REDUCTION OF ZINC OXIDE WITH NATURAL GAS

USING A FLUIDIZATION TECHNIQUE

By

Robert Eugene Lacey

Bachelor of Science

Oklahoma Agricultural and Mechanical College

Stillwater, Oklahoma

1947

Submitted to the School of Chemical Engineering

Oklahoma Agricultural and Mechanical College

In Partial Fulfillment of the Requirements

for the Degree of

MASTER OF SCIENCE

1950

APPROVED BY:

Chairman, Thesis Committee

Member of the Thesis Committee

Head of the Department

Dean of the Graduate School

PREFACE

Because of the decreasing supply of high grade ores, a new technique of refining zinc is needed which can handle large throughputs of lower grade ore efficiently.

This investigation is a preliminary study of the feasibility of using the relatively new technique of fluidization of solids to fill the above need.

ACKNOWLEDGEMENT

The author wishes to take this opportunity to thank all of the members of the Chemical Engineering Staff at Oklahoma A. & M. College for their valuable advice and friendly encouragement.

Thanks are due especially to Mr. Leonard Sheerar, who supervised this work.

TABLE OF CONTENTS

INTRODUCTION

Before an investigation of the use of fluidization for the reduction of zinc oxide, a brief resume of the present status of the zinc industry is in order.

Zinc metal is marketed in the grades shown in Table I.

TABLE I[1]

MARKET GRADES OF ZINC

Grades	Per Cent Maximum			
	Lead	Iron	Cadmium	Sum of Lead, Iron & Cadmium
Special High Grade	0.007	0.005	0.005	0.010
High Grade	0.070	0.020	0.070	0.100
Intermediate	0.200	0.030	0.500	0.500
Brass Special	0.600	0.030	0.500	1.000
Selected	0.800	0.040	0.750	1.250
Prime Western	1.600	0.080	---	---

The three main uses of zinc are in galvanizing, in the manufacture of brass, and in the manufacture of zinc oxide. The zinc used in the manufacture of brass must be of high purity. As little as 0.07% lead or 0.05% iron in the zinc used to alloy with copper for brass will cause the brass to be brittle and subject to cracking under severe mechanical treatment. In the present day manufacture of brass only Special High Grade, and High Grade Zinc are used.

The prices paid for the various grades are listed in Table II.

TABLE II [13][18]

PRICES FOR VARIOUS GRADES OF ZINC

Grade	Price per pound in 1946	Price per pound in 1949
High Grade	$0.0925	$0.1000
Intermediate	0.0915	0.0950
Brass Special	0.0890	0.0925
Prime Western	0.0865	0.0900

Though this demand for high purity has provided an incentive for extension of the electrolytic zinc industry, the distillation processes still are producing the major percentage of the total output of the metal.

In 1946 thirty-nine per cent of the total production of zinc was produced by electrolytic means. Sixty-one per cent of the total production was produced by reduction and distillation processes.[13]

Based on the fuel used, the distillation processes may be divided into two classes, natural gas and coal fired processes. Both classes have the same general steps of roasting the ore in air, reducing the roasted ore and distilling the metallic zinc to separate it from the gangue.

The ores in the United States are mainly sulfide ores containing about 3% zinc. These low grade ores are usually concentrated to about 60% zinc before leaving the mine site. This concentrated material is roasted.

The distillation is carried on in present practice by hand-charging a one to one weight ratio of coal and roasted ore into refractory retorts. The retorts are externally heated to the reaction temperature of approximately 1150°C. The charge is maintained at this temperature for the rest of the 24 hour cycle at which most smelters run.

Of each 24 hour cycle approximately 4 to 6 hours are spent in cleaning, replacing, and recharging retorts. Another 2 to 4 hours are spent in bringing the charge up to the reaction temperature. Thus, only two thirds of each cycle is spent in direct production of zinc.

According to W. R. Ingalls[7] there is only about 70% direct recovery of metal in the present process. Another 20% of the metal is recovered from the reoxidation products formed in the primary distillation. Total recovery of the metal present in the ore is then about 90%. J. L. Bray[1] states that the total recovery of metal from the ore in this country is probably closer to 85%.

Among the sources of loss in the present retorts may be listed absorption of zinc by the retorts and condensers, diffusion of zinc vapor through the walls of the retorts, and the egress of zinc vapors from the end of the condensers.

In the electrolytic production of zinc, the ore is roasted in air. The zinc oxide and zinc sulfate mixture thus formed is leached with dilute sulfuric acid. This solution is neutralized and filtered to remove other metals such as iron, antimony, aluminum, copper, and cadmium. This filtered solution is electrolyzed in wooden tanks using cathodes of pure aluminum and anodes of lead. The zinc collects at the cathodes and is stripped off the aluminum. This cathodic zinc is melted in reverberatory furnaces and cast into fifty pound slabs for market.

With this process, one ton of zinc requires about 3550 kilowatt hours of energy. The equipment used is expensive because the materials of construction must be resistant to sulfuric acid. The greatest expense, however, is the cost of electrical energy.

The main losses in this process occur in the leaching and filtering operations.[1]

Many attempts have been made in the past to reduce zinc oxide with methane or natural gas.

The use of methane as a reducing agent has several outstanding advantages over the present use of carbon for the reduction. Among the advantages may be listed the following items.

On the basis of its reducing power as given by the equation

$$ZnO + CH_4 \longrightarrow Zn + CO + 2H_2 \qquad (1)$$

$$\Delta H_{1323^\circ K} = 105{,}900 \text{ calories per gram mols of zinc}$$

twelve thousand cubic feet of methane will produce one ton of zinc according to J. L. Bray and others.[1][7] The cost of twelve thousand cubic feet of natural gas is less than the cost of the one ton of coal required per ton of zinc in the present process.[7]

As pointed out by H. A. Doerner,[2][3] by burning the effluent gases from a methane reduction reaction, more heat is supplied than is necessary for the reaction.

In reaction (1) 105,900 calories of heat must be supplied to reduce one gram mole of zinc oxide with methane at a temperature of 1050°C. However, the heat of combustion in the gaseous products of the reaction (CO and H_2) is 183,430 calories. This is more than is required for the reduction reaction.

C. G. Maier[8] has shown that, from a thermodynamic viewpoint, methane has several marked advantages over carbon as a reducing agent in the reduction of zinc oxide. In reaction (1) there is a considerable difference between the heat capacity of the products of the reaction and the reactants. Because of this difference, the heat of the reaction and the free energy change are sensitive to an increase in temperature. Maier predicted that it should be possible to carry on the reduction of zinc oxide with methane at temperatures considerably lower than those now used in the reduction with carbon.

H. A. Doerner[2][3] later experimentally verified Maier's predictions and developed a process using a bed of solids in the reduction of zinc oxide with methane.

Despite the promise that methane holds as a reducing agent, no commercial operation has been successful because of certain practical obstacles.

Included in the difficulties to be surmounted before methane reduction can become a commercial success are the following:

There is difficulty encountered in maintaining a gas-tight seal between a ceramic retort and the source of methane because of the unequal thermal expansion. The production per unit of retort volume has not in the past warranted the expense of an alloy retort.

According to J. L. Bray[7] the entrance to the reaction chamber has in the past clogged with carbon formed from the decomposition of methane. Servicing of these entrance pipes has been difficult.

In the methods utilizing a solids bed of zinc oxide difficulty has been encountered in maintaining contact between the reducing gas and the zinc oxide. The beds of zinc oxide have tended to pack in the past and the reducing gas followed the path of least resistance. This resulted in inadequate contact between the reducing gas and the solid.

Another difficulty encountered is the formation of "blue powder". Blue powder is a mixture of zinc and zinc oxide.

Maier[8] pointed out that in the two reactions

$$2CO \longrightarrow CO_2 + C \qquad (2)$$

and

$$CO_2 + Zn \longrightarrow ZnO + CO \qquad (3)$$

reaction (2) is known to be slow below 1100°C., but reaction (3) is perceptible above 300°C. and is very rapid above about 550°C.

R. W. Millar[11][12] introduced pure zinc vapor into pure carbon monoxide at various percentages of each component and at various temperatures between 650°C. and 850°C. He found that in the absence of any active catalyzing surface the reaction between zinc and carbon monoxide was extremely slow. Millar also found that iron, present as metal or as impurities in clay, catalyzed the oxidation of zinc at these temperatures. He also found carbon deposited in the reaction chamber. He concluded that the reaction which was being catalyzed was reaction (2) above, and that the carbon dioxide thus formed, oxidized the zinc.

The other substances Millar tested for catalytic activity were zinc oxide, pure molten zinc, aluminum oxide, iron free clay, and silica. None of these materials showed any catalytic activity.

From the above we may assume that the oxidation of zinc by carbon monoxide proceeds at such a slow rate below 850°C. that it is of negligible practical importance unless a catalyst is present to promote the formation of carbon dioxide.

To minimize blue powder formation it is necessary to keep the concentration of carbon dioxide and water vapor at a minimum.

Doerner[3] overcame this difficulty by using a nickel catalyst to convert the carbon dioxide formed in the reduction to carbon monoxide. He also used a specially designed condenser to keep down reoxidation

The difficulties of maintaining adequate contact between the reducing gas and the solid can conceivably be overcome by a new technique known as fluidization of solids.*

Good fluidization will be defined for the purpose of this work as a well agitated mass of solid particles, which shows no tendency to slug or channel, and which has little tendency of solids carry-over.

Among the features of a fluidized solids technique may be listed the following things.

1. Very large throughputs of solid material may be handled in this way. J. F. Snuggs[18] reports that as much as 13,000 tons of catalyst per day has been handled with little trouble in a fluid catalytic cracking unit. Leva[5] et al state that the ability to handle large amounts of solids with simple mechanical equipment and small energy requirements is one of the features of a fluidized solids technique.

---

*Fluidization of solids is the phenomenon which occurs when a fluid is passed upward at certain velocities through a bed of solids. The solids are violently agitated by the stream of fluid and the system of both solids and fluid takes on the characteristics of a fluid.

2. A very close equalization of temperature is attained throughout a fluidized bed. Mickley and Trilling[10] found in laboratory size equipment that a longitudinal temperature traverse extending 35" along a fluidized bed, gave the following results: The temperature varied from 225°F. at the bottom of the bed to 227°F. at the top of the heating element. From a radial traverse they found that the temperature did not vary except within about 1/8" of the containing walls in a 3" diameter vessel. There was a temperature gradient of about 75°F. from the heat input to the fluidized bed.

   Leva[5] et al found that good temperature equalization is one of the features of fluidized solids beds.

3. Reaction rates in solids-gas reactions are increased because the violent agitation brings about thorough contact between unreacted gas and fresh solids. The finer degree of comminution associated with fluidized solids also increases the solid surface available.

4. Coefficients of heat transfer in fluidized beds are considerably increased over those for gases alone at the same velocity. Mickley and Trilling[10] found that heat transfer coefficients varied inversely with particle size and directly as solid concentration. The coefficient varied inversly as the mass rate of gas flow. The introduction of particles into a gas stream in the form of a fluidized bed increased the heat transfer coefficient

from 3 to 70 times ~~those~~ above that expected from the gas alone. The coefficients found were in the range from 10 BTU/(hr.)(sq.ft.)(°F.) to 120 BTU/(hr.)(sq.ft.)(°F.).

Both Leva[6] et al and Wigton[19] indicate there is an increase in heat transfer, when fluid beds are used, over that expected from the gas alone.

5. Countercurrent flow is not possible with a fluidized bed because of the excellent mixing. Stages of fluidized beds may be arranged, however, so that a semi-countercurrent flow is possible.

6. The gas velocities allowable are a limitation upon the use of fluidized beds. With high velocities, excessive carry-over and entrainment of solids result. Slugging, the phenomenon in which a bubble of gas carries a portion of the fluidized particles up the vessel and subsequently drops the particles back, also seems to depend on velocity. Leva[6] et al state that the factors which influence slugging are the ratio of bed height to diameter of vessel, particle size, distribution of particle size, and the difference in density between the fluidizing gas and the fluidized solid. Leva[5] and his co-workers, in another article, state that channeling depends on the moisture in the bed, the diameter of the reactor, the rate of fluid flow, and the particle diameter.

Considerable difficulty is encountered in using laboratory scale equipment for fluidization studies. With small diameter tubes, violent slugging is encountered. Bridging of the tubes is also encountered at any change in size or direction of the tubes. Continuous systems of small size are difficult to maintain in operation because of this plugging and bridging.

Fluidization studies made in a batch reactor may not accurately predict the operation of a continuous unit.

There are several possible obstacles to the use of a fluidized bed technique for the reduction of zinc oxide with methane.

Foremost among these is the fact that some substances fluidize poorly if at all. Some substances, which fluidize acceptably at one temperature, may tend to become sticky or agglomerate at other temperatures and fail to fluidize.

Another possible difficulty in the application of this technique to the reduction is that the rate of the reduction reaction may be so slow that very little reaction can take place in a practical length of fluidized bed because of the velocity demanded for fluidization, and the resulting short residence time afforded between solid and gas.

Therefore, the two main questions which this investigation is to answer are:

1. Can the commercial zinc oxide sinter be fluidized with methane or natural gas at the temperatures at which the reduction reaction takes place?
2. If the sintered material can be fluidized, is the gas velocity necessary for fluidization such that sufficient contact time is afforded for the reduction reaction to take place?

RAW MATERIALS

The sintered zinc oxide used was obtained from the National Zinc Company, Bartlesville, Oklahoma. It was a sample from the regular sintered material as charged to the retorts for distillation.

H. A. Doerner(3) gives the following average analyses for sintered concentrates obtained from the companies indicated.

TABLE III(3)

ANALYSES OF VARIOUS ZINC OXIDE SINTERS

Constituent	Sintered Concentrates: American Smelting and Refining Co.	Sintered Concentrates: American Zinc and Lead Co.	Calcined Concentrates: Eagle-Pitcher Co.
Zn	69.10%	70.60%	68.68%
Pb	0.43	0.70	1.18
S	0.70	1.00	0.98
Cd	0.01	0.28	0.02
Fe	7.35	----	1.97
Cu	0.80	----	1.07
SiO_2	1.96	----	5.60
CaO and MgO	1.07	0.83	2.12

The sintered concentrate from National Zinc Company was analyzed for zinc. The zinc content was 67.6%.

The reducing gas used was natural gas from the city gas mains in Stillwater, Oklahoma. The gas company furnished the following analysis.

TABLE IV

ANALYSIS OF NATURAL GAS FROM STILLWATER, OKLAHOMA

Constituent	Volume per cent
CH_4	76.5
C_2H_6	17.0
CO_2	1.0
O_2	1.3
N_2	4.2
	100.0

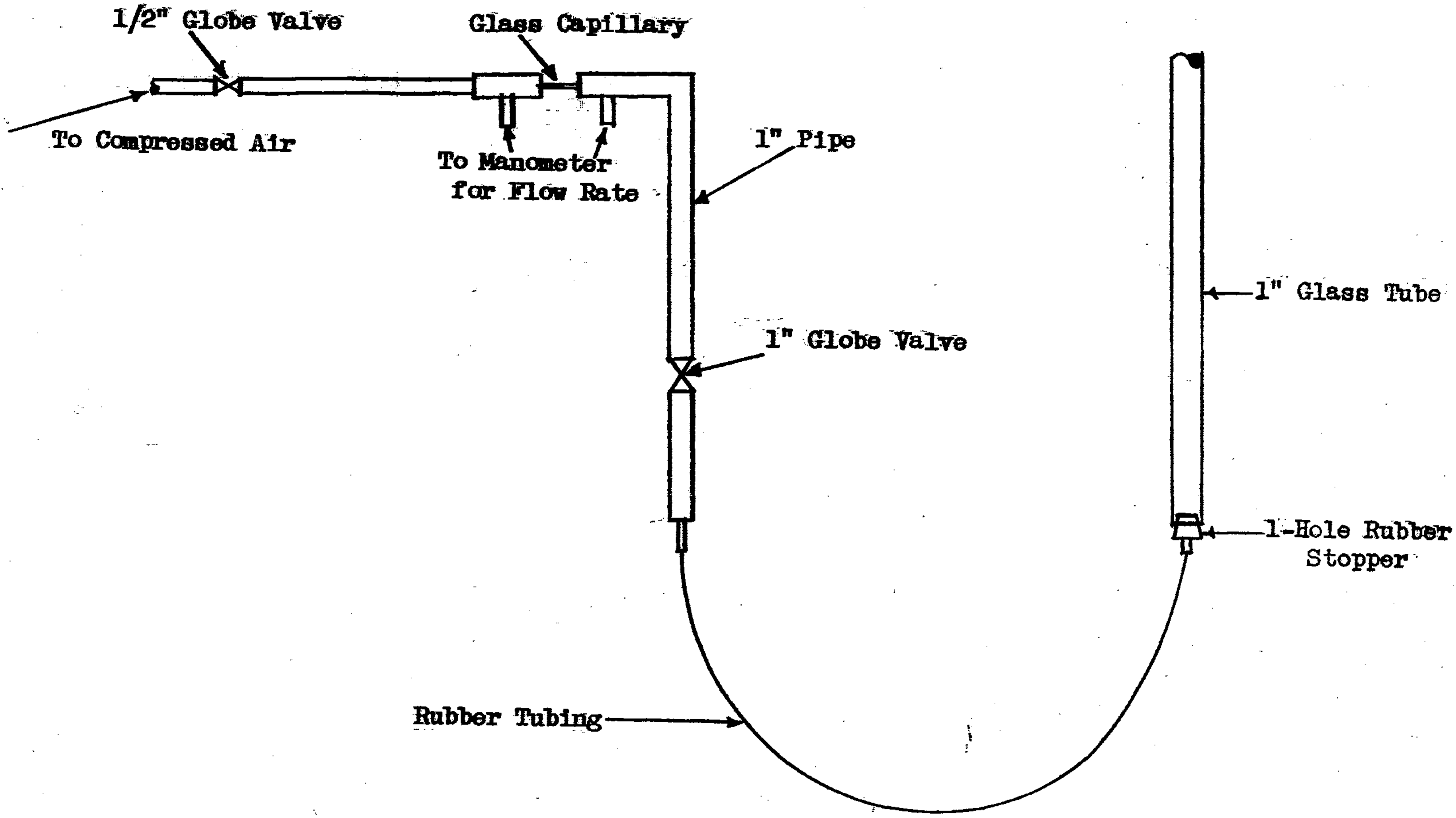
However, it was known that the gas for Stillwater was drawn from three sources and that the analysis might vary from time to time.

The combustible carbon to hydrogen ratio, as given by the above analysis, is 1 to 3.90. Analyses were run on the gas from the mains at different times, and it was found that the combustible carbon to hydrogen ratio calculated from this series of analyses was 1 to 3.88. This is the ratio used in the calculations in the experiment.

PRELIMINARY EXPERIMENTS

Since it was necessary to know if the sintered material would become sticky or agglomerate at the temperature of reduction, a crucible containing the sintered material was placed in a furnace, and the temperature was raised to 1800°F. The sample was cooled and inspected for agglomeration. No tendency to agglomerate was evident. This test was only considered indicative and not conclusive, since the material in this test was open to the atmosphere and the material in the reactor would be subject to a reducing atmosphere. However, from the indication of no agglomeration, experiments were planned to find a particle size and fluidization velocity range to be used in the remaining experiments.

The apparatus for this experiment is represented schematically in Figure 1. Compressed air was introduced into the bottom of a one inch diameter glass tube through suitable throttling valves. The flow rate was measured by the pressure drop across a glass capillary tube. This device had been previously calibrated. (Calibration data may be found in the Appendix.) Previously ground and sieved samples of the sintered material were introduced into the top of the glass tube until the bed height was six inches. Compressed air was admitted at the bottom of the bed, and the velocity was adjusted so that good fluidization was achieved. Various sizes, and ratios of sizes, of particles were studied in this manner. Runs were made at different gas velocities. The range of velocities used was from the velocity which barely supported fluidization, to the velocity at which either slugging or entrainment of solids became



SCHEMATIC DIAGRAM OF APPARATUS FOR
VISUAL STUDY OF FLUIDIZATION CHARACTERISTICS

Figure No. 1

excessive. The fluidization characteristics of the various particle sizes were studied visually and notations as to upper and lower limits of the velocity usable, solids entrainment, channeling and slugging were made.

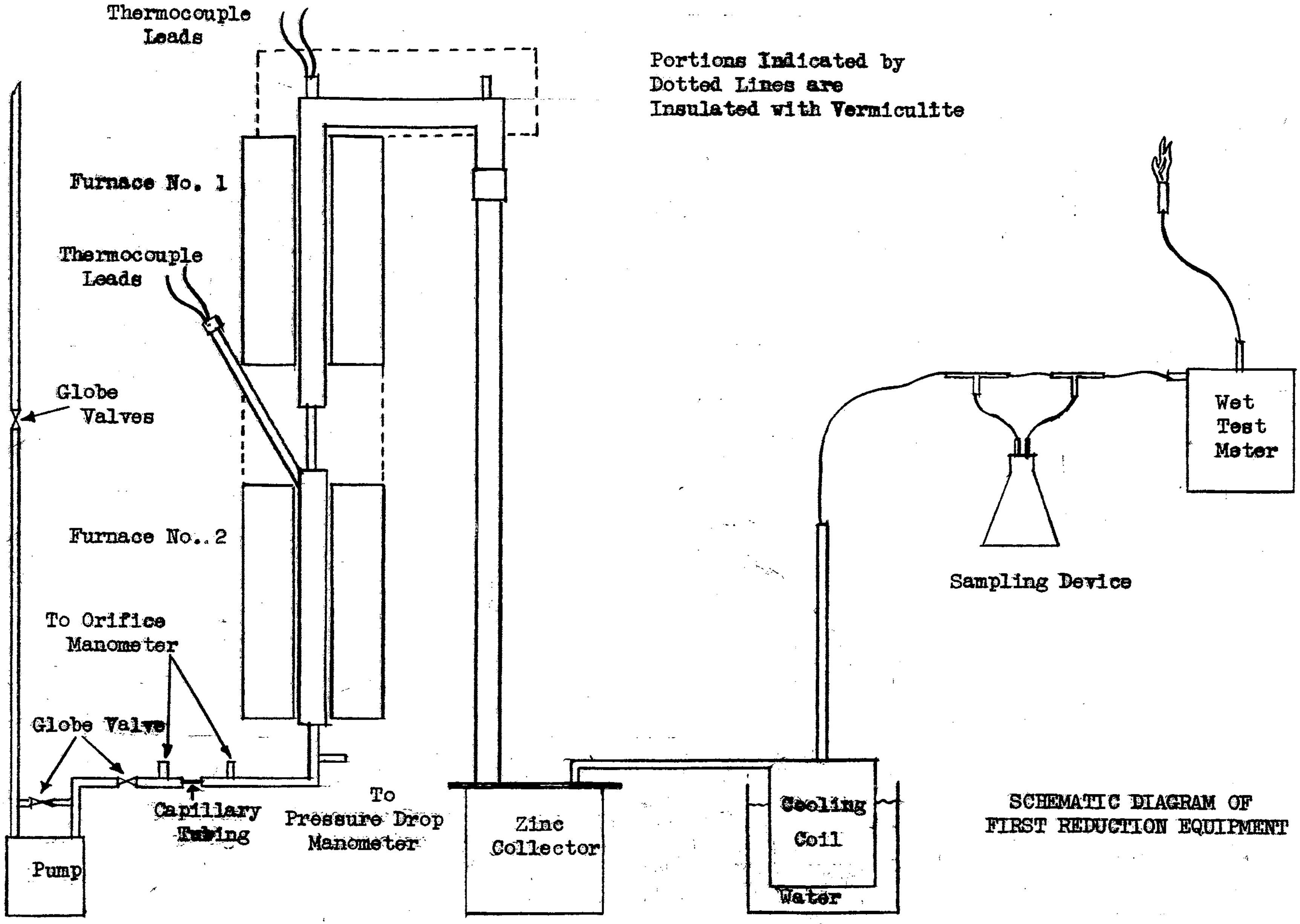
From this visual study it was determined that a 1:1 ratio of the particles, which passed a Tyler standard screen with 28 openings per inch, and which were retained on a Tyler standard screen with 48 openings per inch; to the particles, which passed a screen with 48 openings per inch, and which were retained on a screen with 65 openings per inch, was the size range to be used in the reduction equipment.

EXPERIMENTAL APPARATUS

A porcelain reactor wound with Chromel "A" heating wire was constructed. The heating wire burned out on the first run and cracks developed at the bond between the metal connections and the porcelain reactor. These cracks were due to unequal thermal expansion. Details and drawings of this apparatus are included in the appendix. A discussion of the failure may also be found there.

The next piece of equipment to be designed and constructed is shown in Figure 2. This apparatus made use of two reactors, constructed of 1" iron pipe, 14 3/4" long. The length of the reactors was limited by the heated length of the type CTA-2-9 Burrell high temperature furnaces used to heat the reactors. It was not presumed that the low carbon steel of the reactors would withstand the temperatures involved for any long period of time, but new reactors could be provided upon failure of the ones in use. The bottom reactor was used to fluidize the sintered material. The top reactor was intended for fluidization of the nickel catalyst suggested by H. A. Doerner[5] to keep down the concentration of carbon dioxide. The fluidizing gas for the top (catalyst) reactor was to be the effluent gas from the bottom reactor. From this equipment it was hoped to not only answer the questions originally proposed, but also to obtain data on catalyst efficiency.

Flow rates were measured by the pressure drop across a glass capillary tube. The capillary tube was calibrated in place. The instrument used to measure the pressure drop across the capillary was a differential manometer with carbon tetrachloride and water as fluids. Taps were



SCHEMATIC DIAGRAM OF FIRST REDUCTION EQUIPMENT

Figure No. 2

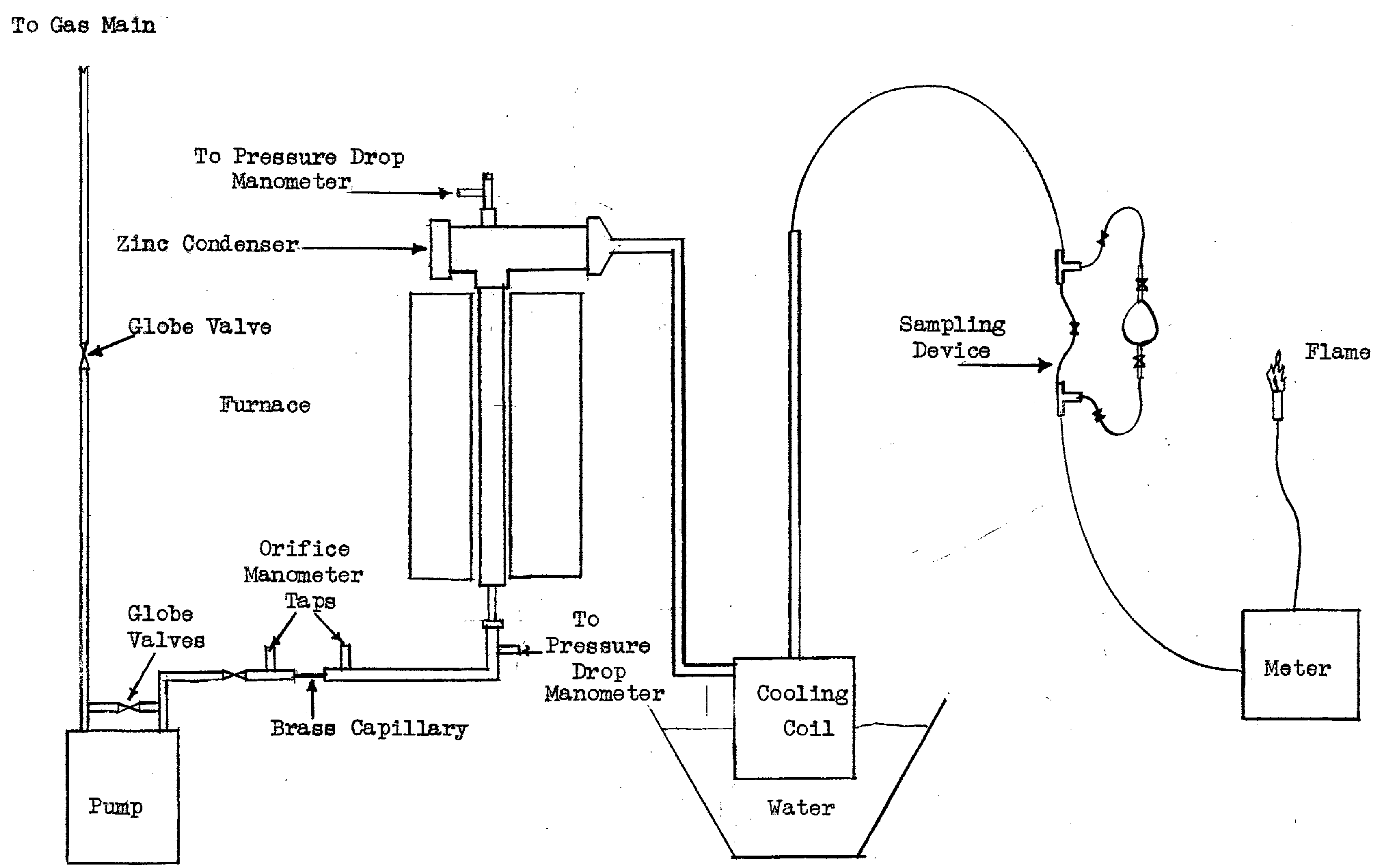
provided to measure the pressure drop across the reaction bed. The mercury manometer used to measure this pressure drop also indicated when good fluidization was occurring by the pulsating characteristics of the manometer fluid.

Temperatures were measured with Chromel-Alumel thermocouples. The potentiometer used was a Leeds and Northrup Company instrument. (Calibration data and curves for these thermocouples may be found in the Appendix.)

Based on the results obtained using the above described apparatus, another reactor was constructed. This apparatus had only one reactor and used only one furnace. Since very little reoxidation occurred in the first run in which no catalyst was used, the catalyst chamber was eliminated.

A schematic diagram of this equipment is shown in Figure 3. As may be seen the general arrangement of the equipment is the same as in the first reactor. The condenser and zinc collector were greatly reduced in size in the new equipment. The shape of the sample bottle was changed. A brass flow rate capillary tube was installed instead of the former glass one. The reactor tube was designed so that it was easily replaced upon failure.

The sample bottles used in the remaining runs were 600 milliliter separatory funnels fitted with a one-hole rubber stopper and a glass stopcock at the top end of the funnel. This revision was necessary because of the inadequate sweepout of residual gases encountered in the original sample bottles. The original ones (Figure A 11) were 800 milliliter Erlenmeyer flasks fitted with two-hole rubber stoppers and two glass stopcocks. This redesigned equipment was used for the remaining runs. The reactor tube was replaced with a new one after the second run made with it.



SCHEMATIC DIAGRAM OF FINAL APPARATUS USED

Figure No. 3

EXPERIMENTAL PROCEDURE

The one run made in the first equipment was performed in the following manner. Gas was admitted to the reactors and adjusted to give a low flow rate. A weighed charge of sintered material was admitted into the bottom reactor through the slanting tube at the top of this reactor. This material was a 1:1 ratio of + 28, -48; + 48, - 65 particles sizes. No catalyst was used. The thermocouples were inserted into the reactors a measured distance. The holes where the thermocouples entered were sealed with high temperature cement. Thermocouples were inserted into the places provided for them in each furnace. Thermometers were inserted in the meter and in the well just preceding the orifice. The water container for the cooling coil had previously been filled. The furnace transformer was adjusted for the correct voltage and the switch was closed. The flow rate was adjusted to a manometer differential of 3.9", or a gas rate of 5.0 gram moles per hour.

Readings of time, temperature at orifice, temperature at meter, meter reading, orifice manometer, pressure drop manometer, reactor thermocouples, and the furnace, thermocouple were taken and recorded at ten minute intervals. The room temperature and the barometric pressure were also recorded. Since the pressure in the meter, as measured by the manometer provided for this purpose, was nil, the uncorrected barometric pressure was used in the calculations.

The condition and color of the flame at the exit of the equipment was noted and recorded also. This flame changed noticeably in color when the reaction started. The color at low temperatures was blue with an orange tip indicating the burning of natural gas. At around 1300°F. the color changed to sooty orange. This was an indication of methane decomposition. The flame color began to turn colorless at about 1600°F. This indicated that the reduction reaction was taking precedence over the methane decomposition at this temperature. The pump was started when the bed had reached about 1600°F. and the flow valve was adjusted to give good fluidization. Fluidization was indicated by pulsations in the pressure drop manometer. At about 1800°F. the pressure drop, as indicated by the manometer measuring the pressure drop across the reactor, started decreasing. The velocity also started dropping. This indicated that somewhere in the equipment the flow was being obstructed. This obstruction eventually built up so that a manometer connection was blown off of the pressure drop manometer. The gas, furnace, and pump were turned off. Samples of the effluent gas were obtained at temperatures of 1784°F., and 1819°F.

When this equipment was dismantled, it was found that the zinc had condensed in the small pipe between the two reactors. This was due to the unheated space between the furnaces. Although this space was insulated with vermiculite, there was sufficient heat loss for the metal to condense. This condensed product was mainly metallic zinc with very little blue powder in evidence.

The natural gas and the samples of the reaction gases were analyzed using the standard method used with a Bureau of Mines type gas analyzer[4].

From the reduction in volume after combustion and the amount of carbon dioxide formed by combustion, the carbon to hydrogen ratio of the gas being analyzed was calculated.

From the carbon to hydrogen ratio of the fuel and of the reaction gas the relative amount of fuel and hydrogen was calculated. The amount of nitrogen was obtained by difference between the amount remaining after all absorptions and the amount brought in with the combustion oxygen. From this the per cent of nitrogen was calculated. For complete calculations, see the appendix.

The procedure used in the second equipment was essentially the same as the one used in the first reactor. The same readings as for the first run were taken with this apparatus.

The major difference in results obtained with this equipment from the results obtained in the first equipment was the form of the product formed. In the new equipment, the zinc vapor was reoxidized far more than in the first reactor.

Runs at four different entrance gas rates were made using this apparatus. Before each run a check calibration was made of the flow metering device. This was necessary since a change of position of the capillary with respect to the pipe would change the calibration of the device. The possibility of such a change of position was present since the reaction tube was dismantled at the completion of each run.

The four entrance gas rates used were 4.1, 4.7, 5.6, and 6.0 gram moles of gas per hour. At the three higher velocities the pressure in the equipment built up until the run was stopped. When the equipment was dismantled after each run this excessive pressure was discovered to be caused by blue powder clogging the exit from the zinc condenser. No evidence of agglomeration was discovered. The thermocouple was removed from the reactor while the bed was still at about 1700°F. It was inspected for agglomerated material. There was sintered material stuck to the thermocouple, but upon closer examination and measurement of the length of sinter formed along the thermocouple and the reactor and condenser, it was determined that the material was not stuck to the thermocouple because of stickiness of the sinter, but because some of the zinc vapor had condensed upon the thermocouple and the sinter stuck to the fluid zinc. It was realized that this was only for one ore and that other ores containing different amounts of impurities may agglomerate.

A tabulation of the important results from the above runs may be found in Table V.

TABLE V

TABULATION OF RESULTS

	Sample Bottle Number	% CO_2	% O_2	% CO	% N_2	% Fuel	% H_2	Temp. at which Sample Taken °F.	% Converted (Based on Hydrogen)	% Converted (Based on Carbon)
Run No. 1										
Gas Rate =										
5.0 g. mole / hr.	2	0.2	6.0	11.9	11.2	45.5	25.2	1784	16.3	19.0
Reactor I	3	0.9	5.4	18.0	38.4	15.5	21.6	1819	56.5	63.1
Run No. 2	1	2.0	1.5	5.1	9.6	71.5	10.3	1648	6.9	9.1
Gas Rate =	2	1.2	3.0	9.2	10.5	61.9	14.1	1748	10.5	14.4
	3	0.7	2.5	15.0	10.6	53.6	18.0	1798	14.9	22.8
5.5 g. mole / hr.	4	2.5	3.7	14.3	13.7	43.6	22.2	1840	20.8	27.8
	5	1.6	1.9	19.0	5.0	38.4	33.9	1885	21.3	35.0
Reactor No. 2	6	1.3	1.4	23.2	6.2	28.7	39.4	1928	41.4	46.1
Run No. 3	1	1.5	5.3	1.6	49.6	42.4	Trace	1645	----	7.0
Gas Rate =	2	1.3	5.2	3.9	43.6	40.2	5.9	1755	7.0	11.5
	3	1.6	5.6	4.7	47.5	23.8	16.9	1795	26.7	21.0
4.8 g. mole / hr.	4	2.1	5.0	9.3	34.1	31.0	17.8	1850	22.4	26.2
	5	3.6	1.2*	18.1	21.7	27.0	28.4	1880	35.2	44.6
Reactor No. 2	6	1.9	3.0	24.2	14.9	15.4	40.8	1895	58.2	63.0
Run No. 4	1	1.2	1.3*	7.1	23.1	54.1	12.5	1649	10.7	13.4
Gas Rate =	2	2.2	2.1	10.4	15.8	50.9	18.8	1774	16.1	19.9
6.5 g. mole / hr.	3	3.3	1.3	12.3	6.7	58.6	19.0	1824	14.5	21.0
	5	2.4	1.5	18.0	14.6	33.4	30.1	1848**	31.8	37.3
Reactor No. 2	6	2.7	2.4	19.3	4.4	35.1	36.2	1870**	34.8	38.5
Run No. 5	1	1.1	4.8	2.5	33.5	43.6	14.4	1626	22.6	8.7
Gas Rate =	2	1.8	0.3*	5.8	35.2	33.0	24.1	1716	22.3	16.4
	3	1.7	1.8	8.0	22.8	47.4	18.5	1766	26.1	20.1
7.0 g. mole / hr.	4	1.4	3.6	6.2	27.9	40.6	19.2	1810	26.7	17.7
	5	1.9	2.1*	8.0	31.4	34.4	22.1	1881	38.8	28.0
Reactor No. 2	6	1.8	1.3	12.4	4.0	43.3	37.3	1943	30.7	24.7

*Oxygen analysis in doubt (See discussion of Results)

**Estimated from furnace temperatures. (Reactor thermocouple burned out)

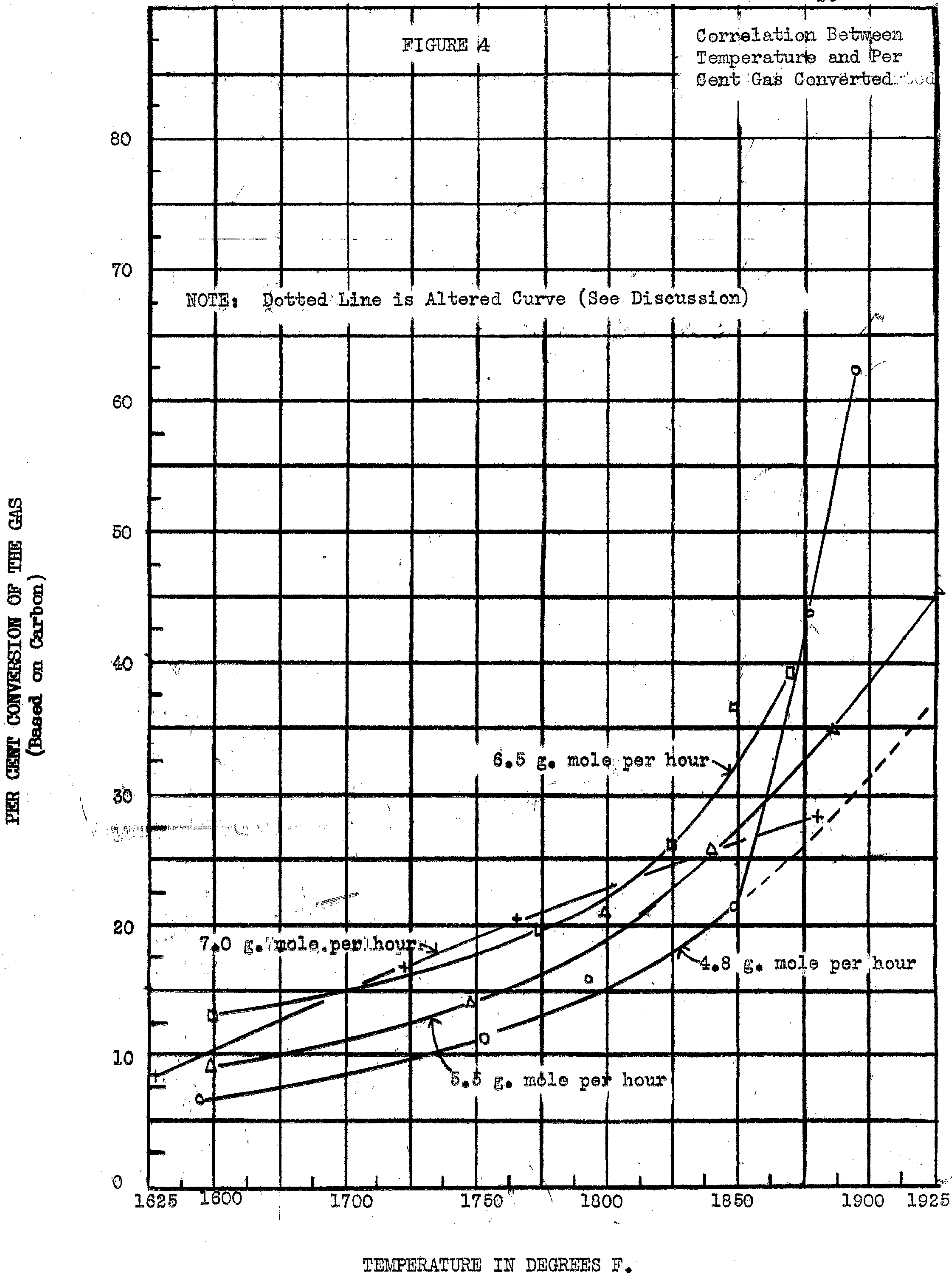


FIGURE 4
Correlation Between Temperature and Per Cent Gas Converted
NOTE: Dotted Line is Altered Curve (See Discussion)
6.5 g. mole per hour
7.0 g. mole per hour
4.8 g. mole per hour
5.5 g. mole per hour
PER CENT CONVERSION OF THE GAS (Based on Carbon)
0
10
20
30
40
50
60
70
80
1625
1600
1700
1750
1800
1850
1900
1925
TEMPERATURE IN DEGREES F.

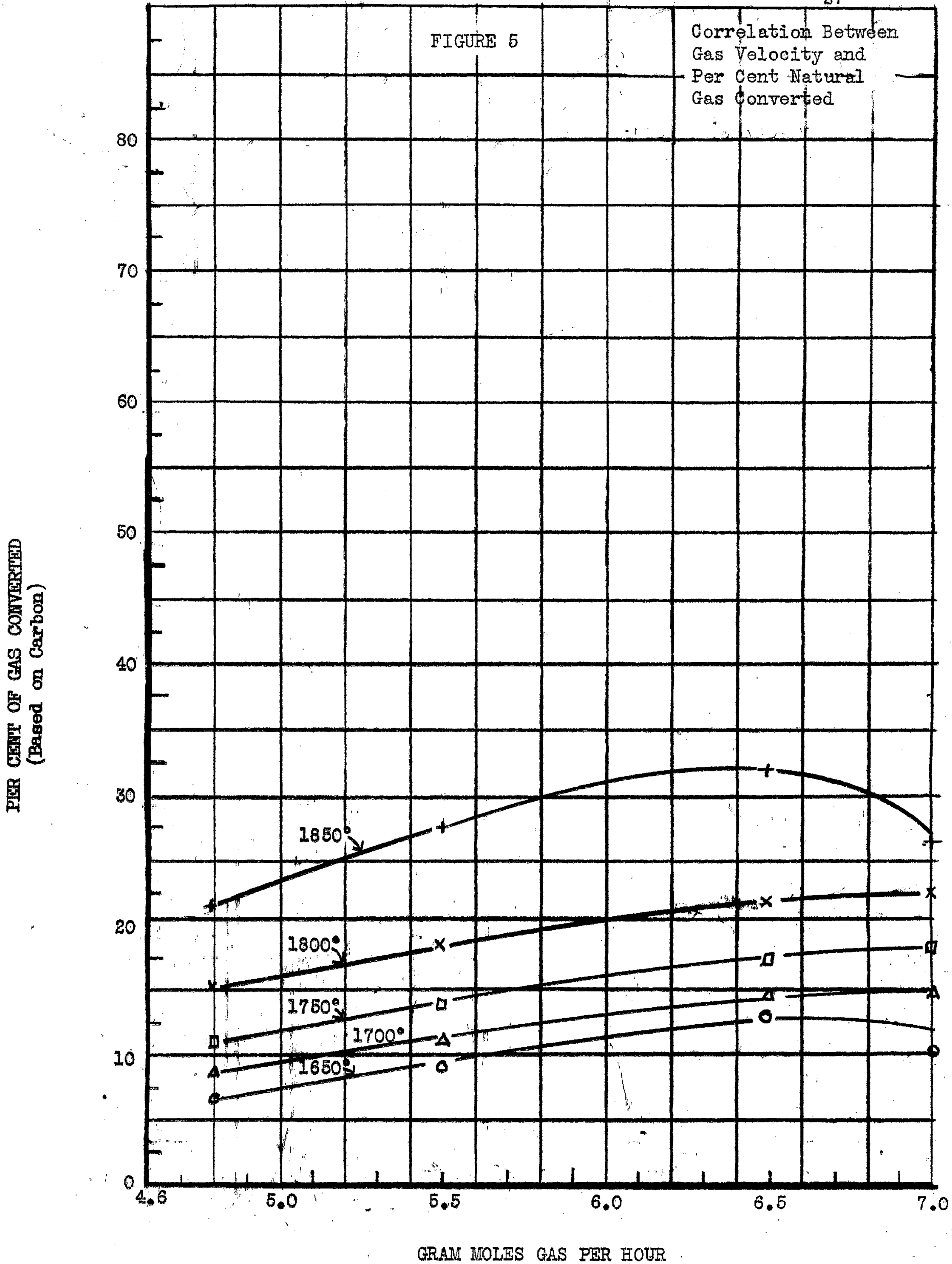


FIGURE 5
Correlation Between Gas Velocity and Per Cent Natural Gas Converted
PER CENT OF GAS CONVERTED (Based on Carbon)
GRAM MOLES GAS PER HOUR
1850°
1800°
1750°
1700°
1650°
0
10
20
30
40
50
60
70
80
4.6
5.0
5.5
6.0
6.5
7.0

DISCUSSION OF RESULTS

The uncertainty of the pyrometer and thermocouples used in this work was ± 5°F. The smallest scale division of the meter was 10°F. Thus, interpolation was necessary to read temperatures any closer than 10°F. (Calibration data may be found in the Appendix.)

The meter used to calibrate the flow device was calibrated with the use of a standard 0.1 cubic foot bottle. (Table XX, Appendix). The correction factor to be applied was found to be 1.075 cu. ft. per 1.0 cu. ft. observed. This correction factor was applied in calculating the velocities for the calibration curves of the capillary tubes.

The capillary tube was calibrated before each run so that any shift in relative position between the capillary and the pipe would be accounted for. The instrument used to measure pressure drop across the capillary was a differential manometer with water as the light fluid and carbon tetrachloride as the heavy fluid. The heights of the liquid in the manometer legs could be read accurately to 0.1 inches. This could be 0.2 inches when both legs of the manometer are considered. Two tenths of an inch pressure differential corresponds to two tenths of a gram mole of gas per hour. The uncertainty of the gas rate measurement was two tenths of a gram mole per hour. The inherent uncertainty of the gas analysis equipment is ± 0.1 milliliter. This is due to the smallest division of the gas measuring burette being 0.1 milliliter.

The figures used in the tables and graphs represent the average of check analyses.

It will be noticed that oxygen and nitrogen appear in the analysis. If this represents the residual air left in the sampling bottles due to incomplete flushing, the nitrogen to oxygen ratio should be 3.76 to 1.0. For none of the analyses does this ratio hold. Thus, apparently either the oxygen or nitrogen comes from some other source or the analyses are in error. The most probably explanation of this discrepancy is that the oxygen percentage is calculated from a small difference between two large numbers. For example, in Sample I, Run II, a sample of 36.68 ml. was analyzed in one check. After the CO_2 was absorbed the reading was 35.94 ml. and after the O_2 was absorbed the reading was 35.40. A cummulative error of less than 0.5% on both of these readings would more than account for the discrepancy in the nitrogen to oxygen ratio in this case. There are several analyses which may be viewed with suspicion despite the above explanation. These analyses have been designated with an asterisk on the results sheet. It is to be suspected that the absorbing solution for the oxygen was exhausted in these cases since the nitrogen to oxygen ratio is very high.

It will be noticed also that the results for Run I are not plotted on Figure 4. The reason for the absence of these results is that Run I was made in a different equipment than the rest of the runs, and the analytical procedure was, at that time, unreliable.

In Figure 4 the curve for 4.1 gm. mole/hr velocity has been altered (dotted lines) since the velocity actually dropped (see Table X) while fluidization remained good. Thus, the extremely high conversion actually measured probably resulted because of the large increase in residence time.

Figure 4 indicates that an increase in temperature increases the per cent conversion at all velocities investigated. This indicates an increase in reaction rate with an increase in temperature.

Figure 5 shows that there is an optimum gas velocity above which the per cent conversion decreases.

This phenomena seems logical upon analysis of the factors affecting the per cent of the gas converted. The per cent of the gas reacted would increase with temperature. It is possible that the per cent of the gas reacted would create an increased agitation of the fluidized bed, and thus an increased surface of solid exposed to the gas. This increase in agitation would probably be more noticeable from low to medium velocities than from medium to high velocities.

There are, then, two possible factors tending to increase the per cent of the gas converted with an increase in entrance velocity. But an increase in entrance velocity not only results in the above factors, it also results in a reduced residence time of the gas in the fluidized bed.

Considering these three factors, it is logical that the per cent of the gas reacted would increase with an increase in velocity because of the first two factors. It is also logical that above a certain velocity the influence of the third factor would predominate and the per cent of the gas reacted would decrease with an increase in velocity.

Calculations from the data obtained indicate that the optimum linear velocity is approximately 0.95 ft./sec.

It will be noticed that both graphs are plotted with "per cent of gas converted" as the ordinate. This is an indirect indication of the amount of zinc formed.

From the equation

$$ZnO + CH_4 \longrightarrow Zn + CO + 2H_2 \qquad (1)$$

it may be seen that one mole of methane gives one mole of carbon monoxide and two moles of hydrogen. The per cent of CO in any analysis of the effluent gas divided by the sum of the per cents of unburned fuel and carbon monoxide (i.e. the total carbon) would then give the per cent of conversion of the gas. However, the above reaction does not give the true picture of the reduction with natural gas. The natural gas is not pure methane. Also, in the actual reduction, carbon dioxide and some water vapor are formed. The conversion of the natural gas then is only an indication of the conversion of the zinc oxide. If the assumption is made that all combined oxygen that occurs in the gas analysis comes from the zinc oxide, it would be possible to estimate the rate of zinc production with considerable accuracy. Because some of the impurities present in the ore occur as oxides, the above assumption is not valid.

POTENTIALITIES OF THE PROCESS AND DIRECTION OF FUTURE WORK

In order to get a comparison between the present production from retort distillation, and the production which might be expected from use of a fluidized technique the following assumptions and calculations were made.

From the work of G. L. Oldright[15] an average production figure of 1.63 pounds of zinc per hour per 10 inch retort was calculated. This total represented production of both blue powder and spelter. The average per cent of blue powder formed was 7.4%.

With a fluidized bed 10 inches in diamter and two feet deep a 50% conversion of the gas might be assumed at a gas velocity of 1.0 ft./second, and a bed temperature of 1900°F.

A gas velocity of 1.0 ft./sec. in this diameter vessel is 1964 cu. ft./hr. at 1900°F. or 1.134 pound moles of natural gas per hour. With a 50% conversion and assuming one mole of gas reduces one mole of zinc oxide 0.567 pound moles of zinc would be formed per hour. This is 37.2 pounds of zinc per hour, or 22.8 times as much zinc per hour as Oldright's data indicates is produced in the retort method.

This increase in production per unit volume of reactor would greatly reduce the heating expense. The lower temperature of reaction (1900°F. instead of 2100°F.) would increase furnace life considerably.

Continuous fluidization would eliminate much labor cost of cleaning, replacing, and hand charging the retorts.

Based on the reducing power and cost of both coal and natural gas, natural gas is by far the more economical reducing agent in regions in which natural gas is available, according to J. L. Bray[1].

The sinter will fluidize in the condition it comes from the roasting operation. However, the velocities needed may be too high to allow reaction to take place. The determination of optimum particle sizes is one of the problems to be solved.

It is possible that an added comminution cost will be necessary to obtain the proper particle size.

The prevention of reoxidation is another problem to be solved. H. A. Doerner[3] and H. K. Najarian[14] both state they have condensed metallic zinc from non-condensable gases with very little formation of blue powder. Doerner controlled the temperature of condensation carefully, but Najarian made use of a liquid zinc bath to keep the condensation temperature above the melting point of zinc. It may be possible that one of their methods may be adapted to this use. The product obtained from runs 2, 3, 4, and 5 contained a high percentage of blue powder. Run 1 contained very little blue powder. The difference between the runs was that the zinc condensed in a narrower space, and presumably at a higher temperature in the first equipment than in the second equipment. The reoxidation in the second equipment was probably due to the lower temperature of condensation in these runs.

Raw material characteristics is another direction of investigation which should be followed. The present investigation was made with only one sintered material from the Tri-State area. The absence of agglomerating tendencies in this particular sintered material is not conclusive one way or another with respect to other ores. An investigation into the tendency of sintered material from various zinc ores to agglomerate should be made.

As pointed out previously, batch fluidization does not reliably predict the operation of a continuous process. Eventually work should be done to develop a continuous process if the above investigations show that a fluidization process can be commercially feasible.

CONCLUSIONS

The following conclusions may be made from the results obtained:

1. Certain commercial sintered materials containing zinc oxide may be fluidized with natural gas at the temperatures at which natural gas reduces zinc oxide to metallic zinc.
2. The velocities at which good fluidization occurs at the reaction temperatures are such that reaction between the natural gas and zinc oxide to produce metallic zinc can take place with a practical depth of bed.

APPENDIX

TABLE VI

CALIBRATION DATA* FOR VISUAL FLUIDIZATION EQUIPMENT

Flow in cu.ft./sec.	Manometer reading inches of mercury	Calculated Velocity** in a 1.125" Diameter Tube -- Ft./sec.
0.01205	11.62	1.74
0.009094	4.54	1.31
0.01323	11.88	1.92
0.01089	6.41	1.57
0.00595	1.82	0.858
0.003656	0.73	0.528

* From J. B. Hocott's notes. (2-21-49)

** Area of tube -- $(1.125/12)^2(3.1416)/(4)$ -- 0.00692 sq. ft.

Ft./sec. -- (cu.ft./sec.) (1/area) or 0.01205/0.00692 -- 1.74 ft./sec.

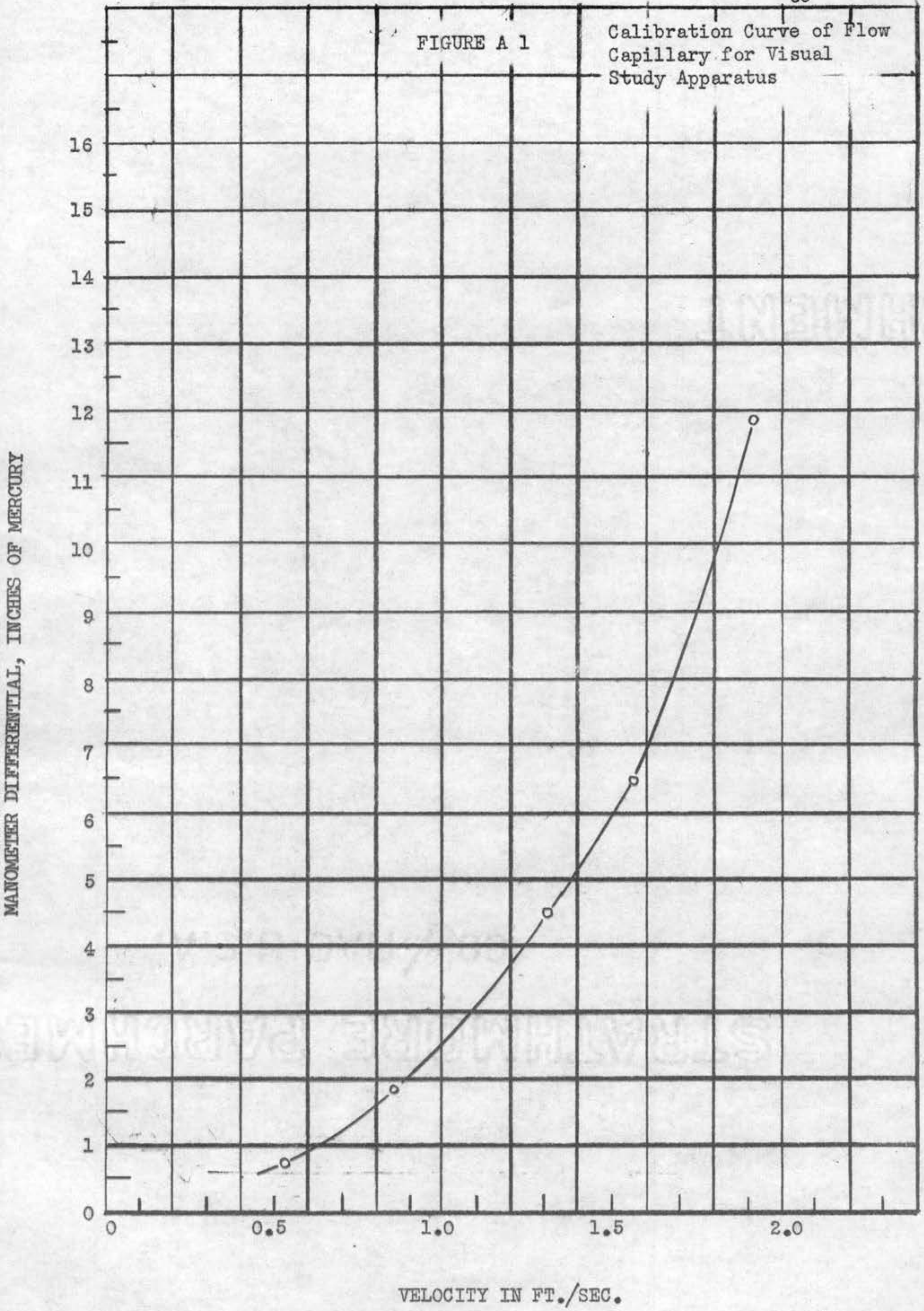


FIGURE A 1
Calibration Curve of Flow Capillary for Visual Study Apparatus
MANOMETER DIFFERENTIAL, INCHES OF MERCURY
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
0
0.5
1.0
1.5
2.0
VELOCITY IN FT./SEC.

FAILURE OF FIRST REACTOR

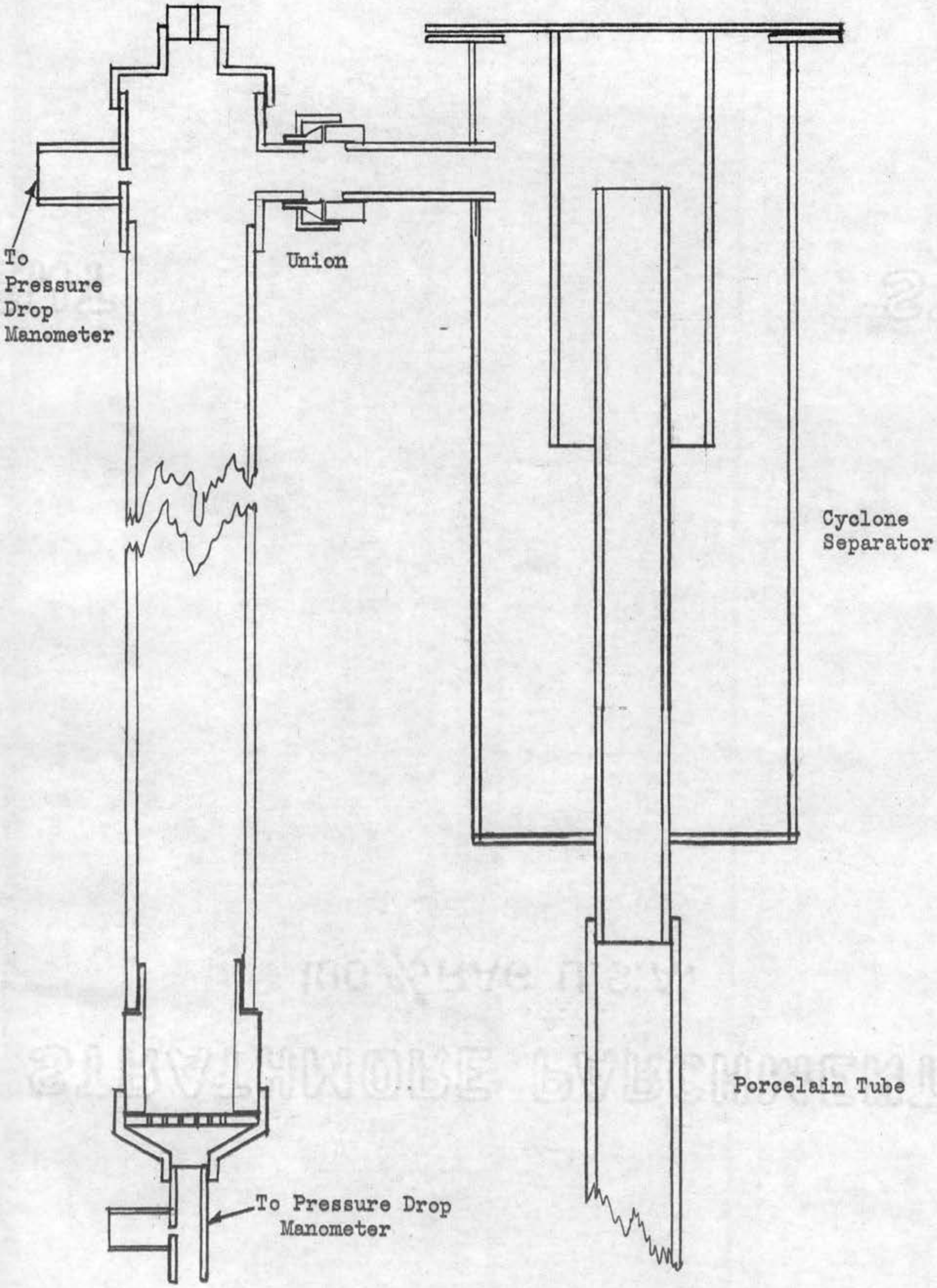
The first reactor that was designed and constructed (Figure A 1) had a porcelain reaction tube wound with Chromel "A" heating wire. The tube was 30" long and 1" inside diameter. The gas entered at the bottom through a distributor with 1/16" holes. The gas left the reactor at the top and entered the tangential feed pipe of a cyclone dust separator. The dust separator was also wound with Chromel "A" wire.

The dust free gas passed downward through a 48" length of porcelain tube used for a zinc condenser. This condenser terminated in a porcelain lined steel container to collect the zinc.

These were the only items that differed from the second reactor.

The reason for the heating element failure was the complete surrounding of the heating wire by material with low thermal conductivity. Thus, though the bed temperature was only slightly higher than 1000°F., the temperature of the wire was above the melting temperature of Chromel "A" wire.

The metal to porcelain bonds developed cracks due to unequal thermal expansion.



FIRST REACTOR

Figure No. A 2

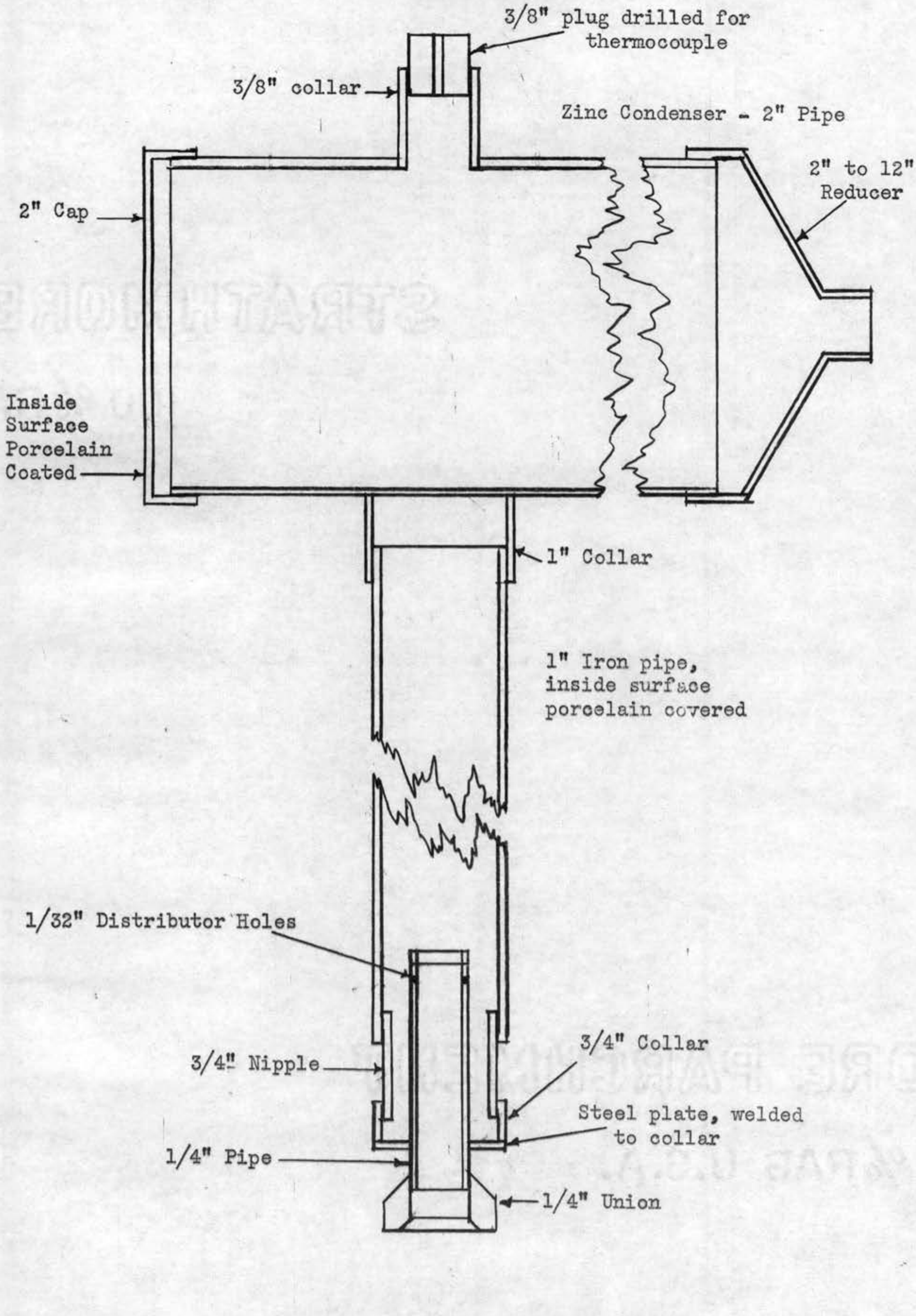

3/8" plug drilled for thermocouple
3/8" collar
Zinc Condenser - 2" Pipe
2" to 12" Reducer
2" Cap
Inside Surface Porcelain Coated
1" Collar
1" Iron pipe, inside surface porcelain covered
1/32" Distributor Holes
3/4" Collar
3/4" Nipple
Steel plate, welded to collar
1/4" Pipe
1/4" Union

Figure A 6.

NOTATION FOR TABLES VII, IX, X, XI, AND XII

θ = Time of Reading in hours and minutes.

T_o = Temperature of gas stream at the thermometer just preceding the orifice, in degrees Fahrenheit.

T_m = Temperature of gas in the meter, in degrees Fahrenheit.

R_m = Meter Reading in cubic feet.

M_{ol} = Reading of left leg of Orifice Manometer.

M_{or} = Reading of right leg of the Orifice Manometer.

M_{pl} = Reading of left leg of Pressure Drop Manometer.

M_{pr} = Reading of right leg of Pressure Drop Manometer.

Tc_{f1} = Reading of the thermocouple in the top furnace, in °F.

Tc_{r1} = Reading of the thermocouple in the top reactor, in °F.

Tc_{f2} = Reading of the thermocouple in the bottom furnace, in °F.

Tc_{r2} = Reading of the thermocouple in the bottom reactor, in °F.

V_t = Voltage applied to the top furnace.

V_b = Voltage applied to the bottom furnace.

TABLE VII

DATA SHEET FOR RUN NO. I

Weight of ore charged - 12 ounces

Room Temperature - 84^{o}F. Barometric Pressure 735.5 mm.

θ	T_o	T_m	R_m	M_{ol}	M_{or}	M_{pl}	M_{pr}	Tc_{f1}	Tc_{r1}	Tc_{f2}	Tc_{r2}	V_t	V_b
8:30	80	86	97.100	15.8	19.7	20.3	19.4	Furnace turned on				40	40
8:40	80	86	97.892	15.8	19.7	20.3	19.4	668	390	464	260	40	40
8:50	80	86	98.500	15.8	19.7	20.3	19.4	778	557	544	370	40	40
9:00	80	86	99.000	16.6	18.9	20.3	19.4	860	670	770	570	40	60
9:10	80	86	99.510	16.6	18.9	20.5	19.2	938	762	868	728	40	60
9:20	80	86	100.000	16.9	18.6	20.5	19.2	1262	1175	1258	1130	90	90
9:30	80	86	100.344	17.0	18.5	20.5	19.2	1238	1130	1372	1290	60	90
			Flame started "puffing".										
9:40	80	86	100.656	17.3	18.3	20.5	19.2	1632	1448	1503	1444	80	90
		Pump started. Noticed pulsations in pressure drop manometer.											
9:50	80	86	101.095	16.3	19.3	20.4	19.3	1790	1690	1610	1580	80	90
10:00	80	86	101.478	16.0	19.4	20.5	19.1	1790	1730	1700	1625	70	90
		Sample Number 1 - taken at 1650° to 1690°.											
10:10	80	86	101.956	16.3	19.2	20.8	19.2	1830	1760	1790	1710	70	90
10:12	pressure drop rose rapidly to			15.6	19.9	22.0	17.7	1830	1760	1780	1695	--	--
10:20	80	86	---	16.0	19.6	22.1	17.6	1870	1805	1852	1700	70	90
		Sample Number 2 - Taken at 1700°F.											
10:30	80	86	103.810	16.0	19.6	22.1	17.6	1895	1837	1890	1710	70	90
10:40	80	86	104.680	16.4	19.1	21.8	17.8	1930	1872	1938	1725	70	90
		Pressure drop started to go down - flame changed color.											
10:49	Trouble with		105.291	manometer		21.2	18.4	1960	1890	1955	1735	70	90
		(The manometer tend to blow off the connections.)											
10:50		Sample Number 3 - Taken at 1735°F.											
10:52		Very feeble flame (orange)									1735		
10:56		Even feebler flame (orange)									1735		
11:00	79	84	105.572	----	----	20.7	19.1	----	1915	----	1735		
11:05	One-half inch flame					20.4	19.2	2000	1933	2033	1710	70	90
		Flame so low it doesn't show over burner.											
11:10	79	84	105.695	----	----	20.3	19.3	2010	1942	2050	1708		

Meter stopped - manometer blew connection and blew liquid out.
Turned gas, electricity and pump off.
Meter reading when stopped - 105.700.
Pressure drop seemed about normal when manometer blew out.
42 grams of zinc was recovered.

TABLE VIII

ORIFICE CALIBRATION FOR RUN I

Manometer Left	Manometer Right	Diff.	Time of Run	Meter Reading Initial	Meter Reading Final	Volume cu.ft./min.	g. moles per hr.	g. moles/hr* Corrected X(1.075)
8.0	27.0	19.0	1 min., 0 sec.	90.400	90.576	0.176		
8.0	27.0	19.0	1 min., 0 sec.	90.800	90.982	0.182	11.9	12.9
8.0	27.0	19.0	1 min., 0 sec.	91.300	91.481	0.181	11.9	12.9
11.4	24.0	12.6	2 min., 0 sec.	91.840	92.131	0.146	9.6	10.0
11.4	24.0	12.6	2 min., 0 sec.	92.200	92.346	0.146	9.5	10.0
13.7	22.0	8.3	1 min., 0 sec.	92.600	92.721	0.121	7.89	8.5
13.7	22.0	8.3	1 min., 0 sec.	92.800	92.919	0.119	7.87	8.5
16.0	20.0	4.0	1 min., 0 sec.	93.100	93.181	0.091	5.40	5.8
16.0	20.0	4.0	1 min., 0 sec.	93.230	93.310	0.080	5.39	5.8
16.9	19.0	2.1	1 min., 0 sec.	93.430	93.486	0.056	3.62	4.0
16.9	19.0	2.1	1 min., 0 sec.	93.530	93.587	0.057	3.73	4.0
17.4	18.7	1.3	1 min., 0 sec.	93.640	93.648	0.044	2.89	3.1
17.4	18.7	1.3	1 min., 0 sec.	93.710	93.754	0.044	2.89	3.1
17.8	18.3	0.5	1 min., 0 sec.	93.800	93.821	0.021	1.35	1.4
17.8	18.3	0.5	1 min., 0 sec.	93.830	93.850	0.020	1.34	1.4

* From Calibration of Meter, Table XVI

The meter temperature stayed constant at 30°F.
Barometric Pressure = 737 mm or 29.2 inches of mercury.
Temperature of entering gas = 82°F.

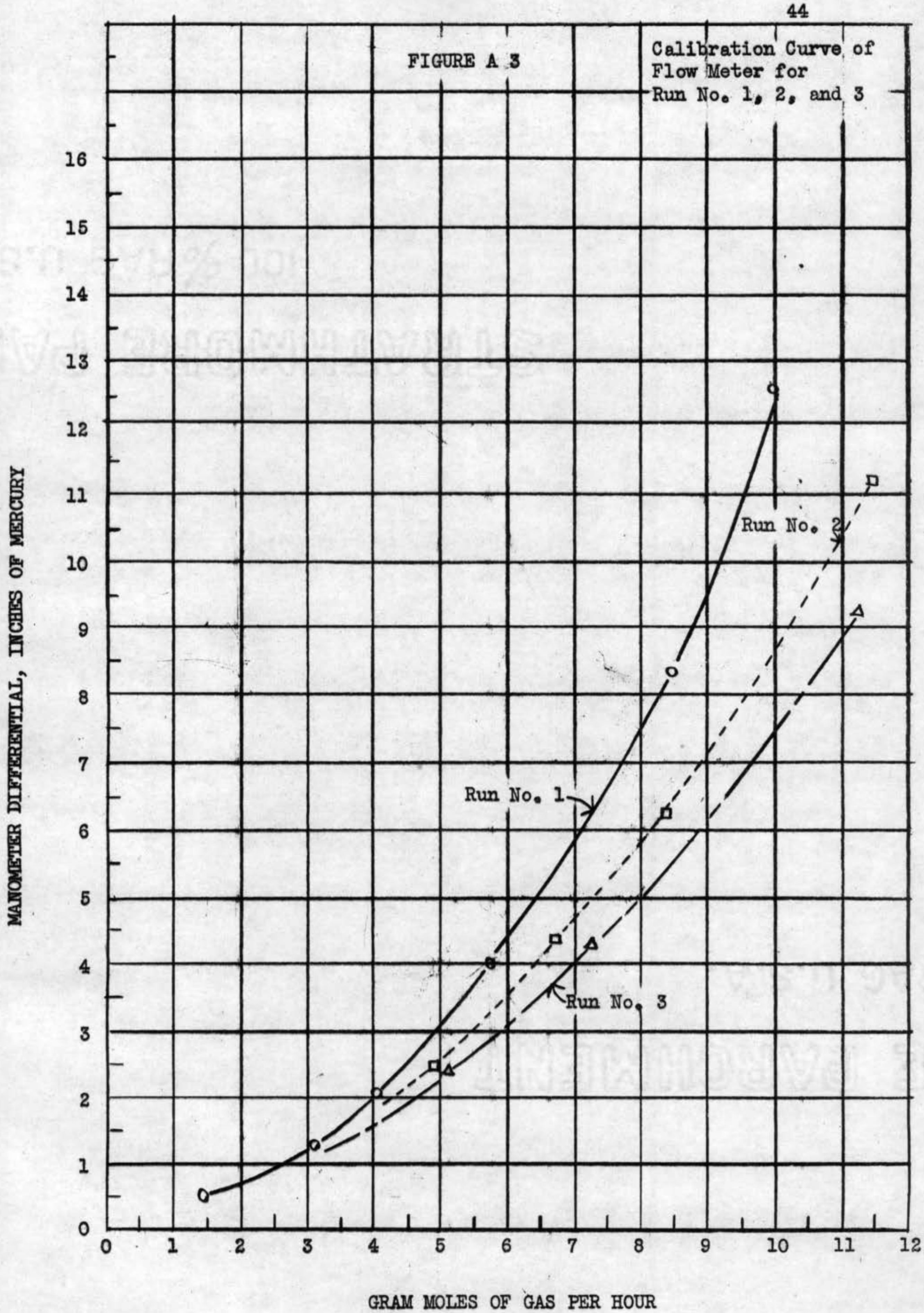


FIGURE A 3
Calibration Curve of
Flow Meter for
Run No. 1, 2, and 3
Run No. 1
Run No. 2
Run No. 3
MANOMETER DIFFERENTIAL, INCHES OF MERCURY
GRAM MOLES OF GAS PER HOUR
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16

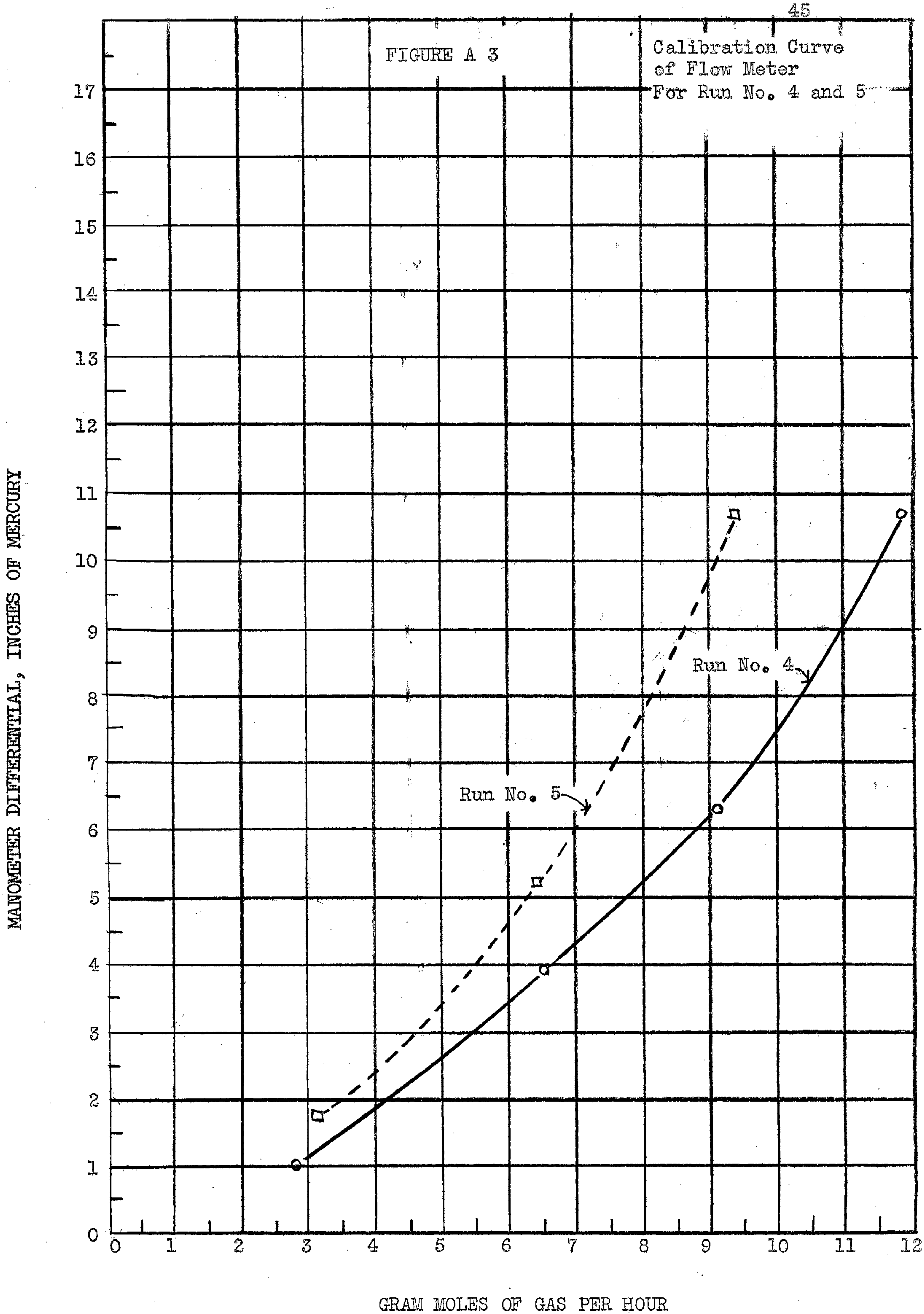


FIGURE A 3
Calibration Curve
of Flow Meter
For Run No. 4 and 5
Run No. 4
Run No. 5
MANOMETER DIFFERENTIAL, INCHES OF MERCURY
GRAM MOLES OF GAS PER HOUR
0
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17

TABLE IX

DATA FOR RUN II

θ	T_o	T_m	R_m	M_{ol}	M_{or}	M_{pl}	M_{pr}	Tc_{f2}	Tc_{r2}	V_b
7:30	83	90	10.700	13.25	16.25	19.9	20.4	Turned furnace on		45
7:40	83	90	11.440	13.30	16.20	19.9	20.4	Changed furnace		60
7:45	--	--	-----	---	---	--	--	560	370	60
				Changed furnace voltage to						80
7:50	83	90	12.200	13.25	16.25	19.75	20.60	815	545	80
7:55				Changed furnace voltage to						100
8:05	Turned pump on to maintain pressure									100
8:10	Attained fluidization by raising velocity and then lowering									
	it back to			13.25	16.25	19.8	20.5	1400	1240	100
8:15				Changed furnace voltage to						120
8:18	Flame began to turn orange (carbon from methane dissociation)									
								1660	1410	120
8:23	83	90	14.600	13.25	16.25	19.8	20.5	1770	1550	120
	Took sample number I between 1550° and 1570°.									
8:28	83	90	15.100	13.25	16.25	19.8	20.5		1640	110
	Took sample number II between 1640° and 1680°.									
8:34	83	90	15.600	13.25	16.25	19.8	20.5	1850	1700	110
	Took sample number III between 1700° and 1720°.									
8:40	83	90	16.380	13.25	16.25	19.8	20.5	1900	1750	110
	Took sample number IV between 1750° and 1755°.									
8:43	Pressure building up - velocity down.									
8:45	83	90	16.940	13.6	15.75	19.9	20.4	--	1790	110
	Took sample number V from 1790° to 1805°.*									
	Flame became colorless (From O_2).									
8:50	83	90	17.250	13.6	15.75	--	--	1970	1830	110
	Started taking sample number VI at 1830°.									
8:55	83	90	17.600	13.6	15.75	20.00	20.30	2100	1858	110
8:58	Flame started to take on orange color.									
9:05	83	90	-----	13.8	15.60	20.00	20.40	2190	1858	120
	Finished taking sample number VI at 1858°.									
9:08	Gas shut off		18.538	13.8	15.60	20.00	20.40	2190	1858	120

Charge - 200 grams of 1:1 $\frac{28-48}{48-65}$ mesh on Tyler Standard Screen.

* Samples V and VI taken while velocity was dropping.

TABLE X

DATA FOR RUN III

Charge - 200 g. of 1:1 $\frac{28-48}{48-65}$ mesh

Room Temperature - 80°F. Barometer - 743.8 mm Hg

θ	T_o	T_m	R_m	M_{ol}	M_{or}	M_{pl}	M_{pr}	Tc_{f2}	Tc_{r2}	V_b
2:30	76	82	22.934	15.9	18.0	19.90	19.75	Turned furnace on		45
2:40	76	82	23.456	15.9	18.0	19.90	19.70	350	152	45
2:50	77	83	24.047	15.9	18.0	20.00	19.70	672	362	65
2:57	Noticed leak in meter.									
3:00	77	83	24.572	16.1	17.8	20.00	19.70	1038	742	85
3:04	Painted meter leak - stopped it. (also change valve)									
3:10	77	83	25.592	16.0	18.0	20.25	19.45	1480	1318	110
3:26	Pump started - fluidization barely perceptible - changed to									115
3:30	77	83	26.198	16.0	18.0	20.20	19.45	1693	1560	
	Adjusted to good fluidization - took Sample No. I from 1560° to 1570°.									
3:40	77	83	26.848	15.9	18.25	20.00	19.45	1783	1670	110
	Took Sample No. II from 1670° to 1680°.									
3:50	77	84	27.692	15.95	18.15	20.25	19.45	1889	1700	110
	Took Sample No. III from 1700° to 1720°.									
	Took Sample No. IV from 1760° to 1780°.									110
4:00	77	84	28.500	16.00	18.00	---	---	----	1800	115
	Pressure drop started to act up at 4:01								1800	
	Took Sample V at 1800°.*									
4:04	77	84		16.25	17.75	20.00	19.30	Flame is colorless		
4:09	---	---	---	16.25	17.50	---	---	2060	1805	115
4:10	77	84	28.867	16.25	17.50	20.00	19.30	2082	1805	115
4:14	77	84	28.989	16.20	17.30	20.00	19.30	2125	1810	115
4:16	Sample No. VI from 1810° to 1820° - Sample off at 4:16*									
4:17	Gas off and switch off at meter reading - 29.049.									

Noticed fine blue powder in glass tees of sampling device.
Removed the thermocouple at about 1700°F.
No trouble encountered. Some metallic zinc formed on it. Also some blue-gray powder and some brown and gray solid matter stuck to the zinc.
Some solid carbon deposited just above the bed height.

20.8 grams of zinc and blue powder was recovered.

*Samples V and VI taken as flow decreases due to pressure built up in equipment

TABLE XI

DATA FOR RUN IV

Room Temperature - 84°F. Charge - 200 g. of 1:1 $\frac{28-48}{48-64}$ mesh Barometer - 742.2 mm Hg.

θ	T_o	T_m	R_m	M_{ol}	M_{or}	M_{pl}	M_{pr}	Tc_{f2}	Tc_{r2}	V_b
1:30	82	88	43.300	15.05	19.05	20.0	19.7	furnace turned on		45
1:40	82	88	44.376	15.05	19.05	20.0	19.7	428	222	45
1:50	82	88	45.272	15.05	19.05	20.0	19.7	842	511	70
	Evidence of fluidization.									
2:00	82	88	46.153	15.05	19.05	20.1	19.6	1178	861	90
2:10	82	88	47.047	15.05	19.05	20.3	19.3	1522	1238	110
2:20	82	88	47.981	15.05	19.05	20.45	19.25	1718	1461	115
	Flame turning orange - started pump.									
	Started collecting sample I at 1545° to 1575°.									
2:30	83	90	48.918	15.05	19.05	19.20	20.5	1840	1610	115
	Flame started to change to colorless - smoky core.									
2:36				15.05	19.05	19.30	20.30	--	1670	
	Took sample II from 1670° to 1710°. Pressure fluctuated and good fluidization started.									
2:40	83	90	49.980	15.05	19.05	19.30	20.30	--	--	-
	Flame changing rapidly to colorless.									
	Took sample III from 1732° to 1748°.									
2:45	83	90	50.610	15.05	19.05	19.50	20.25			
	Flame colorless - Took sample V at 1850°.									
2:50	83	90	50.935	15.05	19.05	19.60	20.10			
	Took sample VI at 1850° to ---									
	Something wrong with Reactor Thermocouple - reads 1200°.									
2:55	83	90	51.054	15.05	19.05	19.70	20.00	2091	1200?	
3:00	Sample 6 taken off. Meter - 51.137									
3:02	Flame absolutely colorless							2170 - still fluidizing		
3:04			Fluidization continued and pressure drop across bed was - -			19.70	20.00			
			when pressure became great enough to blow manometer connection.							
			Shut equipment down and removed thermocouple. No difficulty - no agglomeration - appearance the same as last time except for burned out place.							

TABLE XII

DATA FOR RUN V

Barometer - 739.88 mm Hg. Charge - 200 g. of 1:1 $\frac{28-48}{48-65}$ mesh Room Temperature - 86°F.

θ	T_o	T_m	R_m	M_{ol}	M_{or}	M_{pl}	M_{pr}	Tc_{f2}	Tc_{r2}	V_b
3:00	82	88	55.100	14.1	20.0	20.0	19.7	furnace on		45
3:10	82	88	56.622	14.1	20.0	20.0	19.7	250	230	45
3:20			57.380	14.1	20.0	20.1	19.5	405	405	60
	Found thermocouple trouble - inserted furnace couple the rest of the way and corrected.									
3:30	82	88	59.056	14.1	20.0	20.3	19.3	1102	764	90
3:33	Pump started.									
3:40	82	88	60.234	14.1	20.0	20.4	19.2	1244	998	90
3:50	82	90	61.412	14.1	20.0	20.55	19.05	1518	1292	110
3:53	Adjusted to fluidize - then back to 14.1 and 20.0									
	Pressure drop read					20.25	19.45	(Orange flame)		
4:00	82	90	62.678	14.1	20.0	20.25	19.45	1658	1470	110
4:06			63.448	14.1	20.0	20.25	19.45		1530	110
	Took Sample I from 1530° to 1550° F.									
4:09	84	90	63.752	14.1	20.0	20.25	19.45	--	--	-
4:10	84	90	64.118	14.1	20.0	20.25	19.45	1762	1592	110
4:13	Fluidizing fairly well - (Sample II from 1618° to 1642° F.)									
4:15	84	98	64.728	(Sample III from 1678° to 1682° F.)						
4:18	--	--	65.500							
4:22	--	--	65.800 to 66.044	Sample IV from 1708° to 1740° F.						
	The pressure drop and orifice readings remained constant for all the above at			14.1	20.0	20.25	19.45			
4:25	84	90	66.412	14.1	20.0	20.25	19.45	1911	1761	110
			66.950 to 67.200	Sample V from 1780° to 1800° F.						
4:30	Flame color finally changing from orange to colorless									120
			67.900	Sample VI from 1855° to 1860° F.						
			Pressure building up velocity down.							
			Furnace					2055		
4:39	Orifice manometer blew out.									
4:41	Switch off - gas off - pump off.									
			68.589							

Took thermocouple out of reactor at 4:42, temperature = 1878°.
No trouble with agglomeration. Appearance similar to Runs IV and III.

TABLE XIII

TYPICAL ANALYSIS OF NATURAL GAS

February 19, 1949

Analysis

1.	Volume of Sample - - - - - - - - -	98.30 ml.
2.	Volume after CO_2 absorbed - - -	98.20 ml.
3.	Volume after O_2 absorbed - - - -	97.40 ml.
4.	Volume after CO absorbed - - - -	97.2 ml.

Combustion

1.	Volume of O_2 - - - - - - - - - - -	85.60 ml.
2.	Volume of Sample - - - - - - - - -	31.50 ml.
3.	Volume after Combustion - - - -	54.50 ml.
4 (a)	Volume after CO_2 absorbed - -	22.7 ml.
(b)	Volume after CO_2 absorbed - -	22.6 ml.
(c)	Volume after CO_2 absorbed - -	22.6 ml.
5 (a)	Volume after O_2 absorbed - -	14.3 ml.
(b)	Volume after O_2 absorbed - -	13.9 ml.
(c)	Volume after O_2 absorbed - -	13.9 ml.
6.	Volume after CO absorbed - - - -	13.9 ml.

Analysis of Oxygen

1.	Volume of oxygen sample - - - -	42.70 ml.
2.	Volume after O_2 absorbed - - - -	4.80 ml.

CALCULATIONS FOR ANALYSIS OF NATURAL GAS

Volume of Sample = 98.30 ml.
Volume after CO_2 absorbed = 98.20 ml.

$98.30 - 98.20 = 0.10$ ml. CO_2

$\frac{0.10}{98.30} = 0.1\ \%\ CO_2$

Volume after CO_2 absorbed = 98.20 ml.
Volume after O_2 absorbed = 97.40 ml.

$98.20 - 97.40 = 0.80$ ml. O_2

$\frac{0.80}{98.30} = 0.8\ \%\ O_2$

Volume after O_2 absorbed = 97.40 ml.
Volume after CO absorbed = 97.20 ml.
0.20 ml. CO indicated

(It is improbable that any CO is present. The solution used to absorb CO also absorbs other gases, notably oxygen. However, the calculation is listed.)

$\frac{0.20}{98.30} = 0.2\ \%\ CO$

COMBUSTION CALCULATIONS

Volume of O_2 used = 85.60 ml.
Volume of Sample used = 31.50 ml.
Total volume = 117.10 ml.
Volume after combustion = 54.50 ml.

$117.10 - 54.50 = 62.60$ ml. reduction in volume

Volume after combustion = 54.50 ml.
Volume after CO_2 absorbed = 22.60 ml.

$54.50 - 22.60 = 31.9$ ml. CO_2 formed in combustion

If we start with Y ml. of gas whose carbon to hydrogen molal ratio is 1:x, we may represent the fuel by a formulae of CH_x.

This fuel will burn according to the following equation, if burned completely.

$$(Y)\ CH_x + Y\ (1 + \frac{x}{4})\ O_2 \longrightarrow Y\ CO_2 + Y\ \frac{x}{2}\ H_2O$$

The volume before combustion is:

$$Y + Y\ (1 + \frac{x}{4})\ \text{or}\ Y\ (2 + \frac{x}{4}).$$

The volume after combustion and after the water is condensed is Y (representing the CO_2).

Thus the reduction in volume is:

$$Y\ (2 + \frac{x}{4}) - Y \quad \text{or} \quad Y\ (1 + \frac{x}{4})$$

The volume of CO_2 formed is Y.

From the preceding calculations for this particular analysis:

The reduction in volume = 62.60 ml.

$$62.60 = Y\ (1 + \frac{x}{4})$$

The volume of CO_2 formed is 31.90 ml.

$$Y = 31.90\ \text{ml.}$$

So:

$$62.60 = 31.90\ (1 + \frac{x}{4})$$

Solving the above equation:

$$x = 3.82.$$

Note: From the five analysis of natural gas made, the average carbon to hydrogen ratio may be represented by the empirical formulae $CH_{3.88}$.

TABLE XIV

TYPICAL ANALYSIS OF REACTION GASES

Sample Bottle No. 4, Run 2.

Analysis

1.	Volume of Sample - - - - - - - - - - -	43.94 ml.
2 (a)	Volume after CO_2 absorbed - - - -	42.89 ml.
(b)	Volume after CO_2 absorbed - - - -	42.80 ml.
(c)	Volume after CO_2 absorbed - - - -	42.78 ml.
3 (a)	Volume after O_2 absorbed - - - -	41.18 ml.
(b)	Volume after O_2 absorbed - - - -	41.16 ml.
4 (a)	Volume after CO absorbed - - - -	38.68 ml.
(b)	Volume after CO absorbed - - - -	37.62 ml.
(c)	Volume after CO absorbed - - - -	35.92 ml.
(d)	Volume after CO absorbed - - - -	35.19 ml.
(e)	Volume after CO absorbed - - - -	35.00 ml.
(f)	Volume after CO absorbed - - - -	34.92 ml.
(g)	Volume after CO absorbed - - - -	34.90 ml.

Combustion

1.	Volume of oxygen - - - - - - - - - - -	59.37 ml.
2.	Volume of sample - - - - - - - - - - -	34.90 ml.
3.	Volume after combustion - - - - - - -	42.00 ml.
4 (a)	Volume after CO_2 absorbed - - - -	22.86 ml.
(b)	Volume after CO_2 absorbed - - - -	22.86 ml.
5 (a)	Volume after O_2 absorbed - - - -	17.28 ml.
(b)	Volume after O_2 absorbed - - - -	17.24 ml.
6.	Volume after CO absorbed - - - - - - -	17.16 ml.

Analysis of Oxygen
(From previous analysis)

1.	Volume of oxygen sample - - - - - - -	46.30 ml.
2.	Volume of CO_2 absorbed - - - - - - - -	46.00 ml.
3.	Volume after combustion - - - - - - -	46.00 ml.
4 (a)	Volume after O_2 absorbed - - - -	10.60 ml.
(b)	Volume after O_2 absorbed - - - -	10.60 ml.

CALCULATIONS FOR ANALYSIS OF REACTION GASES
(Reference Table XIV)

Volume of Sample	= 43.94 ml.	
Volume after CO_2 absorbed	= 42.78	
		1.16 ml. CO_2
Volume after O_2 absorbed	= 41.16	
		1.62 ml. O_2
Volume after CO absorbed	= 34.90	
		6.26 ml. CO

COMBUSTION CALCULATIONS

Volume of O_2 used	= 59.37 ml.	
Volume of Sample	= 34.90 ml.	
Combined Volume	= 94.27 ml.	
Volume after Combustion	= 42.00 ml.	
Reduction in Volume	=	52.27 ml.
Volume after CO_2 absorbed	= 22.86 ml.	
Volume CO_2 formed	=	19.14 ml.
Volume after O_2 absorbed	= 17.24 ml.	
Excess O_2	=	5.62 ml.
Volume after CO absorbed	= 17.16 ml.	
Volume CO formed	=	0.08 ml.

ANALYSIS OF OXYGEN

Volume of oxygen sample = 46.30 ml.
Volume of residual N_2 = 10.60 ml.

$$\% \text{ Nitrogen} = \frac{10.60 \times 100}{46.30} = 22.90 \% \ N_2$$

To solve for the carbon to hydrogen ratio:

Assume that for each Y mole of fuel ($CH_{3.88}$), there are X moles of hydrogen.

The complete combustion of the above mixture may be represented by the following equations:

$$Y\ CH_{3.88} + X\ H_2 + \left[Y + \frac{3.88Y}{4} + \frac{X}{2}\right]\ O_2 \longrightarrow YCO_2 + \frac{3.88Y}{2} + X\ H_2O$$

$$\text{or } Y\ CH_{3.88} + X\ H_2 + (1.97Y + 0.5X)O_2 \longrightarrow YCO_2 + (1.94Y + X)H_2O$$

The volume before combustion is:

$$Y + 1.97Y + X + 0.5X \quad \text{or} \quad 2.97Y + 1.5X$$

The volume after combustion and condensation is:

Y (for CO_2).

The reduction in volume is:

$$2.97Y + 1.5X - Y \quad \text{or} \quad 1.97Y + 1.5X.$$

The volume of CO_2 formed is Y.

From the analysis of gas
Reduction in volume = 52.27 ml.
Volume CO_2 formed = 19.14 ml. = Y

Using these values in the above expression:

$$1.97(19.14) + 1.5X = 52.27 \text{ ml.}$$

Solving for X:

$$X = \frac{52.27 - 37.70}{1.5} = \frac{14.57}{1.5} = 9.72 \text{ ml.}$$

The volume of fuel is then the same as the volume of CO_2 formed.

Volume of fuel = 19.14 ml.
Volume of hydrogen = 9.72 ml.

The remaining volume is nitrogen = 43.94 - 37.90 or 6.04.

Complete analysis:

$$CO_2 = \frac{1.16}{43.94} = 2.5\ \%$$

$$O_2 = \frac{1.62}{43.94} = 3.7\ \%$$

$$CO = \frac{6.26}{43.94} = 14.3\ \%$$

$$N_2 = \frac{6.04}{43.94} = 13.7\ \%$$

$$\text{Fuel} = \frac{19.14}{43.94} = 43.6\ \%$$

$$H_2 = \frac{9.72}{43.94} = \underline{22.2\ \%}$$

$$100.0\ \%$$

Solving for Per Cent Conversion:

Total carbon per 100 moles gas.

CO_2 + CO + fuel = Total

2.54 + 14.28 + 43.60 = 60.42

Carbon in Reaction Products = 2.54 + 14.28 = 16.82

$$\text{Per Cent Conversion} = \frac{16.82}{60.42} \times 100 = 27.8\ \%$$

Total Hydrogen present:

(3.88)(43.60) + 2(22.16) = 213.32

Hydrogen reaction product = 44.32

$$\text{Per Cent Conversion} = \frac{44.32}{213.32} = 20.8\ \%$$

TABLE XV

COOLING CURVE DATA

Melting Point of Lead = 621°F. Hoskins Pyrometer - Type AH

C. P. Lead Used Reads in Millivolts and °F.

Chromel-Alumel Couple No. 1				Chromel-Alumel Couple No. 2			
Reading	Time Sec.	Milli-volts	°F.	Reading	Time Sec.	Milli-volts	°F.
1	0	15.0	730	1	0	13.7	675
2	30	14.3	700	2	30	13.6	665
3	60	13.7	675	3	60	13.0	650
4	90	13.5	660	4	90	12.7	630
5	120	12.9	640	5	120	12.6	625
6	150	12.7	630	6	150	12.5	620
7	180	12.6	625	7	180	12.4	615
8	210	12.6	625	8	210	12.4	615
9	240	12.6	625	9	240	12.4	615
10	270	12.4	615	10	270	12.4	615
11	300	12.0	595	11	300	12.0	600
12	330	11.4	575	12	330	11.4	575
13	360	11.0	550	13	360	11.0	550
14	390	10.7	525	14	390	10.7	525
15	420	10.4	500				

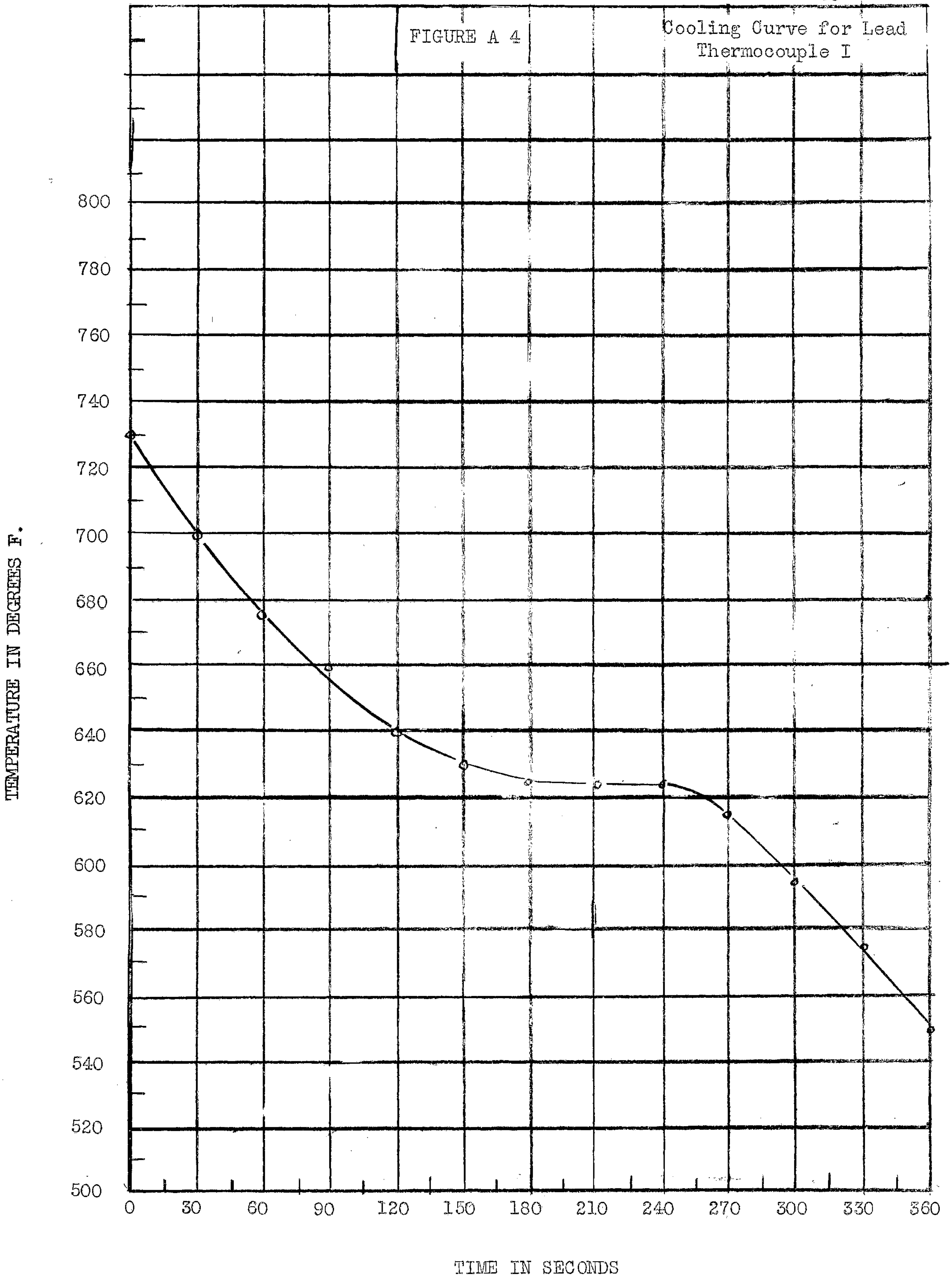


FIGURE A 4
Cooling Curve for Lead
Thermocouple I
TEMPERATURE IN DEGREES F.
800
780
760
740
720
700
680
660
640
620
600
580
560
540
520
500
0
30
60
90
120
150
180
210
240
270
300
330
360
TIME IN SECONDS

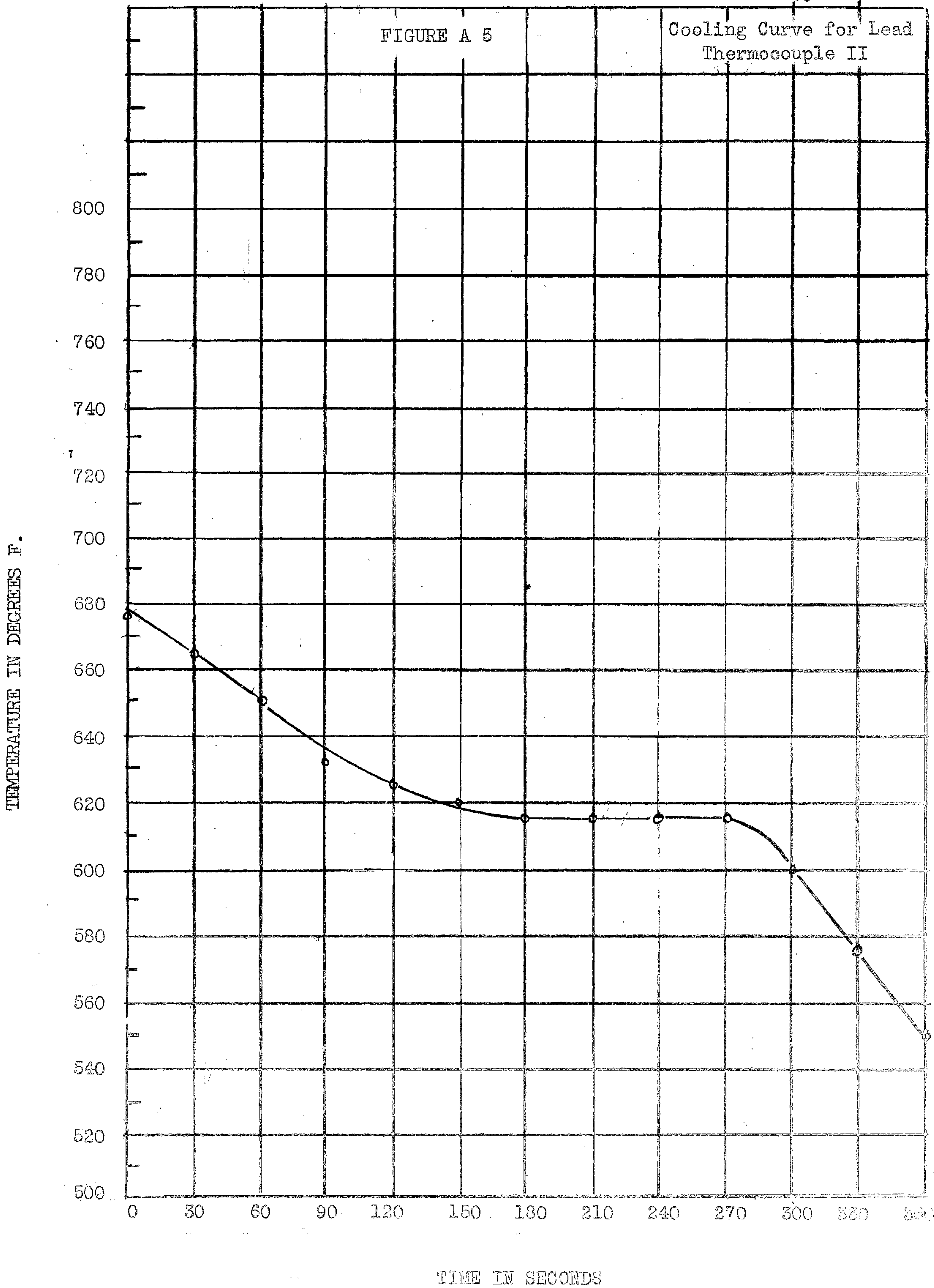


FIGURE A 5
Cooling Curve for Lead
Thermocouple II
TEMPERATURE IN DEGREES F.
800
780
760
740
720
700
680
660
640
620
600
580
560
540
520
500
0
30
60
90
120
150
180
210
240
270
300
TIME IN SECONDS

TABLE XVI

CALIBRATION OF METER

Meter - - - - American Meter Company, Serial No. 1010	
Standard 0.1 cu.ft. bottle - - American Meter Company Serial No. 119	
Temperature of Gas in Meter - - - - - - - - - - -	79°F.
Temperature of Bottle - - - - - - - - - - - - - -	79°F.
Gas Pressure in Meter - - - - - - less than 1/8" H_2O	
Initial Meter Reading - - - - - - - - - - - - -	68.000
Final Meter Reading - - - - - - - - - - - - - -	68.093
Revolutions per 0.1 cu.ft. - - - - - - - - - -	0.93
Correction Factor = 1.075 cu. ft./1 cu. ft. observed	

BIBLIOGRAPHY

BIBLIOGRAPHY

1. Bray, J. L., "Non-Ferrous Production Metallurgy", Second Edition, John Wiley & Sons, 1947.

2. Doerner, H. A., "Reduction of Zinc Oxide by Methane, or Natural Gas", Bureau of Mines Report of Investigation, No. 3091, 1931.

3. Doerner, H. A., "Reduction of Zinc Ores by Natural Gas", Bureau of Mines Report of Investigation No. 3256, 1934.

4. Fieldner, A. C., Jones, G. W., and Holbrook, W. F., "The Bureau of Mines Orsat Apparatus for Gas Analysis"., Bureau of Mines Technical Paper 320, 1925.

5. Leva, M., Grummer, Weintraub, and Pollchik, "Introduction to Fluidization", Chemical Engineering Progress, 44, 511, 1948.

6. Leva, M., Grummer, Weintraub, and Pollchik, "Fluidization of Non-Vesicular Particles", Chemical Engineering Progress, 44, 619, 1948.

7. Liddell, D. M., "Handbook of Non-Ferrous Metallurgy", Pyrometallurgy Section. (Section by W. R. Ingalls)

8. Maier, C. G., "Zinc Smelting from a Chemical and Thermodynamic Viewpoint", Bureau of Mines Bulletin 324, 1930.

9. Maier, C. G., and Ralston, O. C., "The Gaseous Reduction of Zinc", Transactions of the American Electrochemical Society, 51, 339, 1927.

10. Mickley, H. S. and Tribling, C. A., "Heat Transfer Characteristics of Fluidized Beds", Industrial & Engineering Chemistry, 41, 1135, 1949.

11. Millar, R. W., "The Rate of Reaction of Liquid and Gaseous Zinc with CO", Journal of American Chemical Society, 50, 2707, 1928.

12. Millar, R. W., "Condenser Materials and Blue Powder in Zinc Smelting", Mining & Metallurgy, 9, 395, 1928.

13. Minerals Yearbook, Bureau of Mines, 1946.

14. Najarian, H. K., "Weaton-Najarian Vacuum Condenser", Transactions of American Institute of Mining & Metallurgical Engineers, (Reduction and Refining of Non-Ferrous Metals Section), 159, 161, 1944.

15. Oldright, G. L., "Zinc Smelting in the Horizontal Retort", Bureau of Mines Report of Investigation No. 4335, 1948.

16. Rhodes, T. J., "Industrial Instruments for Measurement and Control", McGraw Hill Book Co., 1941.

17. Snuggs, J. F., "Fluid Catalyst Regenerator", Oil and Gas Journal, March 15, 1947, p. 91.

18. Steel Magazine, 125, No. 2, p. 135, July 11, 1949.

19. Wigton, H. H., "Carbonization of Oil-Shale Using a Fluidized Solids Technique" - Master of Science Thesis, Oklahoma Agricultural & Mechanical College, 1949.

Typist: Clara Smith