 per cent of the whole surface. In the former case:

	Per Cent Si
90 per cent eutectic	49.5
10 per cent FeSi	3.33
Total	52.83

In the other extreme, 15 per cent FeSi:

	Per Cent Si
85 per cent eutectic	46.75
15 per cent FeSi	5.00
Total	51.75

Whether one decides 10 or 15 per cent FeSi makes only about 1 per cent difference in the resultant total silicon (compare with 52.3 by chemical analysis). FeSi has a strong metallic luster and a white color. Fig. 5 is a photomicrograph of alloy 21. This alloy is estimated to contain about 34 per cent FeSi.

	Per Cent Si
66 per cent eutectic	36.3
34 per cent FeSi	11.3
Total	47.6

an error of about 1.5 per cent.

In ferrosilicon with silicon content ranging from 48 to 60 per cent a large number of small geodes are found. Fig. 6 shows the largest one found. In occasional pieces a whole series of small geodes were found varying from 0.5 to 1.0 mm. in diameter.

In order to investigate the contents, individual crystals were picked out carefully, avoiding as far as possible taking portions which lay directly upon the solid ferrosilicon alloy, in order not to risk contamination. The fragments gave the following analysis:

	Per Cent Fe	Per Cent Si
1	51.0	50.8
2	49.3	49.1

This corresponds closely to the compound $FeSi_2$.

The first matter which had to be determined was whether geode contents consisted of an actual compound, or if it were only an ordinary alloy which had assumed this form. A small blade from a geode, after etching with hydrofluoric acid, and magnified 100 times, showed individual crystals lying closely together, a homogeneous crystalline formation with no foreign ingredients present. It is, therefore, well established that these geode contents consist of one kind of crystal, which according to the above analyses must be the compound $FeSi_2$.

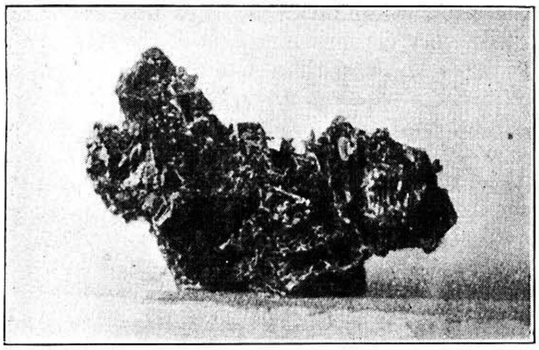


FIG. 7. LARGE GEODE IN 75 PER CENT FERROSILICON. NATURAL SIZE

Fig. 7 shows a crystalline geode found in ferrosilicon about 75 per cent Si. Its analysis gave:

	Per Cent Si	Per Cent Fe
1	82.04	17.48
2	80.95	18.80

If the geodes consisted of homogeneous crystals it would correspond approximately to the compound $FeSi_2$.

Microscopic examination showed at once a compound structure. After observing the section in the microscope it is seen that the geode consists of two distinct constituents—six cornered crystals, lying one on top of the other with an intermingling eutectic; the same eutectic, light gold in color, which was noticed in previous work (55 per cent Si). The maximum eutectic comprised 10 per cent of the whole. For example, suppose 10 per cent eutectic present. Then, if the crystals were to consist of pure silicon we could obtain:

	Per Cent Si
10 per cent of eutectic contains	5.5
90 per cent assured pure	90.0
Total	95.5

Since the analysis gave only an average of 81.5 per cent Si, this hypothesis is excluded.

Assuming that in the average analysis (81.5 per cent Si and 18.5 per cent Fe) all the iron exists as a portion of the eutectic, the distribution of silicon is:

	Per Cent Fe	Per Cent Si
41.1 per cent eutectic contains	18.5	22.6
The chemical analysis is	18.5	81.5
Balance of pure silicon		58.9

The probability is, therefore, that the geode is more nearly constituted as follows:

	Per Cent
Free silicon	58.9
Unresolved eutectic	31.1
Eutectic surrounding the crystals	10.0
Total	100.0

Particles about 5 mm. diameter of alloys 1, 4 and 11 were treated with cold 20 per cent NaOH solution. After a lapse of one day the particles crumbled into small bits, and after a lapse of one week no more dissolved.

The weakly magnetic undissolved residue was filtered off, washed, dried, and analyzed, giving:

Sample	1		4		11	
	Per Cent Si	Per Cent Fe	Per Cent Si	Per Cent Fe	Per Cent Si	Per Cent Fe
1	54.66	45.45	54.90	45.66	55.30	44.80
2	54.45	45.30	55.20	44.97	55.25	44.80

This gives an average of 54.96 per cent Si, 45.13 per cent Fe. The caustic has, therefore, dissolved out the crystallized silicon from the alloy and left remaining an alloy which shows the same constant composition for all three samples. This is the eutectic which is not attacked by the cold caustic. According to this, the composition of the eutectic should be 55 Si, 45 Fe.

In the diagram (Fig. 1) the position of this eutectic is shown at about 60 per cent Si (atomic percentage = 75). The few investigations which they carried out upon this eutectic and the large sources of error which are attached to their work indicate that the position of the eutectic at 60 per cent Si must be wrong. The eutectic must surely not be far from 55 per cent Si and 45 per cent Fe. The curves, therefore, obtain a slightly altered appearance as shown in Fig. 8.

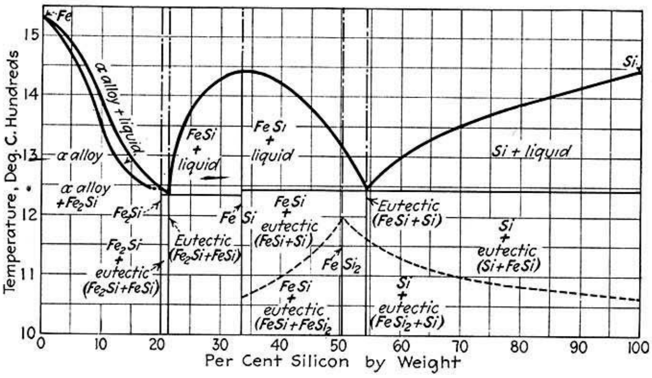


FIG. 8. EQUILIBRIUM DIAGRAM FOR IRON: SILICON ACCORDING TO LOWZOW AND HOUGEN (1919).*

The line *ef* becomes steeper in slope than the line *fg;* also for two alloys lying equidistant from the eutectic and on opposite sides when computed in atomic percentages show a great difference in the relative proportions of eutetic with their respective Si and FeSi.

The undissolved residues from alloys 4 and 11 after one week of treatment with cold caustic were treated with warm 20 per cent NaOH for one week. The warm caustic attacks the small eutectic grains, which then fall into a powder. The powder, washed and dried, possesses greater magnetic properties than the previously discovered eutectic. The analysis gave:

	Per Cent Si	Per Cent Fe
No. 4	33.8	66.3
No. 11	33.9	65.9

This corresponds to FeSi—33.4 Si and 66.6 Fe.

The warm caustic dissolved the silicon from the eutectic and left the FeSi undissolved.

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*TRANSLATOR'S NOTE: The work of T. Lowzow has established the exact composition of the eutectic FeSi and Si and has explained the formation of the compound $FeSi_2$ from this eutectic upon slow cooling. From interpretation of the modified equilibrium diagram the translator has drawn up this constitutional diagram. The dotted line below the solidus line merely indicates the probable manner of formation of the compound $FeSi_2$ and is not intended to even approximate the exact equilibrium conditions.

The specific weights of ferrosilicons given in Hönigschmid's works of 1914, "Carbides and Silicides," are:

Fe_2Si (20% Si)	7.0 (after Moissan) 22°C. 6.75 (after Lebeau) 22°C.
Fe_3Si (25% Si)	6.36 (after De Chalmot)
FeSi (33.33% Si)	6.17
FeSi (50.00% Si)	5.40 (after Lebeau)

De Chalmot gives for technical ferrosilicon the following specific gravities:

	12 per Cent Si	25 per Cent Si	46 per Cent Si
Specific gravity..	6.8	6.36	4.85

To determine specific gravity carbon tetrachloride is used; this does not attack any of the constituents of ferrosilicon. One disadvantage of carbon tetrachloride is its large temperature coefficient of expansion and high vapor tension. The specific gravity of carbon tetrachloride was determined in a Spengels pycnometer at 14.9, 17.1 and 20.1 deg. C. respectively, with parallel investigations of distilled water. Results:

Sp.gr. at 14.9 deg. C.	1.6034
Sp.gr. at 17.7 deg. C.	1.5982
Sp.gr. at 20.1 deg. C.	1.5936

Ferrosilicon is permeated through its whole mass with gas and air spaces. The specific weight must, therefore, be determined in powder form. To determine this a bottle pycnometer was used. It was found absolutely necessary to work in a thermostat. A couple of investigations were made without the thermostat, with reading of the variable temperatures and corrections to the corresponding specific gravity of carbon tetrachloride; this gave very bad results because of cumulative errors. Temperature of the room was held at about 18 deg., maximum 19 deg., and the thermostat was kept constant at 20 deg. C. After filling the pycnometer with CCl_4 and fitting on the cork it was placed in the thermostat. When the pycnometer had been heated to 20 deg. the contents expanded and the overflow was driven out of the pycnometer through the capillary stem. At the moment when no more CCl_4 came out a cap was placed over the capillary and the pycnometer was dried and weighed. During the first investigations a small glass cap was used, but this did not prevent the CCl_4 from evaporating. By fitting on a small piece of rubber tubing, which was closed at one end by a small glass bulb, all evaporation of CCl_4 was prevented.

After this the weighed amount of ferrosilicon was placed into the pycnometer, filled one-third full with CCl_4 and shaken well in order to drive out most of the entrapped air. The remaining air was expelled by evacuation. The pycnometer was then filled with CCl_4, stoppered and set into the thermostat. The operation was continued as described above. Results are given in Table I.

TABLE I. SPECIFIC GRAVITY OF POWDERED FERROSILICON

No.	Per Cent Si	Sp.Gr.	No.	Per Cent Si	Sp.Gr.
1	93.41	2.542	12	66.25	3.453
2	77.50	2.944	13	65.70	3.560
3	76.28	3.010	14	64.10	3.602
4	76.00	3.050	15	61.95	3.780
5	75.90	3.051	16	61.40	3.857
6	74.82	3.060	17	59.70	4.102
7	72.90	3.162	18	56.01	4.260
8	72.55	3.205	19	52.30	4.200
9	72.00	3.220	20	50.90	4.342
10	71.25	3.222	21	49.10	4.630
11	70.32	3.260			

These specific gravities are shown graphically in Fig. 9. The points marked 1′, 2′ and 3′ indicate the specific gravities of FeSi, $FeSi_2$ and Si respectively. Specific gravities are seen to lie fairly regular between 70 and 78 per cent Si. This is to be expected, because these alloys are produced from iron scrap and quartz and contain a very small amount of foreign constituents. No. 4 lies farthest from the curve; its analysis shows 76 per cent Si, but this determination figured from the specific weight curve should be nearer 75.2 per cent Si.

In the production of high ferrosilicon of about 75 per cent Si, very close estimations of the silicon analysis can be made in less than one hour by this specific gravity method, whereas an ordinary chemical analysis takes almost two days. This has a great commercial significance. By one step an approximate analysis can be rapidly made. If compelled to wait two days for an exact analysis there would be a risk of having the operation of the smelting furnace go wrong before being aware of it.

Poorer conditions exist with lower percentages of Si. The dotted portion of the curve represents the mean of the specific gravities. A variation from this line is to be expected since my ferrosilicon alloys were made from iron ore and quartz, naturally giving a larger opportunity for the introduction of impurities.

In order to determine if the constituent minerals would have this effect upon the specific gravities, thin sections were made upon the following samples:

Number	1	2	11	16	18	20
Per cent Si...	93.41	77.50	70.32	61.40	56.01	49.10

These were inspected in the microscope, using transmitted polarized light. In 1, 2 and 11 no minerals were found. On the other hand 16, 18 and 21 contained fairly small mineral grains in various amounts. One would expect that these were unreduced quartz; however, quartz could not be detected. Ca-Mg silicates were found, which accordingly reduce the specific gravity.

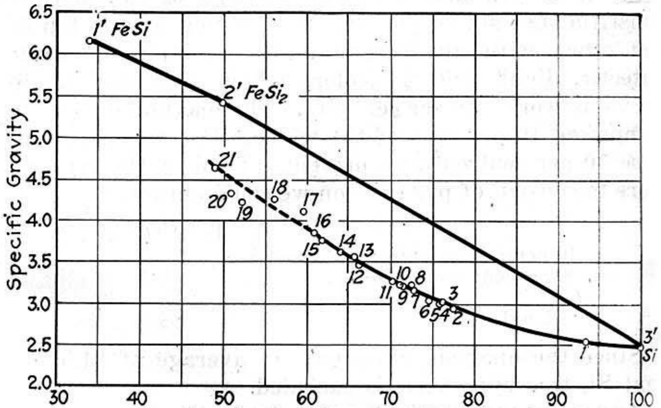

FIG. 9. SPECIFIC GRAVITIES OF POWDERED FERROSILICON

Continuing further with decreasing silicon percentages toward the eutectic (55 per cent Si), the alloy becomes continually duller in appearance. It also becomes more and more friable. No. 18 (56.01 per cent Si) is so friable that it can easily be crumbled with the fingers. Below 55 per cent Si, the alloy changes rapidly in character. Large laminated crystals of FeSi are present and impart to the alloy 50.90 per cent Si a strong metallic luster, a silver white color and great mechanical strength. Alloys which lie a few per cent to the left and up to 10 per cent to the right of the eutectic (55 per cent Si), say between 53 and 65 per cent Si, have, however, fairly little mechanical strength.

How Silica Protection Tubes Cause Contamination of Thermocouples

When Such Devices Are Used in a Reducing Atmosphere at High Temperatures, There Is a Marked Reduction in the emf. of the Thermocouple—This Is Lasting for Base Metal Couples and Temporary for Noble Metal Couples

BY O. A. HOUGEN* AND B. L. MILLER†

IT IS well known that the thermo-electric power of thermocouples is affected by contact with silica protection tubes at high temperatures, especially in a reducing atmosphere. The magnitude of this effect has seemingly not been recorded. It was the purpose of our investigation to determine this effect.

The following procedure was arbitrarily adopted. The couples to be investigated were inclosed in silica protection tubes and calibrated before and after various heat-treatments. Two types of couples were tested—one noble metal couple, platinum-platinum 10 per cent rhodium, and one base metal couple, chromel-alumel. The platinum couple was subjected to the following heat-treatments:

Preliminary annealing — oxidizing atmosphere
50 hours at 900° C. in a reducing atmosphere
50 " " 1,000° C. " " " "
50 " " 1,200° C. " " " "
Annealing at white heat—oxidizing atmosphere
50 hours at 1,000° C. — " "

The chromel-alumel couple was subjected to the same heat-treatments, except for preliminary annealing and the 50-hour heating at 1,200 deg. C.

The reducing atmosphere was obtained by loosely surrounding the silica tubes with graphite powder; the oxidizing atmosphere by the natural circulation of air through the heated tube furnace.

The apparatus for this investigation consisted of a Pt-Pt 10 per cent Rh thermocouple, a chromel-alumel thermocouple, a Type K-L & N potentiometer, storage cell, standard cell, wall galvanometer, tube furnace, resistor force, reactance coil, ammeter, L & N portable potentiometer, graphite, graphite crucibles, pure zinc, pure copper, pure antimony, and silica protection tubes.

New couples were used for these tests, the platinum couple being carefully annealed before initial use. It was understood that the base thermo-elements had been annealed before leaving the factory. The usual precise method of standardization was used in calibrating the thermocouples. The platinum couple was calibrated against the melting points of zinc and copper; the base metal couple against the melting points of zinc and antimony. The metals used were highest purity Bureau of Standards products. The assembly of apparatus for calibration against fixed points is shown in Fig. 1.

After the first calibration the couples were heated for 50 hours at a temperature of 900 deg. C. in a reducing atmosphere. The apparatus and method of heat-treatment is shown in Fig. 2.

Another heat run of 50 hours at a temperature of 1,000 deg. C. was made for both couples, and one at 1,200 deg. C. for the platinum couple only. Recalibrations were made at the end of each heat run.

The couples were then annealed and recalibrated. The couples were annealed by passing a current through the thermo-elements for 15 minutes with the platinum couple at an intense white heat and the base metal couple at a bright red heat. A run of 50 hours at 1,000 deg. C. was made on both couples in an oxidizing atmosphere and then they were recalibrated once more. Recalibration of the noble metal couple was made against fixed points. Recalibration of the base metal couple was made by comparison with a standard noble metal couple.

The calibration curves were computed from the two point equation in each case, $E = at^b$. This equation does not hold exactly over the lower temperature range, but it is useful for comparison of results. The results are given in the accompanying graphs (Figs. 3 and 4) and also in the accompanying tabulation.

WHAT THE TESTS SHOWED

First 50-Hour Run (900 deg. C.), Reducing Atmosphere—There was no change in the emf. of either couple.

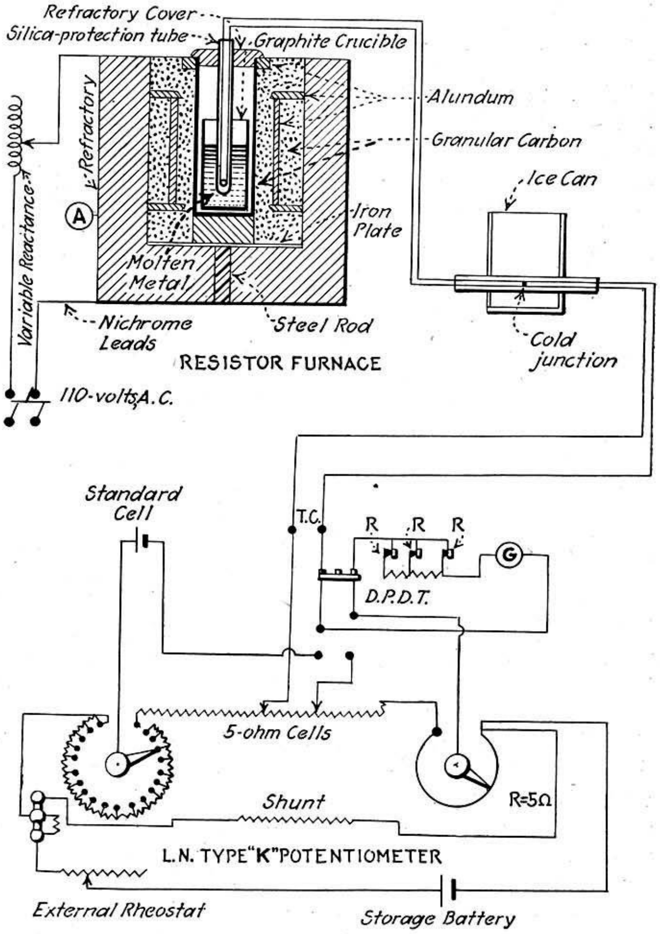

FIG. 1—ASSEMBLY OF APPARATUS FOR CALIBRATION AGAINST FIXED POINTS

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*Assistant Professor Chemical Engineering, University of Wisconsin.

†Chemical Engineering Department, University of Wisconsin.

RESULTS WITH PLATINUM THERMOCOUPLE

Calibration	Treatment	Zinc Point, Millivolts	Copper Point, Millivolts	Equation
Original	Annealed	3.36	10.458	$E = 0.0024365t^{1.1971}$
Second	50 hours at 900 deg. C. reducing atmosphere	3.36	10.46	$E = 0.0024365t^{1.1971}$
Third	50 hours at 1,000 deg. C. reducing atmosphere	3.33	10.40	$E = 0.002374t^{1.207}$
Fourth	50 hours at 1,200 deg. C. reducing atmosphere	3.23	10.21	$E = 0.002128t^{1.213}$
Fifth	Annealed oxidizing atmosphere	3.30	10.36	$E = 0.00227t^{1.206}$
Sixth	50 hours at 1,000 deg. C. oxidizing atmosphere	3.30	10.36	$E = 0.00227t^{1.206}$

RESULTS WITH CHROMEL-ALUMEL COUPLE

Calibration	Treatment	Zinc Point, Millivolts	Antimony Point, Millivolts	Equation
Original	....	16.816	25.564	$E = 0.033366t^{1.03}$
Second	50 hours at 900 deg. C. reducing atmosphere	16.816	25.564	$E = 0.033366t^{1.03}$
Third	50 hours at 1,000 deg. C. reducing atmosphere	16.27	24.479	$E = 0.03121t^{1.036}$
Fourth	Annealing oxidizing atmosphere	17.60	26.06	$E = 0.05121t^{0.966}$
Fifth	50 hours at 1,000 deg. C. oxidizing atmosphere	18.01	26.47	$E = 0.05898t^{0.9474}$

The silica tubes showed no tendency toward crumbling.

Second 50-Hour Run (1,000 deg. C.), Reducing Atmosphere—Both couples showed a reduction in emf. as a result of this run. The thermo-electric power of the noble metal couple was reduced about ¾ per cent, of the base metal couple about 4 per cent. The protection tubes became brittle and even powdered when the surface layer was removed from the tubes.

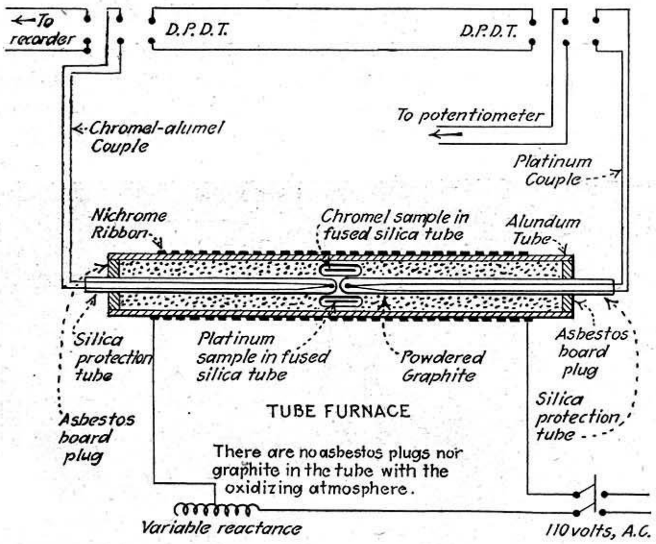
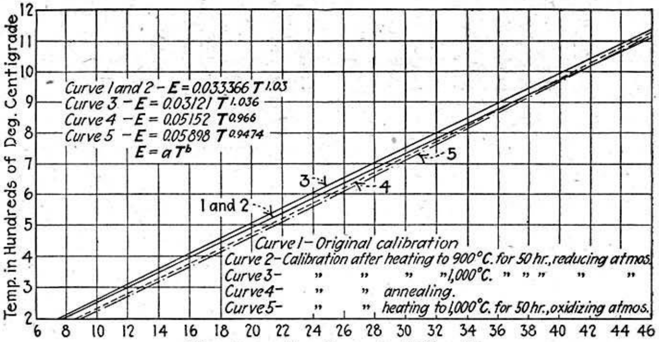


FIG. 2—ASSEMBLY FOR HEAT RUNS IN REDUCING AND OXIDIZING ATMOSPHERES

Third 50-Hour Run (1,200 deg. C.), Reducing Atmosphere—The emf. of the platinum couple showed a marked reduction. The silica tube could be easily crushed and powdered by the hand. The thermo-electric power of the noble metal couple was reduced about 3 per cent from original value.

Annealing, Oxidizing Atmosphere—The platinum couple recovered its emf. to a marked degree. The base metal coupled showed a decided increase in emf. its original value. This indicates that the siliconizing of platinum can be almost completely removed, whereas a permanent alteration takes place in the base metal couple.

Oxidizing Treatment (1,000 deg. C.) — The platinum couple showed no further alteration in emf. The base metal couple showed an increase in emf. again indicating that some permanent alteration had taken place, due to siliconizing. However, visual examination showed that both couples had become brittle in a reducing atmosphere above 900 deg. C., due to contamination by silicon from the reduced silica tubing. Evidence of this is further substantiated by the fact that the silica tubes were brittle and crumbling, and that similar results were not obtained in the oxidizing atmosphere.



Curve 1 and 2 – $E = 0.033366\,T^{1.03}$
Curve 3 – $E = 0.03121\,T^{1.036}$
Curve 4 – $E = 0.05152\,T^{0.966}$
Curve 5 – $E = 0.05898\,T^{0.9474}$
$E = aT^b$

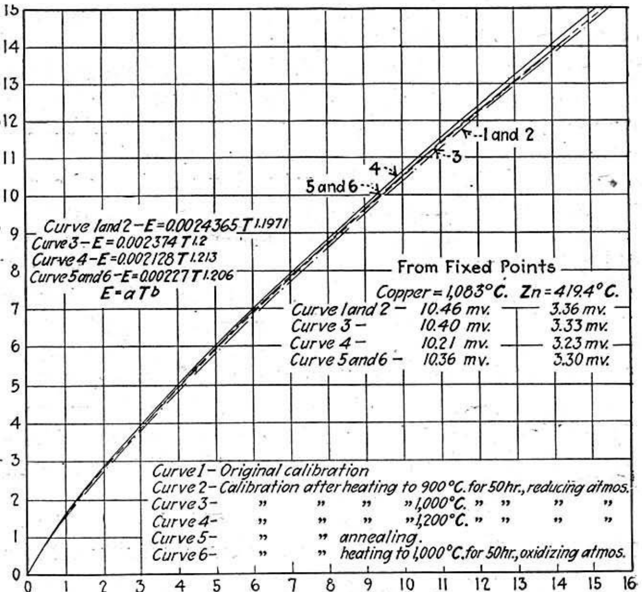
Curve 1 – Original calibration
Curve 2 – Calibration after heating to 900°C. for 50 hr., reducing atmos.
Curve 3 – " " " " 1,000°C. " " " " "
Curve 4 – " " annealing.
Curve 5 – " " heating to 1,000°C. for 50 hr., oxidizing atmos.

FIG. 3—CURVES SHOWING RESULTS OF TESTS ON BASE METAL COUPLE

At temperatures above 900 deg. C., it seems that it is impracticable to use silica protection tubes for precision work in a reducing atmosphere, as the couples become siliconized. The couples show a marked decrease in potential from the original calibrations.

In an oxidizing atmosphere, the emf. of the platinum couple remains unchanged, while that of the base metal couple shows a decided increase when used above 900 deg. C. for any length of time. This indicates that the siliconizing of platinum can be almost completely removed and the thermo-electric power of the couple restored to almost its original value. It also indicates that the siliconizing of chromel-alumel couples produce some permanent alteration in composition which cannot be remedied by subsequent annealing.

It should be made clear that in each case the couples were inserted in new silica tubes, and did not come into direct contact with the surrounding air except when annealed. It seems that, at high temperatures above 900 deg. C., the silica tube becomes porous and permits penetration of the reduced silicon vapor.



Curve 1 and 2 – $E = 0.0024365\,T^{1.1971}$
Curve 3 – $E = 0.002374\,T^{1.2}$
Curve 4 – $E = 0.002128\,T^{1.213}$
Curve 5 and 6 – $E = 0.00227\,T^{1.206}$
$E = aTb$

From Fixed Points

	Copper = 1,083°C.	Zn = 419.4°C.
Curve 1 and 2 –	10.46 mv.	3.36 mv.
Curve 3 –	10.40 mv.	3.33 mv.
Curve 4 –	10.21 mv.	3.23 mv.
Curve 5 and 6 –	10.36 mv.	3.30 mv.

Curve 1 – Original calibration
Curve 2 – Calibration after heating to 900°C. for 50 hr., reducing atmos.
Curve 3 – " " " " 1,000°C. " " " "
Curve 4 – " " " " 1,200°C. " " " "
Curve 5 – " " annealing.
Curve 6 – " " heating to 1,000°C. for 50 hr., oxidizing atmos.

FIG. 4—CURVES SHOWING RESULTS OF TESTS ON NOBLE METAL COUPLE

Oil Absorption by Paint Pigments

An Economical Paint Formula Often Depends on a Balancing of Linseed Oil and Pigment Costs—Here Are Some Comparative Absorption Values With a Definite Bearing on This Relation

BY O. A. HOUGEN AND H. D. HENTZEN
Department of Chemical Engineering, University of Wisconsin

THE amount of oil absorbed by a paint pigment is of importance in the making up of formulas for colors in oil and in estimating the cost of the finished product. This information is necessary in determining the proportion of oil and pigment required for a paste of a definite consistency.

The oil absorption factor is valuable when considering the ratio of the cost of linseed oil and the cost of pigment; thus if the oil were more expensive than the pigment, a low absorption factor would be desirable, while if the pigment cost were greater than the oil cost, a high absorption factor would be desirable. In this respect it is interesting to note the relation of French process zinc oxide and white lead (basic carbonate), the former selling at, say, 10 and the latter at 9½ cents per pound. The oil absorption factor of the zinc oxide, however, is almost three and one-half times that of white lead. With the cost of oil approximately twice that of the pigment, it may readily be seen that the zinc-oxide paste will be the more costly product.

The proportion of oil absorbed by a pigment will vary greatly with different pigments and will also be dependent on a number of factors such as particle size, the extent of grinding and the degree of deflocculation, or dispersion of the pigment. Furthermore, the kind of oil used will affect the oil absorption factor, in that some oils tend to flocculate and others to disperse the pigment particles. In the present investigation raw linseed oil was selected, because it is widely used in practice and also has very little effect on most pigments in dispersing or coagulating the pigment particles.

LIMITATIONS OF PREVIOUS METHODS

The chief difficulty in determining the amount of oil absorbed by a pigment is in obtaining a definite and reproducible end point or degree of consistency. Numerous attempts have been made to determine a suitable method that would overcome this difficulty. These methods have either been unsatisfactory or require too complicated equipment. Gardner and Coleman's test (see Paint Manufacturers' Ass'n of the U. S., Circular 85) consisted in dropping oil from a burette into a round bottom glass tumbler containing a definite weight of the pigment, and stirring with a blunt-end spatula until the pigment has absorbed just enough oil to wet the sides of the beaker. In this test, no grinding action of the oil into the paste took place. According to K. H. Barnard, the results are not comparable to practice, inasmuch as the extent of grinding is a factor in the amount of oil absorbed. (*Paint, Oil & Chem. Review*, 1920, vol. 70, No. 1, p. 8.) The changes in consistency of the samples worked with, the writers observed, were very marked after grinding, which seems to verify the claim of Barnard. As an example, a stiff paste made up of white lead and raw linseed oil was changed to a flowing consistency after grinding. This was true of most of the pigments worked with, though to a varying degree.

K. H. Barnard determined the oil capacity of pigments by grinding with oil and then thinning to such a consistency that 5 drops placed on a clean glass plate will flow 2 in. in 5 minutes when the glass is placed vertically. The criticism of this method is that for a given weight of paste applied over a given area the thickness of the paste film will vary with the density. On the other hand, if the paste were applied as a film of definite thickness, the initial surface covered will be increased, thus increasing the friction between the glass and the paint. Bingham and Green suggested the use of the plastisometer for these tests. (*Proceedings*, A.S.T.M., vol. 19, p. 691; vol. 20, p. 451.) Such an instrument was considered too complicated and expensive for most laboratories.

A NEW METHOD AND ITS ACCURACY

In order to obtain comparable values for a number of representative paint pigments it was therefore necessary to devise a simple reliable method of determining oil absorption. After considerable experimentation, the following method was found to give reproducible results: A definite weight of the air-dried pigment (about 25 grams) was placed in a small brass dish (height 1 in. and diameter 2 in.), and a raw linseed oil was added

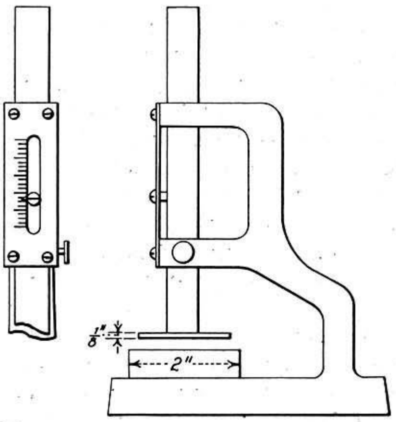


FIG. 1—MODIFIED VICAT NEEDLE APPARATUS

from a burette until all the pigment was taken up. The oil was mixed in with a spatula and after mixing was ground with the pigment with an iron rod ½ in. in diameter and 3½ in. long with one flat end used for grinding. This grinding was continued until no scratches appeared, when a small amount was spread upon a clean glass surface. The relative measure of the consistency of the paste was obtained by means of a Vicat needle apparatus, such as is used in determining the consistency and rate of hardening of cement. However, instead of a needle point a disk, ⅛ in. in thickness and 1⅞ in. in diameter, was attached to the plunger. The weight of the plunger, and consequently the pressure on the paste, was 280 grams. More oil was gradually added from a burette until a consistency was obtained such that the disk under its pressure load of 280 grams penetrated a distance of ½ in. into the paste in 1 minute. This end point consistency corresponds to the consistency of commercial paint pastes.

Factors Affecting Accuracy—Equal weights of the various pigments could not be conveniently used in the various tests due to wide variations in density of the pigments. In each case sufficient pigment was used so as to give a height of about ¾ in. of paste in the dish. Tests were made to determine whether a variable amount of the pigment-oil mixture in the dish affected the results. It was found that within wide limits the total amount of pigment used did not affect the oil-pigment ratio. Thus in the case of zinc oxide (French) a 25-gram sample gave result of 46.96 c.c. oil per 100 grams pigment and a sample of 35.5 grams gave a result of 44.9 c.c. oil per 100 grams of pigment. A smaller amount of pigment did not give sufficient material to run a test and more than 35.5 grams was too great an amount. A similar test on Chrome Green (Deep) on 35 grams gave result of 53.3 c.c. oil per 100 grams pigment, while 25 grams gave a result of 49.84 c.c. oil per 100 grams pigment. In no case was the variation greater than for duplicate tests; the maximum variation due to variation in the amount of pigment used was less than 4 per cent.

Two tests were run on each pigment. The experimental results in the accompanying tabulation show to what degree the tests check. To determine further the accuracy of the reproducibility of the method, the same batch was re-run on the testing apparatus a number of times. The results of these tests showed that the test was accurate on the same sample to within 1 or 2 per cent.

TABLE I—OIL ABSORPTION DATA FOR REPRESENTATIVE COMMERCIAL PIGMENTS

(Raw linseed oil mixed with pigment in air-dry condition)

	C.C. of Oil per 100 Gr. of Pigment	Gal. of Oil per 100 Lb. of Pigment	Lb. of Oil per 100 Lb. of Pigment	Percentage		Rel. Basis ZnO as 1
				Oil	Pigment	
White Pigments:						
Zinc Oxide (American)...	45.93	5.5	41.8	29.5	70.5	1.0
Zinc Oxide (French)......	64.5	7.74	58.5	37.0	63.0	1.4
White Lead (Dutch).....	14.5	1.74	13.2	11.6	88.4	0.31
White Lead (Carter).....	18.33	2.18	16.6	15.4	84.6	0.40
Lithopone..............	36.4	4.36	33.2	25.1	74.9	0.79
Metro-Nite.............	25.6	3.07	23.3	18.9	81.1	0.56
Blue Pigments:						
Ultramarine............	37.23	4.47	34.0	25.4	74.6	0.81
Prussian................	64.85	7.78	59.1	37.1	62.9	1.41
Green Pigments:						
Chrome Green (deep)....	49.24	5.91	45.0	31.0	69.0	1.07
Chrome Green (light)....	51.52	6.20	47.1	31.9	68.1	1.13
Yellow Pigments:						
Chrome Yellow (orange)..	44.00	5.28	40.1	28.6	71.4	0.96
Chrome Yellow (medium)	60.1	7.2	54.7	35.3	64.7	1.31
Chrome Yellow (light)....	72.0	8.65	65.7	39.7	60.3	1.57
French Ocher...........	50.3	6.5	46.0	31.7	68.3	1.1
Brown Pigments:						
Raw Turkey Umber......	91.14	10.94	83.25	45.4	54.6	1.98
Burnt Turkey Umber....	102.0	12.25	91.1	47.6	52.4	2.22
Raw Italian Sienna......	77.99	9.35	71.0	41.5	58.5	1.74
Burnt Italian Sienna.....	67.11	8.05	61.1	37.9	62.1	1.46
Red Pigments:						
Vermillion..............	23.5	2.82	21.4	17.6	82.4	0.51
Indian Red.............	31.5	3.78	28.7	24.0	76.0	0.69
Rose Lake..............	48.0	5.75	43.6	32.4	67.6	1.07
Coach Red (light)........	48.0	5.75	43.6	32.4	67.6	1.07
Red Lead...............	12.1	1.45	11.0	9.9	90.1	0.26
Iron Oxide..............	41.9	5.04	38.3	27.7	72.3	0.92

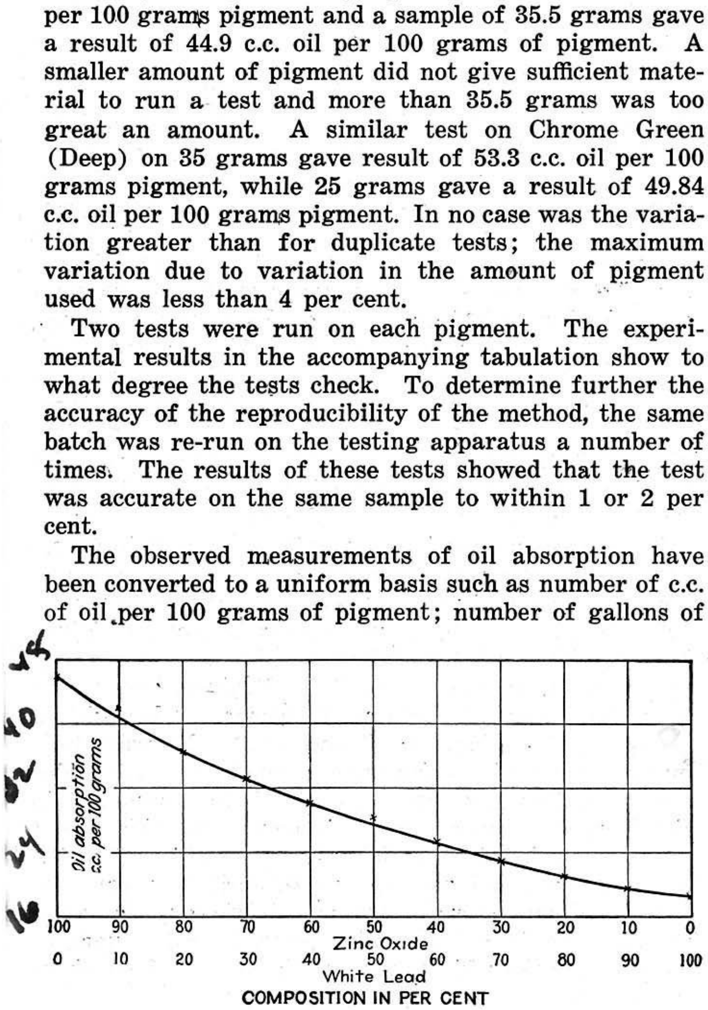


FIG. 2—OIL ABSORPTION CURVE FOR ZINC-OXIDE-WHITE LEAD MIXTURES

The observed measurements of oil absorption have been converted to a uniform basis such as number of c.c. of oil per 100 grams of pigment; number of gallons of oil per 100 lb. of pigment; number of pounds of oil per 100 lb. of pigment; per cent oil and per cent pigment. The results are also expressed on a ratio basis with zinc oxide as a unity.

ABSORPTION BY PIGMENT MIXTURES

In order to determine whether the oil absorption of two combined pigments varied in direct ratio as their percentages in amount by weight, a test was run on mixtures of American process zinc oxide and Carter white lead, the composition being varied at each 10 per cent from 100 per cent zinc oxide to 100 per cent of white lead. The results, which are given in graphical form in Fig. 2, show that the absorption for the mixture is not a direct ratio, but is less than what would be obtained by calculation.

It is of interest to note the relation of the oil absorption factors of the French process zinc oxide and the American process zinc oxide. In the study of sizes of pigment particles, Henry Green found that the French process particles were smaller than the American process particles, the former varying from 0.4μ to 0.6μ and the latter from 0.3μ to 0.4μ. ("Microscopy of Paint and Rubber Pigments," *Chem. & Met.*, Jan. 10, 1923.) The results of this test show a high oil absorption factor for the French process pigment, which is smaller in size than the American process pigment. This would seem to confirm the view that the oil absorption value increases with decrease in size of the pigment particles —that is, increases with the extent of the exposed surface.

A comparison of the above values with published data obtained by different methods of testing is not dependable, since the end point of consistency used in the various tests was not the same. The similarity of some of the writers' results with those of H. A. Gardner seems to be only a coincidence. Gardner used a stiff paste as an end point but did not grind the oil and pigment, while the writers used a more fluid end point and ground the oil and pigment. The similarity of results might be explained by the possibility that for the same amount of oil used the greater fluidity obtained was due to grinding.

The Nitrogen Survey by the Department of Commerce

By Harry A. Curtis
Chief, Nitrogen Division, Bureau of Foreign and Domestic Commerce

From time to time *Chem. & Met.* has commented on the industrial significance of the important raw materials surveys being made by the Department of Commerce under the direction of Secretary Hoover. To date but little has been published regarding the progress of this work, and it is therefore a privilege to be able to present the accompanying article, in which Dr. Curtis briefly reviews the scope and present status of the Nitrogen Survey and explains the manner in which the information has been assembled. The final results and conclusions drawn from these raw materials surveys are to be incorporated in detailed reports to be made to Congress.

Dr. Curtis also requests us to say that in spite of certain unwarranted statements to the contrary, the Nitrogen Division has met with the fullest co-operation from all of the government bureaus with which it had dealings and that its investigators in the field have likewise received the fullest support.—Editor.

The third deficiency appropriation bill passed by the last Congress carried an appropriation to enable the Department of Commerce to investigate and report upon various combinations in foreign countries in control of important commodities that affect the foreign trade of the United States. The general idea back of this Raw Materials Survey, as the project has become known, is to determine the situation with reference to all those raw materials basic to American agriculture or industry which are in any way subject to foreign control as to price or production. While the production of crude rubber is the particular item mentioned in the bill, it was recognized at the time that there are other raw materials in the same class, and the bill was purposely drawn to include these. In general, the Raw Materials Survey is being carried out under the supervision of the various commodity divisions of the Bureau of Foreign and Domestic Commerce. The Nitrogen Division was organized last May to investigate the situation with regard to supply and demand of fixed nitrogen for both agricultural and industrial use in the United States, with particular attention to the relation of our requirements to the Chilean nitrate industry. The urgent need of agriculture for cheaper nitrogenous fertilizer and the fact that the United States is buying more nitrate from Chile than any other country is buying, more in fact than all of Europe combined, without any voice whatever in deciding what the price of nitrate should be, give ample pertinency to the nitrogen survey as a part of the general investigation ordered by Congress.

Scope of the Nitrogen Survey

In planning the nitrogen survey it was recognized at the outset that there is available in technical literature a vast volume of information on various phases of the topic, and that it would be impractical to attempt a review of the whole subject in detail. The problem was to select and assemble such data from existing sources as would be needed, and to supplement these with investigations that would conform with the evident purpose for which the Congressional appropriation was made. Consideration of the proposed nitrogen survey with the above restrictions in mind led to the conclusion that adequate answers to the following questions might satisfactorily cover the ground:

(*a*) What is the agricultural situation in the United States with respect to fixed nitrogen supply?

(*b*) What is the lowest cost at which Chilean nitrate can be produced in Chile, and what range may reasonably be expected in the various factors affecting the cost of Chilean nitrate in the United States?

(*c*) Is there any reason for believing that an air-nitrogen industry will be able to compete with Chilean nitrate in supplying fixed nitrogen for agricultural purposes; and if so, how soon may we expect this competition to develop?

(*d*) What is the general trend in the domestic production of nitrogen compounds in the United States, and is there any likelihood of domestic production being able to meet the demand except through the establishment of an air-nitrogen industry?

In order to establish contact with the agricultural interests of the country, Dr. W. H. Walker and R. F. Bower, of the American Farm Bureau Federation, were added to the staff of the division. During the past summer Dr. Walker visited many of the agricultural experiment stations and agricultural colleges of the United States. Information has been supplied freely by these institutions. In this phase of the survey, and wherever agricultural matters have been involved, we have received most cordial support from the U. S. Department of Agriculture.

Field Investigation Made

Just how cheaply Chilean nitrate might be laid down in the United States is at present a matter of considerable importance, when our air-nitrogen production is getting under way, for the ability of the synthetic products to compete with Chilean nitrate will be the decisive factor in limiting growth of the nitrogen-fixing industry. For this phase of the nitrogen survey the services of Dr. H. Foster Bain, director of the Bureau of Mines, and of one of his assistants, H. S. Mulliken, were secured. These two spent the summer in Chile, observing mining and plant practices and conferring with a large number of the most active executives in the industry. The results of this field investigation are now ready for printing and will probably be issued as Part I of the general report of the nitrogen division.

There has been much progress in nitrogen-fixing processes since the war both in the United States and Europe, and a review of these developments was considered timely. F. A. Ernst was borrowed from the Fixed Nitrogen Research Laboratory for this part of the survey, and, together with Dr. J. M. Braham, also of the laboratory, spent the summer in Europe. They visited nitrogen-fixing plants in France, Italy, Norway, Germany and elsewhere and were cordially received. The results of this field study are now being assembled in the form of a report, and it is hoped that this report will serve to bring up to date the current history of the nitrogen-fixing industry and particularly to answer, as far as present indication will permit, the question as to whether this industry may presently be relied upon to supply a considerable portion of the world's fixed nitrogen demand.

The domestic production of nitrogen compounds from the processing of coal is steadily increasing and leads to

Selection Factors in Choosing Refractories for Industrial Plant Use

The Accompanying Article and Table Contain the Basic Facts Upon Which the Engineer Must Base His Choice of a Refractory

By O. A. Hougen
Assistant Professor Chemical Engineering, University of Wisconsin

IT IS obvious that there is no universal refractory fulfilling all demands, but in the selection of refractory ware a compromise must always be made so as to fulfill the most important requirements at the expense of minor desirable properties.

The general requirements of all refractories for high-temperature work are high softening point, mechanical strength at high temperatures, resistance to sudden temperature changes, chemical inertness toward any solid, liquid or gas with which it may come into contact and permanency of volume in use subsequent to manufacture. This last requirement necessitates that the raw materials should previously be calcined and shrunk, preferably by electrical fusion, to the least volume before bonding and that the bonded ware should be initially fired to a temperature exceeding any temperature to be encountered in subsequent use. It has militated against the development of super-refractories, because it is difficult to obtain uniformly heated commercial furnaces, operating above 1,800 deg. C., for firing such ware. The production of super-refractories will depend largely upon the development of such furnaces.

Certain industrial conditions demand other properties in addition to those listed above. Externally heated crucibles, furnace tubes, muffles and pyrometer tubes require a high thermal conductivity and low permeability to gases. Refractories subject to frequent handling and wear should possess hardness and resistance to abrasion. Electrically heated crucibles and wire-wound furnaces should possess high electrical resistance. Refractories used for thermal insulation should possess a low thermal conductivity and low heat capacity in order to minimize heat losses and effect a more uniform temperature control. Refractories for electrical heating elements should possess sufficient electrical conductivity to enable them to carry a heating current with a reasonably low potential drop.

Usually refractory materials are bonded with various ceramic bonds in order to give the shape mechanical strength during all the processes of manufacture such as molding, drying and baking, and also to permit firing at a low temperature. This is done at the expense of lowering the temperature of softening. Recent progress in manufacture has resulted in producing ware from the pure refractory material by bonding with a portion of material shrunk in an electric furnace which has been rendered plastic by water grinding. In this process the pure refractory material will sinter at a temperature several hundred degrees below its actual melting point. The ware produced from the simple oxides by this process does not possess high mechanical strength at high temperatures above 1,600 deg. C. This is true of magnesia, alumina, zirconia and chromium oxide. However, binary compounds of these simple oxides may be bonded by this method, with the production of ware possessing greater mechanical strength at high temperatures, as well as being more resistant to reduction by carbon, and more resistant to fusion by fused acids and alkalis. This has resulted in the development of such super-refractories as sillimanite, spinel, zircon and chromite.

Attempts have also been made to make pure refractories by casting the fused materials. This process has proved unsuccessful except in the case of glass and silica.

The properties of the common refractory materials, both bonded and unbonded, are tabulated herewith.

Refractories possessing high thermal resistance for use above 1,200 deg. C. have not been developed industrially. Thermal insulation of all refractory materials is decreased with increase in grain size, with calcination and with bonding.

Finely powdered materials such as magnesia, alumina, diatomaceous earth, lime, carbon and graphite, when dry and uncalcined, are excellent heat insulators. Carbon and graphite, however, cannot be used at temperatures above 600 deg. C. in an oxidizing atmosphere. Magnesia, alumina and diatomaceous earth cannot be used above 1,000 deg. C. because of excessive shrinkage. Lime may be used to high temperatures without shrinking.

Finely powdered materials made from the thoroughly calcined or electrically fused refractories possess higher thermal insulation than the bonded form. However, these powders sinter together at temperatures above 1,000 deg. C. and far below their melting point. For this reason they should not be used in contact with furnace parts that require frequent renewal.

Bonded diatomaceous earth possesses the highest thermal resistance of any bonded insulator commercially developed. This material is used on an extensive scale for insulating industrial furnaces. The powdered and bonded forms begin to shrink at 1,000 deg. C. and will not withstand direct flame action. One special type of bonded siliceous material produced by partial calcination may be safely used up to 1,200 deg. C. without shrinking.

The author gratefully acknowledges the generous suggestions of the following men: Dr. E. W. Washburn, of the National Research Council; M. C. Booze, Senior Fellow of the Refractories Manufacturers' Association, and M. F. Beecher, research engineer, Norton Co.

Physical and Chemical Properties of Refractory Materials

Compiled by O. A. Hougen, Assistant Professor, Chemical Engineering Department, University of Wisconsin, for *Chem. & Met.*

Material	Composition	Resistance to Chemical Action 1000° C to 2000° C					Softening Point °C	Fusion Point °C	Deformation Under Load (Under a Compression Load 50 lb./sq.in.)	Coefficient of Expansion (Linear)
		Resistance to Basic Fluxes*	Resistance to Acid Fluxes*	Resistance to Oxidation (by Air)	Resistance to Reduction* (By Carbon and Reducing Gases)	Resistance to Molten Metals (when free from oxides)				
Alumina (Granular)	Al_2O_3	Readily attacked. Soluble in fused alkalis, more readily in fused $K_2S_2O_7$ and $Na_2B_4O_7$. Attacked by strongly basic slags and vapors (12) Resists basic fluxes in lime and cement kilns (82)	Readily attacked. Attacked by fused silica and siliceous fluxes	Not attacked	Attacked appreciably by amorphous C at m.p. but not as readily by graphite (3). Forms carbide slowly at 1800° C (1) Not reduced by dry pure H_2 at 2500° C and 150 atm. (2).	Not affected		2010° C (7) [99.5% Al_2O_3] 2075 ± 25° C (8) 2000 ± 50° C (8) [92-96% Al_2O_3]		$.72 \times 10^{-5}$ (25 to 900° C) (9) $.73 \times 10^{-5}$ (25 to 900° C) (9) $.80 \times 10^{-5}$ (25 to 900° C) (9)
Alumina (Bonded)							1950° C (best grade) (8) 1300° C (inferior grade)	2050° C (14)	None at 1550° C (14)	$.71 \times 10^{-5}$ (9)
Alumina-Silica (Granular)	Chiefly (94) $3Al_2O_3.2SiO_2$, the only stable silicate of alumina at high temperatures (95)	Slowly attacked	Not attacked	Not attacked	Not readily reduced	Not affected		1860° C (42) Eutectic with Al_2O_3 at 1810° C Eutectic with SiO_2 at 1600° C		$.48 \times 10^{-5}$ (25-900° C) (9)
Alumina-Silica (Bonded)							Almost to f.p.		None at 1350° C Rigid to within a few degrees of f.p. (44)	
Porcelain (Bonded) (Refractory Grade)	Chiefly $3A_2O_3.2SiO_2$	Slowly attacked	Not attacked	Not attacked	Not readily reduced	Not affected	1630° C (54) 1650° C (65) 1200-1300° C (inferior grades)	1500°-1550° C (Impervite) 1350-1400° C (Impervite-glazed) Above 1600° C (65)	None at 1350° C (best ware)	$.28 \times 10^{-5}$ (Berlin Porc.) .44× ~~10^{-8}~~ 10^{-5} (20-1050° C)
Magnesia (Granular)	MgO	Not attacked	Readily attacked. Reacts with fireclay at 1600° C (48) and with silica brick at 1610° C (49)	Not attacked	Very slightly reduced at 1450° C. (45); at 1500° C. (46). Forms no carbide (47). Reduced rapidly only above 2000° C.	Not affected	B	2800° C		1.14×10^{-5} (120° C) (50) 1.28×10^{-5} (270° C) (50)
Magnesia (Bonded)							Becomes weak at 1300° C (pyrometer tube)	2165° C (brick) (28) 2250-2800° C (brick) (7)	Shears at 1410° C (brick) (30) Shears at 1555° C (brick) (31) Pure MgO fails at 1680° C with 7.5% SiO_2 at 1870° C (46) (Fired at 2100° C)	1.26×10^{-5} (14° to 1200°C) (83) 1.61×10^{-5} (0° to 1430° C) (88)
Spinel (Granular)	$MgO.Al_2O_3$	Not attacked	Not attacked readily	Not attacked	Not readily reduced	Not affected		2135° C (4) Eutectic with Al_2O_3 at 1925° C Eutectic with MgO at 2030° C		
Spinel (Bonded)							1910° C (brick) 2117° C (best ware)		None at 1350° C Rigid to within a few degrees of f.p.	
Silica (Granular)	SiO_2	Readily dissolved	Not attacked except by fluorides	Not attacked	Very slightly reduced at 1050° C. (57) (58). Forms carbide 1600±50° C. Rapidly at 1840±30° C. (19)	Not attacked by molten Sn, Cd, Zn and S.		β Quartz 1600-1670° C Tridymite (r) 1670° C Crystobalite (β) +1710° C (88)		
Silica (Fused and Bonded)							1400° C Devitrifies at 1100° C (depending upon atmospheric conditions)	1700-1750° C		$.54 \times 10^{-6}$
Highly Aluminous Refractories (Diaspor)		Same as for alumina	Not readily attacked	Not attacked	Not readily reduced	Not attacked		1835-1915° C (96)	1.13% at 1350° C (50 lb./sq.in.) (96) 10.7% (1538-1552° C) = (25 lb./sq.in.) (96)	

Carbon (Amorphous) (Bonded)	C	Oxidized at high temperatures by fused oxides and by fluxes containing combined oxygen	Oxidized at high temp.	Oxidizes in air appreciably at 550° C	Not affected	Not attacked by molten Cu, Zn, Al, Au, Sb, Sn, Ag, Pb, Cd. Contaminates Pt, Fe, Ni, Co, Pd, Cr, Si.	Above 2000° C.	Rapid growth of crystals above 2000° C.	None below 1800° C	$.54 \times 10^{-5}$ (88)
Graphite (Bonded)	C	Oxidized less readily than amorphous carbon	Less readily attacked than amorphous carbon. [Not attacked by fused salts, containing no oxygen, e.g. ~~Caf'z~~] CaF_2	Oxidizes in air appreciably at 640° C (61). [Not attacked by gases such as Cl_2, Br_2, HCl]	Not affected	Same as amorphous C.	Above 2000° C	4400° C Sublimes at 3900° C (1 atm.) (88)	None below 1800° C	$.78 \times 10^{-5}$ (40° C)
Silicon Carbide (Granular)	SiC	Readily attacked. Decomposed by fused alkalis and alkali sulphates. Decomposed by sodium silicate at 1300° C, especially in presence of oxidizing agents. Reacts with CuO at 800° C FeO at 1300° C NiO at 1300° C MnO at 1360° C CdO at 1370° C CaO and MgO at 1000° C	Not readily attacked Reacts with SiO_2 at 2000° C [Not attacked by fused $KClO_3$ or KNO_3.] (16)	Rapidly oxidizes above 1750° C (16). No oxid. in pure O_2 at 1000° C. Slightly in air, 1000-1350° C. Silica formed retards further oxidation 1500-1600° C. CO_2 active above 1800° C. Attacked by Cl_2 at 600° C.	Not affected	Quite similar to C. Not affected by Zn, Cu. Readily contaminates Pt, Fe, Co, Ni, Cr, Pd.		Decomposes at 2220° C (17) 2220°±20° C(18) 2240±5° C (19)		6.58×10^{-6} (15-100° C) (23) 4.38×10^{-6} (700-800° C) (23) 2.98×10^{-6} (800-900) (23) 4.35×10^{-6} (1000 ± 15° C) (23) 5.39×10^{-6} (100-200° C)
Silicon Carbide (Bonded)							Recrystallized ware does not soften below 2200° C. Depends upon bond for other ware (1400°-2000° C)		None at 1650° C (27)	4.7×10^{-6} (100-900° C)
Zirconia (Granular)	ZrO_2	Not attacked Resists fused cyanides and alkalis	Readily attacked by fused fluorides	Not attacked	Forms carbide at high temps. Rapidly at 2400° C (29)	Not attacked		2720° C (87)		$.84 \times 10^{-6}$ (29)
Zirconia (Bonded)							1800-1900° C. (84)	2563-2600° C (27) (29) (brick)	Fails at 1420° C (75 lb.) (brick) Fails at 1520° C (50 lb.) (brick) Fails at 1600° C (25 lb.) (brick)	
Zircon (Granular)	$ZrO_2 . SiO_2$	Not attacked readily by basic slags. Readily destroyed by iron sulphide, fluorspar and caustic	Not readily attacked	Not attacked	Not readily reduced	Not attacked		2550° C (87) Eutectic with ZrO_2 at 2300° C		$.443 \times 10^{-4}$ (40° C) (75)
Zircon (Bonded)									Fails at 1510° C	
Chromite (Granular)	$FeO.Cr_2O_3$	Not attacked readily. Decomposed by fused K- and Na- bisulphates. Attacked by fused NaOH and by CaO at high temperatures	Not readily attacked. Molten silica has a fluxing action (59)	Not attacked	Reduced to ferrochrome at high temps. (59)	Not attacked		2180° C (7)		
Chromite (Bonded)								2050° C (brick) (28)	Bonded Fails at 1510° C (brick) (31) Fails at 1450° C (brick) (30) Fails at 1400° C (brick) (31)	$.902 \times 10^{-5}$ (81) 1.07×10^{-5} (= 1500° C) (88) (040
Fireclay (Bonded) (Brick)		Attacked readily, especially when silica content is high	Not readily attacked	Not attacked	Not readily reduced below 1400° C.	Not recommended above 1300° C.	1500°-1600° C (best ware)	1500-1750° C	Slight deformation at 1350° C (best) Fails 1350-1500° C	$.59 \times 10^{-5}$ (83)
Silica Brick	SiO_2 96%	Readily attacked	Not attacked except by fluorides	Not attacked	Same as for silica	Same as for silica	1700-1750° C	1700-1750° C	Fails at 1700° C (92) (Load 171 lb./sq.in.)	1.21×10^{-5} (14-1200° C) (83) 1.29×10^{-5} (0-1010° C) (88)
		*In general the action of hot conc. caustic solutions is similar to the action of basic fluxes	*In general the action of conc. mineral acids at low temps. is similar to the action of acid fluxes		*Above 2000° C. all oxides and silicates are reduced by C. Bricks containing iron oxide are readily reduced by CO below 550° C. (86)					

Physical and Chemical Properties of Refractory Materials—Continued

Material	Resistance to Spalling	Apparent Density	True Specific Gravity	Thermal Conductivity (Gram calories/cm. cube/° C/second)	Electrical Resistivity (Ohms per centimeter cube)	Hardness (Mohs Scale)	Resistance to Abrasion	Specific Heat	Total Emissivity	Index of Refraction (Na light)
Alumina (Granular)			α 3.93 to 4.01 (3) β 3.03±.01 (4)	0.00162 (47° C) (88)		9+		0.1827 (5) 0.200 (6) 0.279 (20-2030° C) (89)	0.10 (500° C) ~~(87)~~ (97)	α Al_2O_3 Naϵ=1.760 Naω=1.769 βAl_2O_3 Naϵ = 1.63 Naω = 1.66
Alumina (Bonded)	Fair	2.6	3.6	Bonded 0.0083± 0.0004 (1250-650° C) (13) 0.0068 (above 900° C) (15)	47,600,000 (535° C) (8) 4,900,000 (721° C) (8) 2,400.000 (908° C) (8) 750,000 (1040° C)		Good	0.198 (14)		
Alumina-Silica (Granular)			3.23 (44)			6-7		0.1684 (0-200° C) (88)		Naα = 1.638 Naβ = 1.642 Naγ = 1.653 (14)
Alumina-Silica (Bonded)	Good	2.2 (44)	3.23 (44)	0.0044 (at 900° C) (15) 0.00432 ± 0.00015 (15)			Good			
Porcelain (Bonded)	Fair		2.24 to 2.35	0.0045 (100° C) (85)	3.3 × 10^6 (at 1000° C) (71)	6-7	Good	20-200° C 20-400° C 0.202 0.221 (86)	0.5 (500° C) (97)	
Magnesia (Granular)			3.67-3.69 (44) β MgO 3.2 α MgO (83)	0.00047 (powdered) (0-100° C) (79)		5		0.2385 (25° C) (51) -135° C 39° C 61° C 0.1006 0.1933 0.2520 287° C 390° C 0.267 276 (54) (55) 0.355 (20-2780° C) (89)	0.09 (500° C) (97)	1.66 (88) (Periclase)
Magnesia (Bonded)	Very poor (brick) (24)	2.60-2.75 2.27 (16)	3.44-3.60 (brick)	0.00652 ± 0.00012 (14) 0.0071 (at 1000° C) (22) (brick) 0.0085 (at 1000° C) (34) (brick) 0.0080 (at 1000° C) (35) (brick)	6200 (1300° C) (brick) (32) 420 (1400° C) (brick) (32) 55 (1500° C) (brick) (32) 30 (1550° C) (brick) (32) 25 (1565° C)		Very Poor (brick) (25)	~~0.22 (brick)~~ 200° C 400° C 600° C 0.253 0.275 0.290 800° C 1000° C 0.316 0.324 0.340 (1200° C) 0.349 (1300° C) (56)		
Spinel (Granular)			5.37 (88)			8-9		0.194 (15-47° C) (64)		1.7155 (88)
Spinel (Bonded)	Good						Good			
Silica (Granular)			2.20-2.65 (93)	0.00060 (20-100° C) (sand) (79)		7		(0-100) 0.1867-0.2640 ← (0-1100° C) Quartz (90) 0.1882-0.2679 ← (0-1400° C) Cristobalite (90) (0-100)		
Silica (Fused and bonded)	Excellent	2.22 transparent 2.07 translucent			5 × 10^{18} (78) (20° C) 4 × 10^4 (727° C) (88)		Good			
Carbon (Amorphous) (Bonded)	Excellent		1.7-2.0 (88)	360°C 750°C 942°C 1400° C 2000° C 0.090 0.124 0.130 0.137 0.145 (37) Granular 0.00040 (20-100° C) (79)	20° C 360° C 750° C 1400° C 2000° C 0.0046 0.0042 0.0038 0.0037 0.0036 (37) Granular 0.0069-0.0049 (0° C) L.B. Tabellen Granular 0.00403 (0° C) L. B. Tabellen		Good	0.2040 (24-68° C) 0.3145 (20-1040) (67) 0.381 (1297° C) (88)		Opaque
Graphite (Bonded)	Excellent	1.79	2.17-2.32 (88)	390° C 546° C 720° C 1400° C 2000° C 0.337 0.326 0.292 0.277 0.254 (37)	20° C 390° C 546° C 720° C 0.00085 0.00084 0.00082 0.00080 1400° C 2000° C 0.00079 0.00079 (37)	0.5-1.0	Poor	0.467 (977° C) 0.310 (19-1040° C) (67) 0.475 (0-2000° C) (68) 0.535 (0-3000° C) (68) 0.160 (11° C) 0.254 (1380° C)	0.95 (500° C) (97)	Opaque
Silicon Carbide (Granular)			3.12-3.20 (20)	0.00050 (20-100° C) fine 0.00051 (20-100° C) coarse 0.0093 (600° C) (88)		9-10		0° C 300° C 0.140 0.261 600° C 900° C 0.275 0.185 (88)		Naω=2.654 Naϵ=2.697 (14) ω = 2.786 ϵ = 2.832 (88)

quartz 2.65
tridymite 2.27

Silicon Carbide (Bonded)	Excellent (24) Fair (recrystallized)	2.3 (re crystal.) 2.45-2.60 (16)		0.0231 (at 1000° C) (22) 0.0193 (14) 0.0235 (15) 0.024 (at 750° C)	20° C 800° C 1200° C 1500° C 107 6.5 2.45 1.62 (refrax) recryst. 107,200 12,550 4,160 745 (Carbo -B) clay bond 127×10^6 835,000 29,150 8,590 (Carbofrax C)		Very Good(25)			
Zirconia (Granular)			5.8 (fused) (88) 4.75	0.00039 (79)		6.5		0.1076 (0-100° C) (70)	0.09 (500° C) (97)	
Zirconia (Bonded)	Fair (brick) (24)	3.3 (16)		Low (brick) (36)	1200° C 1400° C 1250 300 (29)		Good (brick) (25)	25-600 25-1000 0.137 0.157 25-1200 25-1400 0.167 0.175 (80)		
Zircon (Granular)			4.5-4.6 (88)					0.132 (21°-51° C) (69) 0.146 (15-100) (Regnault)		ϵ = 1.9682 (73) ω = 1.9239 (88)
Zircon (Bonded)	Good			0.0025-0.0067 (1130° C) (brick)	1232 (at 1200° C) (71)		Good (25)			
Chromite (Granular)			4.3-4.5			5.5		0.174	0.99 (1000°C) (97)	2.097 (88)
Chromite (Bonded)	Very poor (24) (brick)	2.83 (16) 3.0-3.2	3.9-4.0 (brick)	0.0034 (brick) (22)	800° C 900° C 1000° C 1200° C 1400° C 2800 760 420 450 410 320 (at 1400° C) (32)		Fair (25)	0.199		
Fireclay (Bonded) (Brick)	Good (best ware)	1.8 to 2.05	2.62-2.75 (brick)	Granular 0.00028 (20-100° C) (79) 0.00169 (100° C) ⎫ 0.00339 (1000° C) (39) ⎪ 0.0034 (at 1000° C) (66) ⎬ Brick 0.0042 (at 1000° C) (22) ⎪ 0.0040 (34) ⎭	600° C 800° C 1000° C 1200° C 21,000 12,000 6,600 2,300 1400° C 1550° C 690 60 (32)	6-7	Good (25)	25-600 25-1000 0.228 0.265 25-1200 25-1400 0.284 0.297 (80)	0.79 (400° C) (97)	
Silica Brick	Very poor below red heat. Excellent above red heat (82)	1.55-1.92	2.30-2.50	200° C 1000° C 1370° C 0.0026 0.00426 0.0050 (66)	20° C 800° C 1200° C 1500° C 125×10^6 2.38×10^6 62,000 8,420 (26)	7	Good	25-600° C 25-1000° C 0.227 0.263 25-~~100~~° C 25-1400° C 0.282 0.294 (80) 1200		
Highly aluminous refractories (Diaspor)	Good; average 9% in 10 dips (reheated brick) (96)	1.91			20° C. 800° C. 1200° C. 137×10^6 5×10^6 193,000 1500°C. 2500 (26)		Good			

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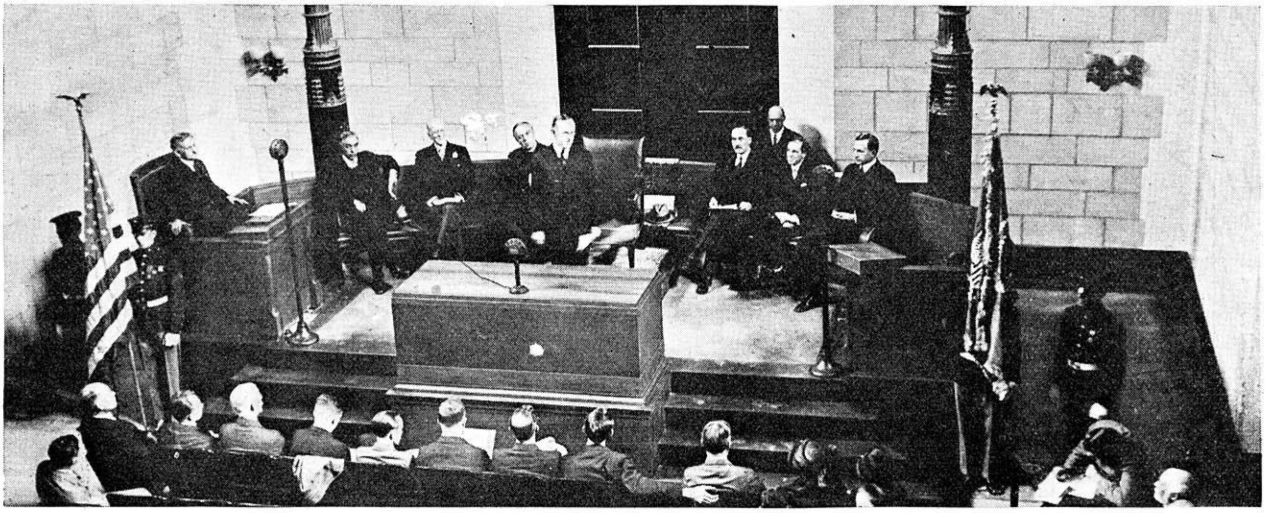

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President Coolidge Speaking at Dedication of New Building of National Academy of Sciences

The platform group, from left to right, is: A. A. Michelson, president of the Academy; C. Bascom Slemp, secretary to President Coolidge; Charles D. Walcott, secretary of the Academy; James E. Freeman, Bishop of Washington; the President; John C. Merriam, president of the Carnegie Institution; Vernon Kellogg, secretary of the National Research Council; Gano Dunn, chairman building committee, National Research Council.

"Science—Pilot of Industry"

The Magnificent Home of the National Academy of Sciences and the National Research Council Dedicated to the Amelioration of Humanity Through the Power of Scientific Research

IN the stern days of the Civil War Congress created the National Academy of Sciences partly with the idea of strengthening the national defense, but primarily to advance knowledge so that it would benefit the nation. This limitless task was begun and carried on by the brilliant individual work of the many distinguished members of the Academy and their colleagues. Then came the World War and the President of the United States called on the National Academy of Sciences to aid the nation in its emergency. This led to the establishment by the Academy of the National Research Council under the same charter. Such marvels in the co-ordination of research were accomplished and such obvious benefits accrued from the work of this body that the President asked for its continuance.

It was peculiarly appropriate that the Carnegie Foundation should have made possible a permanent home in Washington for these two great organizations. It is appropriate, for they represent in full measure one of Andrew Carnegie's ideals—the harnessing of Science to lift the burdens and improve the condition of all the people of the United States.

The ceremony of turning over this beautiful building to the Academy took place on April 28 in the presence of a distinguished gathering. The building is both a workshop and a temple. Here the visitor will find some of the marvelous discoveries of science in actual demonstration. Here, where the great diversity of work undertaken by the National Research Council is carried out, will be found exhibits of ancient and modern scientific advance. The first experiments of Faraday, upon which are based our use of electricity, stand beside the latest developments in radio. Michelson's interferometer, the Foucault pendulum, a Wilson-Shimizu apparatus for observing the tracks and collisions of atoms and scores of other exhibits, which will be changed from time to time and brought up to date, should serve as an inspiration for the visitor and a spur to the scientist.

Here in this temple, for it is more than a building, will burn the fire of "Science—Pilot of Industry, Conqueror of Disease, Multiplier of the Harvest, Explorer of the Universe, Revealer of Nature's Laws and Eternal Guide to Truth."

Here may there be born a spirit that will spread abroad the true beneficence of science. It is unfortunately believed by many that science is responsible for machines of war and destruction and that science will be man's ultimate destroyer. The looseness of thought and tongue that have been responsible for this must have effective counteraction. From such sources as these great agencies and this building must come the controversion. It will be part accomplished if the people of the country come and see the building and its great exhibits. It will be part accomplished by the teachers in school and college, if only they can give some of the thrill, the beauty, the romance of science and even some of its best utility instead of a mere catalog of facts in an obscure language.

The greatest task ahead is not the undertaking and the accomplishing of scientific work now that we have the guarantee of the National Research Council but the insuring of sympathetic understanding by the people.

Searching Chemical Literature

Annotated List of References on Sources of Information Available to the Seeker of Data

By Arthur R. Cade
Industrial Fellow, Mellon Institute of Industrial Research, Pittsburgh, Pa.

The writer has been receiving inquiries recently from several widely different sources for a list of references such as he uses in the lecture course on chemical literature, given by him at the University of Pittsburgh. It would seem therefore that there might be others interested and for that reason it might be of value to the readers of *Chemical & Metallurgical Engineering* to have the following selected list. This list, although not necessarily complete as to every article published on this subject, nevertheless contains references to the most important and useful contributions:

Barrows, Frank E.: "Investigations of the Chemical Literature," *Chem. & Met.*, vol. 24, 1921, pp. 423-428, 477-479, 517-521.
A very valuable treatise on the general subject of chemical literature and its investigation, including a discussion of the use of library facilities and general reference works.

Cobb, Ruth: "Periodical Bibliographies and Abstracts for the Scientific and Technological Journals of the World." *National Research Council Bulletin*, No. 3 (1920).
A list of the several bibliographies, yearbooks, abstracts, etc., available for use in the various branches of the sciences. A section on chemistry is included.

Eason, A. B.: "Sources of Technical Information," *Electrician*, vol. 82 (1919), pp. 326-327.
A rather brief account of a few of the information sources available to technical workers; of particular value to the engineer.

Crane, E. J.: "The Journal Literature of Chemistry," *J. Ind. Eng. Chem.*, vol. 14 (1922), pp. 900-904.
A brief account of the history and distribution of chemical literature; a plea for exactness in writing and improved chemical nomenclature; together with a very thorough discussion of indexes, how to make and how to use them.

Escher, Paul: "Some Observations on Chemical Bibliographies," *Chemical Bulletin* (Chicago), vol. 7, (1920), pp. 43-45; 73-77.
A compilation of the books and periodicals available, including chiefly bibliographies, indexes, catalogs, abstract journals, general reference works, tables of constants and dictionaries most useful to the chemist.

Hamor, William A.: "Bibliography, the Foundation of Scientific Research," *Special Libraries*, vol. 14 (1923), pp. 17-21.
A concise general discussion of the value and scope of bibliography, more particularly of chemical bibliochresis. The writer's course in chemical literature, given at the University of Pittsburgh, is described in this paper.

Hamor, William A., and others: "Chemical Reading Courses," *J. Ind. Eng. Chem.*, vol. 12 (1920), pp. 701-705, 806-812.
A comprehensive list of text-books of chemistry with a brief evaluation of each, arranged according to the specific branch of chemistry involved.

Hibbert, Harold: "The Art of Searching Chemical Literature," *Chem. & Met.*, vol. 20 (1919), pp. 578-581.
A compact treatise giving methods for conducting searches in chemical literature, particularly from the viewpoint of the technical chemist.

McClelland, Ellwood H., and others: "Symposium on Library Service in Industrial Laboratories," *J. Ind. Eng. Chem.*, vol. 11 (1919), pp. 578-589.
A series of articles by various authors—chiefly librarians—on the subject of library service in the different industries which maintain department libraries.

Mack, Harvey F.: "Chemical Literature," *J. Ind. Eng. Chem.*, vol. 11 (1919), pp. 881-882.
A short historic account of the scientific journals which have been or are now published at Easton, Pa.

Noyes, William A.: "Chemical Publications," *J. Amer. Chem. Soc.*, vol. 42 (1920), pp. 2099-2116.
A historic review of the development of the scientific chemical periodicals leading up to those published by the American Chemical Society; the purpose and scope of these latter journals are then discussed to a considerable extent.

Patterson, Austin M., and Curran, Carleton E.: "A System of Organic Nomenclature," *J. Amer. Chem. Soc.*, vol. 39 (1917), pp. 1623-1638.
A rather thorough discussion of the nomenclature as used in the Decennial Index of *Chemical Abstracts.*

Sparks, Marion E.: "Chemical Literature and Its Use."
A pamphlet of 80 pages, privately printed at Urbana, Ill. (1923), 2nd ed. Contains a series of lectures on the subject as given by the author to the third-year students in chemistry and chemical engineering at the University of Illinois. This is the best available treatise on the subject of chemical literature.

Sparks, Marion E.: "Chemical Literature and Its Use," *Science*, vol. 47 (1918), pp. 377-381.
A brief résumé of the lecture course given by Miss Sparks, referred to in reference above.

West, Clarence J., and Hull, Callie: "Manuscript Bibliographies in Chemistry and Chemical Technology," *J. Ind. Eng. Chem.*, vol. 14 (1922), pp. 1075-1077, 1148-1151. See also National Research Council *Reprint and Circular Series*, No. 36 (1922).
A list of some of the many bibliographies and selected lists of references compiled on the different subjects relating to chemistry, with information as to where the individual lists might be obtained. Further work on the compilation of this bibliography of bibliographies is being carried on by the National Research Council.

Using Gasoline for Refrigeration

That natural-gas gasoline can be used to advantage as a refrigerant is suggested by the fact that the "make" tanks and other parts of the equipment of gasoline plants frequently become coated with frost. Experiments recently conducted by the Department of the Interior at the petroleum experiment station of the Bureau of Mines, Bartlesville, Okla, confirm this assumption and indicate that volatile gasoline can be used to advantage in many refrigerating plants.

The Bureau of Mines is making a study of wax distillates in order to find out why satisfactory lubricating oils and waxes can be made easily from certain crude oils and only with difficulty from others. In the commercial distillation of crude petroleum it is customary to separate the distillates into the following groups: (*a*) Gasolines and naphthas, (*b*) kerosenes, (*c*) gas oil, and (*d*) wax distillate (consisting mostly of light lubricating oil, with small amounts of paraffin wax).

Wax distillate is separated into oil and wax by a process of chilling and filtering under pressure, followed by various refining operations. For experimental work of this character the Bureau of Mines has installed an experimental unit consisting of a refrigerating plant, cold room, wax chiller, filter press, sweating oven, etc.

In commercial wax plants ammonia is almost universally used as the refrigerating medium, but the compressor available for use in the bureau's experimental plant was built to handle natural gas containing gasoline vapor.

Serial 2510, just issued and obtainable from the Department of the Interior, Bureau of Mines, Washington, D. C., describes the results of experimental runs using gasoline as a refrigerant. The equipment as installed has proved adequate when using gasoline, and the results of the tests are published to provide data for making similar installations. These should prove useful where natural-gas gasoline is readily obtainable.

Heat Transfer

The Articles Published Herewith Have Significant Bearing on the Technology of This Unit Process and as Such Are of Interest to Production Men in the Chemical Engineering Industries

Effect of Size and Physical Properties on the Heat Absorption of Checkerbrick

An Account of Some Tests on Various Refractories Which Resulted in Establishing Facts of Use to Engineers as to the Relative Merits of Possible Refractory Materials

BY O. A. HOUGEN* AND DAVID H. EDWARDS†

THE chief purpose of brick checkerwork in any heat interchanger, such as in regenerators and hot blast stoves, is to provide a rapid absorption of heat from the hot outgoing gases and rapidly to transfer this absorbed heat to the incoming cold gases when the direction of gas flow has been reversed. It is the purpose of this paper to study some of the factors determining the rate of this heat interchange.

In the selection of refractories for the checkerwork of heat interchangers other properties besides thermal properties, such as fusion point, load-carrying capacity at high temperature, resistance to spalling, chemical corrosion and abrasion, etc., must be given primary consideration. In fact there are usually no refractories possessing all these desirable properties. In most cases the choice of a refractory must be restricted to a single type without consideration of its thermal properties.

The customary construction and design of checkerwork has been based upon years of experience. The use of standard shapes and the attainment of high mechanical strength have usually determined the type of construction.

Despite these restrictions, it was thought desirable to study those properties of a checkerbrick which determine the rate of heat absorption, inasmuch as such a study might suggest possible improvements, either in composition, construction or operation.

In order to study the process of heat interchange it will be convenient to confine our attention to one particular point in the checkerwork. In this discussion a brick located in the middle of the regenerator is chosen. Assume, also, that the regenerator is operating steadily with a constant temperature in the combustion chamber so that the average temperature gradient of the outgoing hot gases and also of the incoming air and producer gas will be the same for each cycle. When such conditions are established, the average temperature of the brick will be constant.

The transfer of heat from the hot gases to the brick will take place by the usual three ways: by radiation, by convection and by conduction. The transfer of heat by radiation can be neglected because this depends upon the emissivity of the hot gases, which is practically zero. If the gas contains suspended material such as soot and slag, its emissivity might be considerable, in which case there would be some transfer of heat by radiation. The presence of such dust is, however, accidental rather than intentional, so this factor is neglected.

Transfer of heat by convection depends upon conduction of heat through a thin film of gas adhering to the surface of the brick. The effect of a high velocity of gas is to reduce the thickness of this film of gas by a shearing action. The thickness of this film will vary inversely as the square root of the velocity (approximately), hence the heat transmission by convection will vary as the square root of the velocity. The average temperature of the surface of the brick will be lower than the average temperature of the hot gases passing by. The temperature actually measured with an optical pyrometer sighted on this brick (assuming that black body conditions prevail) will be the surface temperature and not the temperature of the hot gases. Also, if a properly protected thermocouple were inserted into the regenerator at this point, its recorded temperature would correspond more closely with the surface temperature than with the tempera-

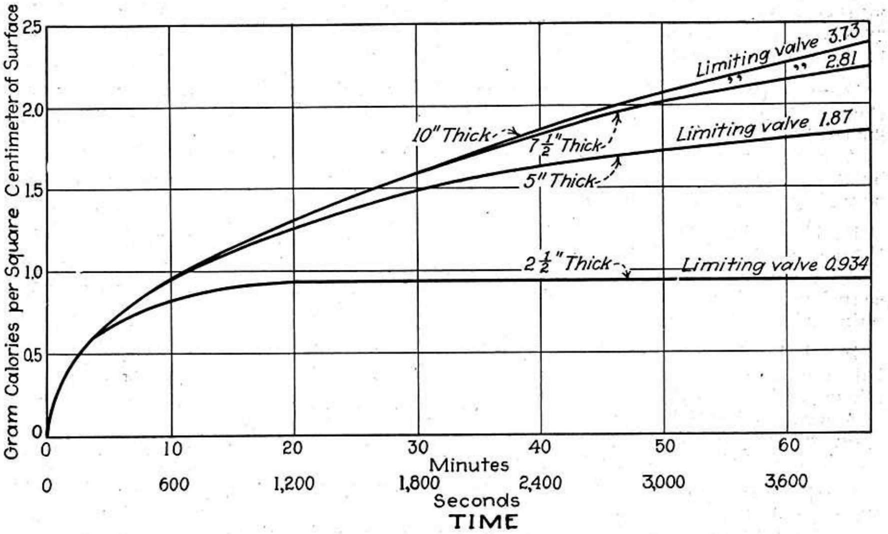

FIG. 1—CURVES OF TOTAL HEAT INFLOW INTO SILICA BRICK

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†Student, 1923, University of Wisconsin.

ture of the hot gases. If the temperature of the surface of the brick is measured instead of the actual temperature of the gases passing by, the temperature of the gases need not be considered.

THEORY OF HEAT CONDUCTION IN CHECKERWORK

The transfer of heat from the surface of the brick to its interior will take place by conduction. The rate at which heat will be stored up in the brick will depend upon its thermal conductivity, density, diffusivity and specific heat. It will also depend upon the thickness of the brick, its shape and specific dimensions. The maximum amount of heat which the brick will absorb will depend upon the original mean temperature difference between the surface and the average initial temperature of the brick; upon its density, specific heat and volume.

The rate of heat flow through any particular area of the brick will be equal to the product of the thermal conductivity and the temperature gradient in the direction of heat flow at that point. As the brick becomes saturated, the temperature gradient at this point approaches zero and no more heat will flow or be absorbed. If, however, the checkerbrick were located on the outside wall, it would be receiving heat from only one side and losing heat from the other side. In this case the brick would never become saturated, but would assume a constant temperature gradient that would correspond to the state of steady flow when it would be losing heat as rapidly as it received it.

The mathematical relation expressing the amount of heat that is absorbed by a brick heated from two sides only when the temperature of the two surfaces is held constant is given by the equation:

$$H = \frac{-4k\theta_o p}{h^2\pi^2}\left\{\left(e^{\frac{-h^2\pi^2 t}{p^2}} - 1\right) + \frac{1}{9}\left(e^{\frac{-9h^2\pi^2 t}{p^2}} - 1\right) + \frac{1}{25}\left(e^{\frac{-25h^2\pi^2 t}{p^2}} - 1\right) + \ldots\right\}$$

where H = gram calories which have flowed through 1 sq.cm. of surface area in time t.

t = time elapsed in seconds.

p = thickness of brick in centimeters.

h^2 = diffusivity $= k/c\rho$ where

k = thermal conductivity in gram calories per centimeter cube per second per degree Centigrade.

ρ = specific heat.

c = apparent density.

$\theta_o = \theta_s - \theta_b$ where

θ_s = temperature of surface of brick.

θ_b = average initial temperature of brick.

The reader must take the above equation for granted or refer to Ingersoll and Zobel's treatise on "The Mathematical Theory of Heat Conduction." The development of this equation in this paper is deemed inexpedient and unnecessary.

Theoretically the above equation holds only for the special case of parallel walls which are heated from two sides only. This approximates the condition encountered in many types of heat interchangers. With a few simple assumptions the equation can be made applicable to the more complicated checker construction as shown later.

In applying this equation to actual cases, the exponential terms after the third always drop out for values of time greater than 5 minutes, and in many cases only the first exponential term need be considered. In evaluating the expression, however, it is necessary to find the sum of the series

$$1 + \frac{1}{9} + \frac{1}{25} + \frac{1}{49} + \frac{1}{81} + \ldots$$

This can be done by remembering that when $t = \infty$ the brick will be uniformly heated to the temperature θ_s. The heat capacity of a brick per degree difference will be $cp\rho A$. where A is the area of one side of the brick. The total heat that has passed into the brick through unit area from one surface is given by the following

$$H = \frac{c\rho p\theta_o}{2}$$

Substituting $t = \infty$ and equating, we obtain

$$\frac{c\rho p\theta_o}{2} = \frac{4k\theta_o p}{h^2\pi^2} \times \left(1 + \frac{1}{9} + \frac{1}{25} + \frac{1}{49} + \frac{1}{81} + \ldots\right)$$

Transposing terms, and remembering that $h^2 = \frac{k}{c\rho}$ the value of the series

$$\left(1 + \frac{1}{9} + \frac{1}{25} + \frac{1}{49} + \ldots\right) = \frac{\pi^2}{8} = 1.232$$

EFFECT OF SIZE AND PHYSICAL PROPERTIES

By application of the above formulas the effect of size and physical properties of various refractories on the rate and amount of heat absorption can be studied. It was decided to study six different bricks of widely differing properties. The bricks selected were carborundum, graphite, silica, firebrick, magnesia, and Sil-O-Cel. These bricks were selected because they represent the very widest variation in properties, though it is obvious that graphite and Sil-O-Cel would be entirely unsuitable as checkerbrick. The thicknesses chosen were 2½, 5, 7½ and 10 in. respectively, because these dimensions represent even multiples of the standard thickness, 2½ in.

The thermal properties of these refractories are not known with any high degree of precision. The best data available are tabulated in Table I. It should be noted that these properties vary with the raw materials used and the method of manufacture, particularly the temperature of firing. The thermal conductivity and diffusivity units were taken at an average temperature of 750 deg. C.

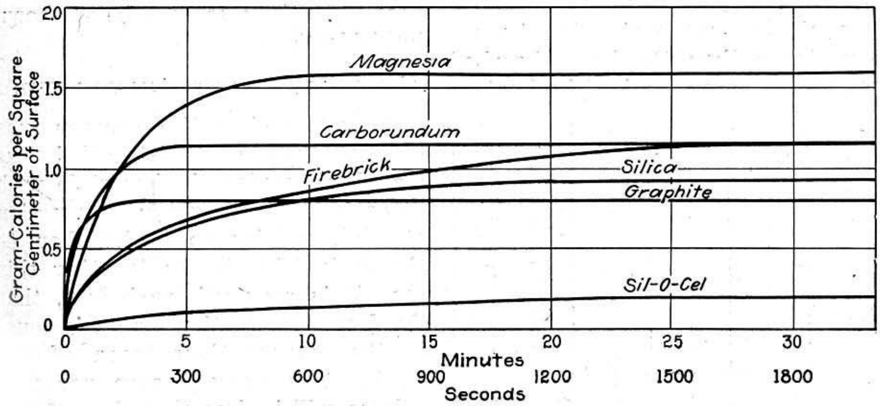

FIG. 2—HEAT ABSORBED BY VARIOUS REFRACTORIES

TABLE I—THERMAL PROPERTIES OF REFRACTORIES

Material	Apparent Density	Specific Heat	Thermal Conductivity	Diffusivity
Graphite	1.79	0.16	0.291	1.02
Carborundum	2.30	0.16	0.024	0.065
Magnesia	2.27	0.22	0.0135	0.027
Silica	1.56	0.19	0.00375	0.0227
Firebrick	1.905	0.19	0.00327	0.00903
Sil-O-Cel	0.48	0.19	0.00024	0.0026

Chemical Rubber Co.'s Handbook.
B. Dudley Jr. in *Trans*. Am. Chem. Soc., 1915.
Celite Products Co. catalog.

TABLE II—TIME REQUIRED TO HEAT REFRACTORIES OF VARIOUS THICKNESSES
(Parallel Walls—Only Two Surfaces Exposed)

Type of Brick	Thickness, In.	Heat Capacity Per Degree Per Unit Area (Gm./Cal.)	Time Required to Reach 95% Saturation, Min.
Magnesia	2½	1.59	6.9
	5	3.18	27.5
	7½	4.77	61.9
	10	6.36	110.0
Carborundum	2½	1.16	3.0
	5	2.35	12.0
	7½	3.53	27.0
	10	4.70	47.0
Silica	2½	0.934	14.5
	5	1.87	58.0
	7½	2.81	131.0
	10	3.73	233.0
Firebrick	2½	1.15	21.0
	5	2.31	64.0
	7½	3.45	188.0
	10	4.62	336.0
Graphite	2½	0.84	0.19
	5	1.68	0.74
	7½	2.98	1.67
	10	3.35	2.91
Sil-O-Cel	2½	0.298	75.0
	5	0.578	296.0
	7½	0.867	671.0
	10	1.156	1,190.0

TABLE III—MAXIMUM PERIOD OF REVERSAL FOR REFRACTORIES—2½ IN. THICK

Material	Time of Reversal of Gas, Min.	Heat Absorbed Per Sq.Cm./Cal.
Graphite	0.2	0.8
Carborundum	3.0	1.1
Magnesia	6.9	1.51
Silica	14.5	0.90
Firebrick	21.0	1.09
Sil-O-Cel	75.0	0.275

Assuming the average initial temperature of the brick as being 750 deg. C. and the surface maintained at a temperature 1 deg. higher by the hot gases passing by, the total heat absorbed at various time intervals through 1 sq.cm. of surface was calculated. These values were obtained for all six different bricks and for the four thicknesses. The results of these calculations are shown in the accompanying Figs. 1 and 2. These graphs indicate the most desirable time interval between gas reversals for checkerwork of a given material and thickness. They also indicate the best material and thickness to employ when the interval between reversals is fixed. For instance, the 2½-in. silica brick, Fig. 2, is found to have absorbed the maximum heat in 15 minutes, while the Sil-O-Cel brick of the same thickness is still absorbing heat at the end of 1 hour.

A comparison of the heat absorbed in various time intervals is also shown in Fig. 2 for a wall 2½ in. thick. These curves indicate that magnesia would make the most desirable checkerbrick. However, the disadvantage of magnesia is that it spalls so rapidly as to make it unsuitable. Carborundum is the next best material. It absorbs heat very rapidly. However, it can be seen from the curves that for a thickness of 2½ in. or less carborundum possesses no advantage over firebrick when the period of reversal exceeds 25 minutes.

From consideration of Fig. 2 it is seen that if a suitable refractory could be constructed possessing the thermal properties of magnesia, it would be an ideal material for checkerbrick. On the other hand, a material like Sil-O-Cel should be entirely avoided. High thermal conductivity, density and specific heat are all desirable in checkerbrick material.

The time required for any brick to attain a constant uniform temperature is theoretically infinite. The time required to absorb a given proportion of the maximum heat possible under given conditions can be computed. Table II shows the time required for the various bricks to absorb 95 per cent of their maximum heat. It can be shown from the equation expressing the relation between total heat and time that for any material, the time required for various thicknesses of brick to absorb a given proportion of its maximum value of heat will vary as the square of the thickness of the brick. From this law, and from the curves above, the heat absorbed for any thickness in a given time interval can be obtained at once.

Table III shows the best interval for reversal for walls 2½ in. thick.

HEAT ABSORBED PER UNIT VOLUME

The heat absorbed per unit of volume of the regenerator is of more importance than the heat absorbed per unit area exposed. The heat so absorbed will vary with the type of construction. Consider first a construction made of parallel walls and assume a ratio of free space to total cross-sectional area in unity. (See Fig. 3.) This ratio corresponds very closely to the values found in practice, such as in hot blast stoves. The free area exposed per cubic meter of volume will be $10^6/p$ sq.cm., where p denotes the thickness of wall. The total heat absorbed per cubic meter per degree initial difference in temperature can then be found by multiplying the values of H obtained previously, by the factor $10^6/p$.

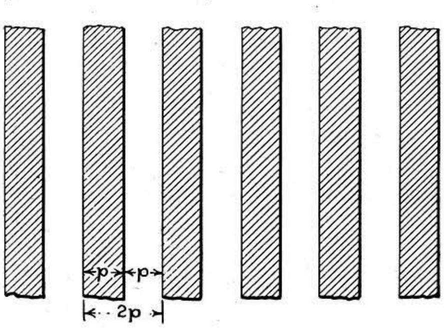

FIG. 3—PARALLEL WALL CONSTRUCTION FOR CHECKERWORK

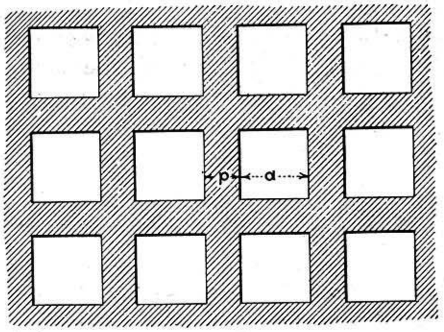

FIG. 4—REGULAR CHECKERWORK CONSTRUCTION

TABLE IV—THICKNESS OF SILICA BRICK, HEATED TO 95 PER CENT SATURATION IN VARIOUS TIME INTERVALS

Time, Minutes	Thickness of Brick, Inches
1	0.7
5	1.55
10	2.18
20	3.08
30	3.78
40	4.36
50	4.88
60	5.35

The resulting values have been plotted for silica brick of various thicknesses in Fig. 5. These curves show that for a given time interval the heat absorbed per unit volume increases with decreased thickness of the material up to the limit of saturation. With a given time interval of heating, the most desirable thickness of brick to use will be as shown in Table IV.

REGULAR CHECKER CONSTRUCTION

In regenerators the common type of construction consists of bricks placed in regular checker style with two sets of parallel walls intersection at right angles to each other as shown in Fig. 4. In treating this case it is assumed, as before, that the free cross-sectional area is equal to the cross-sectional area of the brick. The exposed area per unit volume will be less than for parallel walls. On the other hand, the average heat flow per unit area will be slightly greater, because in this case part of the heat flow is radial. The exact analysis of this case is extremely difficult, but a close approximation can be arrived at by assuming that the average rate of flow for parallel walls multiplied by a factor which is the ratio of the shape factor of the second case to the shape factor of the first case per unit area. The shape factor for the checkerwork for one square opening, 1 cm. long, is given by the formula (Langmuir, *Trans.* Am. Electrochem. Society, 1913, vol. 24, p. 53),

$$S = \frac{A}{p/2} + 0.54\ \Sigma l.$$

Where

A = area;
p = thickness of wall;
m = length of channel;
Σl = the sum of all corner edges.

From Fig. 4 it will be seen that the following relations exist where p = thickness of wall and d = width of opening:

$$2d^2 = (p + d)^2;$$
$$\sqrt{2} \times d = p + d;$$
$$p = 0.434d;$$
$$A = 4dl = \frac{4pl}{0.434}$$
$$S = \frac{\frac{4pl}{0.434}}{\frac{p}{2}} + 0.54\ (4l) = 20.56l.$$

The shape factor for parallel walls for the same area and thickness of wall is given as

$$\frac{A}{p/2} = \frac{\frac{4pl}{0.434}}{p/2} = \frac{8l}{0.434} = 18.4l.$$

Hence the ratio of shape factor is

$$\frac{20.56}{18.4} = 1.12.$$

This ratio indicates that the heat flow per unit area is 12 per cent greater in checkerwork than in parallel wall construction when the thickness of wall and free cross-section are the same in both cases.

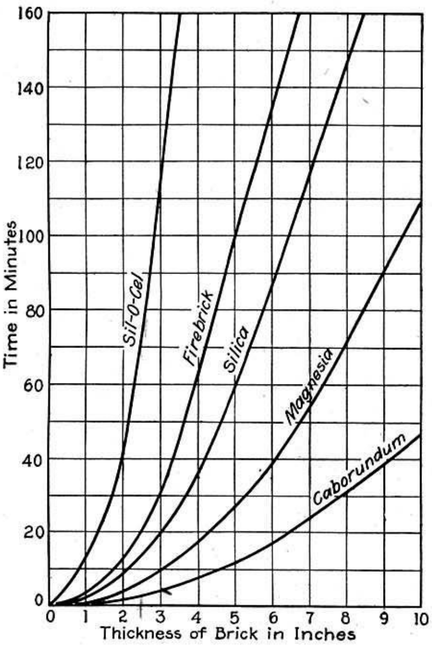

FIG. 5—TIME REQUIRED TO HEAT REFRACTORIES, LONGEST DESIRABLE PERIOD OF REVERSAL

The ratio of the area exposed per cubic volume in the two cases will be found as follows:

First consider parallel wall construction. The number of walls per square meter of cross-section is $\frac{100}{2p}$

The area exposed per cubic meter is then

$$\left(\frac{2 \times 100}{2p}\right) \times 100^2 = \frac{10^6}{p}$$

The area exposed per cubic meter for checker construction is given by the formula

$$\left(\frac{100}{d + p}\right)^2 (100)4d = \frac{0.868 \times 10^6}{p}$$

Hence the ratio of areas exposed by checkerwork and parallel wall construction is 0.868.

Combining these two ratios, we find that the ratio of heat transfer per cubic meter of regular checker to parallel wall construction is $1.12 \times 0.868 = 0.972$.

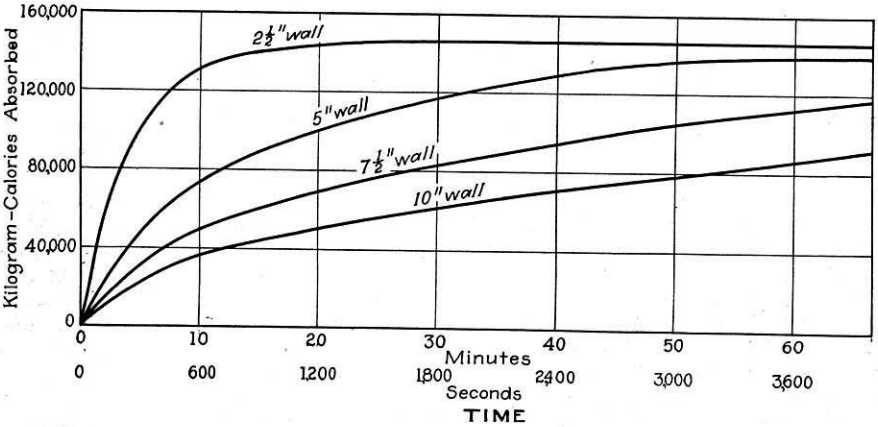

FIG. 6—TOTAL HEAT ABSORBED PER CU.M. OF CHECKERWORK. SILICA BRICK. PARALLEL WALL CONSTRUCTION. AVERAGE TEMPERATURE 750 DEG. C. FOR REGULAR CHECKER CONSTRUCTION ADD 3 PER CENT TO TIME INDICATED

This indicates that the rate of heat flow into regular checkerwork per unit volume is 3 per cent less than for parallel wall construction. The time required for a given heat flow is accordingly 3 per cent greater for regular checkerwork than for parallel walls of the same thickness.

It should be remembered that the values given hold strictly only when the average temperature of the refractory is 750 deg. C. When the average temperature exceeds this value, the rate of heat absorption is slightly greater, whereas for lower temperatures the rate is slightly less. The amount of variation from the given values depends upon the variation in the thermal properties of the refractory material with temperature.

Grateful acknowledgment is extended to Prof. L. R. Ingersoll for his kindly criticism of this paper and for the inspiration of his instruction.

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Insulation of Periodic Kilns

Proper kiln insulation not only results in greatly reduced burning costs but brings about other advantages. According to the facts presented before the American Ceramic Society by J. H. Krusen, a much more uniform distribution of heat is thus made possible, which eliminates the necessity of forcing the fires and overheating the hotter portions of the kiln in bringing the cooler parts up to the desired temperature. The outer walls are protected against rapid temperature changes, reducing the danger of cracks developing with resultant air infiltration.

As is generally known, heat may be transmitted in three ways—namely, by conduction, radiation and convection. Of these, conduction plays the most important part in connection with kiln design and the amount of heat which will be conducted can be reduced or practically eliminated by installing, as a component of the wall, a layer of material having a relatively low conductivity and high thermal resistance.

At least 25 per cent of the heat generated in burning a kiln is lost by conduction through and radiation from the brickwork, and a considerable amount used in heating the large volume of brick in the side walls, crown, flues and the earth on which the kiln is built. On the average yard the fuel loss sustained in this way is more than 25 per cent.

Equipment News

From Maker and User

Radiant Heat Furnace

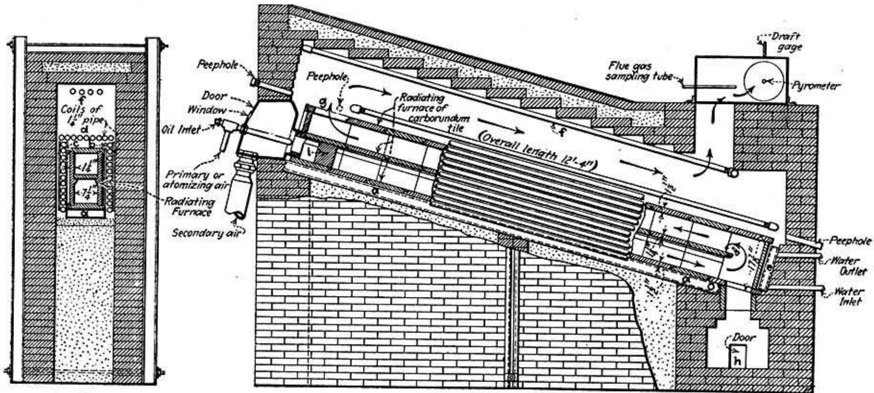
A new type of furnace for use with boilers and other types of heat equipment, called the Cannon Radiating Furnace, and made by the Carborundum Company, Refractory Division, Perth Amboy, N. J., has recently been placed on the market. It is claimed that this new furnace, instead of depending largely on convection for its heat transfer, transmits from 80 to 100 per cent of the total heat transferred by radiation from the outside of the combustion chamber.

Combustion of the fuel used, whether it be gas, liquid fuel or powdered fuel, is accomplished in a two-pass combustion chamber or "radiation flue" of rectangular section and twice the length of the furnace. The walls of this chamber are of carborundum refractory tiles. These tiles are rendered incandescent by the heat and, in accordance with the well-known properties of carborundum, the heat is then readily transmitted through the tiles and radiated from their outside surfaces.

When this type of furnace is used with a boiler, as shown in the illustration, which depicts the unit built at Massachusetts Institute of Technology for test purposes, the heat which remains in the gases after passing through the radiation flue is largely recovered by passing the flue gases through an economizer. This cannot be done when the furnace is used for other purposes, but the maximum amount of heat can be absorbed in the tiles by a more specialized construction.

The illustration of the test furnace does not show the exact commercial application of the furnace, as the outer brick setting here shown need not be employed. The furnace essentially consists of a long, double flue constructed of especially molded carborundum tiles. These are laid with overlapping and interlocking joints—no cement is used. The oil burner is shown at the left end of the lower flue. This could be replaced by a gas burner or powdered coal burner. The wedge block *i* in front of the burner is to facilitate ignition and mixing.

The burning gases travel in the direction of the arrows through the long narrow flue, emerging at *g*. In this passage they are close to the incandescent walls and the air and fuel are continually mixed so that complete combustion is obtained with only about 3 per cent excess air. Water-heating surfaces are placed on all sides of the flue at *a*, *b*, *c*, *d* and *e* and the economizer for utilizing heat in the waste gas is shown at *f*.



SECTIONAL SIDE ELEVATION AND END VIEW OF TEST "RADIANT FURNACE" SET UP AT M.I.T.

In the test carried on at M.I.T. the total radiating surface showed approximately 19,500 B.t.u. radiated per square foot per hour. The temperature of the exit gases at *g* was about 1,270 deg. F. Tests made with oil were at an average rate of combustion of 275,000 B.t.u. per cubic foot per hour. Tests with powdered coal were at combustion rates of 250,000 B.t.u. per cubic foot per hour with a flue gas showing 14 per cent CO_2, 4.5 per cent O_2 and no CO.

Recent Developments in Flameless Combustion

By Eric Sinkinson, B.Sc., D.I.C.
Assistant Professor of Chemistry, Lehigh University

The development of what Prof. W. A. Bone, the inventor, called "flameless incandescent surface combustion" was brought to a point of practical application in 1909 with the "diaphragm" and "incandescent bed" types of heating. Since that day Professor Bone and other inventors have made further developments of surface combustion, until in this country it is successfully used in large-scale industrial furnaces and has received commendation from the U. S. Bureau of Standards, where, in stringent tests, temperatures as high as 1,675 deg. C. in surface combustion furnaces for laboratory purposes have been obtained.

Recently, however, improvements in the method of making "radiophragms," which is the name applied to the modern form of diaphragm, for surface combustion appliances, and the success obtained in using them industrially would indicate an extended scope and usefulness for this system of heating. It is now possible to announce that an important advance has been made in the method of constructing "radiophragms" for the application of surface combustion heating. The improvement is mainly due to F. J. Cox, who, in conjunction with Professor Bone, has undertaken a further development of this branch of the enterprise.

As early as 1909, the so-called "diaphragm" process of burning a homogeneous mixture of gas and air in the right proportions for complete combustion was evolved. By this method the combustible gas and air, fed to a chamber behind the diaphragm, would burn without flame at the exposed surface and keep it in a state of redhot incandescence, thus developing a high degree of radiant energy.

The diaphragm was made of granules of firebrick bound together into a porous and coherent slab by the addition of a small quantity of suitable cement, and the porosity was graded to suit the kind of gas to be used. The diaphragm was mounted in a case in such a way that the space behind the diaphragm and the back of the case constituted a feeding chamber for the gaseous mixture which was introduced centrally to the case.

When the diaphragm was radiating, the combustion was confined to a layer no deeper than ¼ in., and the remainder of the apparatus was comparatively cool. This constituted a most efficient method of developing radiant heat. The combustion was instantaneous and perfect and the ratio of radiating surface to the combustion depth was high.

A new "radiophragm" has now been produced on the lines of the old one, but with certain radical differences. By improved methods of construction, the new radiophragm has not only lost some of the defects of the old ones but also has been found to give new advantages not anticipated.

Experience has shown that in constructing the "radiophragm" the granules comprising it should have perfect regularity of texture and porosity, and

Absorption of Ammonia in Towers

Experimental Determination of Transfer Coefficients of Absorption in Open and Various Types of Packed Towers

By O. L. Kowalke, O. A. Hougen and K. M. Watson
Professor, Assistant Professor and Fellow of Chemical Engineering, Respectively, University of Wisconsin.

OPERATING conditions in the gas and coke industry were chosen as being typical of ammonia absorption. From published data and from private communications it was found that the limits in operation of absorption towers were as follows:

Ammonia concentration of incoming gas, 0 to 1 per cent,
Ammonia concentration of solvent, 0 to 2.5 per cent,
Velocity of solvent flow, 3.9 to 15.7 lb. per min. per sq.ft. total cross section,
Velocity of gas flow, 2.8 to 9.8 lb. per min. per sq.ft. total cross section,
Temp. of gas, 55 to 170 deg. F., and
Temp. of solvent, 54 to 156 deg. F.

The unit of transfer considered most practical and used herein is defined as the number of pounds of ammonia absorbed per minute per cubic foot of tower packing under a mean ammonia vapor pressure difference of 1 mm. of mercury between the gas and liquid phases. The general formula expressing the rate of ammonia absorption in terms of this coefficient, "*ka*" is:

$$W = (ka)V\Delta P_{mean}$$

where W = lb. of ammonia gas absorbed by the entire tower per min.,
V = volume of tower packing in cu.ft., and
ΔP_{mean} = mean vapor pressure difference throughout the tower.

To use this formula, it is necessary to know precisely the value of ΔP_{mean}. That is, the vapor pressure of NH_3 must be calculated for gas and liquid phases at both ends of the tower, and the mean vapor difference accurately determined. The partial pressure of NH_3 in the gaseous phase can be calculated by multiplying the grams of NH_3 per gram of air by the ratio of the molecular weight of air to the molecular weight of NH_3, by the partial pressure of the dry air.

Data on the partial pressure of ammonia in ammonia-water solutions at different temperatures and for low concentrations are incomplete. Some are obtainable from the publications of Abegg and Riesenfeld (*Zeit. Phys. Chem.*, 1902, vol. 40, p. 84), Gauss (*Diss., Breslau*, 1900), Riesenfeld (*Zeit. Phys. Chem.*, 1903, vol. 45, p. 467), Herzen (*Bull. Soc. Chem. Belg.*, vol. 25, pp. 154-7), and Brichaux (*Bull. Soc. Chem. Belg.*, vol. 25, pp. 145-153). The following formula for the partial pressure of ammonia for dilute solutions was based on the free energy concept and the assumption that there is a direct proportionality between vapor pressure and concentration for dilute solutions:

$$\ln_e \frac{p}{m} = \frac{-4425}{T} + 10.82$$

where p = partial pressure of ammonia in atmospheres,
m = mols ammonia per 1,000 gm. water,
T = absolute temperature in deg. C.

The calculated data agree with published experimental data for molalities of ammonia to 4.5 (7 per cent NH_3), showing that Henry's law holds for these concentrations. A concentration of 4.5 mols ammonia is greater than any usually found in the gas and coke industry. It can be proved that the mean vapor pressure difference between the vapor pressure of ammonia in the gaseous phase and in the liquid phase may be expressed by the logarithmic mean. The small variation in temperature due to absorption, and the slight reductions in the volumes of gas and the solvent due to absorption, make no appreciable deviation from this mean.

The apparatus is shown in Fig. 1. The mixture of air and ammonia is forced into the bottom of the tower through a pipe, the end of which is shielded by 2 concentric cones as shown in the diagram. The purpose of the upper cone is to keep water from falling into the inlet pipe and the lower one keeps the incoming gases from being deflected against the layer of water present in the bottom of the tower. After passing up through the packing, the gas is sampled by a closed-end perforated sampling tube. A small metal shield was placed above this tube to prevent entrainment of water in the sample. The water which is sprayed into the tower comes from a mixer, thus providing a means of temperature control. The rate of water flow was determined by weighing the outlet water.

The ammonia gas was led through a trap to an orifice meter, and thence into the main air lines just ahead of

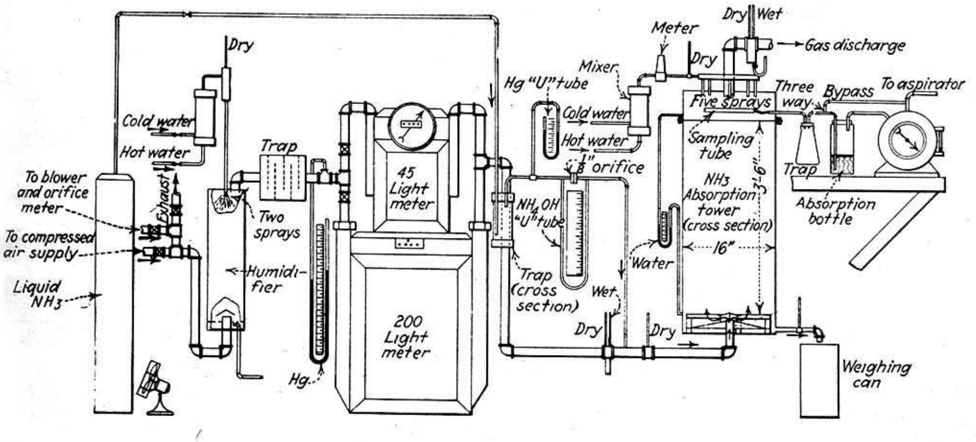


Fig. 1—Gas Absorption Apparatus

The tower proper is a heavy sheet steel cylinder 4 ft. high and 16 in. in diameter. The bottom is a steel plate tapped to receive the pipes. To the top is bolted a crown carrying 5 "Vermorel" spray nozzles arranged in an 8 in. circle. The top is easily removable for changing the tower packing. The packing is supported by a heavy screen on a wooden frame, and extends from 4 in. above the bottom to within 6 in. of the nozzles.

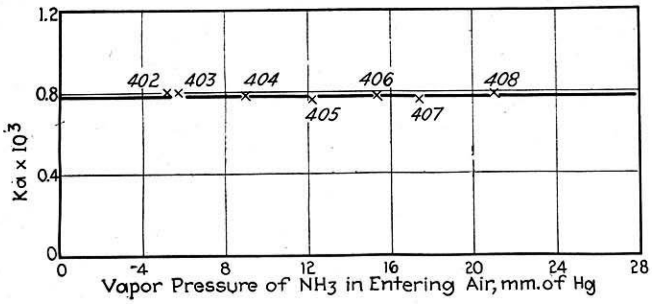


Fig. 2—Ammonia Transfer Coefficient

Variable vapor pressure of ammonia in entering air. Wood grid packing used. Ave. air flow = 0.77 lb. per sq.ft. per min. Ave. water flow = 2.5 lb. per sq.ft. per min.

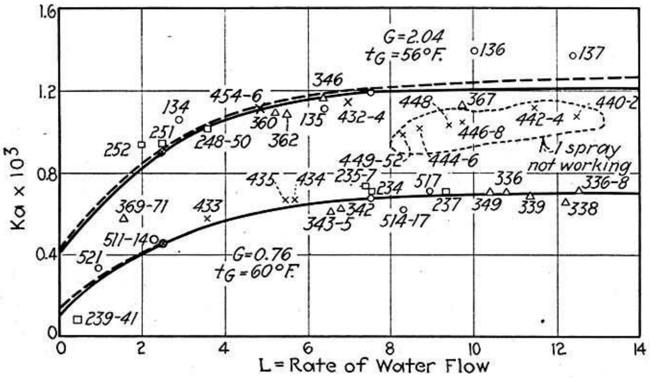


Fig. 3—Ammonia Transfer Coefficient

Empty tower packing and variable water flow. Calculated values in broken lines; experimental values in full lines.

the entrance to the tower. The orifice meter had previously been calibrated for ammonia delivery, and was used as a control and duplicate measure of the total ammonia input. The air was brought to the tower through 2 gas meters, so arranged that either or both could be used. The smaller, a 45-light size, was used for velocities up to about 15 cu.ft. per min. and the larger 200-light meter was used for greater velocities up to about 40 cu.ft. per min. For still greater velocities, the air was measured by an accurately calibrated orifice.

The first experimental work was done with apparatus set up in the form first described, with a packing consisting of 14 basswood grids. The sample of gas leaving the tower was titrated by bubbling it through a known amount of standard sulphuric acid in the wash bottle shown, noting the volume of gas required for neutralization. Sodium alizarin sulphonate was used as the indicator for the titration, as this indicator is not sensitive to carbon dioxide.

The concentration of the ammonia in the liquid leaving the tower was determined on samples taken at intervals and titrated with standard sulphuric acid.

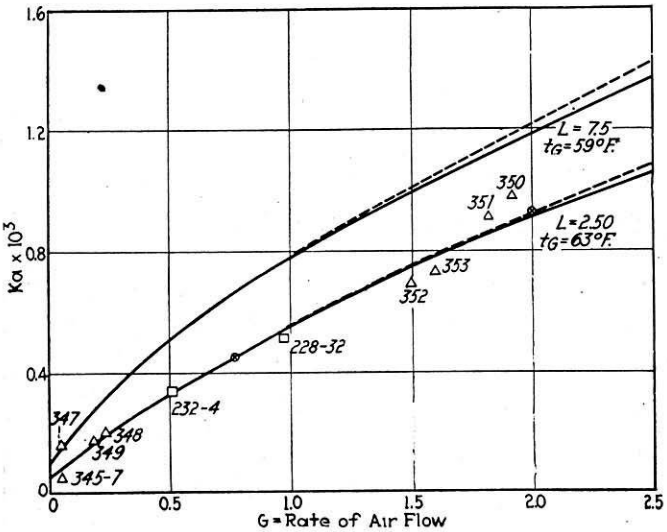


Fig. 4—Ammonia Transfer Coefficent

Empty tower packing and variable air flow. Calculated values in broken lines; experimental values in full lines.

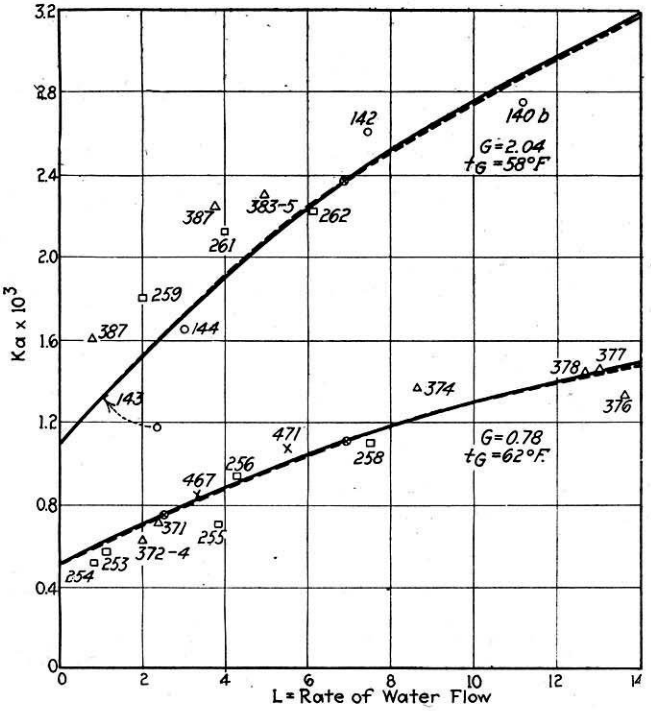


Fig. 5—Ammonia Transfer Coefficient

Stoneware packing and variable water flow. Calculated values in broken lines; experimental values in full lines.

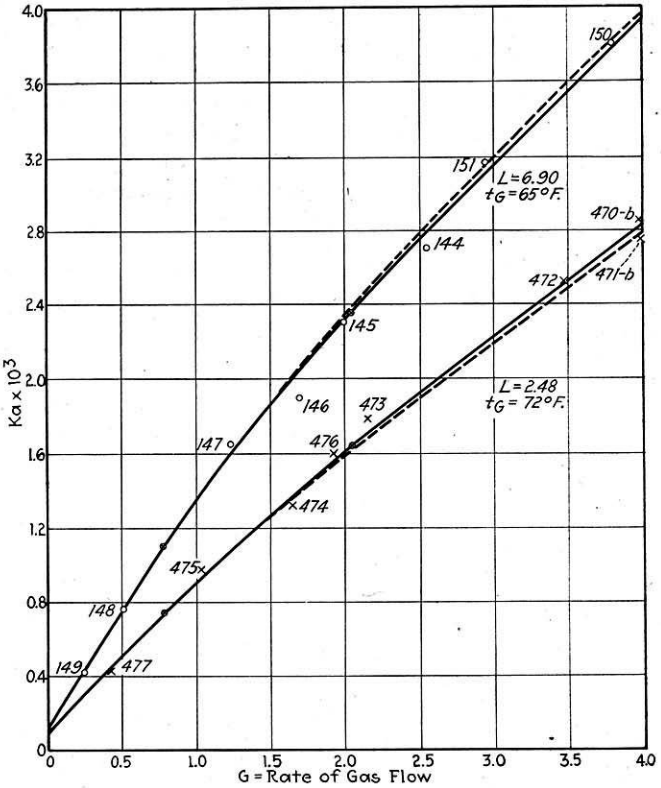


Fig. 6—Ammonia Transfer Coefficient

Stoneware packing and variable rate of gas flow. Calculated values in broken lines; experimental values in full lines.

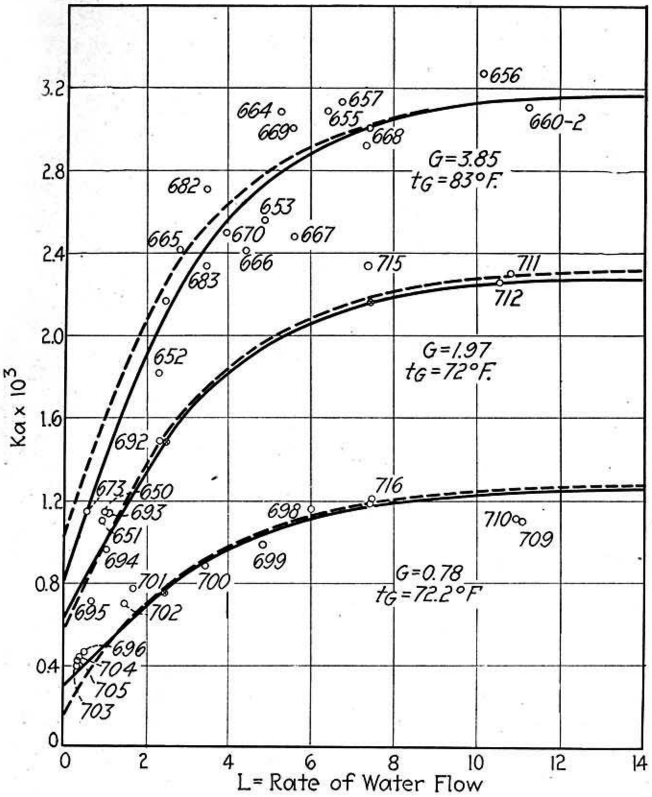


Fig. 7—Ammonia Transfer Coefficient
Stoneware packing and variable water flow. Calculated values in broken lines; experimental values in full lines.

From the above titration and the weight of the liquid leaving the tower during a run, the total ammonia absorbed and leaving in the solution was computed. The total ammonia entering the tower during the same time is the sum of that in the liquid and the amount leaving in the gas, which may be computed from the gas titration and the total volume of air passed. A check on this total input was obtained by means of the ammonia orifice. From this value the partial pressure of the ammonia in the incoming air was obtained.

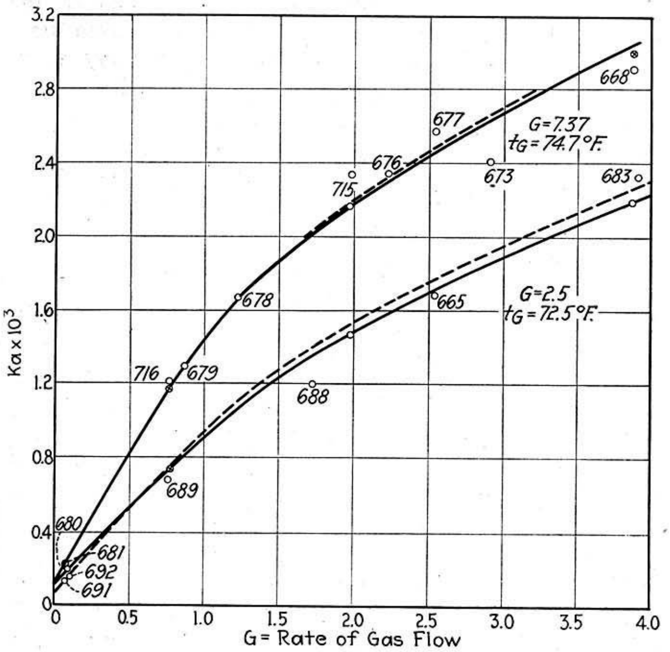


Fig. 8—Ammonia Transfer Coefficient
Stoneware packing and variable rate of gas flow. Calculated values in broken lines; experimental values in full lines.

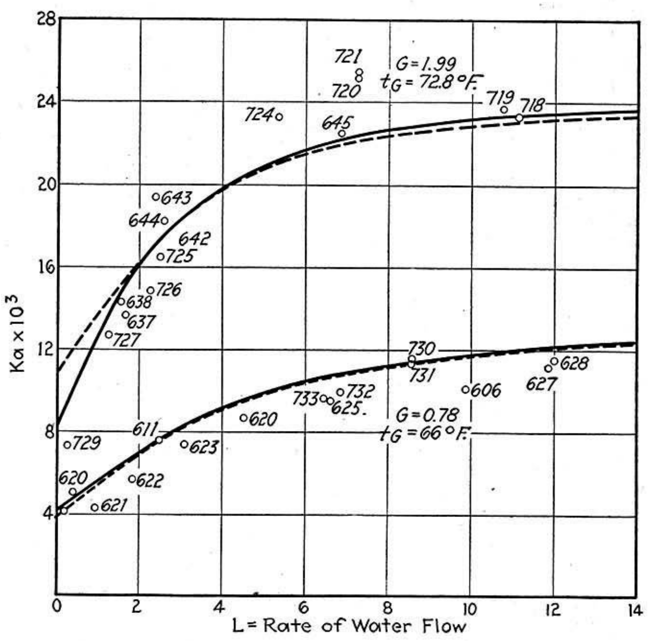


Fig. 9—Ammonia Transfer Coefficient
Paraffined wood grid packing and variable water flow. Extrapolated values in broken lines; experimental values in full lines.

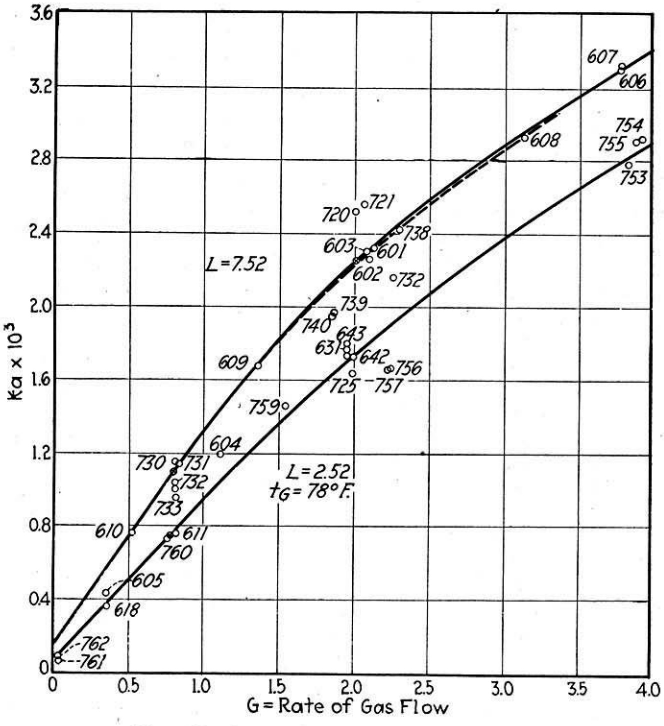


Fig. 10—Ammonia Transfer Coefficient
Paraffined wood grid packing and variable rate of gas flow. Calculated values in broken lines; experimental values in full lines.

Thus the necessary values are determined for calculating the mean vapor pressure difference. The logarithmic mean formula is:

$$Vp_m = \frac{Vp_b - Vp_t}{\ln \frac{Vp_b}{Vp_t}}$$

Where, Vp_m = mean vapor pressure difference,
Vp_b = vapor pressure difference at bottom of tower,
Vp_t = vapor pressure difference at top of tower.

The value of the absorption coefficient may then be computed from the general formula previously given.

Preliminary experiments were made on a wood grid packing. It was found that a time lag existed due to absorption and release of ammonia by the wood.

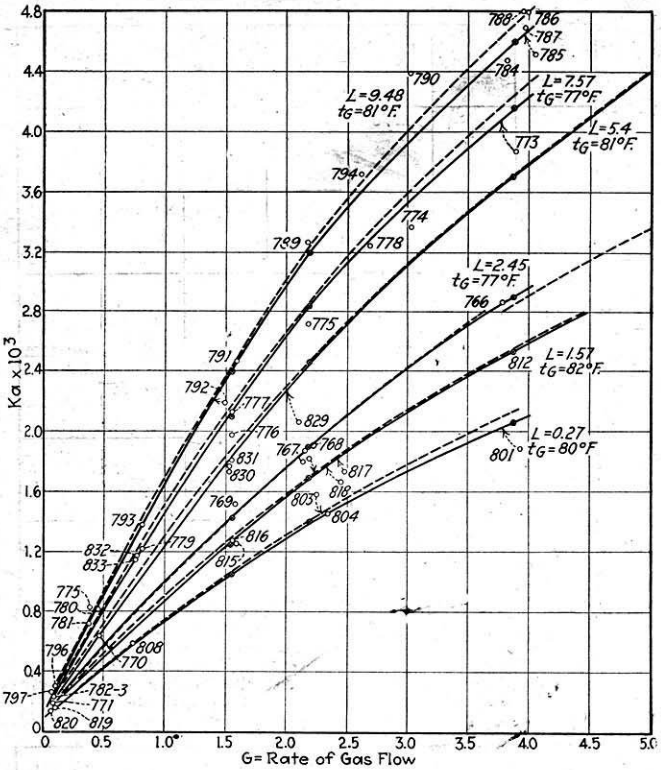


Fig. 11—Ammonia Transfer Coefficient

Quartz packing and variable rate of gas flow. Calculated values in broken lines; experimental values in full lines.

Another appreciable lag was caused by the fluctuations in ammonia concentration in the incoming air. This was eliminated by supplying heat to the liquid ammonia drum sufficient to maintain a uniform pressure of delivery. The time lag for the bare wood grid was found to vary from 1 to 10 hr. Because of this long period of lag, it was deemed expedient to impregnate the wood grid with paraffin, and by so doing the lag was reduced to 15 min.

To indicate the numerous precautions necessary to insure accurate and reliable results, more than 200 preliminary experiments were made before a satisfactory technique, a satisfactory standard of precision of measurement, and suitable mechanical accessories were developed.

A series of experiments, Fig. 2, show that variation in concentration of ammonia in the incoming gas had no effect on the value of *"ka."* The following types of packing were investigated:

Simple Spray Chamber—Water was introduced through 5 "Vermorel" sprays at the top of the tower. No packing was used. Volume = 5.26 cu.ft.; effective height = 3.8 ft.; cross-section = 1.39 sq.ft.

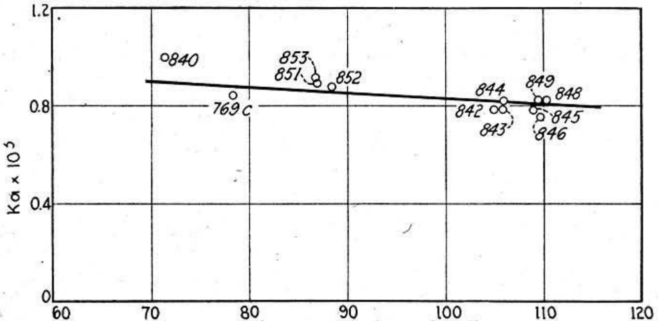


Fig. 12—Ammonia Transfer Coefficient

Variation with temperature when gas rate = 0.77 lb. per sq.ft. per min. and water rate = 2.50 lb. per sq.ft. per min.

No. 1—Stoneware Packing—Volume = 4.75 cu.ft.; height = 3.42 ft.; cross-section = 1.39 sq.ft. This packing consisted of 130 4-in. glazed stoneware rings arranged in 13 layers with 10 rings in each layer. One ring in each layer was split to make the packing more compact. Rings in adjacent layers were staggered to minimize channeling. Total exposed area per cu.ft. of packing = 22.0 sq.ft.

No. 2—Stoneware Packing—Volume = 4.63 cu.ft.; height 3.34 ft.; area = 1.39 sq.ft. This packing consisted of unglazed stoneware cylinders, 3 in. in diameter and 3 in. high with a corrugated outside surface and a spiral ledge on the inside. Weight per cu.ft. = 53 lb.; number of units per cu.ft. = 59; area per cu.ft. = 30.0 sq.ft.

Paraffined Wood Grids—Volume = 4.78 cu.ft.; height = 3.44 ft.; area = 1.39 sq.ft. Fourteen basswood grids impregnated with paraffin, 3 in. high each, and 16 in. in diameter. Consisted of ½x3-in. strips placed on edge and separated by ½-in. spacers. Area exposed per cu.ft. of packing = 32.2 sq.ft.

Quartz—This packing consisted of closely graded quartz, sized to pass a 1¾-in. screen and be retained on a 1½-in. screen. Volume = 4.69 cu.ft.; height = 3.38 ft.; cross-section = 1.39 sq.ft.; weight per cu.ft. = 87.5 lb.; number of units per cu.ft. = 626; estimated area of packing per cu.ft = 30.0 sq.ft.

The results of all tests are shown graphically in Figs. 3 to 12 inclusive.

Early in the experimental work it was noticed that slight variations in temperature of either the gas or the liquid did not seem to alter the values of the ammonia transfer coefficient within the range of experimental error. However, a series of runs was made to determine the general trend of the temperature effect upon the ammonia transfer coefficient. In this series, the rate of air flow, water flow and ammonia concentration in the incoming air were held constant at 0.77 lb., 2.50 lb. and 17 mm. pressure respectively. The temperature was controlled by varying the temperature of the inlet water from 70 to 160 deg. F., thereby varying the average temperature of the gas in the tower from 70 to 110 deg. F. Insufficient data were taken on the temperature effects to warrant any mathematical relationships, but in general it was found that increasing the temperature diminished the values of the ammonia transfer coefficient at 70 deg. F. in the ratio of 0.25 per cent reduction for each degree rise in temperature. This corresponds closely to the change in viscosity of air over the same range.

In another article, to follow soon, the authors will develop a theory of absorption for ammonia in water, and will also discuss practical applications.

◆

Lime for Bleaching Powder

The Interdepartmental Conference on Chemical Lime is engaged in the preparation of specifications for lime employed in various chemical industries. It was found necessary in the preparation of specifications for lime to be used in the manufacture of bleaching powder, to undertake several investigations to determine the properties which such a lime should possess. This work has been undertaken by several agencies including the Bureau of Standards.

The Wisconsin Engineer
UNIVERSITY OF WISCONSIN

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THE THOMAS RECORDING GAS CALORIMETER

By R. A. RAGATZ, ch '20
Instructor in Chemical Engineering

THE quality of manufactured or natural gas distributed in most states and municipalities must now comply with certain standards specified by regulatory commissions. Of the various standards that are usually specified by law, the heating value requirement is one of the most important. It is therefore necessary for the manufacturer of gas to have an accurate device at his disposal for determining whether or not the heating value of the gas is above the prescribed minimum. In small plants such determinations are usually made only once or twice a day, but in the larger plants where gases from several sources may be mixed, a continuous record is a practical necessity.

The calorimeter of the Junkers or continuous flow type, in which the gas tested is burned at a steady rate and the heat of combustion absorbed by a stream of water flowing counter-current to the products of combustion, is the accepted standard of the manually operated gas calorimeters. The heating value of the gas is determined by multiplying the rise in temperature of the water passing through the calorimeter, by the weight of water discharged, and dividing the product by the corrected volume of the gas, which is measured by a meter.

Thus it is apparent that in making a heating value determination with the Junkers calorimeter considerable data must be taken. To obtain the actual figure for the heating value it is necessary to apply various corrections to the readings of the thermometers, barometer, and gas meter, and to go through quite lengthy and tedious computations. Furthermore, the result applies only to the gas passing at the time of making the observations, and the whole procedure must be repeated for every subsequent test. It would be a decided advantage to the gas manufacturer to have a calorimeter which would operate automatically, and which would give a continuous record of the heating value of the gas being manufactured. Such an ideal is realized with the Thomas Automatic Recording Gas Calorimeter, developed by the Cutler-Hammer Manufacturing Co. of Milwaukee.

In general, the Thomas gas calorimeter may be described as a continuous flow calorimeter, in which gas is burned at a steady rate and the heat of combustion absorbed by a stream of air flowing counter-current to the products of combustion. The essential differences between the Thomas and the Junkers calorimeters are that in the Thomas calorimeter air instead of water is employed to absorb the heat of combustion of the gas being tested, and the temperature rise of the heat absorbing medium is measured by electrical resistance thermometers connected to a recording Wheatstone Bridge, rather than by mercurial thermometers.

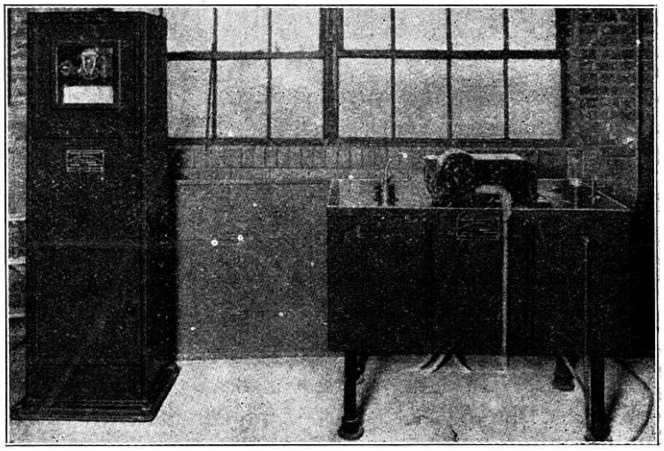


FIG 1. *The Thomas Recording Gas Calorimeter*

The Thomas calorimeter consists of two separate units: the tank unit or calorimeter proper, and the recorder unit. By reference to Fig. 2, let us consider in detail the operation of the tank unit. In a large tank in which a constant water level is maintained by means of a bucket pump and weir overflow, there are

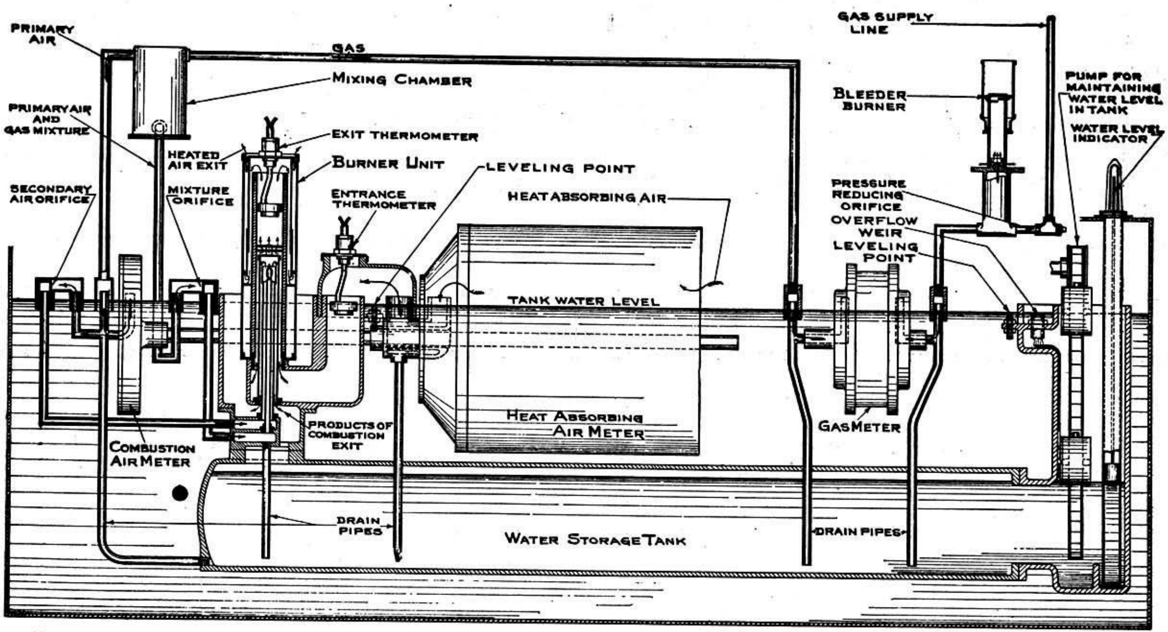


FIG. 2. *Arrangement of Piping and Meters in Tank Unit of Thomas Calorimeter*

immersed three meters, or pumps: one for measuring the gas whose heating value is to be determined, another for measuring the air to be used in absorbing the heat of combustion, and a third for measuring the air supplied for combustion. The three meters are driven by a small motor mounted on the cover of the tank. Since the heat absorbing air meter and the gas meter are geared together and are driven by the same motor, they always deliver in exactly the same ratio with respect to each other, irrespective of the motor speed.

The gas supplied to be tested should be at a pressure of 3 to 6 inches of water and should be freed from objectionable impurities such as hydrogen sulfide or suspended matter before it enters the calorimeter. The gas is admitted to the calorimeter through a pressure reducing orifice and enters a small expansion chamber. On the cover of this chamber is a bleeder flame which serves two purposes: (a) it consumes sufficient gas so that a fresh supply is constantly reaching the calorimeter, thereby preventing any considerable lag in the instrument, and (b) it reduces the gas entering the meter to atmospheric pressure. The volume of combustible delivered by the gas meter is dependent upon the gage pressure of the gas on the inlet side of the meter. Therefore, in order to eliminate the possibility of error due to varying gage pressure at the inlet, the gas pressure is reduced to atmospheric by means of the pressure reducing orifice and the bleeder flame.

The gas upon passing from the small expansion chamber through the gas meter is delivered to a mixing chamber where it is thoroughly mixed with primary air supplied by the combustion air meter. The mixture of gas and air is then delivered to the burner unit. It rises through the central tube of the burner unit and is burned at the top in a small flame. To obtain complete combustion a supply of secondary air from the combustion air meter is delivered to the flame by means of a second tube concentric with the first. The products of combustion are deflected downward and pass through the annular space between the secondary air tube and a third tube, the heat interchanger. As the products of combustion pass downward, they give up their heat to a stream of air which is flowing in the opposite direction along the outside surface of the heat interchanging tube. It should be clearly understood that the products of combustion and the heat absorbing air travel in entirely separate paths and are not mixed with one another. The transfer of heat to the heat absorbing air takes place entirely by conduction through the heat interchanger tube, and is so efficient that the products of combustion are discharged at the bottom of the burner unit at very nearly the temperature of the incoming heat absorbing air. As the products of combustion are cooled, considerable water is condensed which is removed by a drain leading to the water storage tank.

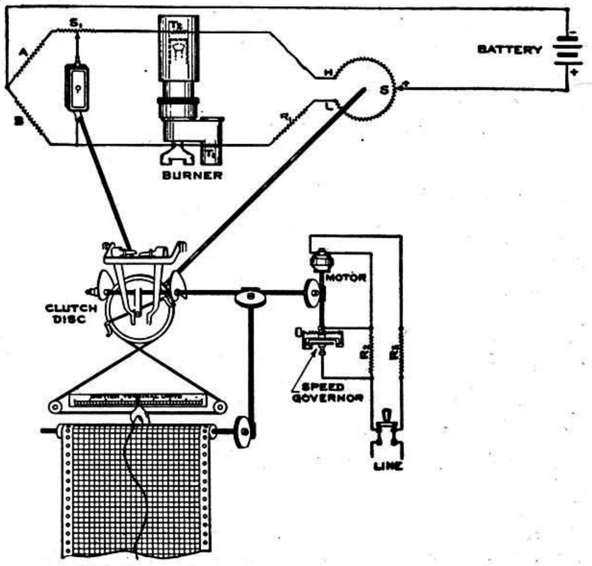
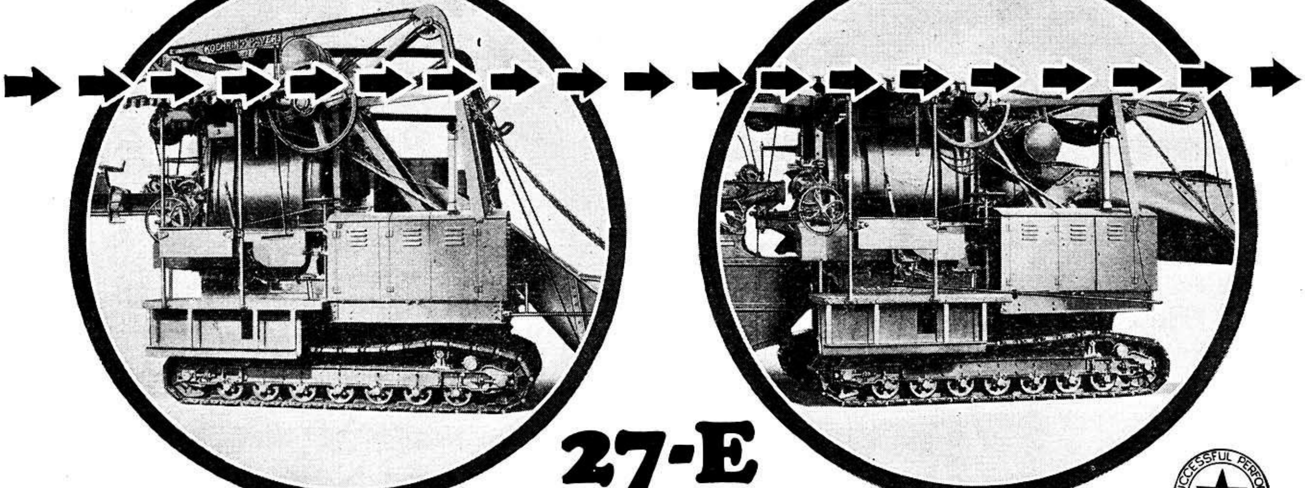


FIG. 3. *Wiring Arrangement of Thomas Calorimeter*

(Continued on page 136)

The Greater KOEHRING



27-E

Upper steel frame is hinged directly above the level of the top of the drum, giving the paver shipping height, with frame collapsed, of 11' 3". Frame is collapsed by taking out a few bolts, pins and unions — about a thirty minute job in the field.

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Construction Mixers—10-S, 14-S, 21-S, 28-S. Steam, gasoline or electric power. Mounted on trucks or skids. Rubber tired wheels optional. 28-S on skids only. Complies with A. G. C. Standards.

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A-3010-I

all connected in parallel by joining the ends. Each of the wires was coated with insulating enamel, and covered with a protecting layer of cotton, three wires being twisted together to form a unit. Three units so formed were twisted together, and the operation repeated until eighty-one wires had been laid together, when the strand was covered with silk. Eighty-one of these strands constituted the cable. From this construction, any wire in a given length of the cable, passes thru the same phases with regard to the longitudinal axis as any other wire, so that the impedances of all wires are equal, irrespective of the skin effect. The insulation of each wire however, prevents the
—Engineering.

ANOTHER METHOD OF TELEGRAPHING PICTURES

Gertrude Ederle, champion swimmer, had hardly left the water in her attempt to swim the English Channel during August, before her picture, taken during this particular swim, appeared in American newspapers.

The public has already become accustomed to seeing telegraphed pictures, but it is impracticable to send these by submarine cable, because a cable does not operate in the same manner as a land telegraph wire. The familiar methods of picture transmission by wire show their own earmarks on close scrutiny, although there is no real objection to this, for it does not injure their news value. If you study closely the pictures transmitted by one of these land processes, you will find that they are made up entirely of parallel lines crossing the picture, each line changing from thick to thin and back again as frequently as necessary to bring out the desired combination of light and shadow. This method is almost automatic.

Pecularities affecting submarine cable transmission make it difficult, however, to employ this process in transmitting pictures across the seas. Hence, another system, not open to these objections had to be devised.

By means of this transoceanic system, which is one of four processes devised by LeRoy J. Leishman, of Ogden, Utah, the picture to be transmitted is divided up into five degrees of tone value, every area of shade being outlined. These boundaries are traced with a stylus attached to two relatively moving scales, the readings on which comprise a record of absolutely every movement described by the stylus in the tracing process.

This mechanical process is based upon the fact that all lines are either straight or curved, and that all curved lines can be divided into components that are arcs of circles. When the arcs change, a single reading of the scales records the fact. All these readings are in letters, instead of figures, and the sum total of them comprises a message that can be transmitted by telegraph or cable. The code also indicates the exact depth of tone of each shaded area. A sample of the code by which Miss Ederle's picture was transmitted to America from England follows:

LONDON COLLECT 233 FIRST 50
NANEWSAL NYK
FOLLOWING FIRST HALF PHOTOGRAPH
EDERLE ABOUT TEN MILES GRISNEZ
CODE BEGINS JDBTD XXBTA XXLGA
JDLGA JDBTD UIGIS UJGGU UGGFU
UFGEA UFFWA UFFSQ UGFLQ UJFDQ
UTEVQ VQEWA VSFAQ VVFDA VXFWA
VXGAQ WAGAQ WBFQ VWGJA VWGKA
VTGKA VQGGQ VMGFQ

At the receiving end, the decoding device is operated and a synthetic picture is built up that is an exact duplicate of the original photograph. So accurate is the reproduced picture that it will superimpose with the original to 1/100 of an inch.

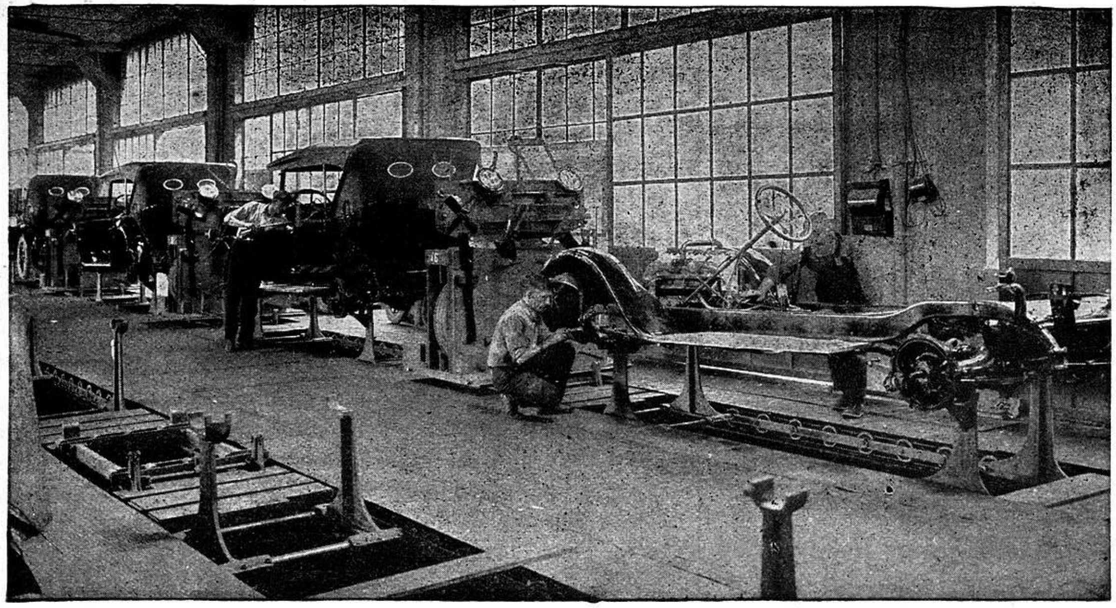
THE THOMAS CALORIMETER

(Continued from page 108)

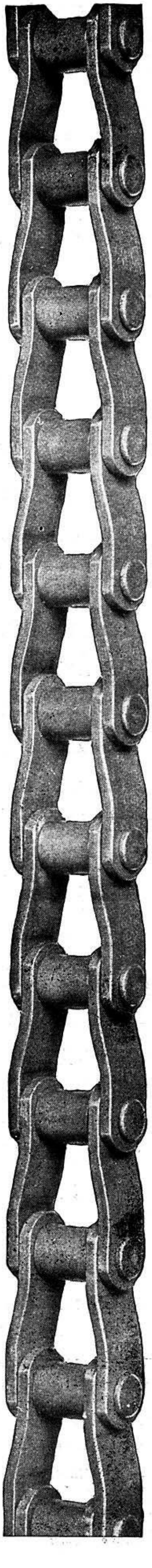
The heat absorbing air meter supplies air to the burner unit in a definite ratio with respect to the gas supplied. An electrical resistance thermometer located near the exit of the heat absorbing air meter gives the temperature of the heat absorbing air as it enters the burner unit. The heat absorbing air passes upwards through the space between the heat interchanger and the outer burner jacket and absorbs the heat from the products of combustion. A second electrical resistance thermometer is employed to obtain the temperature of the heat absorbing air after it has taken up the heat from the products of combustion.

Fig. 3 shows diagrammatically how the recording system operates. Two resistance thermometers, one at the temperature of the heat absorbing air delivered to the burner unit and the other at the temperature of the heat absorbing air after being heated by the products of combustion, are in adjacent legs of a Wheatstone Bridge. The recorder mechanism automatically keeps the bridge in balance by varying the point of contact S. The position of this point of contact when the bridge is balanced depends upon the temperature differences of the two resistance thermometers, which in turn depends upon the heating value of the gas being burned. That is, the higher the heating value of the gas the greater will be the difference in temperature and resistance between the thermometers located at the inlet and the outlet for the heat absorbing air.

The Thomas calorimeter gives a continuous record of the total heating value of the gas supplied to the calorimeter, expressed in B. t. u. per cubic foot at standard conditions: 60°F., a pressure of 30 inches of mercury, and the gas saturated with water vapor. The use of air as the heat absorbing agent in the Thomas calorimeter in conjunction with an electrical system of temperature measurement makes the readings practically independent of variations in tank temperature or barometric pressure within certain limits, or of reasonable variations in the speed of the motor operating the meters. The reading indicated is the heating value of the gas under standard conditions.



Here successive steps of final assembly occur as the cars slowly proceed to the end of the conveyor
The weight of each car is carried on eight chain rollers



THE SWIFT *and* SURE ADVANCE OF MECHANICAL HANDLING

Strictly speaking a conveyor is installed as a means of transporting goods. It would be expected to carry them at least cost.

But that is not all. That alone is not sufficient to account for the rapid advance of mechanical handling in America.

Conveying contributes to the success of industry in many other ways.

In progressive assemblies, conveyors have reduced the cost of building automobiles, stoves, threshing machines, washing machines and tires. They have made labor more efficient and ended much drudgery.

In foundries, conveyors carry the flask while pouring, carry the molds to the shakeouts, handle the sand and the castings, and carry the iron and steel to the furnaces.

In hundreds of industrial plants, Rex Conveyors have broken the bottle necks of production and have balanced production by securing an even flow of material through the plant. They have saved valuable floor space, and cut out idle machine time. In one automobile plant, the conveying system has been developed to such an extent that under the same roof two cars are now produced where one was built before.

The business of building material-handling machinery is still young. Much progress is being made annually in the engineering of this new science. Each year its markets are broader.

Whether you are a student, graduate engineer, or manufacturer, it might be well to see what this expansion of Mechanical Handling holds for you.

The Chain Belt Company will gladly answer the inquires of anyone interested.

REX CONVEYORS

CHAIN BELT COMPANY *759 Park St., Milwaukee, Wis.*

ALSO MANUFACTURERS OF

Rex Chain - Rex Sprockets - Rex Concrete Mixers - Rex Traveling Water Screens
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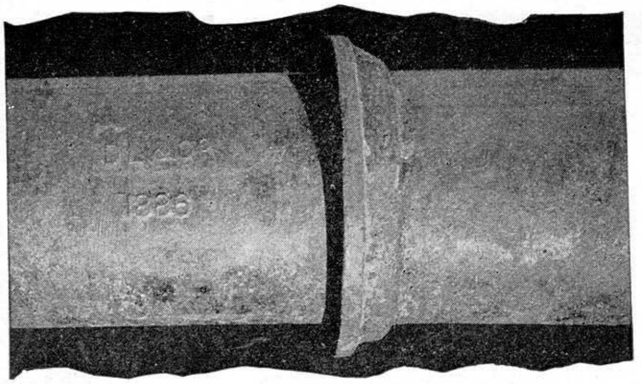

The readings of the calorimeter are not affected by variations in the speed of the motor because the meters delivering gas and heat absorbing air are geared together and always deliver their respective volumes in the same ratio irrespective of the motor speed.

If the meters of the Thomas calorimeter were operating in a fluid having negligible vapor pressure, and if both the gas and the air for absorbing heat were free of water vapor, the temperature rise of the heat absorbing air in passing through the burner unit would be unaffected by barometric pressure or by the initial temperature of the heat absorbing air. This would be the case, for variations in barometric pressure or tank temperature would change the actual weights of gas and heat absorbing air delivered in exactly the same proportion, and hence the temperture rise of the heat absorbing air would be unchanged.

But the meters of the Thomas calorimeter operate in water, which has an appreciable vapor pressure, and the presence of water vapor in the gas and in the cooling air complicates the theory somewhat. The presence of the water vapor makes the temperature rise of the heat absorbing air dependent upon both the barometric pressure and the initial temperature of the heat absorbing air. The effect of barometric pressure upon the readings of the instrument is quite small, a change in the barometer from 30 to 28.5 inches producing a 0.2 per cent change in the heating value indicated, if the tank temperature is 80°F. The tank temperature, however, has quite a pronounced effect upon the temperature rise of the heat absorbing air as it passes through the burner unit. For example, if the calorimeter is operating on a 520 B. t. u. gas, the temperature rise of the heat absorbing air will be 37.20° F. if the inlet temperature is 50°F., but if the inlet temperature is 90°F., the temperature rise will be 35.52°F. However, the nickel wire selected for the resistance thermometers has a resistance-temperature relationship which compensates for this effect quite exactly. That is, though the temperature rise is not the same at different inlet temperatures as shown by the above example, the resistance differences between the inlet and outlet thermometers are nevertheless almost the same, irrespective of inlet temperatures between 55 and 90°F. The net result is that the heating values indicated by the recorder are practically unaffected by variations in tank temperature from 55 to 90°F., or by variations in barometric pressure or motor speed. The manufacturers guarantee the instrument to be accurate within one per cent if the tank temperature is between 55 and 90°F.

The development of the Thomas calorimeter has involved a large amount of research. The Cutler-Hammer Manufacturing Co. has sent several models to the laboratories of the Chemical Engineering Department of the University of Wisconsin to be used for cooperative research. The data obtained in these researches have been factors in changes of design which have improved the precision obtainable.

Protecting Thermocouples by Transparent Silica Tubes

While ordinary fused silica tubes permit contamination in reducing atmospheres the transparent do not

By R. A. Ragatz and O. A. Hougen
Instructor and Assistant Professor in Chemical Engineering
University of Wisconsin, Madison, Wis.

IT IS well known that the use of the ordinary fused silica protection tube of the translucent type permits serious contamination of the enclosed thermocouple when the tube is surrounded by a reducing atmosphere at high temperatures. Apparently this contamination is caused by the porosity of translucent silica which permits the penetration of reducing gases to the interior of the tube. Furthermore, when heated for extended periods above 1050 deg. C. such tubes rapidly devitrify and crumble, as shown in Technical Paper 170, U. S. Bureau of Standards, pages 90 and 91. A previous investigation, reported in *Chem. & Met.*, Vol. 29, p. 662, 1923, showed that this contamination became apparent at temperatures above 900 deg. C., in a reducing atmosphere. When the translucent tubes were heated for 50 hours at 1000 deg. C. in an atmosphere containing carbon monoxide the enclosed noble metal couple showed a ¾ per cent decrease in emf. and the enclosed chromel-alumel couple a 4 per cent reduction in emf.

Because of the recent development of a new fused silica protection tube of the transparent type, it was deemed desirable to perform similar tests upon this new type of material. Twelve such tubes of the following average dimensions were obtained from the Thermal Syndicate: length, 12 in.; diameter, 0.4 in.; bore, 0.2 in.

The experimental equipment used herewith was essentially the same as that used in the previous investigation with the following additional improvements: the use of a solid graphite cylinder instead of powdered graphite for enclosing the protection tubes and maintaining a reducing atmosphere, the use of a glazed alundum tube impervious to gases for the heating furnace and the use of reversing switches to compensate for stray contact emf. in the potentiometer circuit.

Two types of couples were used in these tests, a base metal couple of chromel-alumel and a noble metal couple of platinum—platinum-10 per cent rhodium. These couples were newly constructed and were annealed and calibrated before testing. The plan of procedure was to insert these couples into transparent silica tubes and to subject them to a series of heat treatments of 50 hours' duration each at various temperatures with the tubes surrounded by a reducing atmosphere of carbon monoxide. After each heat treatment both thermocouples were recalibrated at the melting points of zinc and aluminum furnished by the Bureau of Standards. In the testing furnace the protection tube and the enclosed thermocouple were immersed for a distance of 6 in. into the heated reducing zone. Upon calibration, fully 4 in. of this same portion of the thermocouple were in a region of steep temperature gradient, this arrangement readily permitting detection of any contamination which might have occurred in the testing furnace. For each set of heat treatments at a given temperature a different pair of protection tubes were used. Visual examination of the transparent protection tubes after each heat treatment showed no alteration except for the tubes heated at 1200 deg. C. In this case slight surface devitrification was noticed after the end of the first 50-hour period and was more pronounced at the end of 100 hours.

Table I—Effect of Various Heat Treatments Upon the Emf. of Thermocouples Protected with Transparent Silica Tubes Placed in a Reducing Atmosphere Containing Carbon Monoxide

Heat Treatments	Noble Metal Couple		Chromel-Alumel Couple	
	Zinc Point 419.4°C.	Aluminum Point 658.7°C.	Zinc Point 419.4°C.	Aluminum Point 658.7° C.
	Millivolts	Millivolts	Millivolts	Millivolts
Original, after annealing..........	3.432	5.817	17.42	27.64
First 50 hr. period at 1000°C......	3.435	5.822	17.50	27.78
Second 50 hr. period at 1000°C.....	3.435	5.824	17.54	27.82
Third 50 hr. period at 1000°C......	3.435	5.823	17.55	27.85
Fourth 50 hr. period at 1000°C.....	3.435	5.824	17.56	27.84
Fifth 50 hr. period at 1000°C......	3.434	5.823	17.67	27.84
Sixth 50 hr. period at 1000°C......	3.436	5.827	17.77	27.92
First 50 hr. period at 1100°C......	3.432	5.820	17.90	27.95
Second 50 hr. period at 1100°C.....	3.432	5.817	18.01	27.93
First 50 hr. period at 1200°C......	3.431	5.817	Couple* broke	27.96
Second 50 hr. period at 1200°C.....	3.433	5.820	.....	.....
Final after annealing electrically....	3.432	5.817	.....	.....

* Broke due to excessive oxidation by air enclosed in tube.

Table II—The Effect of an Oxidizing Atmosphere Upon Chromel-Alumel Thermocouples

Heat Treatments	Couple 1		Couple 2	
	Zinc Point 419.4°C.	Aluminum Point 658.7°C.	Zinc Point 419.4°C.	Aluminum Point 658.7°C.
	Millivolts	Millivolts	Millivolts	Millivolts
Original, after annealing..........	17.41	27.63	17.39	27.63
First 50 hr. period at 1000°C......	17.52	27.74	17.51	27.75
Second 50 hr. period at 1000°C.....	17.54	27.74	17.53	27.78
First 50 hr. period at 1100°C......	17.67	27.76	17.71	27.81
Second 50 hr. period at 1100°C.....	17.71	27.70	17.72	27.75

The constancy of emf. of the noble metal thermocouple, as noted in Table 1, indicates that no contamination has occurred. The gradual rise in emf. of the chromel-alumel couple was not due to contamination by reducing gases, because as shown by the previous experiments, contamination by such gases causes a reduction in emf. It was suspected that this gradual increase in emf. was due to some other cause, probably the oxidation of the thermoelements by air enclosed in the protection tubes. This supposition was tested experimentally by subjecting two new chromel-alumel thermocouples to a series of heat treatments in an oxidizing atmosphere of air for periods of 50 hours each at various temperatures. The results, given in Table 2, show a steady rise in emf. due to oxidation.

Besides the above method of testing for contamination, homogeneity tests by the traverse method were made on the noble metal thermoelements after the last heat treatment. In this method, as shown in Technical Paper 170, U. S. Bureau of Standards, pages 228 to 232, the used thermoelement was moved in contact with one end of an unused thermoelement of the same composition with the point of contact maintained at 750 deg. C. The contact emf. was recorded at regular distances along the thermoelement under test. The maximum variation in emf. along the used thermoelements was only 6 microvolts, indicating that the thermoelements had suffered no appreciable contamination. In the purest thermoelements, variations of this magnitude may be expected.

Feasibility of Coke-Oven Hydrogen for Synthetic Ammonia

Possibilities of progress depend upon profitable recovery of light oils and utilization of a byproduct ethylene mixture for conversion to alcohol

By Barnett F. Dodge
Fixed Nitrogen Research Laboratory

THE importance of a cheap source of hydrogen in any process for the fixation of nitrogen through ammonia synthesis has been stressed by all who have given attention to this problem. Claude in France was apparently the first to give serious thought to the possibility of obtaining the hydrogen from coke-oven gas. [G. Claude, *Compt. rend.*, vol. 172, p. 974 (1921); *Compt. rend.*, vol. 176, p. 394 (1923); *Chimie et Industrie*, vol. 11, p. 1055 (1924); *J. Ind. Eng. Chem.*, vol. 14, p. 1118 (1922)].

The experiments which he has made toward the separation of hydrogen from coke-oven gas have culminated in the location of a plant at the Bethune Mines which is said to be in successful operation. Claude writes enthusiastically of the great advantages of extracting hydrogen from gas that is otherwise purely a waste product; but all his publications lack any actual figures on the economics of the process. Furthermore, conditions in the coke-oven industry in this country might be quite different from those in France, and distinctly unfavorable to the utilization of this gas as a source of hydrogen. In order to obtain more definite information on this important subject, with particular reference to American conditions a preliminary survey was made at the Fixed Nitrogen Laboratory. The results of this survey, which are summarized below, were obtained with a view to finding some kind of an answer to the questions:

1. How much coke-oven gas might be available for this purpose and what value or values could be assigned to it or the hydrogen contained in it?
2. Having arrived at a value for the hydrogen, how would a liquefaction process for extracting hydrogen from coke-oven gas compared with other methods for preparing the hydrogen for ammonia synthesis, particularly with the water gas catalytic process?

The fixation of 1 ton of ammonia will be taken as a basis for estimation, and 70 deg. F. and 14.7 lb. per sq.in. will be taken as a standard condition for gas volumes. On this basis, the theoretical hydrogen requirement would be 68,000 cu.ft. To estimate the practical coke-oven gas requirement, there has been assumed a 10 per cent loss of hydrogen in ammonia synthesis due to purges and leakage (Report on the Fixation and Utilization of Nitrogen, No. 2041), a 10 per cent hydrogen loss in the water scrubbing to remove CO_2 [R. S. Tour, *Chem. & Met. Eng.*, vol. 26, p. 359 (1922)] and of the hydrogen going into the liquefaction process, there is assumed an extraction of 90 per cent, the remaining 10 per cent being dissolved in the liquid fraction (H. S. Taylor, "Industrial Hydrogen"). For a typical run-of-oven gas containing 48 per cent hydrogen, the above assumptions lead to a gas requirement of 195,000 cu.ft. per ton of NH_3.

The U. S. Geological Survey's yearly publication of statistics for the coke industry furnishes much valuable information on the amount of gas produced and its distribution among various uses. In the following table are collected some of the most pertinent figures covering the period from 1920-24 inclusive.

Table I—Coke-Oven Gas Production and Distribution

(Volumes of gas are expressed as million cu.ft.)

Year	1920	1921	1922	1923	1924
Total gas produced......	476,500	310,200	442,700	601,200	541,100
Gas used for oven heating	235,600	147,000	203,200	....	....
Gas used in steel and affiliated plants.......	151,800	98,400	145,000	200,100	187,200
Gas distributed through city mains...........	53,200	43,800	57,000	65,100	65,700
Gas sold for industrial use	Included in preceding item		10,350	19,500	18,600
Gas burned under boilers.	25,400	12,120	19,120	33,800	29,800
Gas wasted............	10,380	8,860	8,050	....	....
Per cent of total gas used for oven heating......	49.5	47.4	45.9	....	....
Per cent total gas used in steel and affiliated plants...............	31.8	31.7	32.7	34.3	34.6
Per cent gas distributed through city mains....	11.2	14.1	12.9	10.8	12.1
Per cent gas sold for industrial use..........	....	....	2.3	3.2	3.4
Per cent gas burned under boilers.........	5.3	3.9	4.3	5.6	5.5
Per cent gas wasted.....	2.2	2.9	1.9	....	....

The bulk of the gas, about 80 per cent, is thus utilized for oven heating and for various heating purposes in affiliated steel plants. The hydrogen in this gas would suffice for the fixation of very large amounts of nitrogen, but this use of the hydrogen would be competing against a well-established heating use. It is well known that the ovens may be heated with blue water gas and the new Becker type of oven made by the Koppers Co. permits the use of producer gas. In fact the use of producer gas for oven heating has been stated to have several advantages over the use of coke-oven gas (H. C. Porter, "Coal Carbonization"). If all the hydrogen were extracted from the gas used for oven heating and the deficiency in heating value made up by the addition of producer gas, the amount of coke necessary for the production of this producer gas would only amount to 4 per cent of the coal carbonized, which is less than the amount of coke regularly produced in the form of breeze and screenings. This form of coke, which is either wasted or disposed of at a very low figure has been successfully used to make producer gas.

Any satisfactory figure for the value of the coke-oven gas that is used for oven heating or used in steel plants is hard to obtain. In the bulletin of the Geological Survey for 1922 the gas used in steel mills was valued by the coke-oven operators at from $0.06 to

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Ammonia Liberation From $(NH_4)_2SO_4$ Solutions by Various Limes

By R. A. Ragatz and J. M. Spees***

IT is current practice to employ a high calcium lime in distilling ammonia from gas liquors. The experiments described in this paper were executed with the object of determining whether a dolomitic lime would be as suitable for this purpose as a high calcium lime. The question was raised originally by a gas and electric utility company, and during the progress of the experiments financial aid was granted by the Gas Section of the Wisconsin Utilities Association.

Experimental Procedures

Crude ammonia liquor is a complex solution of many ammonium salts. Hence, to avoid unnecessary complications, it was considered advisable to employ a solution of ammonium sulphate as the source of ammonia, in preference to crude ammonia liquor itself. After the ammonium sulphate solution used in these experiments was prepared, its ammonia content was determined by distilling a known volume in the presence of an excess of sodium hydroxide, and absorbing the evolved ammonia in standard acid.

In general, the method employed in making the experiments on the rate of distillation consisted in passing a steady flow of steam through a known volume of the standard ammonium sulphate solution, mixed with a weighed amount of the lime under test. The evolved vapors were condensed and caught in a receiving flask. Successive measured portions of standard acid were added to the receiving flask as the distillation proceeded, and the time was noted when each portion was neutralized.

The detailed procedure followed in making an experiment on the rate of distillation will next be outlined, and may best be understood by reference to Fig. 1, which shows the arrangement of the apparatus in diagrammatic fashion. The lime sample, which had been slaked at least over night, was transferred from the flask in which it had been slaked, to the reaction flask. In slaking the lime, and in transferring it to the reaction flask, definite volumes of distilled water were employed in order to keep the concentration of the ammonium sulphate the same in all of the experiments. The flask containing the lime sample was put into the inner chamber of the water bath and connected to the condenser and steam supply. A thermometer was inserted into the tube used for introducing the ammonium sulphate solution. A separatory funnel containing exactly 100 cc of the standard ammonium sulphate solution, and an Erlenmeyer flask containing 50 cc of distilled water were immersed directly in the boiling water in the outer chamber of the water bath. When the thermometer which had been inserted into the reaction flask read 60 deg. C., the steam was turned on, and the flow adjusted till there was a pressure drop of 31 inches of water across the orifice. After several minutes, the water would start to drip from the condenser delivery tube. After 20 cc had been distilled over, the delivery tube was inserted into the receiving flask, which contained exactly 100 cc of standard acid and a little sodium alizarin sulphonate indicator. A few drops of acid and indicator were put into the guard tube attached to the receiving flask, and also into the guard tube attached to the adapter between the condenser and the flask. The separatory funnel containing the 100 cc. of ammonium sulphate solution was removed from the water bath, and connected to the tube in the reaction flask provided for the introduction of the ammonium sulphate solution. Everything then was in readiness to start the run. The stop cock of the separatory funnel was opened, and at that instant a stop watch was started. After the ammonium sulphate solution had drained into the reaction flask, the separatory funnel was rinsed three times, using the 50 cc of distilled water that had been heated in the water bath. The stop watch was read when the acid in the flask was neutralized. Successive portions of standard acid were added to the flask as the distillation proceeded, and the time was noted when each portion was neutralized. The distillation was continued in each case till 90 minutes had elapsed. At the end of an experiment, the liquid in the receiving flask was titrated back with standard sodium hydroxide. Then the two guard tubes were washed, and the liquid in the flask again titrated with standard sodium hydroxide.

Table 1 gives a list

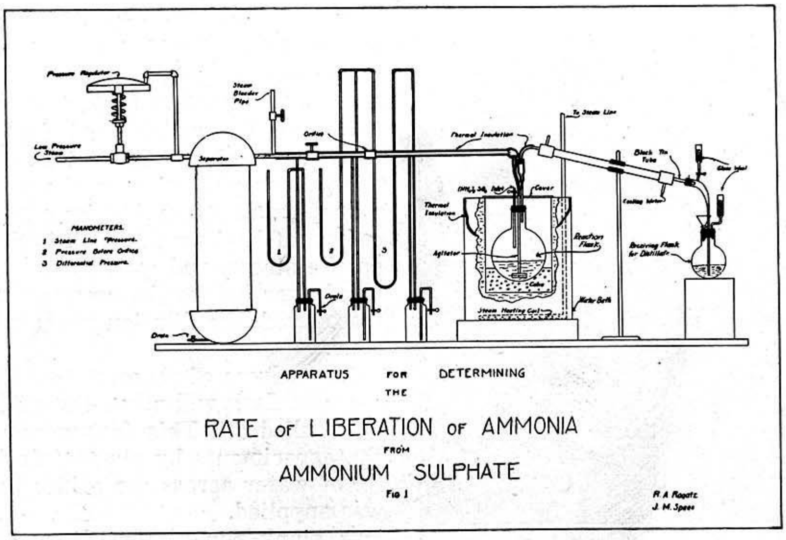

Fig. 1

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*Ass't Prof. Chemical Engineering, University of Wisconsin.

**Fellow Wisconsin Utilities Association Fellowship.

of the bases used in the experimental work, and also the various weights of each base employed. In each case, at least three distillations were made.

Table 1
List of Bases Used

Base	Weight, Grams	Mol. (See Note)
1. Mallinckrodt's "U. S. P." calcium oxide	28.00	0.50
2. Mallinckrodt's "U. S. P." magnesium oxide	20.15	0.50
3. "Synthetic" dolomitic lime		
Mallinckrodt's "U. S. P." calcium oxide	14.00	0.25
Mallinckrodt's "U. S. P." magnesium oxide	10.08	0.25
Total	24.08	0.50
4. Mallinckrodt's "U. S. P." magnesium oxide	28.00	0.695
5. "Synthetic" dolomitic lime		
Mallinckrodt's "U. S. P." calcium oxide	16.28	0.291
Mallinckrodt's "U. S. P." magnesium oxide	11.72	0.291
Total	28.00	0.582
6. High calcium lime A	28.00	
7. High calcium lime B	28.00	
8. Dolomitic lime	28.00	

Note: The figures given in the second column are only approximate, since the "U. S. P." calcium oxide and the "U. S. P." magnesium oxide are not absolutely pure.

Chemical analyses were made of all the limes used in the experimental work, and the results are given in Table 2.

Table 2
Analysis of Limes

	Mallinckrodt's "U. S. P." Calcium Oxide, Per Cent	High Calcium Lime A, Per Cent	High Calcium Lime B, Per Cent	Dolomitic Lime, Per Cent
Loss on ignition	2.77	0.74	0.52	3.11
Insoluble matter	0.21	0.53	0.32	0.52
$Fe_2O_3 + Al_2O_3$	0.92	1.84	1.44	0.97
CaO	95.17	95.65	96.73	55.33
MgO	0.73	0.87	0.81	39.43
Total	99.80	99.63	99.82	99.36

In examining Table 1, it will be noted that in working with the "U. S. P." materials, comparisons were made in two ways. By the first method of comparison, approximately equi-molecular quantities of the various bases were used. That is, instead of employing equal weights, approximately 0.5 mol. of base was used in each case. By the second method of comparison equal weights of the "U. S. P." materials were employed. In working with the commercial limes a comparison was made only on the basis of equal weights. This was considered to be the preferable method of comparison since the cost of lime is based upon actual weight rather than upon molecular equivalence.

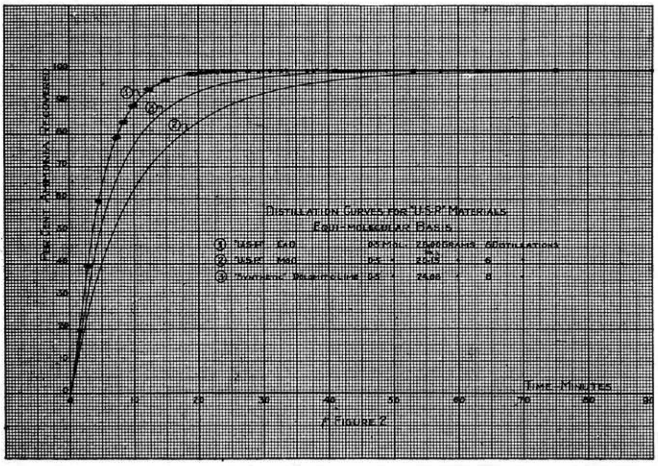

Fig. 2

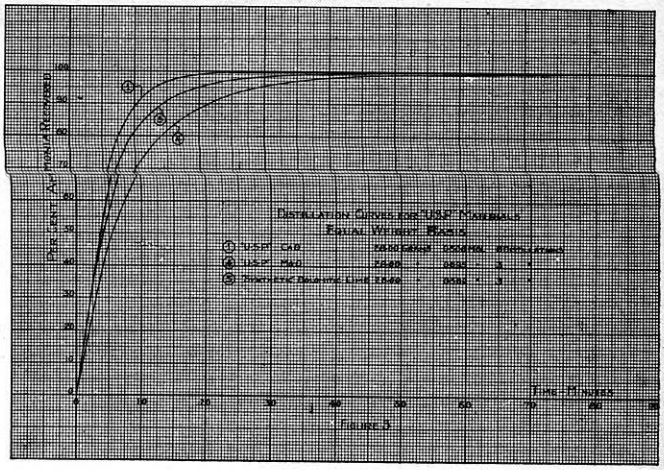

Fig. 3

One-half mol. of either calcium or magnesium oxide or mixtures of the two is capable of liberating one mol. of ammonia. In all of the experiments exactly 100 cc. of ammonium sulphate solution containing 0.504 mol. of ammonia were used. This quantity of ammonia would require 0.252 mol. of base, hence, when exactly 0.50 mol. of base is used, the excess is 98.4 per cent. When 28 grams (approximately 0.695 mol.) of "U. S. P." magnesium oxide are used, the excess is approximately 176 per cent. When 28 grams (approximately 0.582 mol.) of "synthetic" dolomitic lime are used, the excess is approximately 131 per cent.

Each sample of lime was slaked at least over night before being used. This length of time apparently is sufficient to slake the lime to such an extent that the distillation rate has its maximum value. Samples of the same kind of lime slaked for different periods of time were used with no well defined difference in the rate of evolution.

Factors Influencing Rate of Ammonia Evolution

The concentration of the ammonium sulphate solution in the flask at the time of the reaction doubtless has an influence upon the rate of ammonia evolution. Hence the total liquid added to the flask, which includes the water used for slaking, the water used to transfer the base to the reaction flask, the ammonium sulphate solution, and the water used for rinsing the separatory funnel, was always kept at exactly 400 cc. There is, of course, some dilution in the reaction flask due to condensation of steam, but by always adhering to the procedure of heating the flask to 60 deg. C. before turning on the steam, and waiting till 20 cc. of water had distilled over before the ammonium sulphate solution was introduced, the dilution effect was kept constant for all runs.

The volume of steam passed through the liquor in the reaction flask will affect the rate at which the ammonia is distilled off. This factor was kept constant in all of the experiments by maintaining a pressure drop of 31 in. of water across the orifice through which the steam was supplied.

A blank run was made to determine the extent to which the liquor in the reaction flask was diluted, and to determine the volume of steam entering the condenser during a distillation. In making this test the conditions were exactly the same as when making a regular distillation, except that distilled water was substituted for the ammonium sulphate solution. The results are given in Table 3.

TABLE 3
Data on Steam Consumption

Time, Minutes	Steam Entering Condenser Grams	Lb.	Cu. Ft.	Liters
0–30	270.5	0.596	16.48	466
30–60	275.0	0.606	16.75	474
60–90	267.0	0.589	16.28	461
Total	812.5	1.791	49.51	1,401

Total steam condensed in reaction flask, 145 grams. 0.320 lb.

Results Obtained

Figures 2, 3, and 4 show the distillation curves for the different bases experimented with. In Figure 2 the individual points obtained in the various runs with the "U. S. P." calcium oxide are plotted in order to indicate the degree of accuracy of the data. The individual experimentally determined points for the other curves are omitted for the sake of avoiding crowding and confusion.

Figure 2 shows the distillation curves for Mallinckrodt's "U. S. P." calcium and magnesium oxides, and for "synthetic" dolomitic lime In obtaining this series of curves, one half mol. quantities of each base were used rather than equal weights. Hence, a comparison of the three bases was obtained for a constant percentage of excess base. As explained before, when exactly one-half mol. of base is used, the excess is 98.4 per cent. The curves show that the magnesium oxide gives the slowest rate of ammonia evolution, and the "synthetic" dolomitic lime gives a rate intermediate between that of calcium oxide and of magnesium oxide. The curves for "synthetic" dolomitic lime and calcium oxide are practically identical 50 minutes after the start of the distillation, while the curve for magnesium oxide does not reach the other two curves till approximately 80 minutes have elapsed.

Figure 3 shows the distillation curves for Mallinckrodt's "U. S. P." calcium oxide and magnesium oxide, and for "synthetic" dolomite lime when employing equal weights in each case rather than one-half mol. quantities. It has already been mentioned that when 28 gram portions are used, the per cent excess is not the same for each base. For the "U. S. P." calcium oxide, the excess is approximately 98 per cent; for the "U. S. P." magnesium oxide, the excess is approximately 176 per cent; while for the "synthetic" dolomitic lime the excess is approximately 131 per cent. As in Figure 2, the slowest rate was obtained with magnesium oxide, and the intermediate rate with the "synthetic" dolomitic lime. The curves for "synthetic" dolomitic lime and calcium oxide are practically identical after 50 minutes, while the curve for magnesium oxide does not reach the other two till approximately 80 minutes have elapsed.

Figure 4 shows the distillation curves for the three commercial limes tested, the comparison being made on an equal weight of each lime. The curves for the two high calcium limes are practically identical. The dolomitic lime gave a slower rate, but after approximately 50 minutes had elapsed, the curve nearly coincides with the other two.

A comparison between the curves appearing in Figure 2, 3 and 4 yields the following additional information. The curves for the "U. S. P." calcium oxide and the two high calcium limes, all for 28 gram batches, are practically identical. The curves for the "synthetic" dolomitic lime and the commercial dolomitic lime, both for 28 gram batches, are practically identical. In comparing the two curves for "synthetic" dolomitic lime, the one for a 28 gram batch and the other for a 24.08 gram batch, it is observed that the larger quantity of base gives a distinctly faster rate of ammonia evolution, but the two curves practically coincide after 40 minutes have elapsed. Similarly, in comparing the two curves for the "U. S. P." magnesium oxide, the one for a 28 gram batch and the other for a 20.15 gram batch, it is observed that the larger amount of base gives the faster rate of ammonia evolution. However, the two curves do not coincide till approximately 70 minutes have elapsed.

The figures assembled in Table 4 are presented to show more clearly how the distillation rate is affected by the base used. The values given in this table were obtained from the curves of Figures 2, 3 and 4.

TABLE 4
Time Required for Various Percentage Yields When Using Different Bases

Base	Weight of Base Grams	Per Cent Ammonia Recovery 80% Min.	90% Min.	95% Min.	99% Min.
"U. S. P." calcium oxide	28	7.5	10.3	13.0	20.0
High calcium lime A	28	7.5	10.1	12.8	20.0
High calcium lime B	28	7.2	10.0	12.6	18.5
"Synthetic" dolomitic lime	28	9.5	14.3	19.5	33.0
"Synthetic" dolomitic lime	24.08	11.2	16.7	22.7	37.5
Commercial dolomitic lime	28	9.5	14.3	19.5	33.5
"U. S. P." magnesium oxide	28	14.2	21.5	29.0	47.5
"U. S. P." magnesium oxide	20.15	17.4	26.0	35.0	57.5

Amount of Total Ammonia Recovery

Within the limits of experimental error, the total ammonia recovery at the completion of the 90-minute distillation period is the same for all bases. This is shown by the figures given in Table 5.

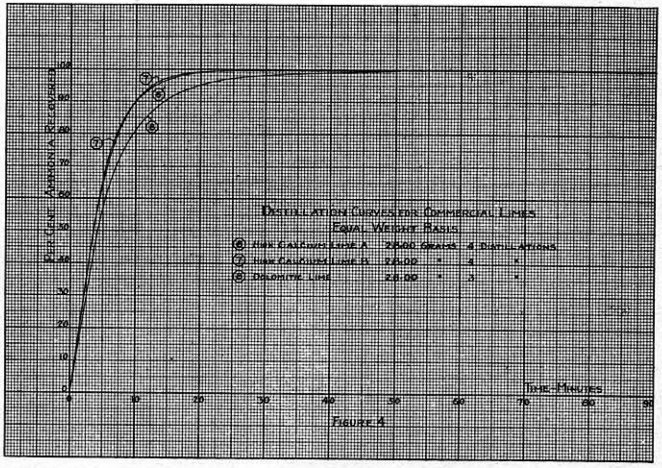

Fig. 4

TABLE 5

Per Cent Ammonia Recovery at the End of the Ninety Minute Distillation Period When Using Various Bases

	Weight of Base, Grams	Number of Runs	Per Cent Recovery at End of 90 Minutes
"U. S. P." calcium oxide	28	6	99.92
High calcium lime A	28	4	99.83
High calcium lime B	28	3	99.91
Average			99.89
"Synthetic" dolomitic lime	28	3	99.89
"Synthetic" dolomitic lime	24.08	8	99.94
Commercial dolomitic lime	28	3	99.83
Average			99.89
"U. S. P." magnesium oxide	28	3	99.89
"U. S. P." magnesium oxide	20.15	6	99.83
Average			99.86

Conclusions

The presence of magnesium oxide in a lime slows up the rate at which ammonia is evolved. Dolomitic lime gives a lower rate of evolution than high calcium lime, but the distillation curves practically coincide after 50 minutes. Within the limits of experimental error, the total yield at the end of the 90 minute distillation period was the same for all of the bases experimented with.

In closing, the writers wish to acknowledge the assistance of C. T. Greenidge and R. E. Harr in carrying out the experimental work.

10

Some Characteristics of Pyrometers Useful in the Gas Industry

By O. L. Kowalke

Annual Meeting, Wisconsin Gas Association,
March 15, 1916

The use of electrical pyrometers as instruments for scientific measurement of temperature and means of its control has been extended over a wide field during the past ten years. The factors which have aided in this development are decrease in cost, convenience of operation, reliability of service, and a better understanding between the manufacturer and the user. Perhaps the most potent factors among those mentioned are the appreciation of the manufacturer of the needs of his customers respecting the precision of measurement required and the conditions of service. This appreciation has lead to marked improvements in measuring devices so that determinations can be made by most any intelligent workman, and has also resulted in a very satisfactory protection and choice of the material, upon which measurements are made.

Electrical pyrometers may be grouped under four classes: (1) electrical resistance, (2) thermo-electric, (3) radiation, and (4) optical.

The electrical resistance thermometer consists of a coil of wire, either of nickel or of platinum, wound on a mica frame, provided with suitable leads, and enclosed in a protecting tube of metal or refractory material. This thermometer is then connected to a wheatstone bridge of special design upon which the change in electrical resistance due to the change in temperature is measured. The measurement of electrical resistance by means of a wheatstone bridge can be made with the highest precision. Thus if the relation of change in electrical resistance of a metal to change in temperature is known, a most delicate and precise measurement of temperature can be made. Measurements of the highest precision can be made only at moderate temperatures and through a limited range, say 5 deg. C. or 10 deg. F.

At temperatures above 1000 deg. C. or 1800 deg. F. most metals show a tendency to volatilize, and this effect is quite marked when the metals are thus exposed for extended intervals of time. Volatilization of the metal reduces the size of the wire and hence increases its resistance, therefor the upper limit of temperature for the resistance thermometer is about 1000 deg. C. or 1800 deg. F.

The resistance thermometer is particularly well adapted for measuring the temperatures of brine solutions for cooling, steam, gas in mains, flue gases, or coal in storage.

The thermo-electric pyrometer consists of two wires of dissimilar metals fused together at one end, the

other ends being attached to the two terminals of a voltage measuring device. This combination so arranged is called a couple. When heat is applied to the fused junction of two such wires an electromotive force is generated whose magnitude is a function of the temperature, and which can be measured by means of a milli-voltmeter or potentiometer. Such devices constitute an accurate, convenient robust and flexible means for measuring temperatures.

There are many combinations of metals now in use and in general fall into two classes: (1) precious metals, such as platinum and the alloys of platinum with iridium and rhodium, (2) base metals, such as iron, nickel, copper cobalt, and alloys composed of nickel-chromium, nickel-copper, nickel-aluminium, nickel-aluminium-manganese, etc. For accurate work it is essential that the wires composing the couple be pure and homogeneous, so that the only source of electromotive force be the fused junction. If there is any lack of purity and homogeniety, parasite electromotive forces will be set up whose magnitude depends on the temperature of the particular spot, and whose effect may tend to oppose or augment the electromotive force at the fused junction.

Couples made of the precious metals were the first to be used in the industries, and for the most accurate work and for temperatures to 1500 deg. C or 2700 deg. F. are still used. They are fragile, easily con-

taminated by carbon and by metallic vapors, have a comparatively low electromotive force, and a high cost. They must be carefully protected by glazed porcelain or fused silica tubes which are easily broken.

Base metal couples are the result of a demand for a cheap, robust, reasonably accurate couple which can be used continuously up to 1100 deg. C. or 2000 deg. F. or intermittently to about 1350 deg. C. or 2450 deg. F. There are a number of combinations which meet the first requirement above, among which may be mentioned:

1. Iron vs. (Copper - 60%) Nickel - 40%)

2. (Chromium - 10%) Iron - 30% (Nickel - 60%) vs (Aluminum - 3.3%) Nickel - 96.4%

3. Iron vs (Aluminum - 1.17) Nickel - 98.37

4. (Nickel - 96.8) Iron - 0.7 (Manganese - 1.8) vs (Chromium - 9.7) Nickel - 61.2 (Iron - 24.2) Manganese - 3.5 (Silicon - 0.7

These couples are reasonably accurate for most technical requirements. Service tests on them have shown that they remain constant well within 40 deg. C. or 72 deg. F. when heated to 800 deg. C. or 1470 deg. F. for periods of 24 hours.

There are other couples on the market whose cali-

bration changes, after about three exposures to 1000 deg. C. for one-half hour so that an error of 150 deg. C. or 270 deg. F. is made. This change may be due to several things, one of which is a segregation of the metal crystals when silicon is alloyed with nickel. Hence a combination of silicon and nickel is not satisfactory.

The use of a low resistance milli-voltmeter for the measuring device may also give rise to serious errors. Suppose that the diameters of the wires of a couple are each 0.064 inches and its length five feet; that for calibration purposes only three inches of the couple is heated, and when in use about four feet of the couple is heated, an error of 25 deg. C. or 45 deg. F. may easily result. The increase in resistance of the circuit due to a longer portion of the couple being heated cuts down the current proportionately and a low reading of temperature is obtained. With large wires the possibility for errors are greatly minimized. Furthermore the millivoltmeters, themselves, do not hold their calibration and thus introduce another source for error.

It is now possible to obtain portable potentiometers at reasonable prices which are much superior to milli-voltmeters. Since the potentiometer system is a zero system, the length and diameter of wires are immaterial. When the instrument is not in order, a measurement is impossible and thus no misleading result can be obtained.

The millivoltmeter may operate, but its indications may be greatly in error due to friction and fatigue of the regulating springs.

The effect of reducing gases at high temperatures on couples has not been very fully investigated, but in general the couple should be protected by a metal or porcelain tube which is impervious to gas. Nickel is quite susceptible to deterioration in a hot gas containing carbon monoxide. The metal becomes porous and brittle and is easily broken. In water gas machines all couples had best be protected.

Hot carbon in contact with most couples will form carbides of the metals and produce a decided change in calibration.

The thermocouple is a most convenient temperature measuring device; it is quick acting, occupies a small space, is robust, does not require skilled attendance, and is reasonable in cost. It can be used for most combustion work, retort temperatures, flue gas temperatures, and give indications correct to within about 30 deg. C. or 54 deg. F.

The limit of temperature to which a thermocouple can be used with accuracy is about 1100 deg. C. or 2000 deg. F. Beyond this point radiation or optical pyrometers must be used. Our scale of temperature is known fairly accurately to the melting point of platinum 1750 deg. C. or 3155 deg. F. and the higher temperatures are extrapalated. The great majority of the industries, however,

do not employ temperatures in excess of 1500 deg. C. or 2700 deg. F.

The radiation pyrometer is based on the Stefan-Boltzman law which states that the total energy radiated from a "black body" is proportional to the difference of the fourth powers of the absolute temperatures of the body radiating energy and the body receiving such radiations, i.e., $E = lc (T^4 - T_1^4)$. For practically all purposes the effect of the fourth power of the absolute temperature of the body receiving the radiations may be neglected as being negligible in comparison to the radiating body. Hence it may be stated that the energy radiated from a "black body" is equal to a constant multiplied by the fourth power of its absolute temperature. A "black body" is defined as one which absorbs all energy falling on it, reflects none, and radiates as much as it absorbs. The interior of uniformly heated furnaces, combustion chambers and retorts approximate this theoretical condition close enough for all practical purposes.

The radiation pyrometers on the market at present consist of a tube blackened on the inside, and in one end of which there is placed either a spherical or conical mirror, the other end being left open. A very small and sensitive thermocouple, usually made of iron vs. constantan is located in the tube in such a manner that the fused junction is at the focus of the mirror. The two ends of the couple are attached to a galvanometer or sensitive millivoltmeter. The radiant energy of all

wave lengths entering the tube is focused on the junction of the thermocouple, thereby raising its temperature and producing an electromotive force which is measured on the milli-voltmeter.

Radiation pyrometers are of two types:- the fixed focus, and the adjustable focus. In the fixed focus pyrometer the receiving tube is about 30 inches long and 1 inch inside diameter. The adjustable focus type has a receiving tube about 5 inches long by 3 inches inside diameter.

It is evident that the mirror in this type of pyrometer plays an important role. Tarnish, dust and dirt, and displacement of focus may produce serious errors. A fixed focus radiation pyrometer is one of the University laboratories gives indications too low by 200 deg. C. or 360 deg. F. due to tarnishing of a cone mirror made of aluminum. The mirror in the adjustable focus type is usually gold plated on the front side and gives very satisfactory service.

It is generally assumed that radiation pyrometers, as constructed, obey the Stefan-Boltzman law respecting the fourth powers of the absolute temperatures. Some recent tests made at the Bureau of Standards show that the exponent instead of being 4 varies from 3.28 to 4.22 for different instruments and even from 3.50 to 4.50 in the same instrument depending on the conditions of operation. Hence, absolute confidence can not be placed on the temperature scale furnished by the maker. The safest way is to have the same calibrated.

In a perfect radiation pyrometer the distance of the source of radiation to the pyrometer should be immaterial. The adjustable focus type of radiation pyrometer may be open to serious error due to two conditions. The first condition relates to the construction of the mirror and the receiving disc on the fused junction of the couple, and the second to the size of the image produced on the receiving system. The Bureau of Standards has recently found that the energy received by the thermocouple when the focusing distances were 80 c.m. and 300 c.m. respectively, differed by 9 per cent. Hence, if the pyrometer were calibrated at a focusing distance of 80 c.m. and used at 300 c.m., the temperature so measured would be too high by 2 per cent, or 35 deg. C. at 1500 deg. C. The size of the image on the receiving system produces the most serious error due to heat conduction and conviction to the thermocouple. Thus for an extreme case the Bureau of Standards found that an instrument which was calibrated by sighting on a source 3 c.m. (1¼") diameter at a distance of 150 c.m. (60") and used to sight on an opening 11 c.m. (4¼") diameter would be in error 32 per cent of the absolute temperature, and at 1500 deg. C. or 2700 deg. F. would read 2070 deg. C. or 3726 deg. F., that is 570 deg. C. or 1036 deg. F. too high. An average diameter of image of 0.4 c.m. is more often employed in calibration, and in general use the size of the image will vary from 0.2 c.m. to 1.1 c.m. diameter. Such variation will result in temperature readings too low by 2 per cent for

the small image and too high by 4 per cent for the large image. Thus with ordinary use the errors may amount to several hundred degrees for extreme cases, but in general to 50 deg. C. and more.

The various fixed focus radiation pyrometers are also open to errors. In one make under favorable conditions an error of 3 per cent in temperature was observed. In general the readings decrease for increased sighting distance. In another make the error in temperature reading amounted to 12 per cent when calibrated on a 12 c.m. (4¾") diameter source at a distance of 115 c.m. (45") and afterwards used with the tube close to the source.

Various recording devices have been devised for radiation pyrometers, but their usefulness has been limited to recording variations in temperature from a fixed point.

Of the various forms of optical pyrometers only one has proved to be of any considerable commercial importance. This instrument is really a spectro-photometer in which the intensity of a certain wave length of polarized light in the red spectrum from a furnace is matched in intensity by a similar wave length of polarized light emanating from a standard, 6 volt, electric lamp operated on a storage battery.

Obviously, it is important that the standard electric light must be of constant brightness, hence the voltage of the battery should be constant. To bring the electric lamp to the required intensity, it is compared

with a standard flame of amyl acetate. If the storage battery is small the chances for changes in voltage are large and an error of 50 deg. C. or 90 deg. F. may easily creep in.

Since polarized light is compared with respect to intensity it is easy to show that below 900 deg. C. or 1620 deg. F. the instrument is insensitive, and that above 1600 deg. C. or 2900 deg. F. the setting is difficult to make accurately. The temperature scale is given in terms of degrees of arc on a dial attached to the analyzer of the polarizing system. This dial is about 4 inches in diameter and the size of each degree of arc is about 1/16 inch at 1000 deg. C. or 1800 deg. F., one degree Centigrade corresponds to 1/10 of a degree of arc, while at 1800 deg. C. or 3240 deg. F., seven degrees Centigrade corresponds to 1/10 degree of arc.

It will also be seen that the accuracy of a temperature determination by means of this pyrometer depends on the sensitiveness of the eye to changes in intensity of light. Individuals differ materially in ability to distinguish light intensities, so it follows that duplicate readings by various persons are not easy to obtain.

In spite of the large errors possible in measurement of high temperatures with the pyrometers discussed in this paper it should not be forgotten that all of them have a wide field of usefulness and have given excellent service. The intention is to point out the limitations of the various pyrometers, the precision of measurement possible

and the conditions for operation. Some pyrometers are poorly designed and constructed; these give trouble. Yet each year's investigation brings out some new property of material, and new applications of scientific facts to pyrometric equipment. The art is still in the transition stage. The past five years have brought out some fine improvements and in the near future, it is hoped, pyrometers will be as well standardized as electrical instruments.

11

PROGRESS REPORT ON THE WORK OF WISCONSIN GAS ASSOCIATION FELLOWSHIP AT THE UNIVERSITY OF WISCONSIN.

March, 1918

O. L. Kowalke

The grant of $500 by this Association for a fellowship in gas engineering at the University of Wisconsin is a manifestation of much good will and confidence. The University desires to express its appreciation of this grant and to assure the Association of its earnest endeavor to carry on the work. When last April your executive committee announced the grant and requested that steps be taken to engage a man for this work, Mr. Howard E. Sweet, a graduate of the chemical engineering course of the University of Wisconsin was chosen.

Early in October, 1917, Messrs. Cross, Lyons, and the writer met to decide on the problem most desirable and suitable for investigation; one which could be worked out in Madison. At that time it appeared desirable to make a study of the advisability of lowering the B.t.u. standard for gas in Wisconsin. It was suggested that if some plant were operated so that the heating value of the gas could be varied, much valuable information could be obtained.

The project was discussed in several meetings with the Commissioners, but they, while in sympathy with the plan, finally decided that it was not desirable at

this time to sanction a temporary suspension of the regulations at Madison.

Meanwhile, the fuel and labor situations had become acute and altogether it seemed best to discontinue the work on this problem, because the data would not be comparable to that obtained under normal conditions. The plan was abandoned about December 20. Up to this time Mr. Sweet was engaged in gathering information from the literature and familiarizing himself with the situation. He has gathered material which will be valuable later if the problem is again attacked.

The problem determined upon after the B.t.u. question was abandoned was the investigation of gas furnaces with respect to the best methods of obtaining high temperatures, the behavior of various refractory materials used in the construction of these furnaces, and the heat treatment of steel. Experiments are now in progress to determine how high a temperature and how quickly the same may be obtained with various gas and air pressures in a standard American Gas Company furnace having a chamber 12" by 14" by 18". The gases forming the atmosphere in the furnace are analyzed and the appearance of the flame noted to determine a relation, if there is one, between flame appearance and atmosphere in the furnace. It is also planned to determine the effect of the atmosphere in the furnace on the microstructure of the steel under treatment. The furnace has also been adapted to test out the

feature employed by the Surface Combustion Company, where the burners direct the flames onto a mass of broken refractory material from which they are reflected to the roof and then back onto the work. The data so far warrant more tests of the surface combustion feature. At this time the results in general are as yet too inconclusive to warrant a statement, but by the end of the school year enough data will have been obtained to make a full report.

The investigations under the Fellowship are for the benefit of the Association, and it is hoped that this progress report will bring out suggestions and helpful criticisms.

Grateful acknowledgment is here made to the Eclipse Fuel and Engineering Company for many courtesies extended and for the loan of apparatus.

Chemical Engineering Department.

12

CHEMICAL INDUSTRIES OF WISCONSIN

By O. L. Kowalke

Chemical and Metallurgical Engineering, Vol. 21, p. 338(1919)

A wide variety of chemical industries is represented in Wisconsin, but among these the leather and paper industries are the most important on the bases of value of product and number of men employed.

The leather industry of Wisconsin ranks fourth among all the industries of the State and third in the leather industry of the United States. The employees constitute 10.5 per cent and the value of the products, $42,200,000, constitutes 11.5 per cent of the total for the country in 1914. Milwaukee is the second city in the country on the bases of size of tanneries and the value of the products. The principal product is "calfskin upper," 2,292,800 sides, of which more is made here than in any other State; sole leather, with 1,122,200 sides, comes next in order, and is followed by harness leather, with 631,787 sides. Of the latter more is made in Wisconsin than in any State in the Union.

Wisconsin is one of the leading pulp and paper producing States in the country, being surpassed in the consumption of wood for this purpose only by Maine and New York in the order named. There are 30 ground wood, 20 sulphite and 5 sulphate pulp mills in the State, which in 1917 produced about 400,000 tons of pulp, consisting of 45 per cent unbleached sulphite, 38 per cent mechanical,

8 per cent sulphate and 9 per cent bleached sulphite. Besides the wood pulp paper, such as news, writing, book, tissue, wrapping, etc., considerable amounts of rag paper and container board are made, amounting in all to 480,851 tons in 1917. A number of specialties were developed in Wisconsin for war purposes, such as cellu-cotton, a wood pulp substitute for absorbent cotton; special waterproof containers for packing and shipping shells and other war supplies, and the use of waste hemlock bark, produced from the rossing of wood, for the manufacture of hemlock extract. Other specialties, not for war purposes, are fiber rugs, filter mass (the plant being the largest in the United States), and molded pulp products.

There are several chemical industries that rank well to the front in the country. Of these the rubber industry ranks sixth in the value of products, $7,382,108, for five establishments in 1914, the principal product being automobile tires. The 11 soap factories, with an output valued at $2,894,000, rank tenth in the country in this industry on the bases of persons employed and value of the products. The increase in value of the finished products over the raw materials is 117 per cent. In this respect Wisconsin is led by only one State, which gives a measure of the high grade of soap made. Gas for domestic and municipal consumption made in 47 plants is valued at $5,294,000, which puts the group in tenth place in the industry. Not included in the group of 47 gas plants are

two by-product coke-oven plants, in one of which 250 ovens are in operation, producing 1800 tons of coke daily.

The census of 1914 ranks Wisconsin nineteenth in a group called chemical industries, comprising 395 establishments engaged in the manufacture of acids, sodas, alums, coal-tar products, cyanides, bleaching materials, chemicals by electrolysis, plastics, compressed and liquefied gases, and other chemicals. Most of these materials are made here. Sulphuric acid is made in two plants, one using the contact process; nitric acid is made in one plant; three plants are engaged in making bicarbonate and sal soda. The compressed and liquefied gas industry has kept pace with the growth of the foundry and machine tool industry; two plants make compressed acetylene, two make compressed oxygen and hydrogen, while at one plant of considerable size compressed oxygen is obtained from the air.

MISCELLANEOUS OTHER INDUSTRIES

Another group of industries not included in the above list but of equal importance is worthy of consideration. Of major importance in this group are four beet sugar factories having a combined daily capacity of 2800 tons of beets; one glue factory capable of handling all the wastes from the Wisconsin tanneries in addition to large amounts of raw materials shipped in from other sources; and a match factory of large capacity. The dry battery industry ranks third in its group and its output

is about 2 per cent of the total in the country. In the manufacture of dynamite and permissible explosives, Wisconsin ranks sixth among the seven States producing nine-tenths of these commodities. Other industries on which statistics are not available include the following:

Industry	Number of Establishments.
Lime........................	30
Fertilizers..................	8
Paints ready to use..........	6
Iron buff and other colors...	3
Zinc Oxide...................	1
Varnish......................	1
Wood alcohol and acetate of lime......................	3
Glycerine....................	2
Insecticides.................	2
Baking Powder................	2
Electroplating...............	10
Glass bottles................	1

A number of industries were established as a result of the war. Among these is the production of potash from wood ashes. In 1917 21 plants were in operation in Wisconsin and 25 in Michigan, which together produced 1035 short tons of crude potash, or 2 per cent of the total potassium oxide production in the United States. The initial cost of the average sized potash plant, including the building, was between $3000 and $4000.

The production of high explosives in Wisconsin in 1916 amounted to 6,515,032 lb., which was 2½ per cent of the total manufactured in this country. Closely associated with the production of high explosives is the

manufacture of coal-tar dyes and dye intermediates in one large plant. This plant made a number of intermediates in large quantity and is now well established for peace-time production.

Laboratory of Chemical Engineering,
University of Wisconsin.

"The Gas Industry, A Good Customer of the University".

by O. L. Kowalke

Annual Meeting Gas Section, Wisconsin Utilities Association, March 22, 1921.

It is unusual that you are asked to consider an educational problem. But the problem is one in which you are vitally interested; it concerns your employment of a product from the University. You are now a good customer and it is necessary that you continue to be so. To retain your patronage, satisfactory service must be rendered; you must know the capacity of the product; your confidence and good will must be retained.

To aid in the presentation of this topic certain analogies will be suggested between the gas industry and the University. Your business is sometimes called a public utility. Utility is synonymous with service; so you give a public service. What would justify a University if it were not public service?

The gas industry and the University each have a technical staff. In the University the function of the staff is to train young men for engineering and industrial service. Your raw materials now come to you from variable sources, and it is not always known how best to treat them, although they may obey certain well-known laws of chemistry, physics, and mathematics. The University also draws on many sources for young men of variable capacity and previous training and the technical staff is not always able

to meet requirements in the matter of standards because the laws governing the workings of the human mind are not perfectly understood. Some companies are managed more successfully than others; some instructors are more successful than others in the training of young men.

Your sales and complaint departments are complementary. The first sells the product to your consumers; the second gives the customer an opportunity to express dissatisfaction with the commodity sold or service rendered, but at the same time strives to retain his good will. In a like manner the University after disposing its product among the industries, strives, through its representatives, to determine whether the service rendered by the young men is satisfactory. This is one of the opportunities which the University seeks for a discussion regarding inadequacies in its technical training. A frank expression of opinion is therefore invited.

You get new business through advertisements, demonstrations, and personal solicitation. You believe that the better the prospective customer understands what he can do with your product, the more likely he is to buy your commodity. The University publishes a general catalog and bulletin regarding special courses; it may also make personal explanations regarding specific advantages offered.

This opportunity is therefore taken to speak specifically about the training offered for chemical engineers, which, it is believed, is particularly suited for the gas industry today. The training is not that of a chemist; it is more along the lines of engineering than of chemistry.

It is intended that the student shall be able to make a chemical analysis, but not that he be only a analyst in chemistry. Besides liberal instruction in theoretical chemistry, the student is also required to take the basic courses in drawing, mathematics, physics, mechanics, and machine design that are required in the curricula for mechanical and electrical engineering.

The following tabulation of the curriculum in chemical engineering is self explanatory.

First Year

First Semester			Second Semester		
General Chemistry	3	credits	General Chemistry	3	credits
Drawing	3	"	Drawing	3	"
English	3	"	English	3	"
Mathematics	5	"	Mathematics	5	"
Shop work	2	"	Shop work	2	"

Second Year

Mathematics	4	credits	Mathematics	4	credits
Physics	5	"	Physics	5	"
Machine Design	4	"	Mechanics	5	"
Quant. Chem. Analysis	5	"	Gas & Fuel Analysis	2	"
			Engineering Materials	2	"

Third Year

Organic Chemistry	3	credits	Organic Chemistry	3	credits
Steam & Gas Engineering	3	"	Steam & Gas Engineering	5	"
Mechanics	5	"	Descriptive Geometry	3	"
Metallography	3	"	Electrical Engineering	2	
Pyrometry	2	"	Chemical Machinery	2	
Electives	3	"	Strength of Materials	2	"
			Electives	3	"

Summer work in Chemical Engineering....5 weeks

Fourth Year

Electrical Engineering	4	credits	Machine Design	3	credits
Physical Chemistry	3	"	Contracts	2	"
Electrochemistry	5	"	Industrial Organ Chem	2	"
Industrial Chemistry	3	"	Thermochem. Calculations	2	"
Thermochem. Calculations	2	"	Special problems	4	"
Steam & Gas Engineering	1	credit	Electives	5	"
Electives	2	credits			

In the elective courses opportunity and encouragement are given for the student to broaden his vision and interests. He is encouraged to study economics, business methods, English, history, and the like. Among the electives, he may choose a course in gas manufacture and distribution. In this course the fundamental principles of chemistry, physics, and mechanics are emphasized as applied to the carbonization of coal and oil, heat conduction, refractory materials, and the distribution of gas. The technique of this industry can best be learned in the plant.

You have repeatedly employed the graduate in chemical engineering, hence you are a good customer. Customer is synonymous with patron. But a patron is defined as one who supports, one who helps a cause, a work. You have done more than support; you have given liberally from your funds to establish a Fellowship in Gas Engineering in the Department of Chemical Engineering. Thus you have a vital interest in this matter of training young men.

The question may well be asked, "Why did this Association establish the Fellowship?" Two reasons may be suggested; first, to obtain information of value to the Association, second, to train men for subsequent employment in the industry. Up to this time the chairman of the Chemical Engineering Department chose and nominated to the Board of Regents the most promising candidate for the Fellowship. The chairman also took the initiative in the choice of problem, but consulted with the President of this Association and other members. Informal discussions have been held as

the work progressed, and the final reports have been presented at the annual meetings of this Association.

The following suggestions are offered for your consideration in order to obtain better results and greater interest on the part of students in the gas industry. Because the men hitherto appointed to the Fellowship have had neither knowledge or the problem to be studied nor practical experience in the gas business, considerable time had to be spent by each Fellow to become familiar with his problem. There should be some way in which the student could become more familiar with the practices in the gas industry before beginning work on his problem.

During the summer following the junior year, the student in chemical engineering is required to work at the University eight hours each day for a period of five weeks in a laboratory course in chemical manufacture. This is a most favorable opportunity to observe the ability and initiative shown by the student.

It is proposed to select from this group three or more men of proper personality and good records as students to take temporary summer employment in your plants, that is, from about the middle of July to the middle of September. During this time the men are under your supervision. Reports on such summer work will be required of the student; reports from your executives to the chairman of the chemical engineering department regarding the record made by the student would be highly desirable. By the end of the senior year it would be possible to make a choice

for the Fellowship from those who have shown aptitude for the work. During the summer following the fourth year the student should have the opportunity again of working in a gas plant so that he may become more familiar with the problem he is to study during the coming scholastic year.

It is hoped that this proposal will provoke some discussion and that suggestions will result from it. This is a matter in which you are vitally interested and your views are earnestly sought. The Chemical Engineering staff desires to give an account of its stewardship of the patronage which you have so generously extended.

14.

SOME INTERESTING SIDELIGHTS ON HOUSEHOLD REFRIGERATION

By O. L. Kowalke

Presented before Annual Convention, Gas Section,
Wisconsin Utilities Association, February 26-27, 1925

During the past fifteen years great progress has been made in the development and the use of appliances for the household for cooking, water heating, washing and ironing, sweeping, space heating, refrigeration, and the like. In the cities, gas service and appliances for cooking are considered necessities; appliances for mechanical refrigeration, however, are a newer development and still belong to the class of conveniences; they are now in the Pierce-Arrow class, but the Ford may be just around the corner. Much time and money have been spent to make household refrigerating machines reliable and automatic in operation and for a price that is attractive to the customer; and it appears that these machines are here to stay.

Mechanical refrigeration is accomplished either by the compression or the absorption system. In the compression system, either an electric motor or a steam engine is required; in the absorption system, a motor or engine can be omitted, but energy in the form of heat must be supplied. The absorption system,is, therefore, of interest to a gas company.

How can refrigeration be accomplished with the aid of a gas flame? This question can be answered best by describing the procedure followed in a specific machine

such as the "Common Sense Ice Machine", which enjoys a unique distinction. Data presented by H. D. Valentine before the American Gas Association, 1923, and by "Ice and Refrigeration" in the issue for October 1923, regarding this machine are here freely used.

A solution of ammonia in water (about 35 per cent by weight of ammonia) is in the absorber-generator (A). The water from the city supply is admitted at (Y) through the shifting valve (Z), into the pipe (W), through the controlling valve (S), into the condenser jacket (D), and thence to waste. The controlling valve (S) admits only a relatively small amount of water so that the main pressure may open the gas valve (K). By means of a pilot light, the gas flowing through the valve (K) is ignited at the burner (M). The ammonia vapor generated by heating the solution in (A) is conducted through the separator in the dome (B), thence through the check valve (C) into the coils in the condenser (D). Here the ammonia gas is liquified through cooling and the liquid water-free ammonia is collected in the receiver (E).

When the boiling off operation has proceeded to the point where the ammonia content in the generator-absorber (A) is reduced to about 20 per cent., the pressure (about 190 lbs.) in (A) is high enough to actuate a mechanism in the pipe (Q) so as to shift the water valve (Z). The water supply is thus directed into the pipe (U), which means that the gas valve (K) closes because the pressure has been removed and that the water no longer

runs through the condenser (D).

The water now runs through the pipe (U) and the controlling valve (T) into the cooling coils (N), and thence to waste. The residual weak ammonia in the absorber-generator (A) is thereby cooled to about room temperature, and the pressure in (A) drops to atmospheric or below.

When the ammonia has been boiled off from the solution in (A) to a predetermined concentration and the cooling of the residual weak ammonia has commenced, the liquid water-free ammonia from the receiver (E) can be allowed to pass through the expansion valve (F) into the expansion and refrigerating coils (G) in the brine tank. Another valve controlled by a thermostat immersed in the brine allows ammonia to pass from the expansion valve (F) into the expansion and cooling coils (G) in case the brine is warmer than the temperature desired, or it shuts the ammonia off altogether when the brine temperature has fallen as low as desired. As the liquid water-free ammonia enters the coils (G), where the pressure is the same as in the generator-absorber (A) or at atmospheric, it is changed from a liquid to a vapor, and in doing so absorbs heat from the surrounding brine. Water-free liquid ammonia under atmospheric pressure will boil and form a saturated vapor at 28 degrees below zero Fahrenheit. If the brine is at 28 degrees above zero Fahrenheit, it is then 56 degrees warmer than the ammonia vapor. Thus the brine furnishes the heat required to change the ammonia from the liquid to the vapor condition.

About one-half as much heat is required to change a pound of liquid ammonia to vapor as to change a pound of water to vapor.

The ammonia vapor formed in the expansion and cooling coils (G) is now conducted through the pipe (I) into a perforated pipe (H) in the bottom of the absorber-generator (A). By the time the ammonia is allowed to enter (G), the weak ammonia solution in (A) has been cooled and will readily take up additional ammonia vapor. This procedure continues until all the liquid water-free ammonia from the receiver (E) has passed through the expansion coils (G). The pressure in the receiver (E) then falls to a low value and so does the pressure in the pipe (R) attached to the shift valve (Z). When a fixed minimum pressure in (R) against the shift valve is reached, the mechanism in (Z) operates. It shifts the water <u>from</u> the pipe (U) and the cooling coil (N) <u>to</u> the pipe (W), the gas valve (K), and the condenser coils (D). The gas valve (K) is opened as the water pressure comes on and allows gas to flow to the burner (M) and be ignited. This marks the beginning of the second cycle.

The question may now be asked: How far has the the development of mechanical refrigerating appliances for the household proceeded with respect to price, cost of operation, safety, automatic working, and reliability? There are now on the market about 52 different machines for household refrigeration, costing from $150 to $700, the average price being about $400.

Of all the household refrigerating machines

now on the market, only two makes have been found to operate on the absorption system, and of these only one, the "Common Sense Ice Machine", uses gas; all the other makes of machines operate on the compression system. For the present, a gas company desiring to sell appliances of the absorption type for household refrigeration is much restricted in the choice of machines. The "Common Sense Ice Machine" is made in three sizes, rated at 125, 250, and 500 pounds of refrigeration per 24 hours on the basis of 4 complete cycles. A pound of refrigeration is defined as the amount of heat absorbed by the melting of one pound of ice at 32 degrees Fahrenheit to water at 32 degrees Fahrenheit. The consumption of gas for each of the above sizes respectively is 45, 90, and 150 cubic feet per hour. The water consumed will depend on its temperature; for the 125 pound machine from 300 to 350 gallons of water per 24 hours are required.

On the other hand, there are many different machines operating on the compression system. The manufacturers of these machines, it is estimated, have spent at least $60,000,000 to bring their products to the present state of perfection. The inherent mechanical difficulties such as frictional losses, leakage of refrigerating fluid through stuffing boxes and joints, lubrication, regulation and control of refrigerant have been overcome in many instances. Manufacturers now also recognize that if the customer is to enjoy satisfactory and continuous service from his machine, the manufacturer or the sales agent must stand ready to make periodic in-

spections, adjustments, and repairs. It is also a policy to place these machines only in good boxes. If the customer's box is in poor condition, he is urged to purchase a more efficient one.

It was estimated* that at the end of 1923 there were 80,000 household refrigerating machines in use in this country, and that the number manufactured during 1923 was about 25,000.

'What is the probable market for mechanical refrigeration? Dr. Mary Pennington of the National Association' in May 1924** that from her investigations she believes that not over 30 per cent of the people in Boston had refrigerators in their homes. In the department stores she found that refrigerators could be purchased for $35 to $50. Thus it would seem to follow that 70 per cent of the people have found it hard to pay $35 for a refrigerator. Some of the 30 per cent might buy a mechanical machine if the price came down to $100, but the 70 per cent could not do more than get an ice box. Leslie C. Smith, Sec. of the National Association, told the Massachusetts dealers at this meeting that a survey of 162 cities having populations from 10,000 to 500,000 showed that 45 per cent of the regular telephone subscribers were only <u>regular summer</u> users of ice; that 53 per cent of the telephone subscribers could be canvassed

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* "Ice and Refrigeration", November, 1924.
** "Ice and Refrigeration", May, 1924.

for ice.

In the second largest consuming district in the U. S., the average amount paid for ice for domestic use was $16.92 for the year 1922. The per capita consumption[*] of ice in 26 of the larger cities averages 1150 pounds per year, ranging from 2000 pounds per capita per year in Dallas, Texas, to 600 pounds per year per capita in Los Angeles. An investigation at Kansas City, where ice was selling for 60 cents per hundred in 1923, showed that the revenue varied for different classes of homes as shown in the following table:

1. Homes - Regular Users.

Class A - 10 rooms or over	$243.96	per year
" B - under 10 rooms	63.24	" "
" C - 7 to 8 rooms	41.38	" "
" D - 5 to 6 rooms	40.68	" "
" E - under 5 rooms	29.00	" "

II. Apartment Houses.

Class One with kitchenetee	36.00	" "
Class Two " "	28.00	" "
Class Three " "	27.00	" "

III. Necessity Class - Customers who do not take ice till May 1.

Houses 7 to 8 rooms (include boarding)	$27.27
Houses 5 to 6 rooms	18.00
Houses under 5 "	15.00

Mr. L. C. Smith[**] estimated for a machine costing $200, the cost of mechanical refrigeration for 300 days would be $37. In Kansas City[*] it was estimated that mechani-

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[*] "Ice and Refrigeration", April, 1924
[**] "Ice and Refrigeration", May, 1924

cal refrigeration can complete successfully when the ice bill amounts to $40 per year.

Information* was gathered from 160 cities in 41 states to show the amount of ice business done each month by the dealers. These data were then averaged and the percentages of the whole year's business for each month computed. The results are set forth in the following table:

January	-	2.6	per cent.	of	year's	business
February	-	2.0	"	"	"	"
March	-	3.76	"	"	"	"
April	-	5.54	"	"	"	"
May	-	9.57	"	"	"	"
June	-	13.50	"	"	"	"
July	-	17.00	"	"	"	"
August	-	16.20	"	"	"	"
September	-	17.40	"	"	"	"
October	-	6.21	"	"	"	"
November	-	3.52	"	"	"	"
December	-	2.7	"	"	"	"

This table shows that nearly 2/3 of the year's business is done in 4 months. The decrease for August is indicative of vacations and gives additional suggestions regarding prospective customers.

These data seem to point to the conclusions, (1) that those people whose ice bill is about $40 per year are good prospects for mechanical refrigerating machines, (2) that the electrically driven or compression machines have a strong hold on the market, (3) that the volume of gas which can be sold for refrigeration is, for the present, very small.

There seems to be no reason why automatic ab-

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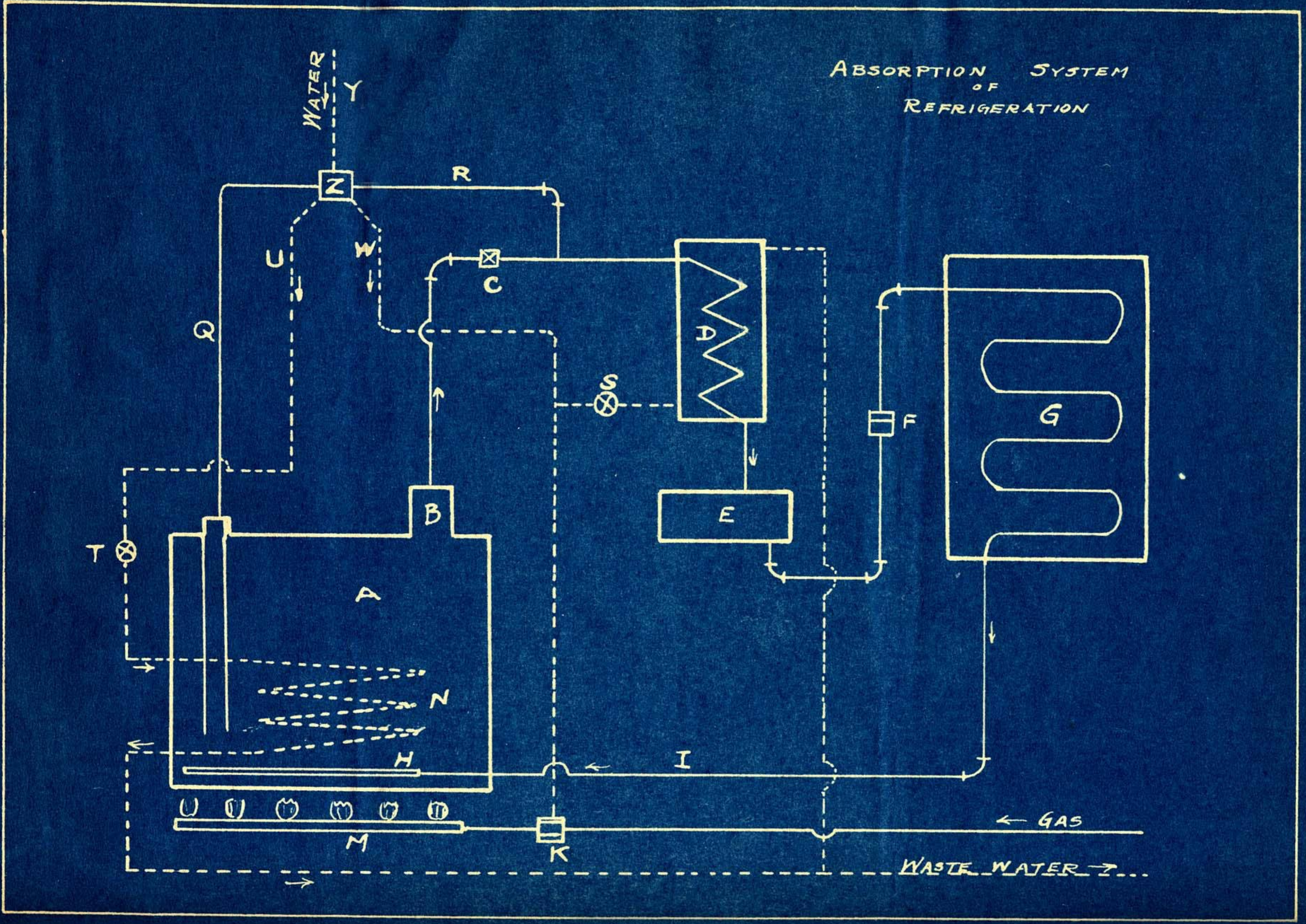
* "Ice and Refrigeration", 62 364 (1922)

sorption refrigeration devices using gas can not be made to operate at least as effectively as those of the compression type.

Chemical Engineering Department,
University of Wisconsin,
Madison.



ABSORPTION SYSTEM OF REFRIGERATION

15.

PROGRESS REPORT ON THE COMBUSTION SPACE REQUIRED IN INDUSTRIAL FURNACES FOR BURNING CARBURETTED WATER GAS

Annual Meeting Gas Section, Wisconsin Utilities Association
May, 1926

by O. L. Kowalke and A. W. Carlson

These experiments are the co-operative efforts of the Gas Section of the Wisconsin Utilities Association and the Chemical Engineering Department of the University of Wisconsin in connection with the Research Fellowship maintained by the Gas Section.

The objects of these experiments were two-fold; first, to obtain data on the behavior of burners when attached to a furnace; second, to determine the maximum amount of gas which could be completely burned per unit volume of combustion space. To gain these objectives it was desirable to measure the total volume of combustible mixture introduced into the furnace; to observe the nature of the flame issuing from the chimney; to determine the presence of carbon monoxide in the flue gases; and to measure the pressures in the burner tube and in the combustion chamber.

A carburetted water gas having the following analysis was used:

CO_2	3.4%	Ch_4	8.01
O_2	1.2	C_2H_6	1.78
H_2	32.9	Illuminants	8.60
CO	33.3	N_2	10.81
			100.00%

The furnace used, as shown in Fig. 1., had a combustion chamber $4\frac{1}{2}$" x $4\frac{1}{2}$" x 9", whose walls and floor were made of standard fire brick and whose top consisted of a moulded slab of crushed firebrick bonded with sodium silicate. This brick combustion chamber was set inside a galvanized iron box 14" x 14" x 18" and the space between the sheet iron and brick filled with loose magnesia asbestos. Suitable openings in the sides were provided for the burner and the pressure measuring tube. A chimney 6" high and $1\frac{3}{4}$" inside diameter was mounted on the cover over the opening opposite from the burner.

Two types of burners were used. The first type, No. 1, used is shown in Fig. 2. It consists of a cast iron $\frac{3}{4}$" tee (B) into which was screwed a brass nozzle (C) soldered onto a brass nipple (E). Between the two pieces of $\frac{3}{4}$" pipe (A) there was inserted an explosion box (F), (4" x 4" x 4"), made of galvanized iron and fitted with a paper blow-out disc (G). This explosion head served as a protection against destructive back firing while adjustments of the air supply were being made. Air under pressure was introduced at (E) and gas under 5" water column entered at (D). The mixture of gas and air then passed through the explosion box (F) and thence to the burner pipe. (A).

The second type, or atmospheric burner No. 2 is shown in Fig. 3. It consists of an injecting tube (A) mounted in a 1½" pipe (B); one end of this pipe was threaded to take a 1½" x 2½" reducing coupling (C) which was fitted with a cross piece (D) so as to support the gas supply pipe (E); the other end was threaded so that a 1¼" pipe (G) screwed into it. A perforated plate was fitted into the end of the pipe (G) for the purpose of increasing the port velocity and to prevent back firing. The perforations were evenly spaced and their diameters were that of a No. 40 drill. To regulate the air supplied to the mixing tube, a disc shutter (H) was mounted on the gas supply pipe (E). By turning the disc shutter in the threads on (E) the opening for the air supply could be enlarged or completely shut off. The gas supply pipe (E) was rigidly supported by the bar (D) in such a manner that the gas stream emerging from the orifice (F) always passed through the axis of the injecting tube (A).

To measure the air inspirated by the gas stream discharged at (F) a wooden box (M) with a removable cover was placed to enclose the air inlet. This box arrangement is similar to that described in Bur. Stand. Tech. Paper 193. With the cover on the box a measured volume of air was admitted through the ½" pipe (K) while gas was admitted from (F). The 1/8" pipe (J) was connected to a gage to measure the pressure of the air-gas mixture in the burner tube.

The burner was operated with gas delivered at desired pressures from a rotary compressor. A dry meter on the suction side of the compressor measured the volume

of gas delivered to the burner.

To eliminate pulsations in pressure caused by the compressor, the gas was passed into a receiving tank located between the compressor and the burner.

A mercury manometer was used to measure the gas pressure at the orifice. Pressures in the burner tube and furnace were measured by slope gages filled with xylene.

A 10-light Maryland meter was used to measure the gas volumes and a 45-light Maryland meter for the air.

Procedure:

With Pressure Burner No.1.

In all these experiments air was admitted only as primary air mixed with the gas in the burner tube. The burner was lighted outside the furnace and the air supply adjusted to the desired amount. Then the burner was inserted into the furnace and sealed into place with magnesia asbestos cement. To keep the burner end cool a stream of water was made to flow over it. No data was taken until the furnace was red hot inside. These data included observations of pressures in the burner pipe and the differential pressure between the burner pipe and the furnace as shown by two slope gages. The gas rate was found by observing the time necessary for 2 cu. ft. to flow. In a like manner the air rate was found by observing the time necessary for the flow of 5 cu.ft. of air. A series of tests was made using different air-gas ratios. In order to get the desired ratio the air rate was first determined and then the volume of gas was regulated to correspond with the predetermined air-gas ratio. In experiments with the

pressure burner, No. 1., the effect of furnace back pressures upon the behavior of the burner was investigated. The furnace back pressures were increased by placing fire clay discs on top of the chimney flue.

Experiments were next made to determine the amount of gas which could be burned completely within the furnace. The burner was operated with a certain setting of the gas valve and a high air-gas ratio. The air rate was then progressively decreased until carbon monoxide began to appear in the flue gases. The presence of carbon monoxide was determined by drawing flue gases through a tube in which a piece of filter paper moistened with palladium chloride was placed. Carbon monoxide reduces the palladium chloride to metallic palladium which is black and is easily distinguishable.

With Atmospheric Burner, No. 2.

Tests of the atmospheric burner were made to determine the effect of the size of the orifice opening upon the air entrainment, and the effect of the furnace back-pressure on the air entrainment. The method of procedure was quite similar to that described above. The burner was lighted, then placed in the furnace, sealed with moistened magnesia asbestos, and cooled by a water jet. All the air used for combustion was drawn into the burner by the gas stream. The following data were taken during a run: pressure of the gas at the orifice; pressure in the burner pipe as measured by a slope gage; pressure in the furnace

by a similar gage; and the gas rate as determined by the time necessary for the flow of 2 cu. ft.

In order to obtain the air inspirated by the burner the cover was screwed onto the box (M) enclosing the burner head and the measured volume of air introduced through the pipe (K) Fig. 3 until the pressure in the burner was the same as when the box was open. When this condition was obtained it was then known that the air was being supplied at the same rate as the burner was inspirating air under normal operation.

Results.

From the experiments with the No. 1 pressure burner it was found that the pressure inside the furnace had little effect upon the operation of the burner. The burner operated in a satisfactory manner with back pressures as high as 2½ inches of water.

When operating with the atmospheric burner No.2 it was found that furnace back pressures influenced greatly the amount of air inspirated by the burner. An increase in the furnace back pressure caused the air entrainment to fall off. This is shown graphically by the curves in plate II. Curve (1) shows the amount of air entrained by the burner when operating in the open, with an orifice made by a #32 drill (area - 0.0106 sq. in.). When the burner was placed in the furnace and operated the air entrainment was found to be less as shown by curve 2. In this case the flue opening for the furnace was 1¾ inch, but when the opening was reduced to 1 - 3/8 inch, the entrainment of air was less as shown in curve 3; and when the flue opening

was still further decreased to 1 inch the air entrainment decreased again as shown in curve 4.

Curves 1 and 2 are straight lines or very nearly so. This means that the amount of air entrained is directly proportional to the amount of gas flowing through the burner. Curves 3 and 4 show that the amount of air entrainment per unit volume of gas flowing decreases as the gas flow is increased. This is probably due to the fact that as the amount of mixture sent into the furnace is increased the pressure built up is enough to cause a progressive decrease in the volume of the air entrained per unit volume of gas introduced.

The size of orifice used for admitting gas into the burner has a large effect upon the amount of air entrained per unit volume of gas flowing. It is shown very definitely in Plate III that the smaller the orifice used, the greater will be the air-gas ratio of the resulting mixture. By selecting the proper size of orifice the composition of the combustible mixture can be altered so as to have either oxidizing, reducing, or neutral atmospheres inside of the furnace.

The pressures which existed in the furnace with various rates of combustible mixture supplied to the furnace are shown in Plate IV. This curve is an average of all points obtained when using various sizes of orifices. Since a different air-gas ratio results from each orifice used, it would be expected that a separate pressure curve would be obtained for each orifice. This would be true

only when the temperatures were the same for each run. In these experiments it was not possible to maintain exactly similar temperature conditions in all runs, the differences being enough to hide the effect of the air-gas ratio on the pressure in the furnace.

The maximum air-gas mixture which could be burned per minute per cubic foot of combustion space was fixed in the following manner. For a given volume of gas the air supply was gradually reduced until the carbon monoxide was detected in the flue gas and the air-gas ratio producing this condition was taken as the limit of the voluem of gas that can be burned completely in that space. These data were then recalculated on the basis of cubic feet of gas per minute per cubic foot of combustion space.

The amount of gas per minute which can be burned per cubic foot of combustion space depends upon the air-gas ration which is used. When air is present in excess of that theoretically required for complete combustion, the rate of reaction between the gas and the oxygen is increased. The graph in Plate V. shows the number results of these tests. This graph must necessarily straighten out and approach a horizontal line which represents that ratio of air to gas theoretically necessary for complete combustion. If this limiting ratio is not exceeded, there will always be some carbon monoxide present in the flue gases, no matter how slow the rate of combustible mixture sent into the furnace may be. From the curve it can be seen that as the rate of gas to the furnace is increased, the amount of excess air required increases rapidly.

Chemical Engineering Dept., Univ. of Wis.- Feb. 1926

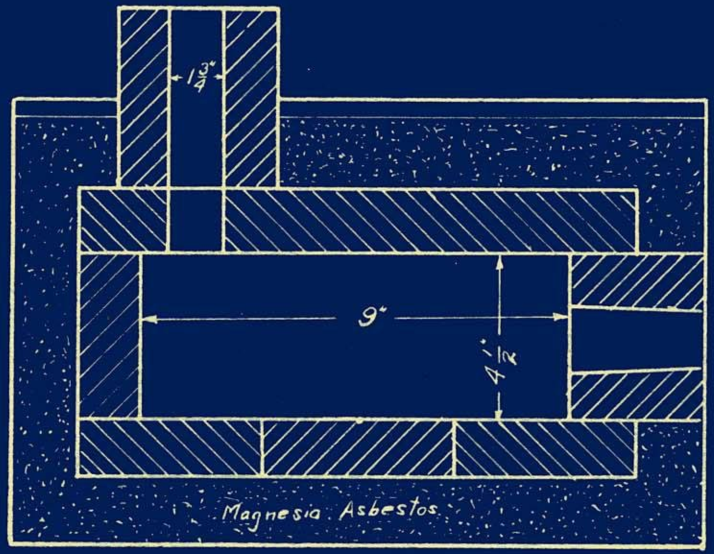


Fig 1. Furnace.

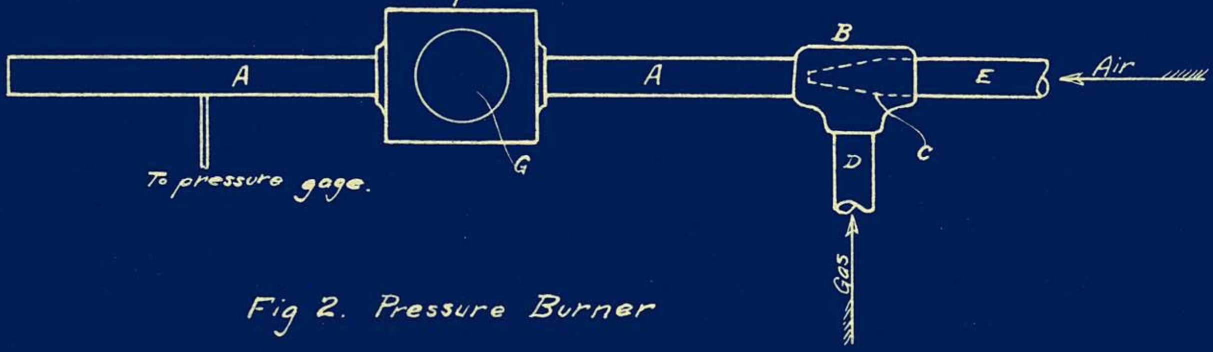
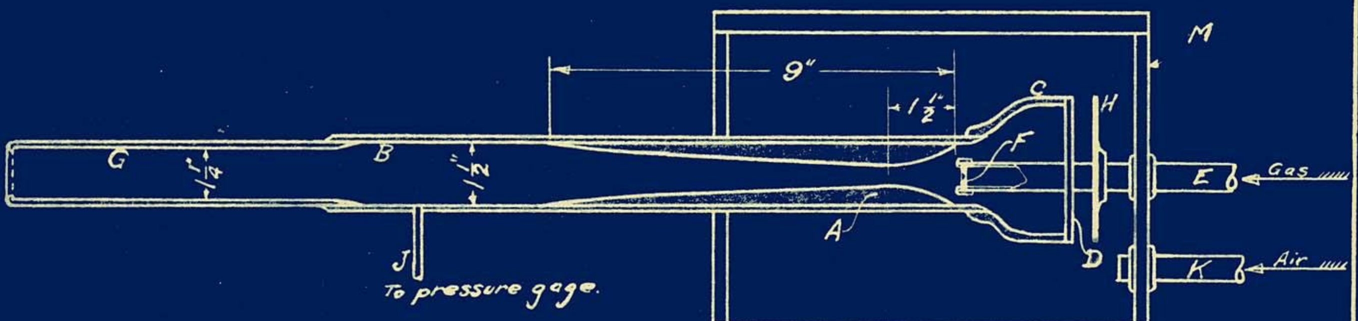


Fig 2. Pressure Burner



Area of burner port openings — 0.80 sq. in.

" " Air " " — 5.2 sq. in.

Diam. of throat of injecting tube — 5/8"

Distance from orifice to throat — 1 1/2"

Fig. 3.

Atmospheric Burner.

PLATE I

PLATE II

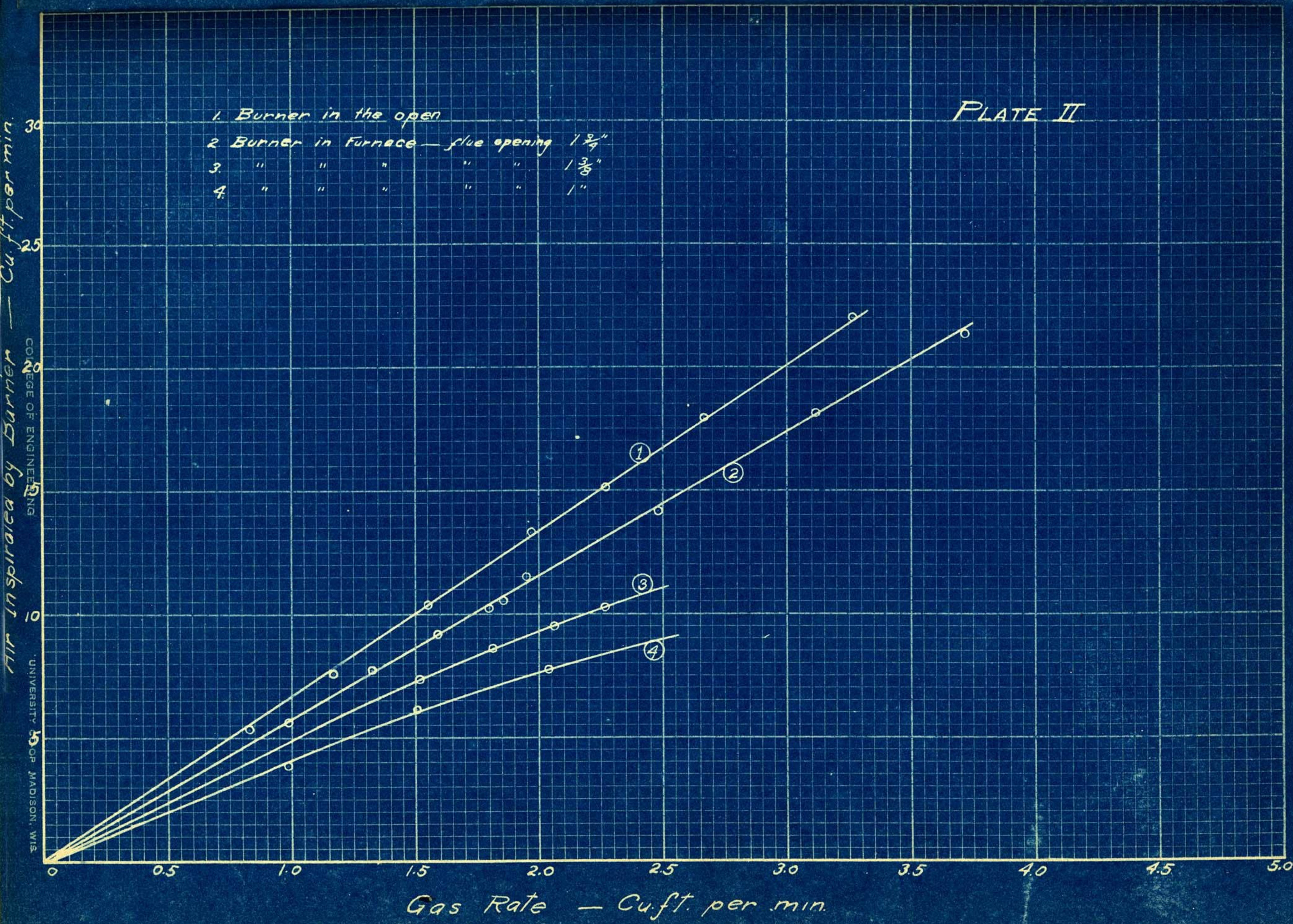
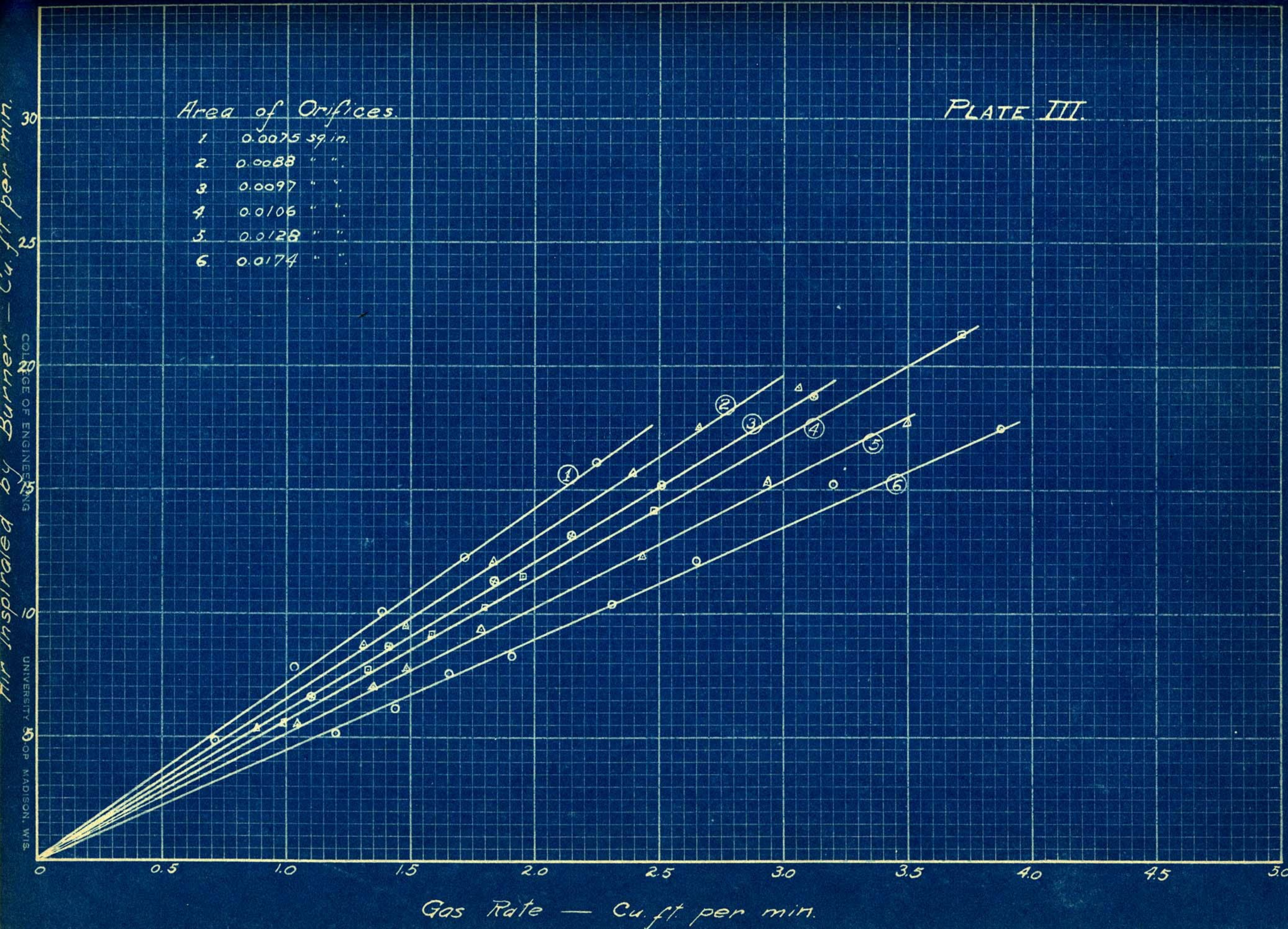

1. Burner in the open
2 Burner in Furnace — flue opening 1 3/4"
3. " " " " " 1 3/8"
4. " " " " " 1"
Air Inspirated by Burner — Cu.ft. per min.
Gas Rate — Cu.ft. per min.
30
25
20
15
10
5
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
①
②
③
④

PLATE III.


Area of Orifices.
1. 0.0075 sq. in.
2. 0.0088 " ".
3. 0.0097 " ".
4. 0.0106 " ".
5. 0.0128 " ".
6. 0.0174 " ".
Air Inspirated by Burner — Cu. ft. per min.
Gas Rate — Cu. ft. per min.
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5
10
15
20
25
30
①
②
③
④
⑤
⑥

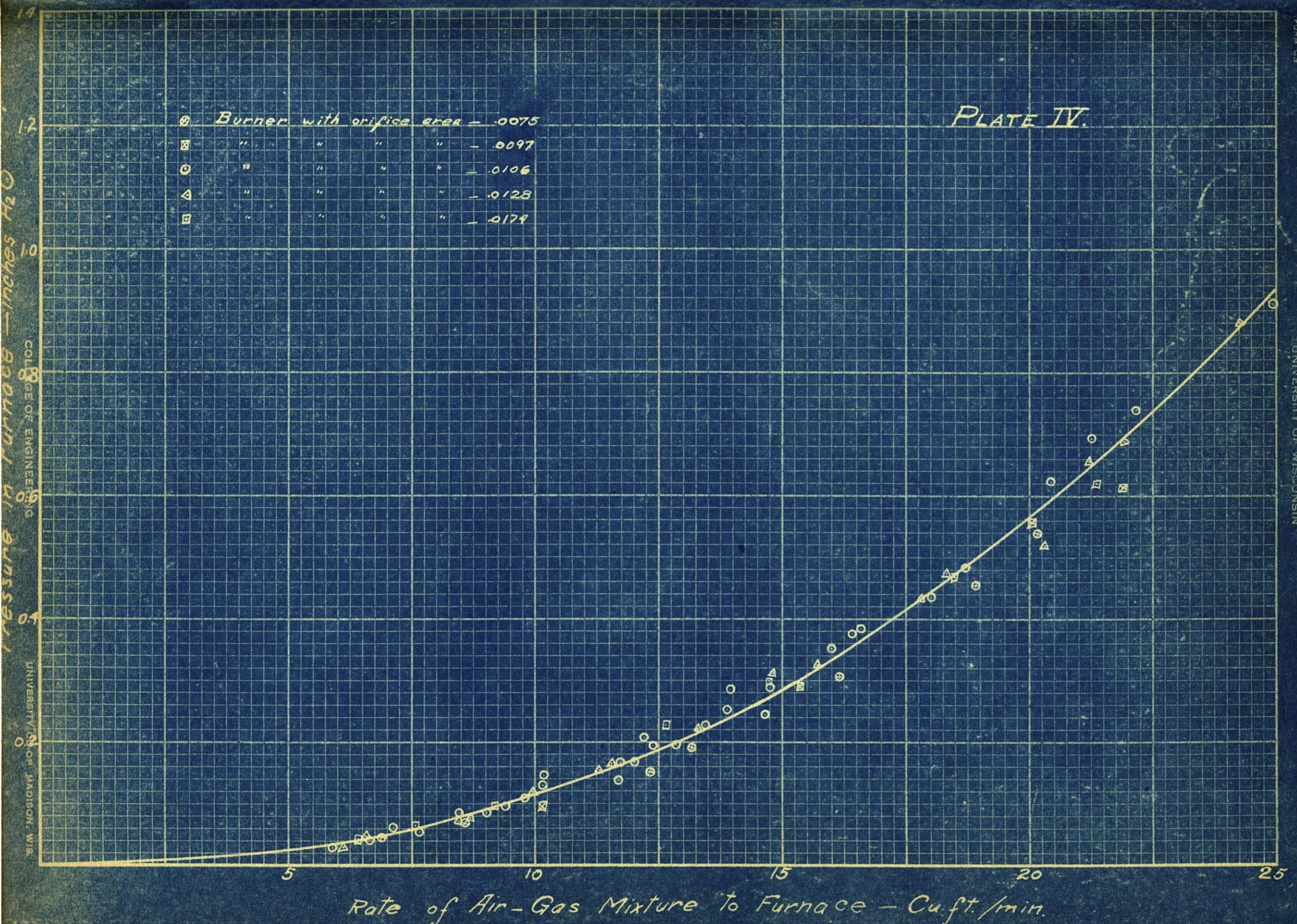

1.4
1.2
1.0
0.8
0.6
0.4
0.2
Pressure in Furnace — Inches H2O
5
10
15
20
25
Rate of Air-Gas Mixture to Furnace — Cu.ft./min.
⊗ Burner with orifice area — .0075
⊠ " " " " — .0097
⊙ " " " " — .0106
△ " " " " — .0128
⊡ " " " " — .0174

PLATE IV.

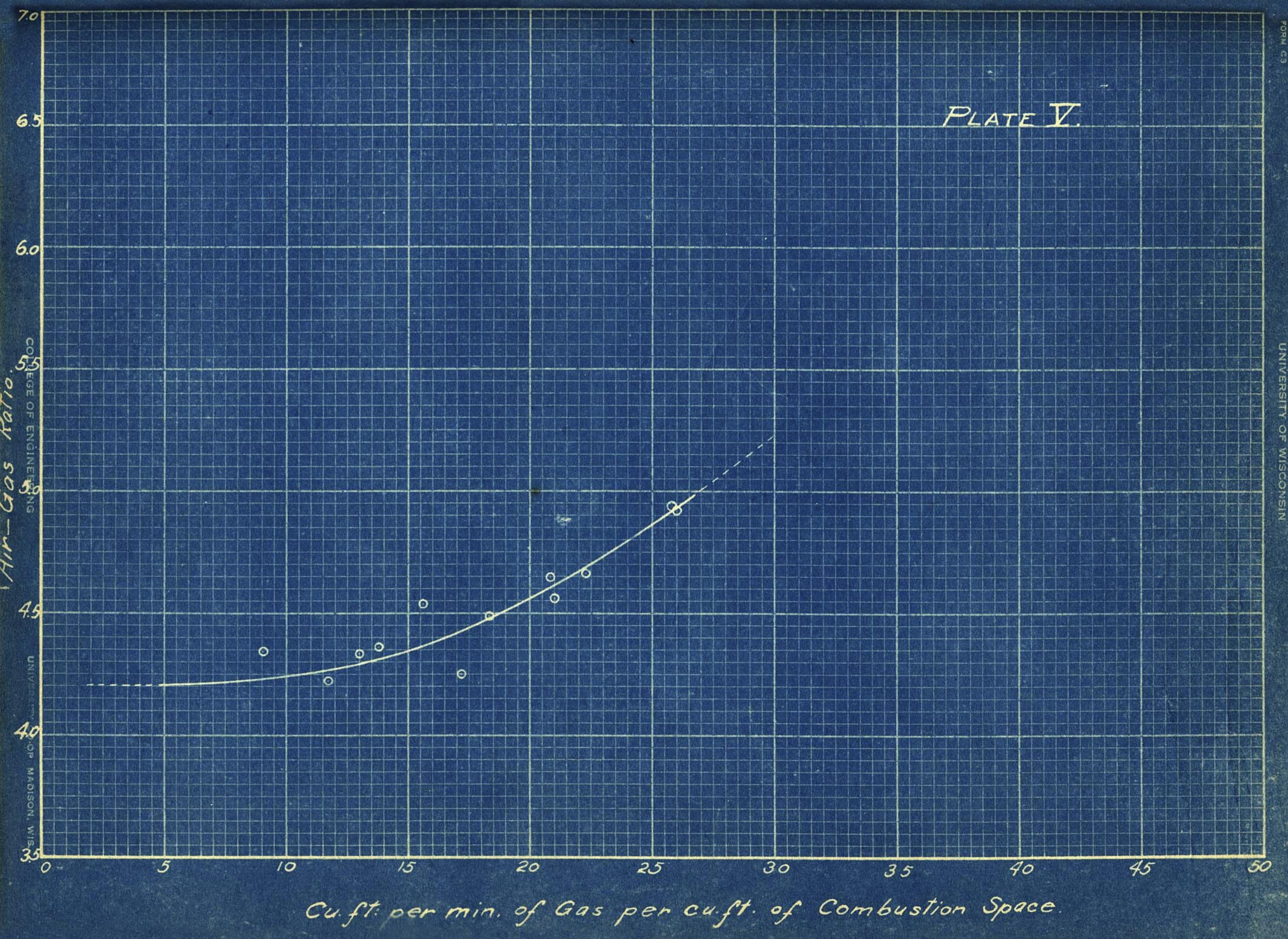


PLATE V.

Air-Gas Ratio.
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
0
5
10
15
20
25
30
35
40
45
50
Cu. ft. per min. of Gas per cu. ft. of Combustion Space.

16

Some Characteristics of Gas Combustion.

By. O. L. Kowalke.

Illinois Utilities Association Meeting, Springfield,
March, 1926.

How a gas flame is propagated and maintained is a question that has received theoretical and experimental study from a host of brilliant scientists. Within recent years particularly, these investigations have been concentrated on the Bunsen flame with special regard to the advancing needs of industry.

Among the early experimenters were Mallard and Le Chatelier (1) who showed from photographic evidence that when an explosive mixture of gases and air is ignited in a horizontal tube closed at one end there is first set up at the point of ignition an initial accelerating propagation of the flame; this is followed by a vibratory movement like sound waves; and then detonation sets in with a rapid, luminous pressure wave which is propagated at a constant velocity. If a stream of gas, not previously mixed with air, issuing from a pipe is ignited, it burns with a luminous flame. In this case the air from the surroundings must diffuse into and mix with the combustible. The form and size of the flame depend on the speed of mixing, the air supply required, and the speed with which the gas escapes from the pipe. If the gas stream is mixed with air beforehand in the pipe and then ignited, the familiar Bunsen flame is obtained. The Bunsen flame is of greatest

(1) Compt. Rend. 91, 825; 93, 145; 95, 566

importance industrially and will be the one treated in this discussion.

It was Bunsen (2) who first pointed out the possibility of getting a smokeless flame by mixing air with gas in a tube and burning the mixture at the outlet. He pointed out that if the air-gas mixture is supplied rapidly enough no striking back of the flame would occur. He was the first to suggest a dynamic method of experimentation regarding the determination of the speed of flame propagation, and he measured the velocity of the gas-air mixture escaping from a small orifice at which the flame struck back.

Gouy (3) suggested that at the surface of the inner cone of a quietly burning Bunsen flame, there is a continuously renewable dynamic equilibrium. The velocity of flame tending inward is identical with the velocity of the gas stream emerging from the top of the burner. Gouy also showed that under the conditions of quiet combustion the velocity of flame propagation normal to the cone surface must be equal and opposite to the component of velocity of the gas stream normal to the surface. It was also assumed that the inner cone was a geometrical cone and that the velocity of flame propagation was uniform over the entire surface. Fig. II illustrates this point.

It was on the basis of these ideas that Ubbelohde (4)

(2) Pogg. Annal. 131, 161
(3) Ann. chim. phys. 18, 27.
(4) Jnl. Gasbel. 56, 1232

and his associates investigated the speed of propagation in Bunsen flames. They showed that

$$u = \frac{V}{3.1416r\,(r^2 + h^2)^{\frac{1}{2}}}$$

where, u = speed of flame

V = volume of gas-air mixture per unit time

r = radius of cone

h = height of cone.

Thus by measuring the heights of the inner cones of Bunsen flames supplied by different gases, with various amounts of air, and at different rates, they were able to determine the speed of flame. The results of their tests on the speed of propagation of flames are given in Fig. 1. The remarkable thing about these results is the high flame velocity of hydrogen in contrast with methane and carbon monoxide. Another interesting point is that the maximum velocity in flame is not obtained with the theoretical mixtures of gases with air for complete combustion. In every case the maximum velocity occurs at a concentration of the gas materially higher than that required for complete combustion.

When each of these gases is mixed with hydrogen the flame velocity is materially increased; in fact, some of their experiments with mixtures of hydrogen and carbon monoxide proved that it was possible to obtain a velocity of ignition that was greater than with hydrogen alone. For example, a gas mixture of 93.4% by volume of hydrogen and 6.6 parts by volume of carbon monoxide gave a flame velocity of 220 centimeters per second as compared with 202

centimeters per second for pure hydrogen on the basis of 45% combustible and 55% air. A 50% hydrogen - 50% carbon monoxide mixture on the basis of 45% combustible and 55% air gave a flame speed of only 137 c.m. per second.

The rate of flame propagation in a carbon monoxide-air mixture may be increased by the addition of water vapor. Various investigators including Wheeler (5) and Ubbelohde (6) showed that by adding approximately 7% by volume of water vapor to all carbon monoxide-air mixtures, the maximum flame velocity can be obtained. Inerts like carbon dioxide and nitrogen operate to reduce the flame speed.

The self propagation of flame through a mixture has been shown by Wheeler and Mason (7) to be possible when the speed of reaction of between the combining gases is sufficient to overcome loss of heat by radiation, convection and conduction under the conditions of combustion. The speed of reaction is dependent on the temperature that the portion which is burning can impart to the adjoining layer about to burn. Hence preheating of the gas mixture increases the speed of ignition, increases the range of explosive mixtures, and also involves a decrease in the air supply necessary for obtaining the maximum speed of ignition. A mixture of gas and air either at the upper or lower limits can be made to ignite more rapidly if preheated than

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(5) Jnl. Gasbel. (1902) 286
(6) " " 57, 759
(7) Jnl. Chem. Soc. 113, 15

if at room temperature. The preheating of the gas-air mixture gives the flame a form such that the products of combustion from the outside pressing toward the inner cone are presented with a much more unattractive angle of approach. With warm feed mixture the flame is taller and thinner than the flame resulting from unpreheated mixture.

Wheeler (8) showed that with an ethane (6%)-air mixture the speed of flame propagation could be increased from around 200 c.m. per second for quiet gas to around 510 c.m. per second for turbulent conditions in the mixture.

It is ordinarily supposed that in a Bunsen burner all the air necessary for combustion should be supplied in the tube with the gas. This condition may possible be realized if in the burner both the air and the gas are admitted under pressure; but in the ordinary atmospheric burner, air from the room surrounding the flame must also supply oxygen necessary for complete combustion. Ubbelohde (9) and Dommer using pure carbon monoxide-air mixtures showed that the composition of the gases taken from various places at or near the appex of the inner cone showed considerable variations from the theoretically possible. For a mixture of 32.0% CO in air, they computed what the products should be and compared the observed results with the calculated.

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(8) Jnl. Chem. Soc. <u>115</u>, 81

(9) Jnl. Gasbel. <u>57</u>, 736

Percents

	CO_2	CO	O	N_2
Calculated				
	32.9	4.5	0.0	62.6
Found				
1 m.m. above apex inner cone	24.5	10.5	3.0	62.0
5 m.m. " " " "	29.0	5.9	2.1	63.1
10 " " " " " "	29.1	3.8	3.0	64.5
20 " " " " " "	27.5	1.0	3.5	68.1
5 " " " " " " and 3 m.m. from axis	29.0	4.1	2.8	64.5

Rembert and Haslam (10) working with city gas determined the relation between the supplied air-gas ratio and the used air-gas ratio. In all cases investigated, the ratio of utilized to supplied air passes through a maximum with respect to supplied air, the actual values depending on the port velocity. The fraction of the supplied air that is utilized for combustion increases with both port velocity and diameter, owing probably to an increased rate of mixing. Ubbelohde and Dommer (9) using burners having diameters from 0.19 c.m. to 2.45 c.m. and carbon monoxide-air mixtures varying from 40%CO to 80% CO found that for burners greater than 2 c.m. diameter the influence of the secondary air has practically ceased.

Chemical Engineering Department,
University of Wisconsin,
March, 1926.

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(10) Jnl. Ind. & Eng. Chem. 17, 1238
(9) Jnl. Gasbel, 57, 739

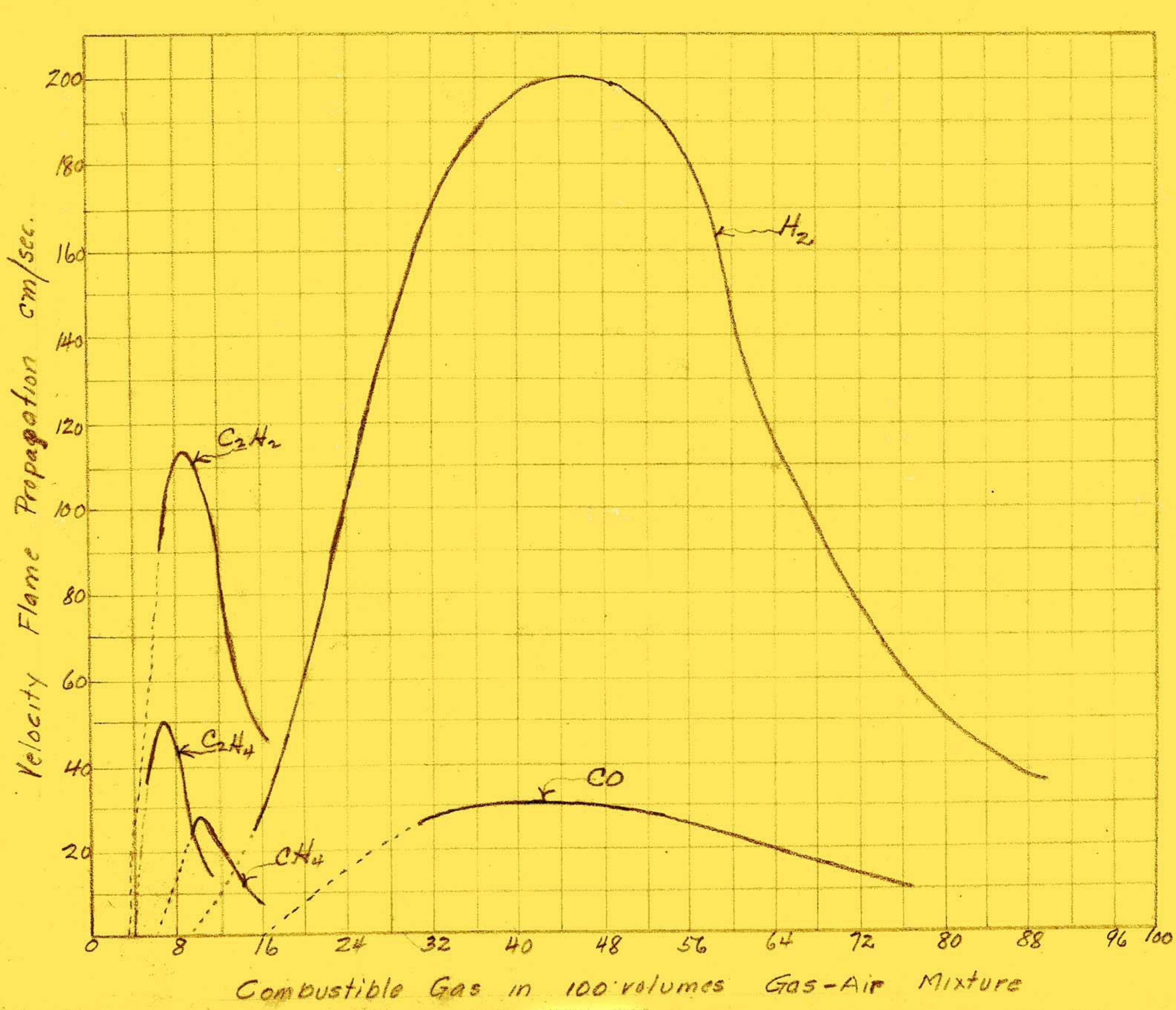

Velocity Flame Propagation cm/sec.
200
180
160
140
120
100
80
60
40
20
0
8
16
24
32
40
48
56
64
72
80
88
96
100
H_2
C_2H_2
C_2H_4
CH_4
CO
Combustible Gas in 100 volumes Gas-Air Mixture

Fig. I.

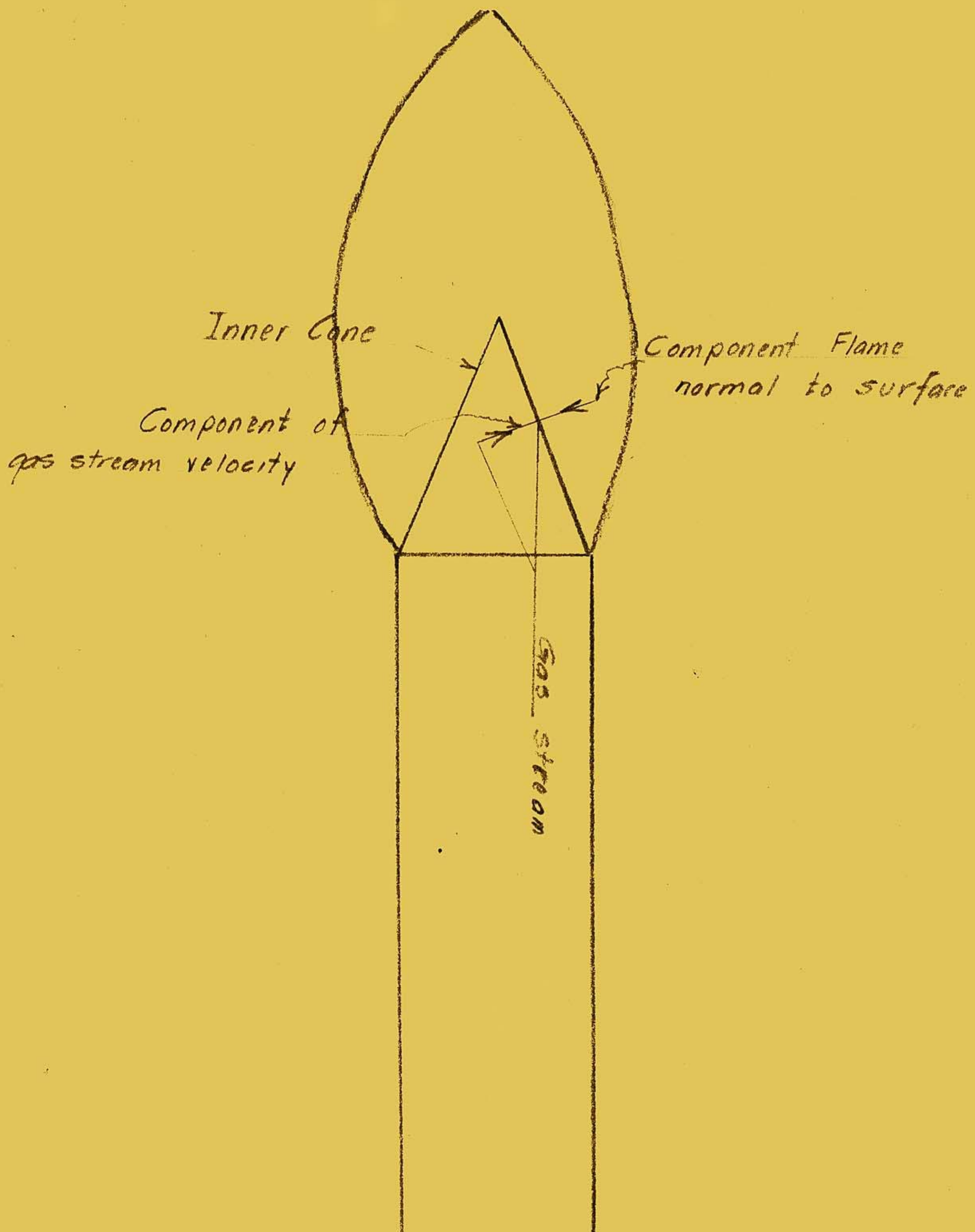

Inner Cone
Component Flame normal to surface
Component of gas stream velocity
gas stream

Fig. II.

17.

PROGRESS REPORT ON THE WORK
OF THE FELLOWSHIP
GAS SECTION, WISCONSIN UTILITIES ASSOCIATION

February 25, 1927

by O. L. Kowalke.

The report read today by Mr. J. M. Spees on the use of limes of various kinds for liberating ammonia from ammonium sulphate solutions constitutes the conclusion of that effort. Mr. Spees as an undergraduate could not qualify for the fellowship under the original agreement, so he worked at his problem in fulfullment of a requirement for graduation. Following his graduation in February, he was appointed to the Fellowship for the second semester, 1926-1927.

During the period from June to October 1926, various written communications passed among Messers. S. B. Sherman, A. A. Schuetz, and the writer relative to the problems to be studied for the current year. At a conference held in Milwaukee in November, it was decided to continue the studies on combustion space required in furnaces, on which a report was made at the 1926 meeting of the Gas Section.

In connection with the studies on combustion space, it was decided to investigate suitable means for aspirating the air required for combustion if the gas were under pressure. Multiple jet aspirators were suggested

by the Eclipse Fuel Engineering Company of Rockford, Illinois, who also offered to give its services gratis for patterns, machine work, etc. At present the first set of jets are being assembled for tests; the orifice meters are made and calibrated; and other accessories are ready. There is no printed information which can be used as a guide and the present designs are made from suggestions obtained from devices used on gas producers.

Last year Mr. Schuetz presented a problem in case hardening with gas to the Chemical Engineering Department and some progress was made toward the solution. It seemed to the Committee that the study on this problem should be continued. Mr. Spees for his work on the fellowship will devote his time to this problem for the current semester under the supervision of Professor R. A. Ragatz. These men hope to find out which of the hydrocarbon constituents in manufactured gas are most active in the case-hardening process. Their methods of attack will be to introduce the various constituents separately into a gas known to be incapable of producing case hardening.

Both of these problems present peculiar difficulties and it is not easy to predict when the conclusion will be forth coming. The action of the Gas Section in May 1926 making the funds for the fellowship available for equipment and services has been of great help to the work on hand."

Madison, Wisconsin.
Chemical Engineering Department,
University of Wisconsin.

18

TEMPERATURE MEASUREMENTS OF HOT FLOWING GAS

K. M. Watson and O. L. Kowalke.

Published in Gas Age-Record, April 21, 1928

The measurement of the temperature of gas flowing in a well insulated pipe or conduit presents no unusual difficulties. However, if the confining walls are at temperatures different from that of the gas, several types of errors may be introduced, due to the interchange of heat between the measuring instrument and the walls. Study of some recently published data on temperature measurements of gas flowing in iron pipes showed errors of considerable magnitude and suggested the desirability of making rather extended experiments which included studies of the factors contributing to such errors when ordinary temperature measuring equipment is used. As a result methods have been devised whereby accurate values may be obtained. The errors in measuring temperature of gases flowing in pipes may be due to radiation, to conduction, and to position of the thermometer or pyrometer.

Radiation Errors

R. T. Haslam and E. L. Chappell(1) measured the temperature of a relatively cool gas flowing through a small pipe, (one inch diameter) the walls of which were at red heat. They proposed expressions whereby the coef-

(1) Ind. and Engr. Chem. 17; 402-0 (1925)

ficient of heat transfer could be calculated from data on the velocity and the temperature of the gas and the dimensions of that part of the instrument in contact with the gas. By means of the formulae proposed and data on emissivities, it was possible to calculate the correct gas temperature from observations with ordinary equipment

Conductance Errors

In case the above formula, which assumes interchange of heat only by radiation and by transfer due to contact of gas with the thermometer, is applied to ordinary technical methods of temperature measurement, a third manner of heat transfer must be considered. Ordinarily the instrument is metallic and is inserted through the confining wall, in good thermal contact with it. There must thus exist a temperature gradient along the instrument and a corresponding flow of heat, governed by the thermal conductance. In many cases the conductance loss may be far more important than that due to transfer by radiation.

To include consideration of heat transfer due to the conductance of the instrument in the equilibrium equation of Haslam and Chappell would lead to expressions too complicated for practical work.

Variations in Temperature Traverse:

Another difficulty is encountered when the mean temperature of a gas stream is to be determined. In the film concept of flowing fluids it is postulated that at the boundary between a flowing fluid and a confining wall

there exists a thin, stationary film of the fluid whose thermal conductivity may be very low. It is therefore customary to assume that the entire temperature drop takes place through the thin, stationary film at the boundary. This condition is approached where the velocity is well above the critical value, and where the turbulent flow makes possible a high effective conductivity of the main portion of the stream. Although there will always be a temperature gradient across all parts of the stream, that gradient across the central, turbulent portion will represent only a small part of the total difference in temperature between gas and walls.

In the case of a gas flowing in a circular pipe this relatively small temperature gradient is greatly magnified in its effect on the mean temperature of the gas, because the cross sectional area of rings near the walls represents a large portion of the total. The decrease in the linear velocity near the walls, on the other hand, tends to counteract the effect of the increased cross-sectional area, but, under many conditions encountered in practice, the disregard of the entire effect may result in large errors.

The measurement of temperature of a gas stream thus resolves itself into two parts. Special precautions must be observed to determine the true gas temperature correctly at any one point in the cross section of the stream. In addition, if the mean temperature is desired, account must be taken of the variations in the temperature from point to point in the cross-section of the stream.

To obtain a general, qualitative idea as to the most desirable characteristics in protecting tubes, a set of conditions was arbitrarily adopted approximating some which might be met in practice. The errors produced by varying the diameter, the emissivity, and the longitudinal conductance of the well, each independent of the others, were observed. Even though the relative order of magnitude of the effects of the different variables might be reversed under other conditions, interesting information as to the importance of recommended precautions in the design of wells for thermometers was obtained.

Experimental Apparatus:

The apparatus used in all of the experimental work is diagrammatically shown in Figure 1. A stream of air was supplied by a Sturtevant blower driven by a 1 H.P. motor. Regulation of the volume delivered was obtained by an adjustable sleeve covering openings in the discharge pipe of the blower and by inserting a wedge shaped damper into the stream.

For heating the gas stream electric energy was dissipated in grids made of "chromel" ribbon, constructed in two sections to permit switching in either series or parallel; the flow of current was regulated by a reactance coil in series with each section. The entire heating unit was encased in a sheet metal box which was thermally insulated by means of fire-brick. From the heater the gas passed around a right-angle bend and into a 36" x 36", carefully insulated, expansion chamber provided with two perforated plates, set at right angles to the direction

of gas flow. The purpose of this expansion chamber was two-fold; (1) it eliminated the possibility of radiant heat from the heating chamber reaching the cooled test section of pipe, and (2) it smoothed out the velocity disturbances caused by the bend in the pipe line, giving a test section in which velocity conditions approximated those of a long, straight pipe.

A second expansion chamber for gas was placed at the outlet end of the test section and was identical in construction and insulation to the first. From the second expansion chamber the air stream was discharged into the room.

The test section proper consisted of a thin, sheet iron pipe, 6 inches in diameter and 6.71 feet long, surrounded by a 1-inch water-jacket divided into two parts, the first one being 4.62 feet long. The water-jacket of each section was connected to a mixing chamber into which hot and cold water could be admitted in regulated proportions. In this way, by using a high rate of water flow, it was possible to hold the inner walls of the test section at a desired temperature, almost constant throughout its length.

Four openings through water-jacket and pipe were provided near the junction between the two sections and through these all instruments to be tested were inserted. To determine the velocity of the gas stream, a Pitot tube, calibrated by direct comparison to a Thomas meter, could be inserted through one of these openings and moved about to traverse the cross-section. To measure the temperature

of the inside walls of the test portion, copper-constantan thermocouples were carefully soldered to the walls at three points along the length of the section. Each element was individually joined to the wall by flattening the end to a very thin sheet and pressing it against a thin coat of molten solder on the galvanized pipe surface, thus making a portion of the pipe wall form a part of each thermoelectric circuit.

As a basis for comparison, the true, mean temperature of the gas stream at the test cross-section was also desired. To eliminate both radiation and traverse errors a nickel resistance thermometer in the form of a grid of fine wires across a 3½ inch annular ring of "Transite" asbestos was inserted in a carefully insulated section of the 5-inch pipe line leading into the first expansion chamber. Due to the high velocity and mixing of the air stream in passing through the orifice of the ring, combined with the temperature equalizing action of the wire grid, such an instrument should indicate a close approximation to mean temperatures. A similar resistance thermometer was placed at the outlet from the second expansion chamber. The resistance thermometers, along with the other thermometric apparatus used in the investigation, were calibrated in an oil bath against a standard, platinum, resistance thermometer.

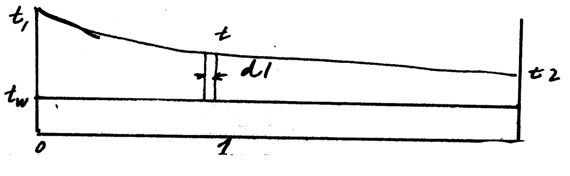
By means of the resistance thermometers it was thus possible to determine the true, mean temperature at the entrance to the first expansion chamber and at the outlet from the second. The assumption was made that the

heat losses from the carefully insulated expansion chambers were negligible in producing a temperature drop in the air stream. On this basis the resistance thermometer readings represented the mean air temperatures at respectively the inlet and the outlet of the water-jacketed test section. This assumption was verified by carefully regulating the water-jacket so that the walls of the test section were at the same temperature as the gas stream. It was found that, at the high air velocities used, the heat losses were so small that they might be neglected without introducing errors beyond the desired limits of accuracy.

If the inside walls in contact with the gas of the test section were kept at a uniform, known temperature by the rapid circulation of the jacket water, it was possible from the resistance thermometer readings, to calculate the mean air temperature at any cross-section in the test pipe, as follows:

Let t_1 = temperature of gas entering test section
t_2 = temperature of gas leaving test section
t = average temperature of gas at any point in test section
H = Heat transfer coefficient between gas and pipe/unit time/unit length/unit temp. diff.
t_w = Wall temperature
l = Dist. from inlet of test section
w = Weight of air/unit time flowing through pipe
c = Specific heat of air.

Consider a small element with width dl and height $t - t_w$, lying between the two curves representing respectively the variation of gas and wall temperatures along the length of the pipe.



The heat interchanged in this elemental length of section may be expressed by the equation:

$$dQ = Hdl\,(t - t_w) = cw(dt)$$

or

$$dl = \frac{cw}{H}\,\frac{dt}{(t-t_w)} = K\,\frac{dt}{(t-t_w)}$$ if the term cw/H

is assumed to be constant with length.

Integrating this expression between the limits $l = 0$ where $t = t_1$ and $l = l$ where $t = t$:

$$l = K\left[\ln(t-t_w) - \ln(t_1-l_w)\right] = K'\left[\log(t-t_w) - \log(t_1-t_w)\right]$$

When $l = 6.71$, $t = t_2$, from which K' may be evaluated.

$$K' = \frac{6.71}{\log(t_2-t_w) - \log(t_1-t_w)}$$

The complete expression relating the gas temperature at any cross-section in the pipe to the distance from the inlet and then becomes,

$$l = \frac{6.71\left[\log(t-t_w) - \log(t_1-t_w)\right]}{\log(t_2-t_w) - \log(t_1-t_w)}$$

In order to measure the true temperature of the gas at any point in the cross-section of the stream, the thermocouple devised by R. T. Haslam and E. L. Chappell (1) was used. A copper constantan thermocouple was inserted in a small-bore, glass tube in the form of a Y having one branch much longer than the other two. The couple was so placed that its junction was about ¼" from the end of the long branch, which was open. The thermocouple leads were passed through a seal in one of the short branches of the Y, while to the second short branch was connected a tube leading to the intake of a small, impeller-type, laboratory blower. The blower served to draw a stream of gas at a very high velocity past the junction of the couple.

Effects of Protection Tube Construction:

The effect of the longitudinal, thermal conductance of the thermometer protecting tube on the indicated temperature was studied by preparing a set of tubes of varying conductances each being of one-half inch outside diameter and 5 inches long. The thermal conductances were varied by varying the wall thicknesses and materials of construction. The emissivities were kept constant by coating the outside of each tube with a special, flat, black paint having an emissivity assumed to be approximately unity. In all, six tubes were constructed using iron, brass, and wood, having conductances ranging from 0.000478 to 0.322 B.t.u. per hour per degree Fahrenheit difference in temperature between the ends of the tube. The con-

(1) Ind. and Engr. Chem. 17; 402-9 (1925)

ductances were calculated from conductivity data in engineering handbooks.

For supporting the tubes in the test section of pipe, a brass sleeve was fitted into one of the openings through the water jacket into which the tubes were pressed, placing them in good thermal contact with the pipe walls. The end of the tube was adjusted to the center of the pipe. A drop of mercury was placed in the bottom of each tube and its temperature measured by a separate, copper-constantan thermocouple, making contact through the mercury.

The following conditions were arbitrarily adopted for all of the tests relating to the construction of protection tubes:

Pipe Diameter = 6"

Gas Velocity (center of Pipe) = 29 ft. per sec.

Temperature of Pipe Walls = 30°C

Temperature of Gas (center of pipe) = 100° at test cross-section.

Temperature of gas (Mean) = 90°C at test section.

Maintaining these conditions and taking care to allow sufficient time for equilibrium to be established, duplicate determinations were made of the temperatures at the bottoms of the various tubes. The results are shown graphically in Figure 2, in which tube conductance is plotted against indicated temperature.

In order to test the effect of the diameter of the protecting tube, a second set of experimental tubes was made, painted black as before and mounted and used as in the preceding tests. In this case the tubes were de-

signed with different wall thicknesses and materials, so that all had the same conductance but varied in outside diameter from 3/8 inches to 5/8 inches. The results are shown graphically in Figure 3.

The effect of the emissivity of the protection tube was determined by making up a set of tubes of the same sizes and conductances but finished to produce surfaces having emissivities varying from 0.05 to practically 1.0, and tested as in the preceding. The surfaces were metallic finished, and their emissivities were taken from the Smithsonian tables. In Fig. 4 are shown the results of the measurements together with the type of surface used for the production of the various emissivities.

From a study of the curves of Figures 2, 3, and 4, it may be seen that, under the conditions of the test, both the emissivity and the conductance of the well have marked influence on the indicated temperature. However, over the range investigated, the effect produced by varying the diameter of the tube was less than the experimental error encountered in making the measurements and constructing tubes of constant conductance. The relative magnitudes of the errors introduced due to radiation and conductance for any particular tube construction may be roughly estimated from these curves. Considering Fig. 2, it will be seen that the temperature error introduced due only to the conductance of any well is approximately represented by the difference between the temperature corresponding to zero conductance and that corresponding to the

actual conductance of the well in question. Thus under the conditions of the test, the error which would be introduced by each effect might be roughly estimated for a well of any particular emissivity or conductance within the range investigated. It must be emphasized that the magnitude of the errors thus determined would apply only to the conditions of temperature, velocity and pipe size for which the data were obtained. However, an idea as to the relative magnitude of the two contributing effects may be obtained which will apply over more general conditions.

Were the pipe size larger, the conductance of the well would be of less importance. On the other hand, at higher temperatures or greater temperature differences, the effect of radiation errors would become relatively greater. It becomes obvious that under conditions approximating those of these tests, it is important to consider both conductance and emissivity of the protecting tube as well as its size, which may assume secondary importance.

Comparison of Central and Mean Temperatures:

Thus far, consideration has been given only to the problem of determining the true temperature of the gas at the center of the stream or at some definite point in the cross-section. Even though some accurate device such as the "high velocity thermocouple" is used for such measurements, an additional problem is met where it is desired to obtain the true mean temperature of the stream.

Reference to Figure 2 shows that the true mean temperature of the gas stream is 90°C and the true gas temperature at the center of the pipe is 100°C, a difference of 10°C or about 15% of the total difference in temperature between the gas and the walls.

To make a further, qualitative study of the nature of temperature traverses, a wire-wound laboratory furnace with a 2" by 24" cylindrical core was connected to a compressed air line. At mid-length of the furnace a small hole was drilled through the wall of the core through which a small, "high-velocity type", chromel-alumel thermocouple in a quartz tube might be inserted. Air at room temperature was blown through the furnace at a velocity measured by a Pitot tube set in the center of the outlet end of the tube. The walls of the furnace were heated to a temperature of about 700°C as estimated with an optical pyrometer. Under these conditions temperature traverses of the stream were made at four different velocities of flow, ranging from 4 ft. to 50 feet per second at the center of the pipe. The results are plotted in Fig. #5. It will be noted that at the lower velocities the variations are very large. There is also marked evidence of convection in the displacement of the point of minimum temperature to a position below the center of the pipe. The critical velocity under such conditions is about 2 ft. per second. At the higher velocities the temperature variations become much smaller and the convection effect disappears. It is evident that at even the highest

velocity there is a very definite difference between mean and central temperatures.

The mean temperatures of a gas stream in a circular pipe may be readily calculated if both the linear velocity and the temperature are known at every point in the cross-section. With this information the cross-sectional area of the pipe may be divided into a number of elements in the form of annular rings and a calculation made of the heat content of the gas passing through each element per unit time. The total heat content of the stream per unit time, above the reference temperature, is then obtained by the summation of that passing through each of the elements. The total volume of gas per unit time may be calculated in a similar way. The mean temperature of the stream, above the reference value, is then obtained by dividing the total heat content of the stream by the product of the total volume of gas, and neglecting its variations with temperature. For ordinary work this assumption is sufficiently accurate where large temperature differences are not encountered. The specific heat of the gas then drops out of the calculations entirely and the mean temperature is represented by the summation of the products of the temperature and volume of gas passing through each element per unit time, divided by the total gas volume per unit time. The major source of error in such calculations lies in the uncertainty in the determination of both the temperature and the velocity of the gas at the walls where the cross-sectional

area is the greatest and accuracy most important.

This traverse method of determining mean temperatures was tested experimentally in the apparatus used for the tests, previously described. Thus, the calculated mean temperature might be compared to the value obtained from the two grid resistance thermometers. In the first runs the gas stream was maintained at a mean temperature of approximately 90°C with wall temperature of about 30°C. After the apparatus had reached equilibrium, temperature traverses of the stream were taken by means of the "high velocity" thermocouple. Velocity traverses were then determined at the same cross-section by means of a calibrated Pitot tube. The results of two of these runs are shown graphically in Figure 6. The mean temperatures were calculated by dividing the cross-section of the pipe into annular rings one half inch in width. The product of the temperature, linear velocity, and area of each of these rings was then calculated and all added together. This sum was then divided by the sum of the products of the linear velocities and areas of the rings. It will be seen that the mean temperature of the gas as indicated by the grid resistance thermometers was in each case 90.0°C. The value calculated from the traverses was in one case 90.3°C and in the other 90.4°C. Other comparisons made at somewhat different conditions of velocities and temperatures resulted in similar correspondence between calculated and observed values of mean temperatures. This indicates an agreement between the two methods which is within the limits of errors which would be expected

from either. As a result of this evidence of accuracy under rather extreme conditions, it would seem that such a traverse method might be considered as reliable for all ordinary requirements. In industrial work satisfactory results might be obtained by permanently installing Pitot tubes and thermocouples at a limited number, for example three, points in the cross section of the stream. Curves might be plotted from such data by which fair values of mean temperature could be determined.

Integrating Thermometers:

In many cases it is not feasible or convenient to determine traverses in the flowing stream; in any case the necessary calculations are laborious. It is therefore desirable that some method of measuring directly and easily the mean temperatures be available. Such an instrument must be of an integrating type and the wire grid resistance thermometer seemed to offer the greatest possibilities. By using wire of small diameter, errors due to radiation may be minimized, while the relatively good thermal conductivity of the wire tends to equalize its temperature to a value approximating the mean. By mounting the grid in a ring thermally insulated from the pipe walls, conductance errors become negligible. Still greater accuracy may be obtained by mounting the grid in a sharp constriction or orifice. In such a case the velocity of the gas past the wires is greatly increased, thus increasing the coefficient of heat transfer and rendering radiation transfer less important. The integrating action is also greatly improved by the violent turbulence and

mixing of the gas in passing through the orifice.

A resistance thermometer grid was constructed upon an annular ring of ¼" Transite board with an inside diameter of 3½" and an outside diameter of 6". The resistance element was of #22 B. & S. gauge nickel wire, strung across the supporting ring at ¼" intervals. The resistance was measured by means of a portable potentiometer and a standard resistance. The thermometer and standard resistance were connected in series with a rheostat and a dry cell so that a current in the neighborhood of 0.01 amperes would flow through them. The potential drop was then alternately measured across the standard resistance and the thermometer. The thermometer was calibrated, with the electrical apparatus, in an oil bath against a standard resistance thermometer.

This resistance thermometer was mounted in the water-jacketed test portion of pipe of the apparatus shown in Figure #1. With the walls of the section regulated to about 30°C, gas at a mean temperature of about 90°C was passed through the apparatus. The reading of the resistance thermometer was noted and both a temperature and velocity traverse determined at a cross-section one half inch down-stream from the thermometer. The traverse data for two of the runs, at different gas velocities, are plotted in Figure #7. The mean temperature of the gas stream was then graphically calculated as described above. It will be noted that in each case the resistance thermometer indicated a temperature of 88°C

while in one case the calculation gave a result of 89.4 and in the other of 89°.0. This agreement is as good as could be expected in consideration of the difficulty of determining traverse data in a jet of gas issuing from an orifice. The resistance thermometer, mounted in an insulating orifice would thus seem to be a direct method for determining mean temperatures, with accuracy sufficient for ordinary industrial purposes. A still better average temperature measurement might be obtained by winding the resistance thermometer in the form of a spiral, thus distributing the length of the wire in proportion to the volume of gas passing it.

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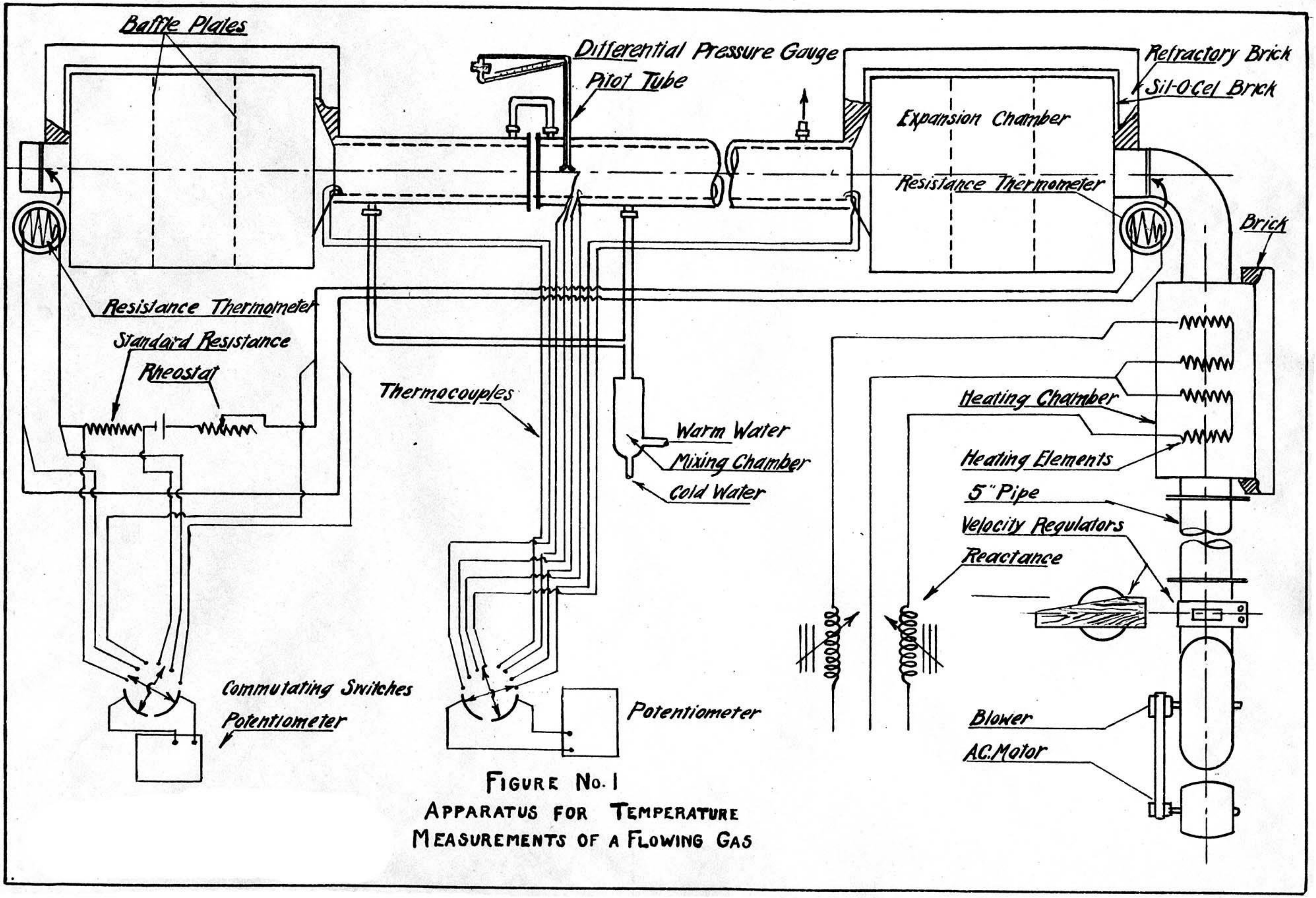


FIGURE No. 1
APPARATUS FOR TEMPERATURE
MEASUREMENTS OF A FLOWING GAS

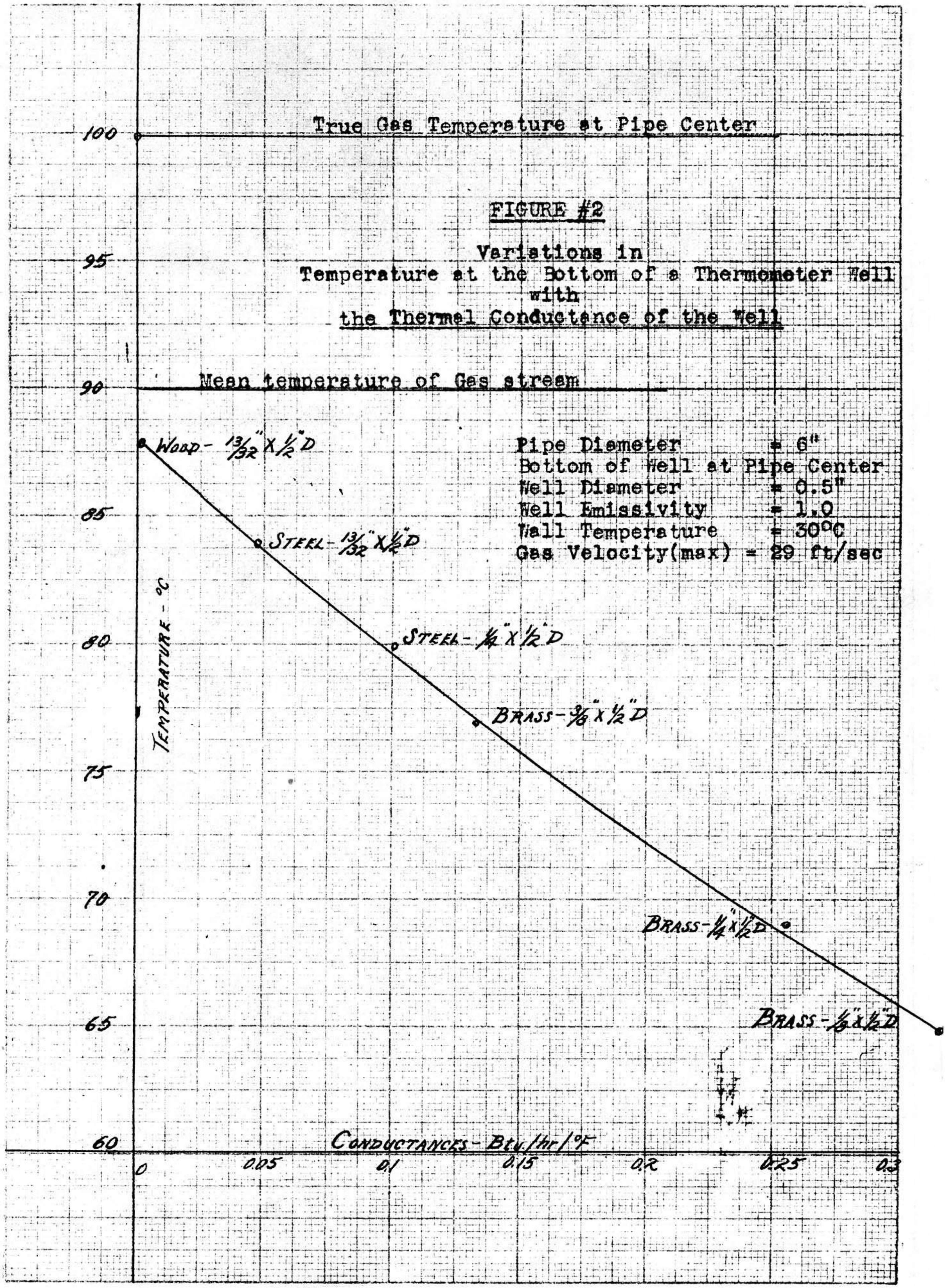


FIGURE #2

Variations in
Temperature at the Bottom of a Thermometer Well
with
the Thermal Conductance of the Well

Pipe Diameter = 6"
Bottom of Well at Pipe Center
Well Diameter = 0.5"
Well Emissivity = 1.0
Wall Temperature = 30°C
Gas Velocity(max) = 29 ft/sec

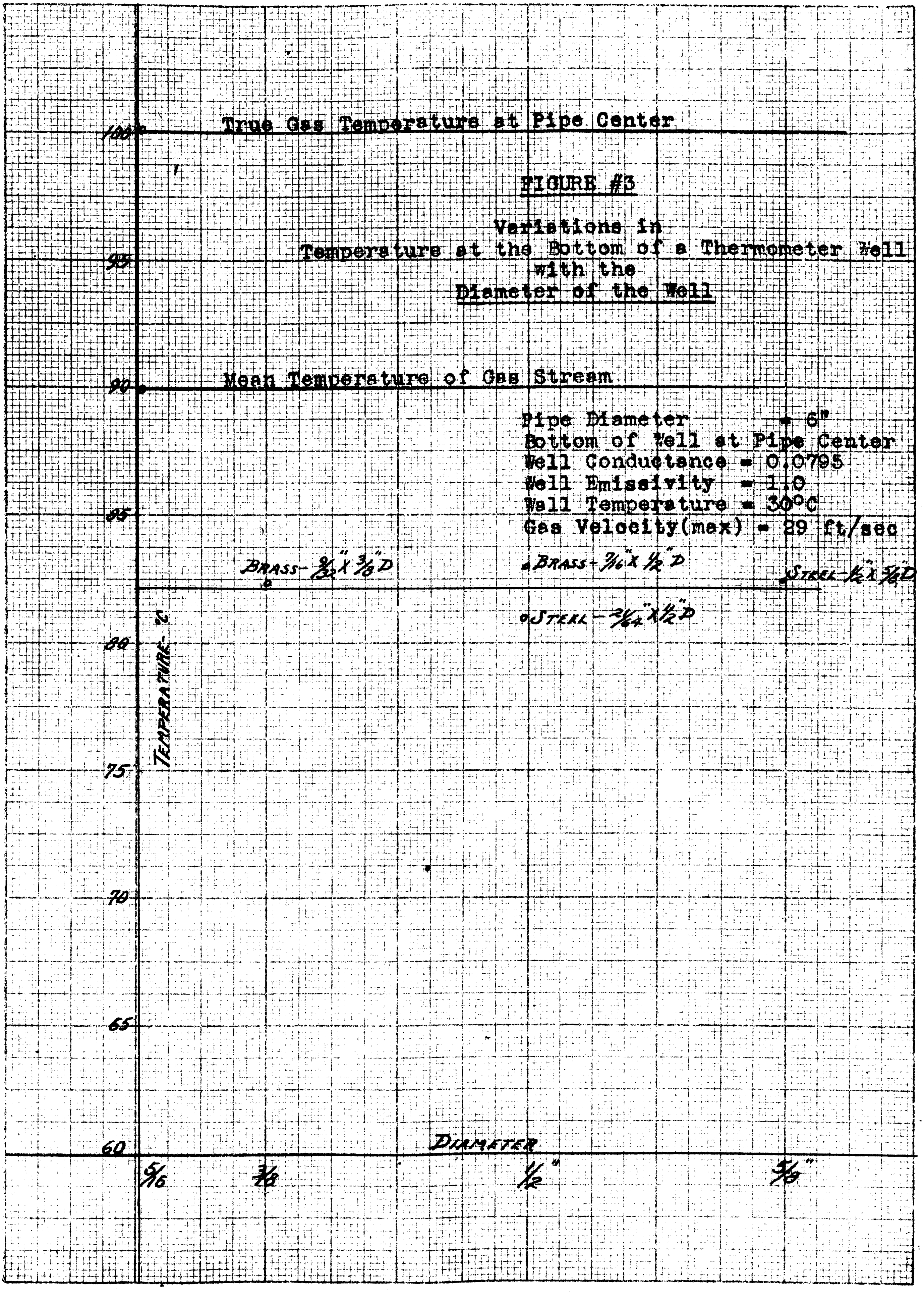


FIGURE #3

Variations in
Temperature at the Bottom of a Thermometer Well
with the
Diameter of the Well

Pipe Diameter = 6"
Bottom of Well at Pipe Center
Well Conductance = 0.0795
Well Emissivity = 1.0
Wall Temperature = 30°C
Gas Velocity(max) = 29 ft/sec

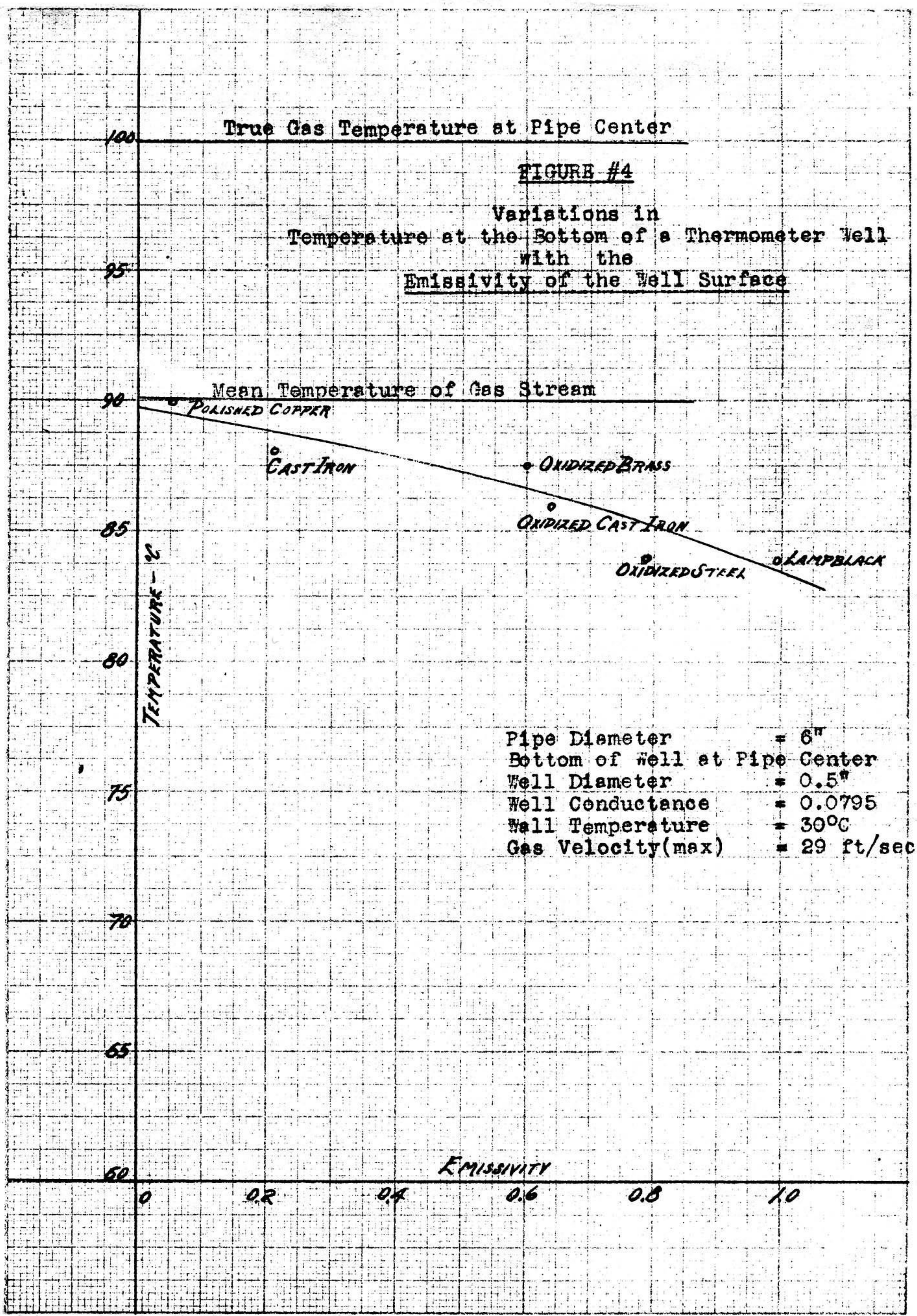


FIGURE #4

Variations in Temperature at the Bottom of a Thermometer Well with the Emissivity of the Well Surface

Pipe Diameter = 6"
Bottom of Well at Pipe Center
Well Diameter = 0.5"
Well Conductance = 0.0795
Wall Temperature = 30°C
Gas Velocity(max) = 29 ft/sec

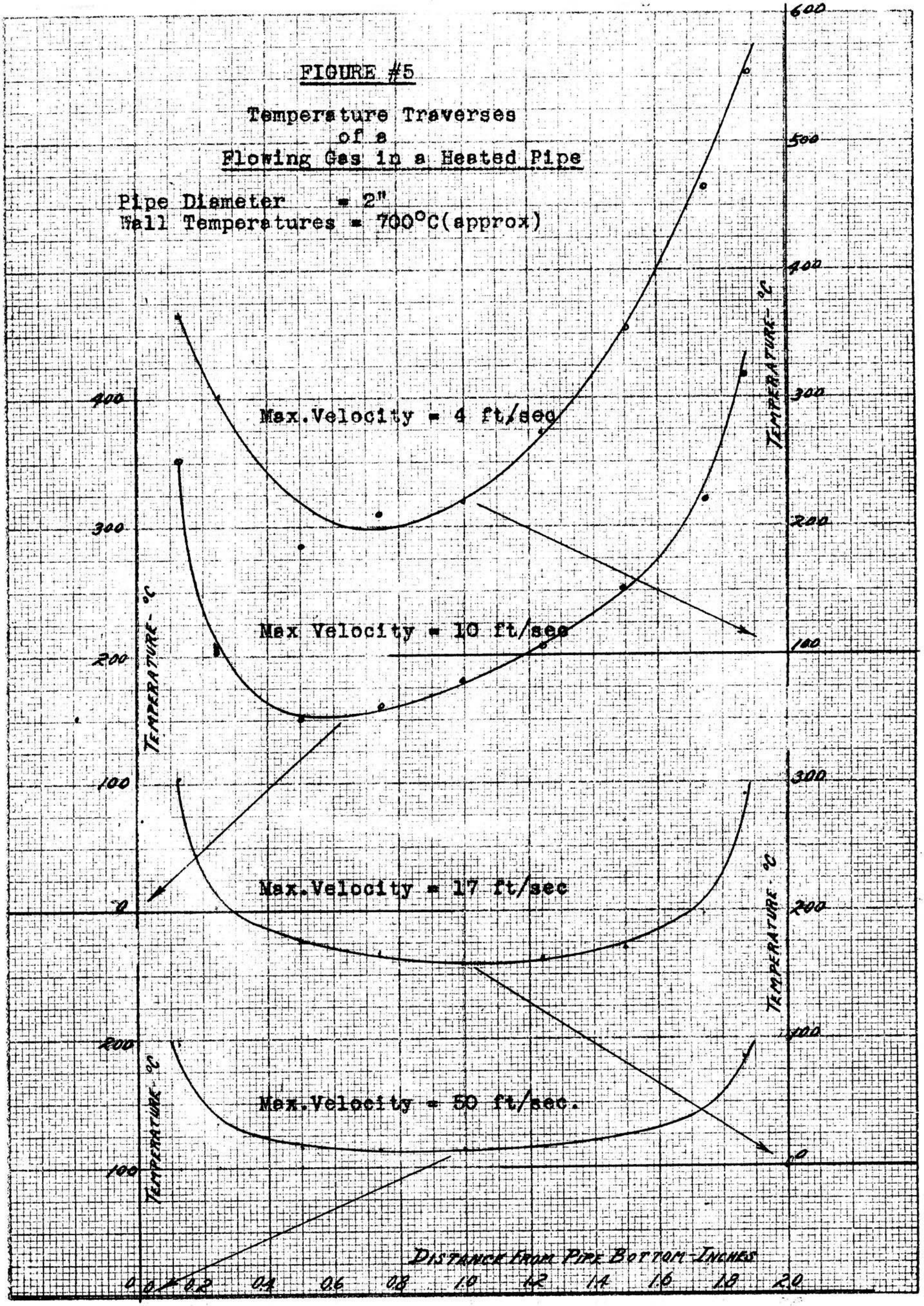


FIGURE #5

Temperature Traverses
of a
Flowing Gas in a Heated Pipe

Pipe Diameter = 2"
Wall Temperatures = 700°C(approx)

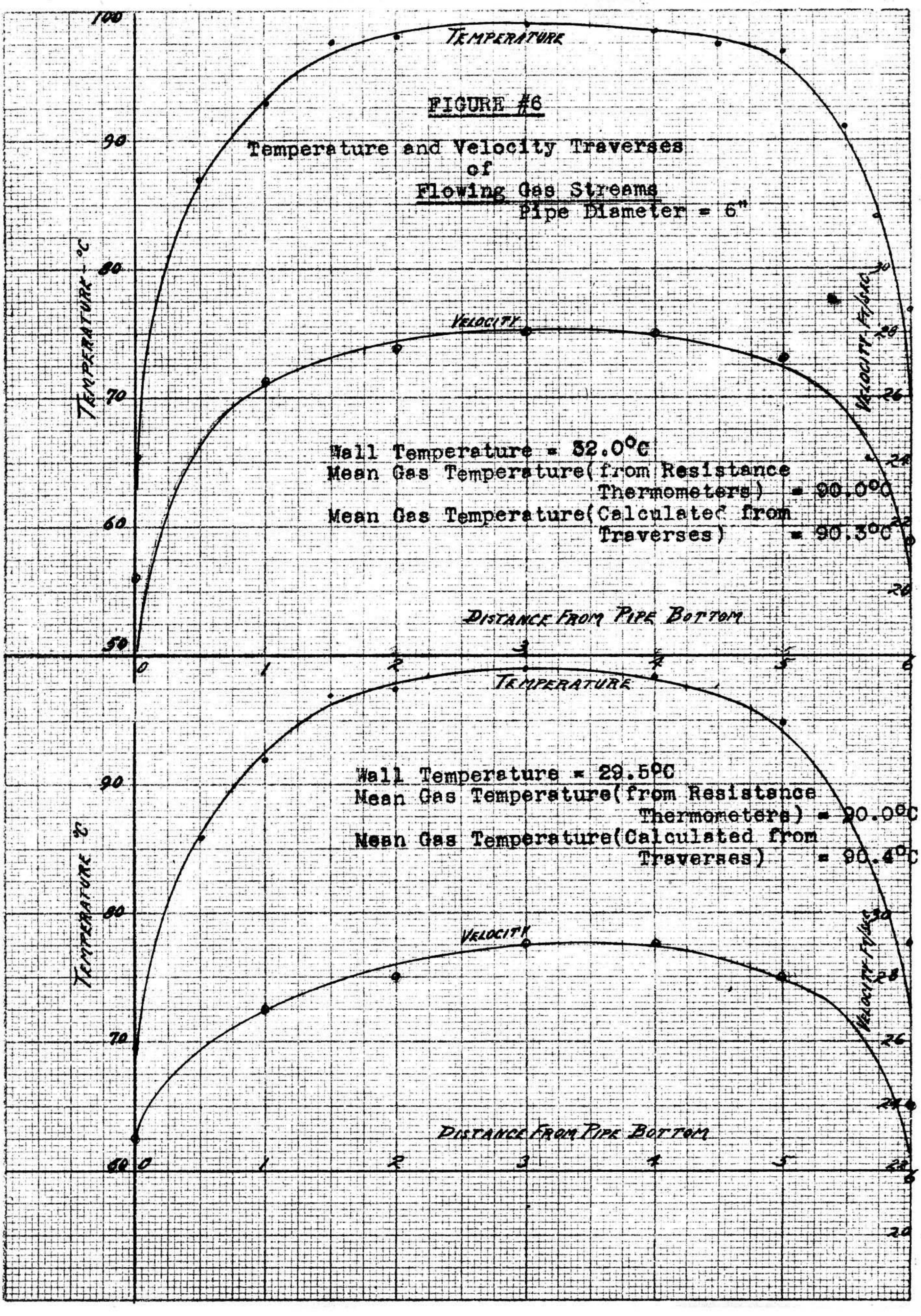
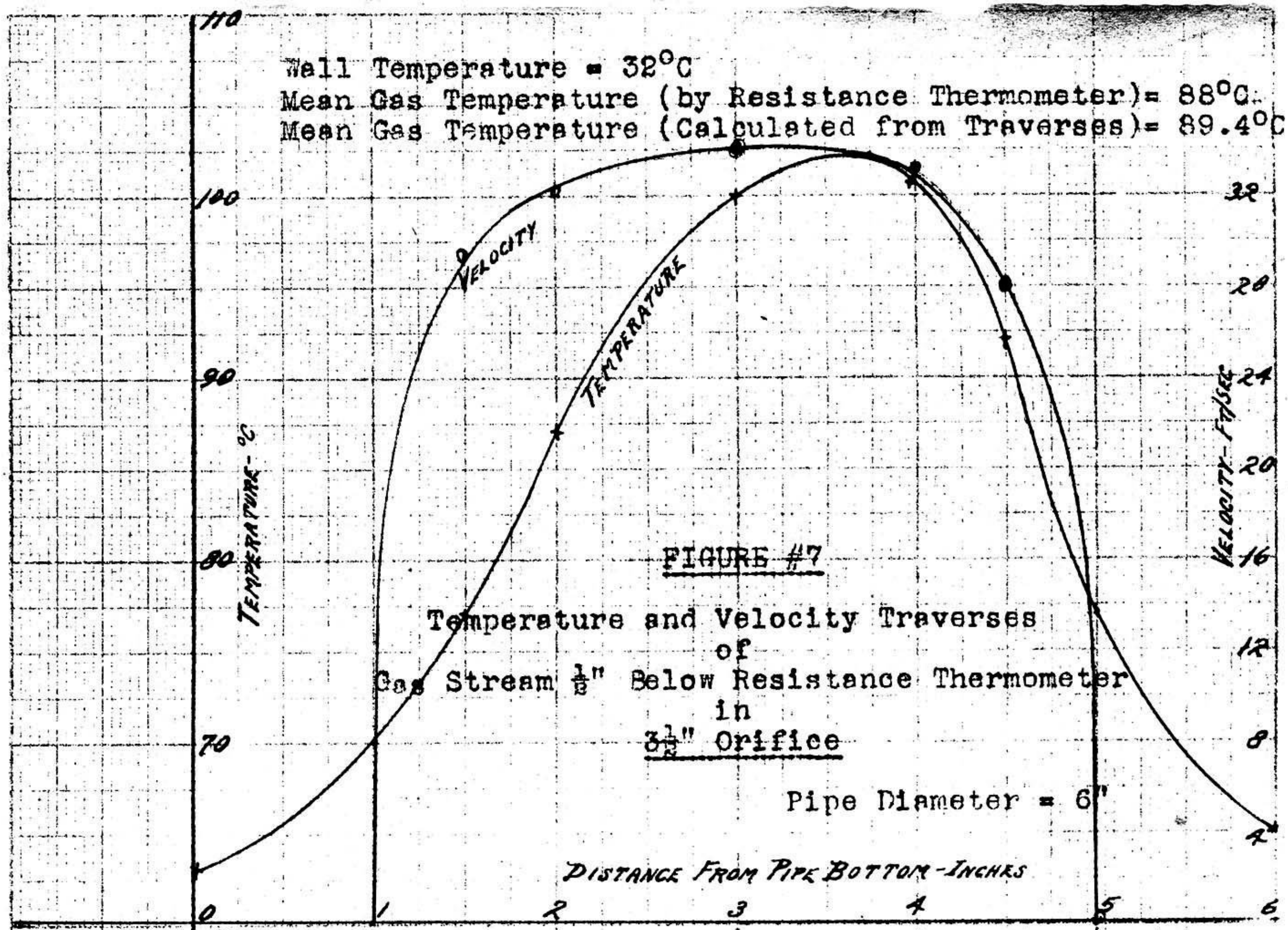


FIGURE #6

Temperature and Velocity Traverses
of
Flowing Gas Streams
Pipe Diameter = 6"

Wall Temperature = 32.0°C
Mean Gas Temperature(from Resistance Thermometers) = 90.0°C
Mean Gas Temperature(Calculated from Traverses) = 90.3°C

Wall Temperature = 29.5°C
Mean Gas Temperature(from Resistance Thermometers) = 90.0°C
Mean Gas Temperature(Calculated from Traverses) = 90.4°C

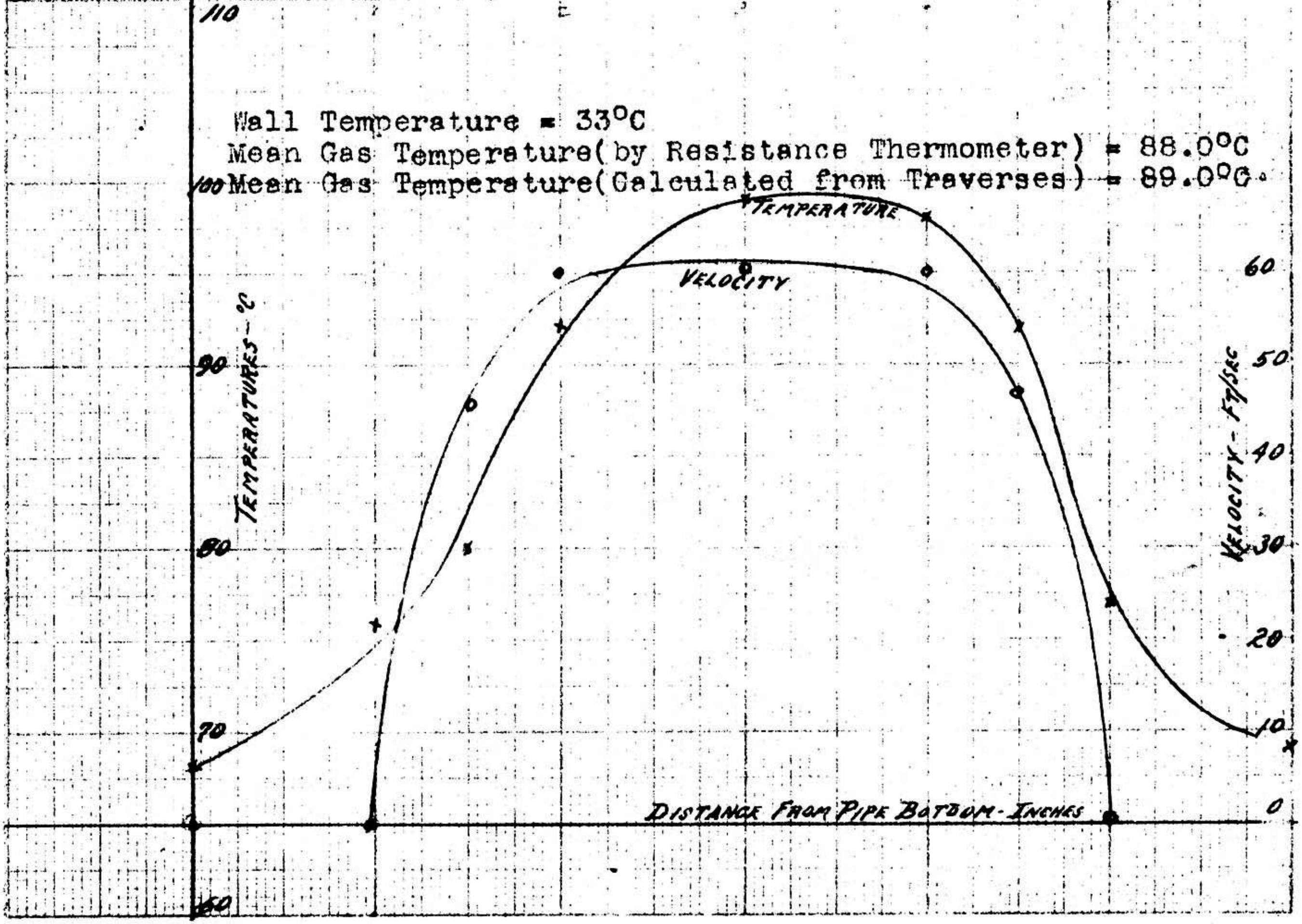


Wall Temperature = 32°C
Mean Gas Temperature (by Resistance Thermometer) = 88°C.
Mean Gas Temperature (Calculated from Traverses) = 89.4°C

FIGURE #7

Temperature and Velocity Traverses
of
Gas Stream ½" Below Resistance Thermometer
in
3½" Orifice

Pipe Diameter = 6"



Wall Temperature = 33°C
Mean Gas Temperature (by Resistance Thermometer) = 88.0°C
Mean Gas Temperature (Calculated from Traverses) = 89.0°C.