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DIRECT REDUCTION OF ZINC SULFIDE

UNDER VACUUM

by

MERRITT E. LANGSTON

A

THESIS

submitted to the faculty of the

SCHOOL OF MINES AND METALLURGY OF THE UNIVERSITY OF MISSOURI

in partial fulfillment of the work required for the

Degree of

MASTER OF SCIENCE IN METALLURGICAL ENGINEERING

Rolla, Missouri

1952

Approved by



Professor of Metallurgical Engineering

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Introduction

That the application of vacuum equipment and technique has gained a firm position in the field of science in general and in metallurgical engineering in particular is an unquestionable fact. Although its importance was recognized by a few investigators some years ago⁽¹⁾, it was

(1) Whitney, W. R., The Vacuum-There's Something in It, Smithsonian Institute Annual Report, pp. 192-206 (1924)

not until recently that much attention has been devoted to the study of high vacuum processes on an industrial scale. The Pidgeon process⁽²⁾

(2) Pidgeon, L. M., and Alexander, W. A., Thermal Production of Magnesium-Pilot Plant Studies on the Ferrosilicon Process, Trans. A.I.M.E., Vol. 159 (1944)

for the vacuum reduction of calcined dolomite by ferrosilicon to produce magnesium metal is a classic example of the birth out of necessity of a new metallurgical process during wartime when operational costs were considered secondary to the need for a large quantity of metal. It was found that magnesium could be reduced from its oxide by adding ferrosilicon and by heating under reduced pressure at elevated temperatures to cause metallic magnesium to vaporize and then condense in a retort. Further work in the field of vacuum metallurgy brought forth such processes as the preparation and reduction of lithium oxide to lithium metal by Kroll and Schlechten⁽³⁾, and the production of titanium by Kroll.

(3) Kroll, W. J., and Schlechten, A. W., Laboratory Preparation of Lithium Metal by Vacuum Metallurgy, A.I.M.E. T.P. 2179, Metals Tech., June, 1947

In regard to the metallurgy of zinc it has long been known that the ordinary zinc retort smelting practice has certain definite disadvantages⁽⁴⁾: (1) high heat loss and large fuel consumption; (2) high

(4) Brown, O. W., and Oesterle, W. F., The Electric Smelting of Zinc, Trans., Am. Electrochem. Soc., Vol. 8, pp. 171-182 (1905)

maintenance costs; (3) considerable loss of zinc (10% or more) through pores and cracks in the retort, through blue powder formation, and by the retention of zinc in the retort charge because of insufficient temperatures and the presence of sulfur; (4) limited retort capacity; (5) necessity of roasting and sintering the zinc concentrates; and (6) only pure ores are used because iron and calcium produce highly corrosive slags which corrode through the walls of the retort. With so many obvious disadvantages to the present distillation process, it is only natural that attempts have been made to perfect more suitable methods for the production of zinc by distillation and condensation. Earlier investigators turned their attention to direct methods of ore reduction in hope that the costly roasting and sintering operations might be eliminated. Their reports were none too encouraging as will be pointed out in the following review of previous literature. However, the work received renewed interest when it was found that by using reduced pressures an electrothermic reduction of zinc sulfide could be carried on at temperatures between 920 and 1000 degrees centigrade. Within this range of temperature the ratio of zinc sulfide vapor to zinc vapor in contact with iron was small, and the rate of exothermic reaction between zinc sulfide vapor and beta iron was sufficiently large.

The present work is a continuation of the previous investigations

of Gross and Warrington⁽⁵⁾ and Liu⁽⁶⁾ in which the effect of various re-

(5) Gross, P., and Warrington, M., The Reduction of Zinc Sulfide by Iron under Reduced Pressure, Trans. Faraday Soc., July, 1948

(6) Liu, T-2., Reduction of Zinc Sulfide, Thesis, Missouri School of Mines and Metallurgy, Rolla, Mo.

ducing agents on the vacuum reduction of zinc sulfide was studied. The author became interested in this topic while reading the papers by these investigators in which they recommended that further work be performed in an attempt to prevent zinc sulfide from distilling over during reduction, thereby contaminating the zinc condensate. The original plan was to perform a few runs for the purpose of duplicating the results that were reported by Liu, and from this point carry on the work using reducing agents other than iron. Soon after the work had been started, it was found that the results of Liu for the reduction of zinc sulfide could not be duplicated, particularly at the lower reaction temperatures; therefore, the previously reported results were cast aside and a considerable amount of work was performed for two purposes: (1) to determine the reasons for the lack of agreement, and (2) to investigate thoroughly several of the operational variables in order that this work might be given more justification for being acceptable than the previous work by Liu. In addition to using several other reducing agents at various reaction temperatures and for specified times at temperature, experiments were made to determine the effect, if any, of the crucible shape and the degree of charge compaction on the recovery of metallic zinc.

The latter phase of the work was concerned with an attempt to improve the zinc condensates that were produced in previous iron reduction runs by redistilling a carefully selected composite charge for various

times at certain temperatures. It shall be seen that certain reducing agents were very effective in reducing zinc sulfide directly to metallic zinc; however, a portion of the sulfur in the charge also distilled into the condensing region as zinc sulfide. Moreover, the majority of the condensates that were produced were extracted either as a loose powder or as thin brittle sheets. Sometimes a suitable metallic sheet was produced, but only if a high reaction temperature was used. Therefore, the purpose for redistilling the condensates as a composite charge was two-fold: (1) to improve the physical characteristics of the condensates by attempting to produce zinc as strong metallic sheets, and (2) to determine the extent of evaporation of sulfur as zinc sulfide from the composite and its effect on the purity of the resulting condensate.

Review of Previous Literature

The pyrometallurgical process for the production of zinc involves the reduction of zinc oxide by carbon at a temperature above the boiling point of zinc. During the reduction process zinc is volatilized in a retort and then caused to condense to a liquid in a pool at the bottom of a condenser. The condenser is emptied into drawing kettles, the zinc is then dumped into larger dressing kettles, and finally it is ladled by hand and cast into standard slabs. The shortcomings of the retort method for distilling zinc led several investigators to seek some other means for producing zinc. As early as 1907 Imbert⁽⁷⁾ patented a process for

(7) Imbert, A. M., Process for Treatment of Sulfide Ores by Precipitation by Means of Iron, German Pat. 2,323,295, August 1907

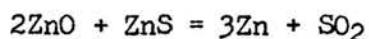
producing zinc directly from its sulfide ores by means of iron precipita-

tion. And in the United States two co-workers were granted a patent on an electric furnace which extracted zinc from its ores by a continuous process⁽⁸⁾. A proposal by Maier⁽⁹⁾ was to heat a mixture of zinc oxide

(8) Cote, E. P., and Pierron, P. R., Electric Furnace for the Continuous Extraction of Zinc from Its Ores, U. S. Pat. 944,774, December, 1909

(9) Maier, C. G., Zinc Smelting from a Chemical and Thermodynamic Viewpoint, U. S. Bureau of Mines Bull. 324 (1930)

and zinc sulfide in a manner analogous to copper matte converting according to the reaction



At low temperatures it was found that the free energy for the reaction was a large positive value, indicating that zinc must reduce SO_2 to ZnS and ZnO . At 727°C Maier found that the reaction was still to the left; that no appreciable amount of zinc vapor could exist in equilibrium with SO_2 . At 1227°C , the temperature for zinc retort smelting, the reaction proceeded to the right as written but to a very small degree and upon cooling in a condenser, the products reverted to ZnS and ZnO .

Another method that was investigated was the reduction of zinc sulfide by carbon. Gin⁽¹⁰⁾ stated that the reaction would proceed to the

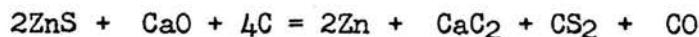
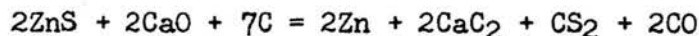
(10) Gin, Gustav, The Electrometallurgy of Zinc, Trans., Am. Electrochem. Soc., Vol. 12, pp. 118-139 (1907)

right at high temperatures, but that it was reversible as the temperature decreased.

Brown and Oesterle⁽¹¹⁾ described experiments on the electric smelt-

(11) Brown, O. W., and Oesterle, W. F., *op. cit.*, pp. 171-182

ing of zinc ore, lime and carbon according to the reactions



Their results showed a superior recovery of zinc when stoichiometric amounts were used instead of equal amounts of constituents. A lengthy description of the furnace used, its dimensions, materials, and construction, was presented but no specific data was given concerning the temperatures and times used for the reaction. Their original purpose was to produce pure CaC_2 and to distill zinc simultaneously, but because of certain impurities present in the ore, sulfur-free carbide could not be obtained. The reactions were proven to be possible in the laboratory but they remained untried on an industrial scale. In a similar experiment it was reported that zinc sulfide could not be reduced at high temperatures by silica and carbon.

Considerable work on unroasted zinc sulfide ores was presented in a paper by Peterson⁽¹²⁾ using an electric zinc furnace. In an initial ex-

(12) Peterson, P. E., The Electric Zinc Furnace, Trans., Am. Electrochem. Soc., Vol. 24, pp. 215-239 (1913)

periment a charge of zinc sulfide and iron was heated in a small electric furnace which had a single vertical electrode, no external openings, and no condensing unit. A 99.8 percent recovery of zinc as spelter encouraged the author to proceed further. By putting a condenser on the furnace and operating under the same conditions as before, only blue powder was obtained and no spelter. Using a larger furnace that had a vertical carbon electrode from the top and a horizontal iron electrode from the side near the bottom and a rectangular condensing chamber with a baffle arrangement,

Peterson was able to produce only blue powder as before. An unsuccessful attempt to tap the furnace resulted in the withdrawal of a matte containing 1.3 percent zinc and a slag of 0.4 percent zinc. Finally, a fourth experiment was made using the larger furnace and a circular iron pipe for the condensing unit. Two different charges were tried: a zinc sulfide concentrate, lime, and coke charge gave a 50 percent zinc recovery; a zinc sulfide and scrap iron charge gave a 90 percent recovery. In both cases mention was made of the formation of a matte and a slag within the furnace.

Gin summarized the results of previous experiments in which iron was used as the reducing agent by saying that the reaction temperature was too high to be utilized in a closed container; moreover, he stated that it seemed impossible to obtain intimate contact between the ore and the iron particles.

Parravano and Agostini⁽¹³⁾ investigated the reduction of various

(13) Parrovano, N., and Agostini, P., The Reduction of Metallic Sulfides by Means of Aluminum, Florence Gezz, Chim ital., Vol. 49, I, pp. 103-105 (1919)

sulfides by aluminum at atmospheric pressure. A known amount of aluminum in a clay crucible was brought to its fusion temperature. The sulfide was added and the temperature was slowly raised to maintain the mixture in fusion, and the entire operation was performed in an atmosphere of some inert gas. Their findings showed that the sulfides of lead, copper, tin, cadmium, zinc, antimony, silver, bismuth, nickel, and cobalt reacted to a large extent and some completely with aluminum. The authors stated that in the case of PbS, CuS, SnS, Ag₂S, and Bi₂S₃ the amount of metal obtained was approximately the theoretical. For CdS and ZnS the

amount of metal was considerably less than the theoretical due to the volatility of zinc and cadmium. NiS and CoS gave a lesser amount due to an extremely high reaction velocity that caused a large part of the charge to be projected out of the reaction container.

Up to this point all of the previous work had been performed at atmospheric pressure. Within the past ten years the direct reduction of zinc sulfide has been given renewed attention chiefly because of the development of vacuum equipment which permits the reduction to occur at pressures considerably below atmospheric and also because of the increased application of the concepts of free energy to metallurgical reactions. In 1946 Gross and Prytherch⁽¹⁴⁾ patented a process for the

(14) Gross, P., and Prytherch, W. E., Zinc, Brit. Pat. 575,336, February 13, 1946.

vacuum reduction of zinc sulfide by iron. In short, the process involves heating zinc sulfide or zinc sulfide ore, preferably under sub-normal pressure, to above the volatilization temperature of the zinc sulfide material and passing the vapor over iron turnings maintained at a temperature of about 950°C, thereby forming zinc vapor which is condensed to metallic zinc.

Another patent that was issued to Parry⁽¹⁵⁾ in 1950 described an

(15) Parry, V. F., Recovery of Metals, U. S. Pat. 2,497,096, February 14, 1950

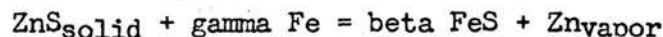
apparatus for the recovery of such metals as mercury, magnesium, and zinc from their ores by endothermic chemical reactions. The ore is passed down through an externally-heated elongated reaction zone, and the spent ore is removed at the bottom of this section. The gases formed

during the reaction are drawn off from the center of the reaction vessel and are passed up through a heat-exchanger zone which is located within the reaction chamber. Then the gases are passed downward through a condenser that is within the heat-exchanger zone. The metallic vapors are cooled and the metal is recovered at the bottom of the condenser. Unfortunately, no information could be found giving specific operational data such as temperature, time, and efficiency.

The recent work by Gross and Warrington⁽¹⁶⁾ is one of the first ar-

(16) Gross, P., and Warrington, M., op. cit.

ticles published which presents an analytical description of the reduction of solid zinc sulfide by gamma iron under a vacuum according to the equation



They stated that the above reaction will go to completion at reduced pressures and at a temperature below that of the ZnS-FeS eutectic because the reaction system becomes nonvariant. The procedure involved heating small cylindrical briquettes composed of zinc sulfide and iron in a vacuum resistance furnace to temperatures ranging from 920 to 1000°C. Furthermore, they stated that thermodynamic data show that the ratio of zinc sulfide vapor to zinc vapor in contact with iron is small in the range of temperatures used, and that the rate of exothermic reaction between zinc sulfide vapor and beta iron is sufficiently high.

A slight disagreement exists between various workers in regard to the thermodynamic equations and data for the reduction of zinc sulfide by iron under reduced pressures. Two equations exist for the free energy of the reaction:

- (1) $G^\circ = 48,500 - 34.50T$ (Kelley)⁽¹⁷⁾
 (2) $G^\circ = 55,000 - 34.50T$ (Gross and Warrington)

(17) Kelley, K. K., Contributions to the Data on Theoretical Metallurgy, VII, The Thermodynamic Properties of Sulfur and Its Inorganic Compounds, U. S. Bureau of Mines Bull. 406, pp. 137-146 (1937)

Table I shows the variations in the data which result from the use of these two equations in calculating the temperatures which correspond to certain vapor pressures of zinc and the vapor pressures of zinc sulfide using Veselowski's equation.

TABLE I

Calculated Vapor Pressures of Zinc Sulfide and
Temperatures for Various Vapor Pressures of Zinc

| PZn mm Hg | Equation (1) or (2) | Temperature | | PZnS equation | PZnS data |
|--------------|------------------------|-------------|------|----------------------|----------------------|
| | | °K | °C | | |
| 1 | 1 | 1018 | 745 | 3.5×10^{-5} | 5.0×10^{-4} |
| | 2 | 1150 | 877 | 1.4×10^{-3} | 9.6×10^{-3} |
| 10 | 1 | 1125 | 852 | 9.5×10^{-4} | 8.3×10^{-1} |
| | 2 | 1275 | 1000 | 2.0×10^{-2} | 2.0×10^{-1} |
| 100 | 1 | 1260 | 987 | 2.0×10^{-2} | 1.6×10^{-1} |
| | 2 | 1430 | 1157 | 4.5×10^{-1} | ----- |

The temperatures above were calculated by relating the term $RT \ln p_{Zn}$ to equation (1) or (2), substituting values of p_{Zn} , and solving for T in °K. The last two columns show the lack of agreement between Veselowski's equation and his actual data. His equation states that

$$\log P_{ZnS}(\text{mm}) = - \frac{14,200}{T} + 9.495$$

In order that the equation be made to fit his actual observations, the equation should read as follows

$$\log P_{ZnS}(\text{mm}) = - \frac{14,200}{T} + 10.495$$

The importance of the consideration of the partial pressure of zinc

sulfide is seen by the preceding table. At relatively low temperatures, say, 745°C, the partial pressures of zinc sulfide and zinc are very small. As the temperature increases there is an increase in the quantity of zinc metal distilled and in the amount of zinc sulfide which vaporizes. This increase in the loss of zinc sulfide by sublimation from the charge results in a contamination of the total zinc distilled by sulfur.

The latter part of the paper by Gross and Warrington dealt with the rate of the reaction. If the rate of evaporation exceeds the rate of reaction, then the effect of zinc sulfide must be considered. The equilibrium constant K is a measure of the amount of zinc sulfide left in the charge after the system comes to equilibrium.

Additional information regarding the free energy change and the reducibility of sulfides and oxides was found in the papers by Osborn⁽¹⁸⁾, Ellingham⁽¹⁹⁾, and Dannatt⁽²⁰⁾. The variation of the standard free ener-

(18) Osborn, C. J., The Graphical Representation of Metallurgical Equilibria, Journal of Metals, Trans., A.I.M.E., Vol. 188, March, 1950

(19) Ellingham, H. J. T., Reducibility of Oxides and Sulfides in Metallurgical Processes, J. Soc. Chem. Ind., pp. 125-133, May, 1949

(20) Dannatt, C. W., and Ellingham, H. J. T., Roasting and Reduction Processes, Trans. Faraday Soc., No. 4, England, (1948)

gy with temperature are presented graphically and correction curves are provided for pressures other than the standard pressure. The task of determining the feasibility of a proposed metallurgical reaction is greatly simplified by using these graphs and then correcting for pressure.

A limited amount of information was found on the vapor pressure of pure zinc. Table II shows the variation in the boiling point of pure

zinc with pressure. (21)

(21) Vapor Pressure of Pure Substances, Ind. Eng. Chem., Vol. 39, No. 4 (1947)

TABLE II

Variation in Vaporization Temperature
of Zinc with Pressure

| | | | | | | | | | | |
|-------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| Pressure mm Hg | 1 | 5 | 10 | 20 | 40 | 60 | 100 | 200 | 400 | 760 |
| Temp. °C | 487 | 558 | 593 | 632 | 673 | 700 | 736 | 788 | 844 | 907 |

St. Clair and Spendlove⁽²²⁾ recently published their results on the

(22) St. Clair, H. W., and Spendlove, M. J., Rate of Evaporation of Zinc at Low Pressure, U. S. Bureau of Mines R. I. 4710, June, 1950

rate of evaporation of zinc under reduced pressures, and in their summary they stated that the maximum rate of evaporation of molten zinc is given by the equation

$$W_0 = \frac{28.30 P_0}{\sqrt{T}}$$

where W_0 equals the maximum rate of evaporation, P_0 is the vapor pressure of zinc and T is the absolute temperature. It was observed that the rate of evaporation was always less than the maximum rate, the difference depending largely upon the pressure of the residual gases in contact with the metal. At temperatures below the boiling point (907°C), the evaporation rate was slow, but under reduced pressure (less than 1 mm Hg) rapid distillation took place at 500°C.

In commenting on the appearance of the condensed metal they stated that at low rates of evaporation or at relatively high pressures, the condensate was a loosely compacted dendritic crystal, suggesting direct

condensation from the vapor to the solid state. At higher evaporation rates the condensate was more dense and had smooth rounded surfaces, suggesting a vapor to liquid to solid change during condensation.

EXPERIMENTAL WORKI. Apparatus and EquipmentA. List of Apparatus and Equipment

The list that follows includes the apparatus and equipment used in performing the experimental work. For certain pieces of equipment listed below a detailed discussion is to follow, including principles of operation, photographs, schematic drawings, and cut-away views, all of which aid in the understanding of their integral role in the overall arrangement of the equipment.

Mechanical Pump, Welsh Duo-Seal type, 330 rpm, ultimate vacuum-0.02 microns Hg.

Motor, General Electric Co., 110/220 v., a.c., 5/25 amp., 1/3 HP, 1725 rpm, 60 cycle, single phase.

Metal Diffusion Pump, Distillation Products Inc., Type MC-275, 200 gms. (193 cc.) butyl phthalate, forepressure-0.100 mm Hg, heater current-3.50 amp., heater voltage-115 v., speed-275 liters per sec., ultimate vacuum-0.005 microns Hg.

Variable Transformer, Powerstat (or Variac), Superior Electric Co., type 1256, input-110/220 v., 50/60 cycle, single phase; output-0 to 270 v., 26 amp., 7.5 kva.

Ammeter, Triplett Instrument Co., model 337 S C, 0 to 50 amp.

Furnace, Porcelain Tube, McDanel Porcelain Co., 40 inches in length, 2 and one-eighth inches inside diameter.

Furnace Heating Element, resistance-type using Smith No. 10 alloy wire wound on an alundum core, encased in magnesia cement, packed in silica brick, and surrounded in a steel case 11 inches outside diameter and 18 inches high. Maximum temperature-1300°C.

Water Cooling Coils, copper tubing, for diffusion pump and furnace joint.

Metal Cap, ground to fine finish, for sealing lower opening of furnace.

Thermocouples, C/A, provided with 10 feet of compensated lead wire to Wheelco Millivoltmeter Pyrometer and Brown Potentiometer.

Vacuum Release Valve, rubber stopper.

Millivoltmeter Pyrometer Controller, Wheelco Instrument Co., C/A

thermocouples, 110 v., 0 to 1000°C, 1.51 external resistance.

Potentiometer Recorder, Brown Instrument Co., C/A thermocouple, 110 v., 60 cycle, single phase, 0 to 1600°C.

Clock, Tork Clock Co., Inc., a.c. only, single pole, 115 v., 60 cycle, 24-hour face plate, 20 amp. at 115 v. or 10 amp. at 250 v.

Switch, C-H Co., single pole, single throw, 1 1/2 Hp, a.c.-d.c., 125-250 v., 10 amp. at 250 v., 15 amp. at 125 v., for mechanical and diffusion pumps.

Switch, C-H Co., single pole, double throw, 3/4 HP, 115/230 v., a.c., 10 amp. at 230 v., 15 amp. at 115 v., for clock and pyrometer.

De-Ion Line Starter, Westinghouse Electric Co., mechanical style, single or polyphase, 1 to 5 HP, 110 to 600 v.

Switch, Safety, Westinghouse Electric Co., single or polyphase, 30 amp. capacity, 230/25° v., a.c.

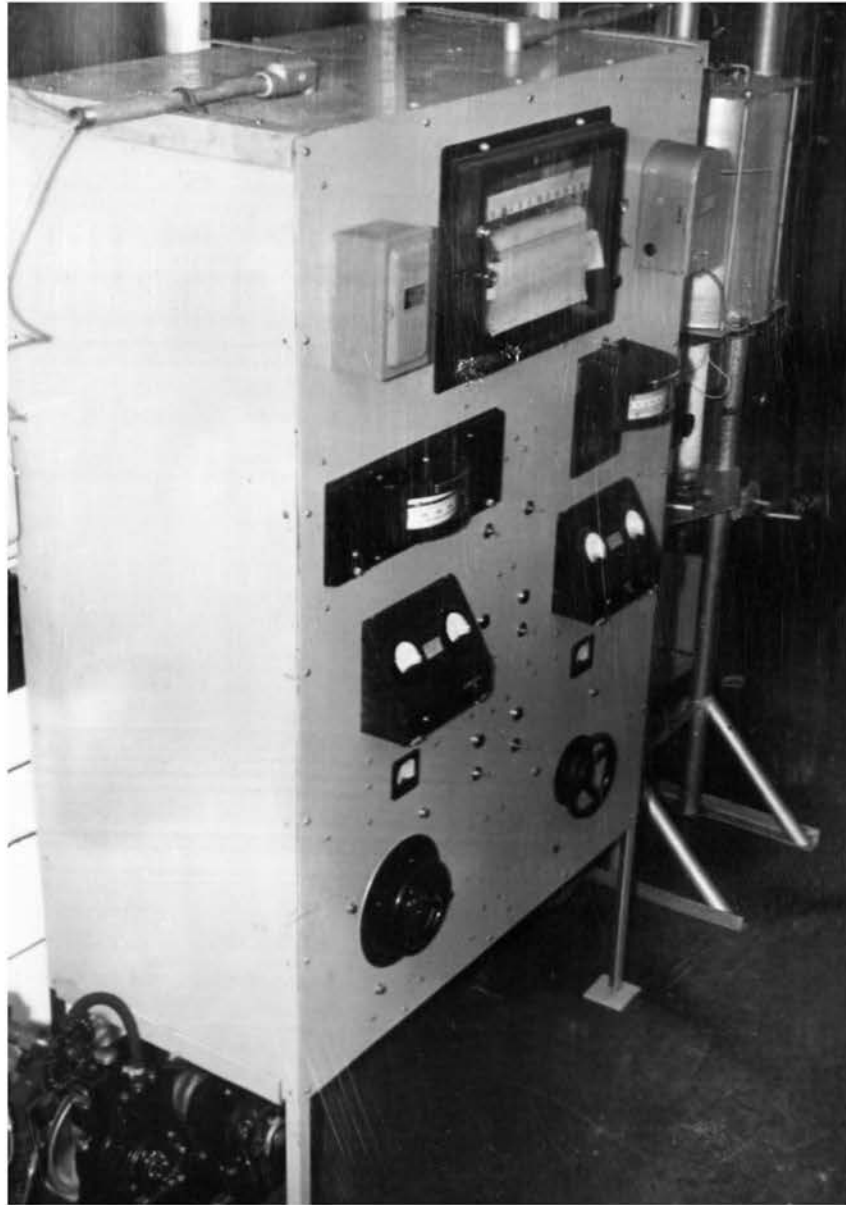
Pirani Tube, Distillation Products, Inc., for pressure measurement below the vacuum valve.

Pirani Gauge, Distillation Products, Inc., type PG-1A, voltage input-115 v. a.c., bridge voltage-3 v. a.c., scale no. 1 - 0 to 20 microns, scale no. 2 - 0 to 0.75 mm Hg.



GENERAL ARRANGEMENT OF APPARATUS AND EQUIPMENT

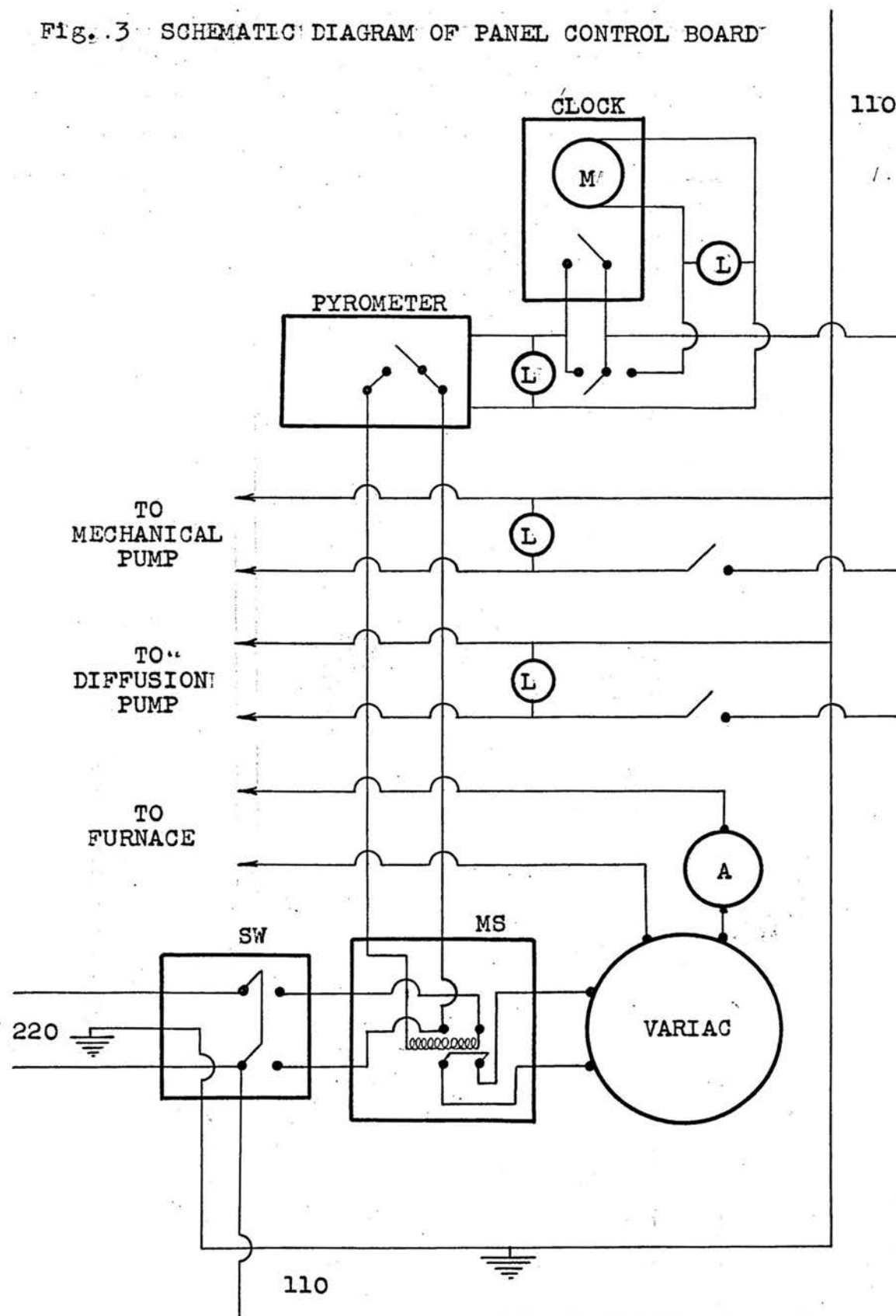
Figure 1



PANEL CONTROL BOARD

Figure 2

Fig. 3 SCHEMATIC DIAGRAM OF PANEL CONTROL BOARD



B. Electrical Resistance Furnace

The electrical resistance furnace used in the experimental work is shown in sectional view in Figure 4. A porcelain tube approximately 40 inches in length and $2 \frac{1}{8}$ inches inside diameter is supported vertically by a metal head, which, in turn, is fastened to a steel plate held in place by three vertical pipes. Figure 5 shows the junction of the porcelain tube and the metal head. The junction is kept cool by circulating water through coils to prevent the vacuum sealing wax from melting. Near the bottom of the metal head there is a side opening through which vacuum connections are made between the furnace and the diffusion pump. The lower end of the metal head is tapered slightly to fit a ground metal cap, which, when removed, provides the means for introducing the sample to the furnace.

Figure 4 shows that only the upper portion, or approximately 12 inches of the porcelain tube, is surrounded by the heating element. Heat is applied by passing a current through the Smith No. 10 resistance wire which is wound on an alundum core, covered with magnesia cement, and packed in crushed silica brick. The use of Smith No. 10 wire limits the temperature to a maximum of 1300°C , but this was of little importance because no runs were made in excess of 1000°C .

Graphite tubing was used within the porcelain tube for three purposes: (1) to support the crucible containing the charge at a level within the zone of heating, (2) to provide a surface for the condensation of any volatile material, and (3) to provide an inert surface that would not alloy with zinc during condensation. The

Fig. 4 ELECTRICAL RESISTANCE FURNACE

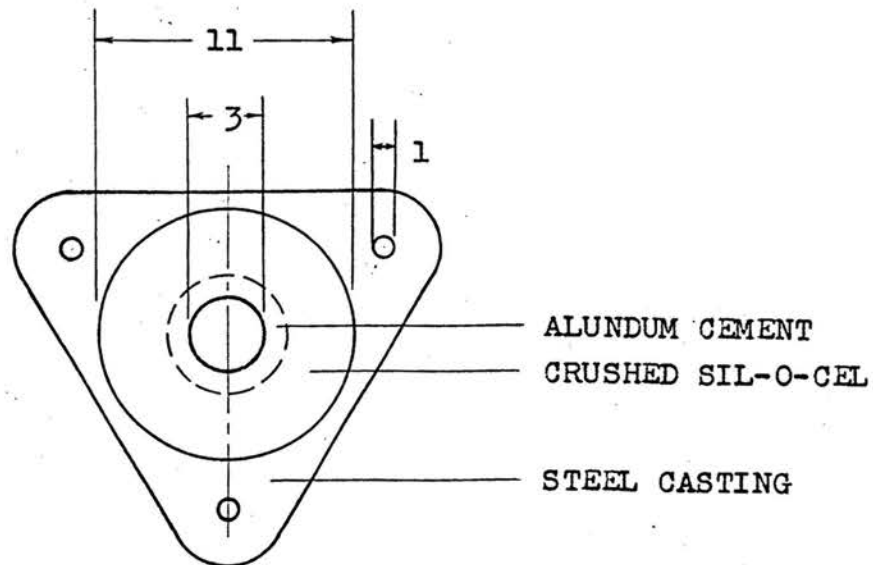
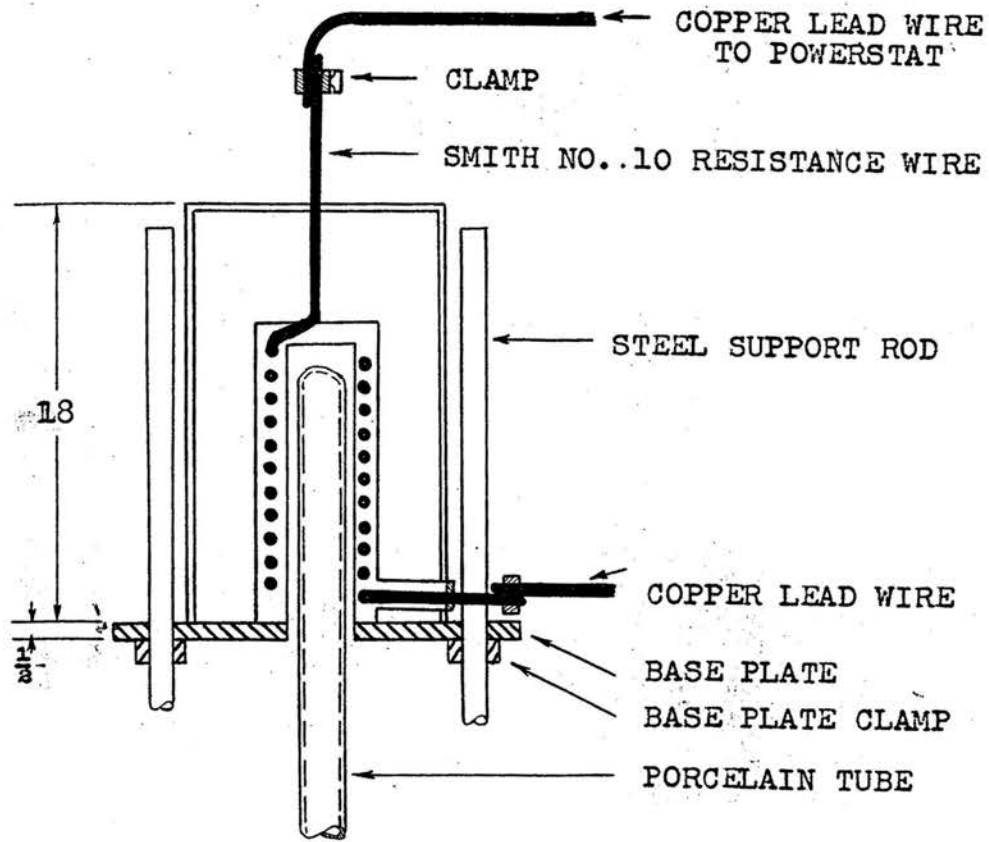
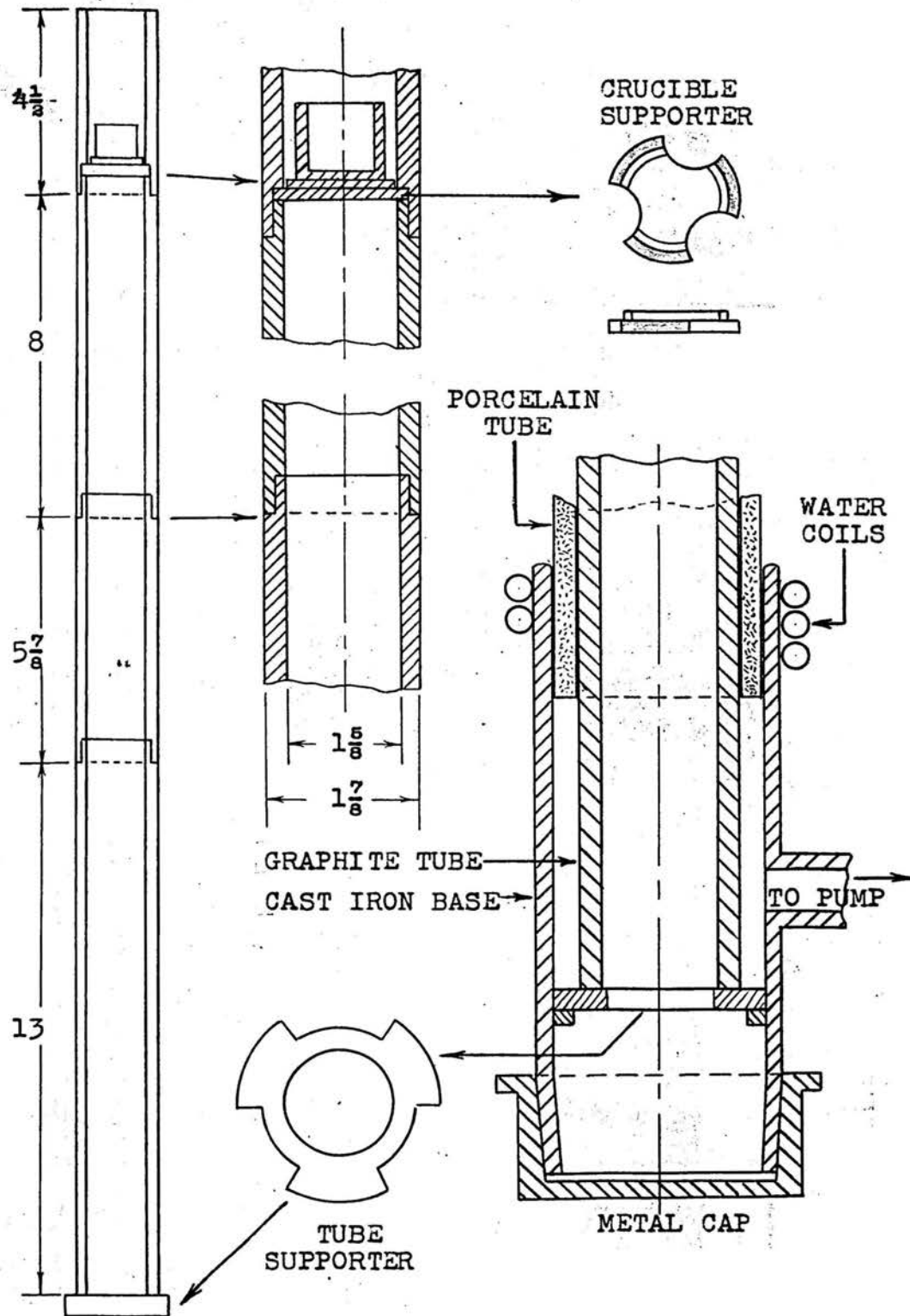


Fig. 5 GRAPHITE TUBE ARRANGEMENT



sectioned graphite tube, its accessories, and their general arrangement in the furnace are shown in Figure 5.

C. Metal Diffusion Pump

The metal diffusion pump shown diagrammatically in Figure 6 is relatively simple in construction and both fast and efficient in operation. A vertical metal cylinder is provided with two openings, one of which is connected to the forepump and the other to the furnace. By applying heat through a coil at the bottom of the cylinder the oil is caused to vaporize. The vapor passes upward through a chimney and is deflected by jets and is thus directed downward and outward against the water-cooled walls of the cylinder. In its downward movement the vapor entraps molecules of gases and causes them to be directed toward the outlet where the forepump continues the exhaustion. After striking the cold wall the vapor condenses to a liquid which flows downward to the boiler where it is once more vaporized by the heating coil.

Type MC-275 is a two-stage semi-fractionating metal diffusion pump and operates only when the forepressure is below 100 microns. The pump is equipped with a coil around the boiler to cool the oil before exposing it to the atmosphere; however, the schedule used during the experiment did not necessitate its use. Moreover, the manufacturer recommends the use of a Type WB-8 Water-Cooled Baffle between the diffusion pump and the chamber being evacuated, but this was left off because it was believed it would only introduce another potential source for leaks. Such a baffle is generally employed in a system to inhibit the direct flight of scattered oil vapor molecules into the furnace which results in an oil loss and a vacuum

contamination. Finally, a water-cooled trap on the side arm of the pump makes the diffusion pump semi-fractionating by preventing the diffusion of oil vapor into the forepump.

D. Mechanical Pump

A diagrammatic sketch of the Welsh-Type Duo-Seal mechanical pump is shown in Figure 7. This pump contains a rotor that is mounted eccentrically with reference to a stator and is equipped with two metal vanes which move in and out of their slots during the revolution of the rotor. The vanes maintain constant contact with the inner walls of the stator and in this manner cause a crescent-shaped air space to be swept out twice during each revolution. A thin seal of oil separated the inlet and outlet ports. Gas molecules from the diffusion pump enter through the inlet port, pass between the rotor and stator, and are ejected to the atmosphere through the outlet port as shown in Figure 7.

E. Pressure Measurement - The Pirani Gauge

Pressure measurement is made by use of the Pirani gauge which provides a simple and convenient method for measuring vacuums directly and continuously within a range from 0 to 750 microns of mercury. The operation of this gauge is based upon the principles that the conductivity of a gas is proportional to its pressure, that the filament temperature is proportional to the gas conductance, and that the resistance of the filament is proportional to its temperature. Conductivity is measured in an indirect method by determining the change in resistance of a hot filament with pressure. A change in the pressure on the filament causes a variation in the rate of heat conductance away from the filament, which, in turn,

Fig. 6 OIL DIFFUSION PUMP

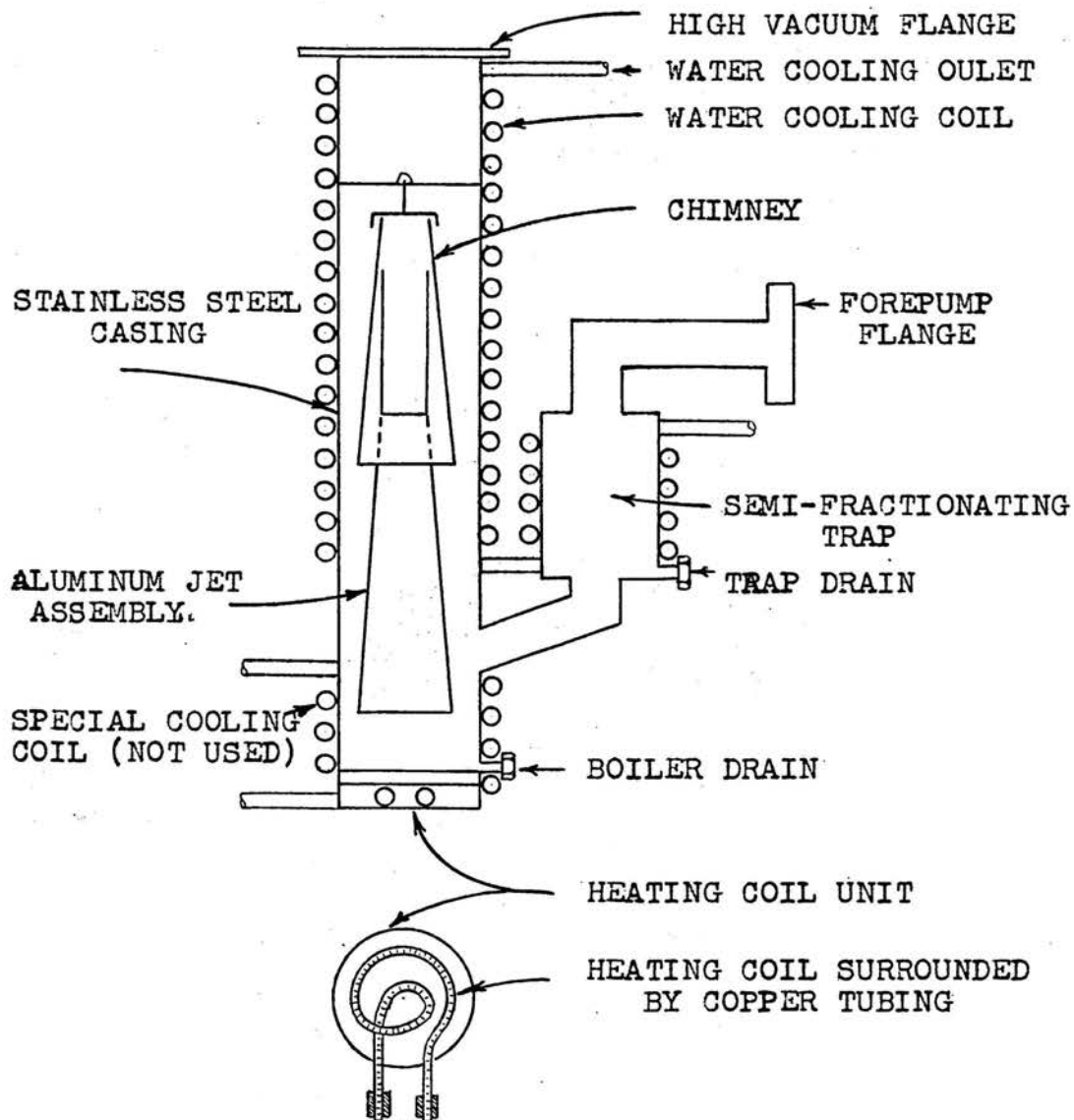


Fig. 7 WELSH DUO-SEAL MECHANICAL PUMP

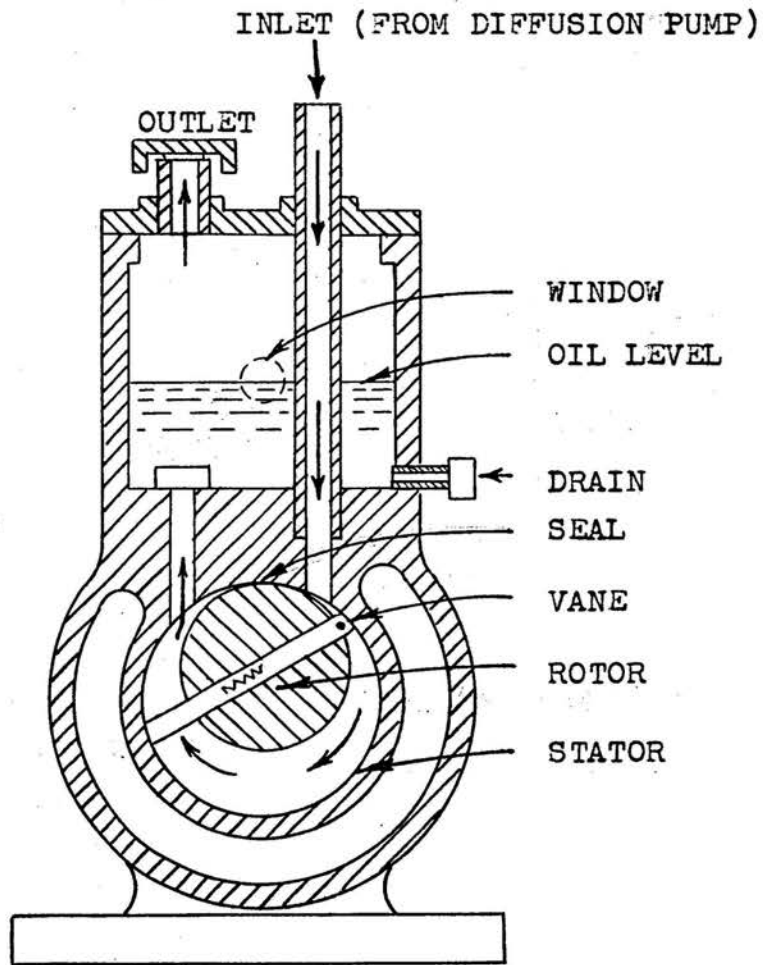


Fig. 8 PIRANI GAUGE - PRESSURE INDICATOR

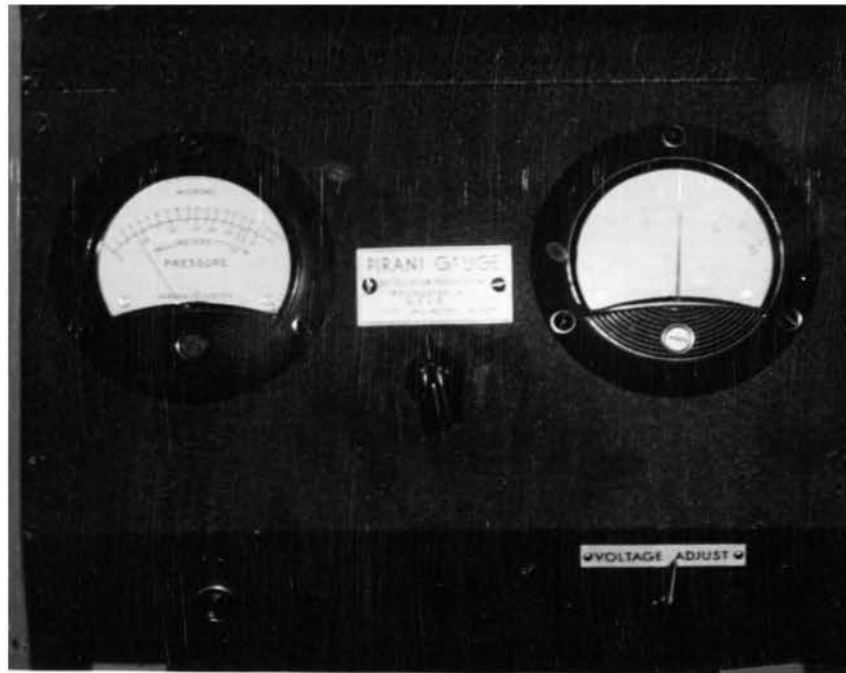
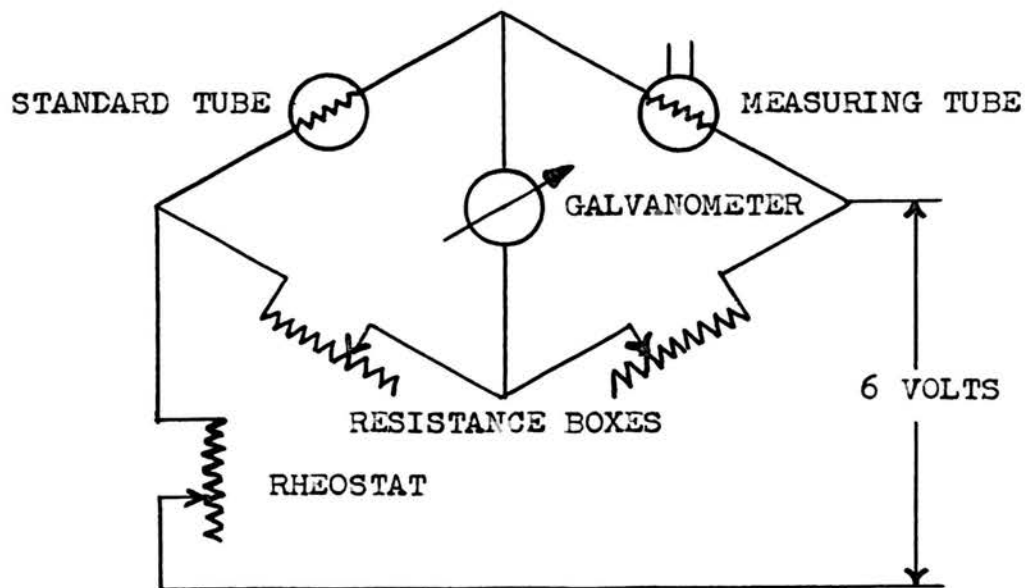


Fig. 9 PIRANI GAUGE - SCHEMATIC DIAGRAM



causes a change in the temperature and the resistance of the filament. To measure the resistance change a Wheatstone bridge arrangement is used as shown in Figure 9. Two filaments are used as shown, one being a standard filament enclosed in a glass bulb which has been evacuated to a very low pressure and sealed off, and the other filament having the same enclosure but with one end open through which a connection is made to the system being evacuated. The filament is heated at constant temperature by keeping the voltage at three volts as read on the D. C. Voltmeter, Figure 8. If the Wheatstone bridge is in balance at this filament temperature, a change in the thermal conductivity of the residual gases will cause the bridge to become unbalanced. In this manner the deflection of the bridge galvanometer measures the pressure of the residual gases in the system directly and continuously. The gauge has two scales from which the pressure may be read: scale No. 1 ranges from 0 to 20 microns, scale No. 2 from 0 to 0.75 mm Hg.

Pressure measurements are made at a point directly below the vacuum valve that is located just above the diffusion pump. Measuring from this point proved to be effective in determining rapidly whether a leak was above or below the valve, thus simplifying the maintenance of the equipment. The minimum pressure obtainable was not controllable in this apparatus; it was entirely dependent upon the efficiency of pumping on one hand as counteracted by the existence of leaks on the other.

F. Temperature Measurement, Control, and Recording

Temperature measurement was made by using a chromel-alumel thermocouple which was attached to the outer wall of the porcelain

tube and whose hot junction was located at a level corresponding to the midpoint of the crucible held within the furnace. To this thermocouple was connected 10 feet of compensating lead wire which led to the Wheelco indicating pyrometer. Temperature control was maintained by the pyrometer which contained an electronic tube whose function was to make or break the circuit of the De-Ion line starter as required. The general arrangement of the furnace, powerstat, and line starter is presented diagrammatically in Figure 3.

Although it was never used as such, a Brown potentiometer was available to record temperature-time readings. Instead, the potentiometer was employed to act as a second source of temperature measurement to check the readings given by the Wheelco pyrometer. A second c/a thermocouple was attached to the porcelain tube about an inch below the first and temperature readings were taken periodically on the potentiometer. At times the potentiometer lagged the pyrometer by as much as 50°C during heating to the reaction temperature, but generally the range of deviation between the two instruments was from 5 to 25°C after the reaction temperature was reached. The potentiometer always gave the lower reading. To avoid an error the temperature of the Wheelco pyrometer was always taken as the reference value because this instrument was the controlling device in the experiment.

G. Rate of Heating

The rate of heating of the furnace was regulated by setting the powerstat, or variac, at such a position as to cause a preselected amperage to pass through the resistance wire, the exact amperage being read on the a.c. ammeter. At a powerstat setting of about 15

the furnace was supplied with 10 amps., resulting in a heating rate of 3 to 4 degrees per minute. 20 amps. at a setting of about 38 gave a heating rate from 15 to 20 degrees per minute. After reaching the reaction temperature, the powerstat was usually set back to 32 to allow 17.5 amps. for holding at a constant temperature.

II. Experimental Procedure

In discussing the procedure used in this work the general procedure will be presented first, then the variations from this procedure, and finally a special procedure for the distillation of the zinc condensates. The raw materials used in this work are listed in Appendix I.

Stoichiometric amounts of zinc sulfide and the reducing agent(s) were weighed, mixed carefully to insure a homogeneous mixture throughout the charge, and briquetted in a Buehler specimen mount press using 1000 psi at room temperature. To accelerate the procedure the mechanical pump was usually left running between runs or it was turned on shortly before the charge was prepared. In either case the vacuum valve was closed and the lower half of the system was evacuated prior to charging the furnace. The charge in the form of a briquet whose dimensions were one inch in diameter and about three-eighths of an inch in height was inserted in an alundum crucible in such a manner that its diameter was perpendicular to the base of the crucible. This method provided a maximum surface area for evaporation. Then the crucible was placed on the crucible support ring, the graphite tubes were assembled as shown in Figure 5, and the whole assembly was pushed up into the furnace where it remained in a fixed position by a supporting ring located at the bottom of the furnace. The metal cap was coated with a thin film of high vacuum

grease and pushed onto the conical joint of the metal head to secure a tight fit. After inserting the rubber stopper which served as the vacuum release valve, the vacuum valve above the diffusion pump was slowly opened and the system was evacuated by the mechanical pump to approximately 100 microns pressure. The water valve was opened to allow a steady stream of water to circulate through the cooling coils around the diffusion pump and at the junction of the porcelain tube and the metal head, and the diffusion pump was turned on.

When the Pirani gauge indicated no further decrease in pressure, the heating cycle was started by throwing the pyrometer switch and by setting the variac to a position which permitted 10 amps. to pass through the furnace. At 400°C the amperage was increased to 20 amps. and held at this value until the reaction temperature was reached, after which the current was decreased to 17.5 amps. The Tork clock was set to shut off the furnace at the end of a preselected reaction time, but the pumps were left running until the furnace had cooled to room temperature, which usually required that the sample be left in the furnace overnight.

In discharging the furnace the diffusion pump was turned off first and allowed a 20 to 30 minute cooling period before proceeding to the next step. Then the vacuum valve was closed and the rubber stopper was removed slowly and carefully to destroy the vacuum in the furnace. The metal cap was slipped off and the graphite tubes were lowered from their suspended position within the porcelain tube. The sections of tubes were carefully separated and then examined to check both the appearance and the relative position of the condensate(s) produced. By using a spatula the condensate was scraped from the inner surface of the graphite tube and saved for future use. The residue and crucible were weighed to de-

termine the extent of loss during reduction by vaporization. Then the residue was pulverized and analyzed for zinc and sulfur. The results of the runs made by this procedure are tabulated and discussed in the subsequent section of this paper.

In performing the experiment on the reduction of zinc sulfide by calcium oxide and carbon it was necessary to use a special technique in preparing the charge. After weighing and mixing the charge as before, a small amount of collodion was added as a binder to the mixture. After briquetting, the charge was preheated in a Globar furnace to 375°C to remove the collodion which would contaminate the vacuum if it were left in the charge. Another variation from the general procedure arose several times during heating to temperature when it became necessary to shut off the diffusion pump because of a pressure increase in excess of 100 microns. At such times of considerable pressure fluctuation, the temperature was held constant until the vacuum was restored to the original minimum value, then the diffusion pump was started and the heating to reaction temperature was resumed. This procedure was followed for the reduction of zinc sulfide by iron and carbon as lamp black.

In preparing the composite of zinc condensates that were produced in previous zinc sulfide-iron reductions, a series of condensates were selected on the basis of a wide variation in their reaction temperatures and times for the purpose of obtaining a considerable amount of composite of nominal composition. The chosen condensates were ground to about minus 65-mesh and mixed thoroughly. The first composite was mixed in a rotating agitator for 20 minutes. The second composite could not be given the same treatment because the agitator was not usable at the time; however, the condensates were rotated by hand in a glass jar in a manner

analogous to the action of the mechanical agitator. Because of the lower temperatures used for distillation, the current was held at 10 amps. for the entire period of each run. Otherwise, the procedure was identical to the general procedure.

Discussion

I. Reduction of Zinc Sulfide by Iron

A. Effect of Time and Temperature

Considerable work on the reduction of zinc sulfide by iron under reduced pressure has been reported previously by a number of investigators who are mentioned in the review of literature. It was suggested by Dr. Schlechten at the outset of this experiment that several runs should be made using a charge of $ZnS + 2Fe$ and under conditions similar to those used by Liu for the purpose of checking his results. Previous investigations by Liu showed that a charge composed of $ZnS + 1Fe$ contained an insufficient quantity of iron for a maximum thermal reduction of zinc sulfide; that $ZnS + 3Fe$ only slightly improved the results obtained by using $2Fe$.

To eliminate the effect of the quantity of sample on the comparison of results, a 13-gram charge was used throughout the experiment to approximate the amount of charge used by Liu. The calculation of the relative amounts of charge constituents are found in Appendix IV. Graphite tubes were used within the furnace to provide an inert surface for the condensation of zinc vapor, thus eliminating any alloying action which would have occurred had stainless steel tubes been used. The reaction temperatures were varied from 800 to 1000°C; the time at the chosen reaction temperature was kept constant at 4.5 hours in accordance with the time used by Liu. After each run the residue was analyzed for zinc and sulfur, and the amount of zinc and sulfur distilled was calculated from the loss in weight and the difference in analyses between the charge and the residue.

Before discussing the results of this experiment quantitatively, it would be well to consider the behavior of zinc sulfide during the reduction

process. There are two assumptions which can be made in regard to the thermal behavior of zinc sulfide under reduced pressure. The first assumption is that there is an appreciable degree of dissociation of zinc sulfide as indicated by the equation



In an investigation made by Hsiao⁽²³⁾ it was found that the dissociation

(23) Hsiao, Chi-mei, The Volatility of Metallic Sulfides and Their Treatment by Vacuum Metallurgy, Thesis, Missouri School of Mines and Metallurgy, Rolla, Mo. (1948)

rate was very small as compared to the measured volatility; practically all of the zinc sulfide would sublime before any dissociation could occur. Moreover, the sublimates from his experiments were investigated by X-ray diffraction methods and were found to be pure zinc sulfide. If it were possible to drive off the free sulfur formed by the dissociation of zinc sulfide, then pure metallic zinc could be produced merely by heating zinc sulfide to some elevated temperature, condensing the zinc vapor, and pumping sulfur away from the zinc condensate. Another argument against the dissociation of zinc sulfide is that it is rather difficult to believe that after dissociation all of the sulfur and the zinc will revert to zinc sulfide in the cold region of the condensing chamber. Therefore, from the described theoretical behavior of zinc sulfide and from the actual experimental evidence, Hsiao concluded that the vapor consisted of molecular zinc sulfide. Table III gives the sublimation data for zinc sulfide as reported by Hsiao.

TABLE III

| <u>Sublimation Data for Zinc Sulfide</u> | | |
|--|----------------------------|----------------------------|
| <u>Temp</u> <u>°C</u> | <u>Time</u> <u>sec.</u> | <u>Loss</u> <u>gms.</u> |
| 704 | 2900 | 0.0338 |
| 704 | 12900 | 0.0387 |
| 804 | 1560 | 0.0375 |
| 804 | 5520 | 0.1483 |
| 804 | 17340 | 0.2294 |
| 904 | 3360 | 0.4050 |
| 904 | 14580 | 1.8915 |
| 904 | 20760 | 2.8313 |
| 1006 | 300 | 1.2920 |
| 1006 | 2520 | 3.8280 |

Evaporation Area = 5.52 sq. cm.

The significance of the above data will become apparent in the paragraphs to follow.

The results of the series of runs using the ZnS + 2Fe charge are tabulated in Table IV and are presented graphically in Figure 10. In calculating the percent zinc distilled as metal and the percent zinc metal produced, it was assumed that any sulfur that distilled over into the condensing zone during the reduction did so in the combined form of zinc sulfide. This is the second and most valid assumption: that zinc sulfide does not decompose to any appreciable extent during the reduction process. As the reaction temperature increases, the total percent zinc distilled increases; however, the percent metallic zinc produced increases at a decreasing rate because of an increase in the rate of sulfur distilled as zinc sulfide. Referring once again to Table III it is seen that this statement is substantiated by the results reported by Hsiao; that the loss of zinc sulfide increases considerably as the temperature approaches 1000°C.

TABLE IV

ZnS + 2Fe Reduction: Reaction Time Constant - 4.5 Hours

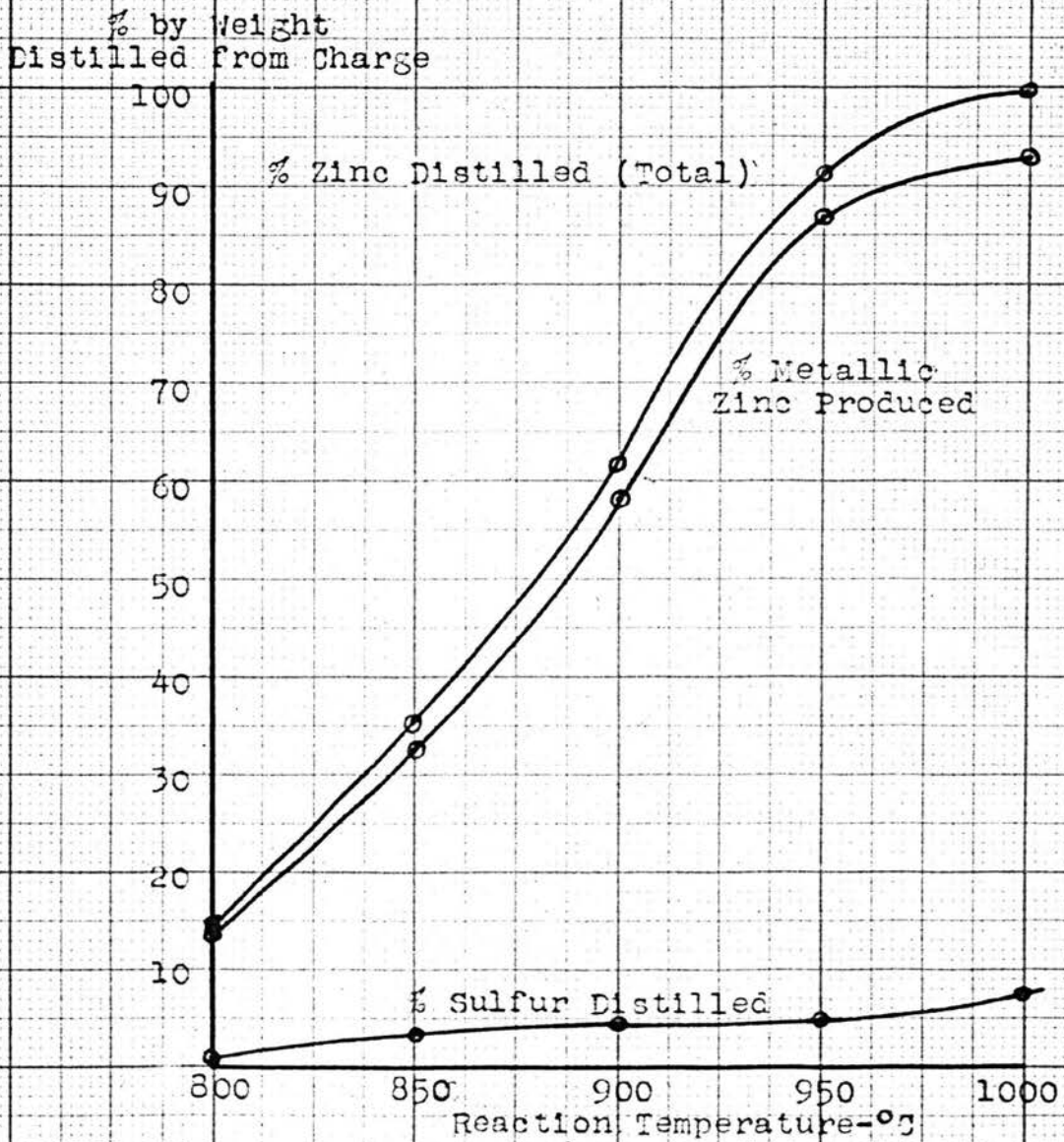
| Temp °C | Gms. Sample | Gms. Residue | Gms. Loss | Gms. Zinc in | | | % Zn Dist. |
|------------|----------------|-----------------|--------------|--------------|---------|-------|---------------|
| | | | | Sample | Residue | Loss | |
| 800 | 13.104 | 12.550 | 0.554 | 4.190 | 3.602 | 0.588 | 14.0 |
| 850 | 13.106 | 11.757 | 1.349 | 4.191 | 2.698 | 1.493 | 35.6 |
| 900 | 13.101 | 10.538 | 2.563 | 4.189 | 1.612 | 2.577 | 61.5 |
| 950 | 13.113 | 9.241 | 3.872 | 4.193 | 0.360 | 3.833 | 91.4 |
| 1000 | 13.108 | 8.979 | 4.129 | 4.192 | 0.030 | 4.162 | 99.3 |

| Temp °C | Gms. Sulfur in | | | % S Dist. | % Zn Dist. as metal | % Zn Metal Produced |
|------------|----------------|---------|-------|--------------|------------------------|------------------------|
| | Sample | Residue | Loss | | | |
| 800 | 1.936 | 1.930 | 0.016 | 0.8 | 94.5 | 13.3 |
| 850 | 1.936 | 1.873 | 0.063 | 3.2 | 91.0 | 32.6 |
| 900 | 1.935 | 1.861 | 0.074 | 4.2 | 94.2 | 58.1 |
| 950 | 1.937 | 1.843 | 0.094 | 4.8 | 95.1 | 86.9 |
| 1000 | 1.937 | 1.801 | 0.136 | 7.6 | 93.5 | 92.8 |

| Temp °C | Pressure microns Hg |
|------------|------------------------|
| 800 | 18 |
| 850 | 23 |
| 900 | 23 |
| 950 | 14 |
| 1000 | 35 |

Figure 10

ZnS + 2Fe Reduction
Reaction Time Constant: 4.5 Hours



The experimental data on the thermal behavior of FeS as reported by Hsiao showed that only about 0.3 percent of the FeS was lost from the charge at 1000°C. Moreover, the major portion of the weight loss was due to a dissociation of FeS into Fe and S and the evaporation of S; the remainder was due to the sublimation of FeS. Consequently, the effect of FeS on the purity of the zinc distilled can be considered to be negligible in comparison to the effect of ZnS.

One might wonder how zinc sulfide could be distilled when iron was added to the charge in an amount sufficient to reduce virtually all of the zinc sulfide present. One reason might be that the rate of sublimation of zinc sulfide is so great at temperatures between 900 and 1000°C that there is not sufficient time for the complete reduction of all of the zinc sulfide. A second explanation is that there were certain regions within the compacted charge that were high in iron content and other adjacent regions that were high in zinc sulfide, even though the charge was believed to be thoroughly mixed. A third reason was suggested by Gin when he said that it appeared impossible to obtain intimate contact between the zinc sulfide and the particles of iron. These three reasons may have acted individually or collectively to cause the two curves representing zinc to differ by an increasing amount as the temperature increased.

Figure 11 shows a comparison of results for the reduction of zinc sulfide by iron between the temperatures of 800 and 1000°C that were obtained independently by Liu and the author. According to Liu, the total percent zinc distilled increased rapidly from 27.8 percent at 800 to 85.7 percent at 850, reached a maximum value of 91.4 percent at 950, and then decreased slightly to 90.4 percent at 1000. The sulfur curve shows

Reaction Temperature -
 800 850 950 1000

% Sulfur Distilled

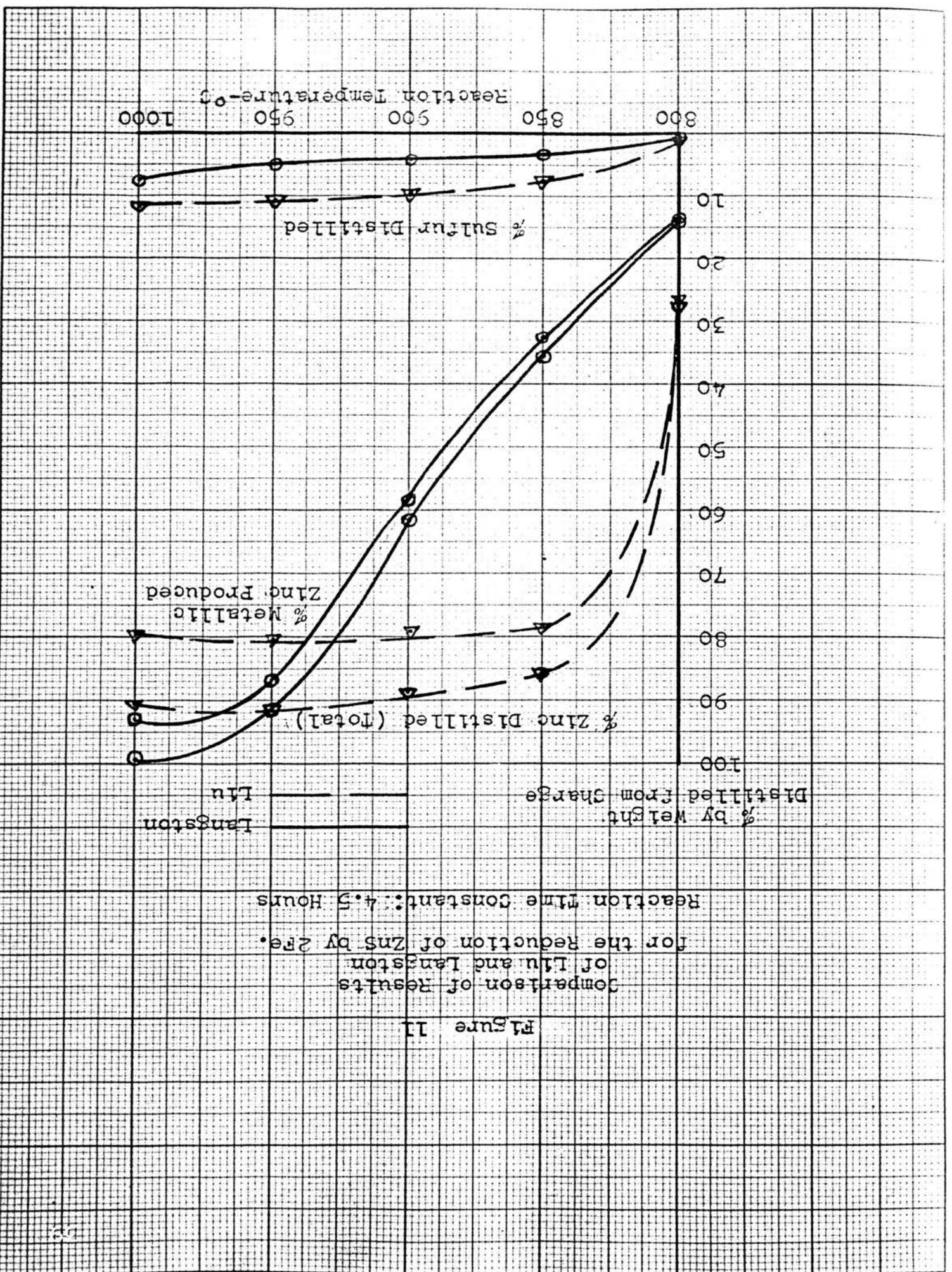
% Zinc Distilled (Total)
 % Metallic
 Zinc Produced

% by weight
 Distilled from charge
 Ltn
 Langston

Reaction Time constant: 4.5 Hours
 for the reduction of ZnS by 2Fe.

Comparison of Results
 of Ltn and Langston

Figure 11



a similar trend in that it increased from 1.5 to 11.8 percent quite rapidly. In contrast to these curves are the curves reported by the author. The total percent zinc curve increases gradually from 14.0 percent at 800 to 99.3 percent at 1000. Between 900 and 1000 the slope of the curve decreases to approach the abscissa asymptotically. The sulfur curve shows a gradual increase from 0.8 percent at 800 to 4.8 percent at 950, and then it increases rapidly to 7.4 percent at 1000. In view of the results of Gross and Warrington who reported that the reduction of zinc sulfide occurred most readily between 920 and 1000, and on the basis of the data obtained by the author in this series of runs, this writer was inclined to doubt the validity of the data reported by Liu.

Actually this single series of runs just discussed were not regarded as being conclusive proof to completely disprove the results of Liu; it showed that a more thorough investigation was necessary. The fact that Liu mentioned the use of only a 4.5-hour reaction time led the author to believe that additional runs should be made to determine the effect of both the reaction time and the reaction temperature on the recovery of zinc. Consequently, two more series of runs were made, one for three hours and another for six hours. All other operating conditions were kept the same as before. The data for these two series of runs are presented in Tables V and VI; Figures 12 and 13 show the graphical representation of the results. For the three-hour period the slope is not as steep as for the previous 4.5-hour period, indicating that the reaction time was not sufficient; moreover, the resulting curve does not level off at 1000. Using a six-hour period at temperature, the percent total zinc distilled increased more rapidly than for the 4.5-hour runs. At 950 the curve shows an abrupt change in slope which results in a maximum

TABLE V

ZnS + 2Fe Reduction: Reaction Time Constant - 3 Hours

| Temp °C | Gms. Sample | Gms. Residue | Gms. Loss | Gms. Zinc in | | | % Zn Dist. |
|------------|----------------|-----------------|--------------|--------------|---------|-------|---------------|
| | | | | Sample | Residue | Loss | |
| 800 | 13.097 | 12.762 | 0.335 | 4.188 | 3.792 | 0.396 | 9.4 |
| 850 | 13.106 | 12.218 | 0.888 | 4.191 | 3.150 | 1.041 | 24.8 |
| 900 | 13.103 | 11.104 | 1.999 | 4.190 | 2.232 | 1.958 | 46.7 |
| 950 | 12.997 | 9.805 | 3.192 | 4.156 | 0.941 | 3.215 | 77.3 |
| 1000 | 13.108 | 9.007 | 4.101 | 4.192 | 0.046 | 4.146 | 98.9 |

| Temp °C | Gms. Sulfur in | | | % S Dist. | % Zn Dist. as Metal | % Zn Metal Produced |
|------------|---------------------|---------|-------|--------------|------------------------|------------------------|
| | Sample | Residue | Loss | | | |
| 800 | 1.935 | 1.927 | 0.008 | 0.4 | 96.0 | 9.1 |
| 850 | 1.936 ^{''} | 1.898 | 0.038 | 2.0 | 92.7 | 23.1 |
| 900 | 1.936 | 1.899 | 0.037 | 1.9 | 96.2 | 45.1 |
| 950 | 1.920 | 1.864 | 0.056 | 2.9 | 96.5 | 74.8 |
| 1000 | 1.937 | 1.828 | 0.109 | 5.6 | 94.5 | 93.7 |

| Temp °C | Pressure microns Hg |
|------------|------------------------|
| 800 | 15 |
| 850 | 14 |
| 900 | 13 |
| 950 | 12 |
| 1000 | 35 |

TABLE VI

ZnS + 2Fe Reduction: Reaction Time Constant - 6 Hours

| Temp °C | Gms. Sample | Gms. Residue | Gms. Loss | Gms. Zinc in | | | % Zn Dist. |
|------------|----------------|-----------------|--------------|--------------|---------|-------|---------------|
| | | | | Sample | Residue | Loss | |
| 800 | 13.101 | 12.462 | 0.639 | 4.189 | 3.577 | 0.612 | 14.6 |
| 850 | 13.110 | 11.455 | 1.655 | 4.193 | 2.440 | 1.753 | 41.8 |
| 900 | 13.104 | 10.482 | 2.622 | 4.190 | 1.520 | 2.670 | 63.7 |
| 950 | 13.110 | 8.977 | 4.133 | 4.193 | 0.099 | 4.094 | 97.6 |
| 1000 | 13.105 | 8.979 | 4.126 | 4.190 | 0.028 | 4.162 | 99.3 |

| Temp °C | Gms. Sulfur in | | | % S Dist. | % Zn Dist. as Metal | % Zn Metal Produced |
|------------|----------------|---------|-------|--------------|------------------------|------------------------|
| | Sample | Residue | Loss | | | |
| 800 | 1.935 | 1.895 | 0.040 | 2.1 | 86.8 | 12.7 |
| 850 | 1.937 | 1.833 | 0.104 | 5.4 | 88.0 | 36.8 |
| 900 | 1.936 | 1.829 | 0.107 | 5.5 | 91.5 | 58.5 |
| 950 | 1.937 | 1.861 | 0.076 | (3.9) | (96.1) | (94.0) |
| 1000 | 1.936 | 1.706 | 0.230 | 11.4 | 88.9 | 88.3 |

| Temp °C | Pressure microns Hg |
|------------|------------------------|
| 800 | 23 |
| 850 | 23 |
| 900 | 23 |
| 950 | 20 |
| 1000 | 35 |

Figure 12

ZnS + 2Fe Reduction
Reaction Time Constant: 3 Hours

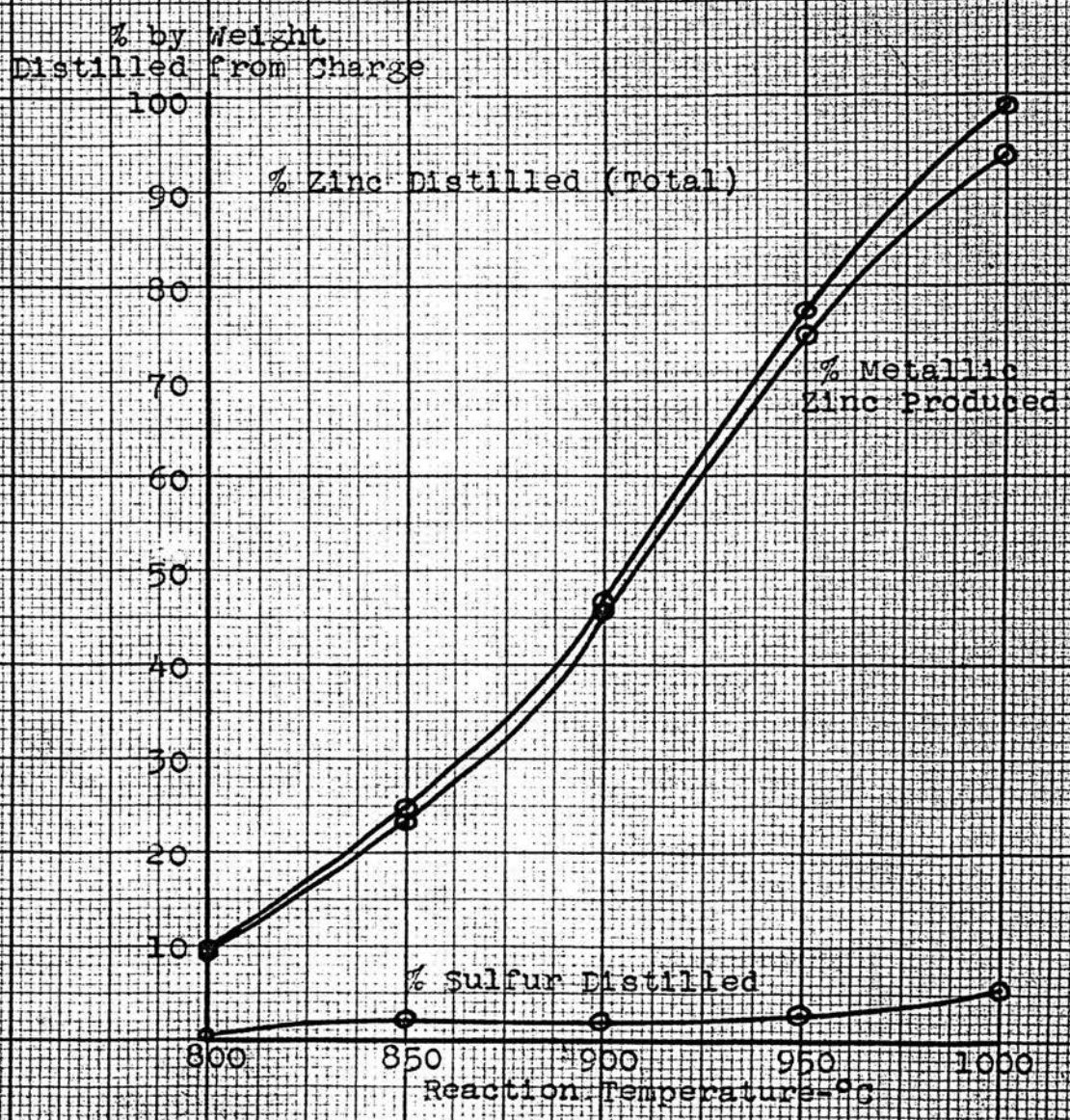


Figure 13

ZnS + 2Fe Reduction
Reaction Time Constant: 6 Hours

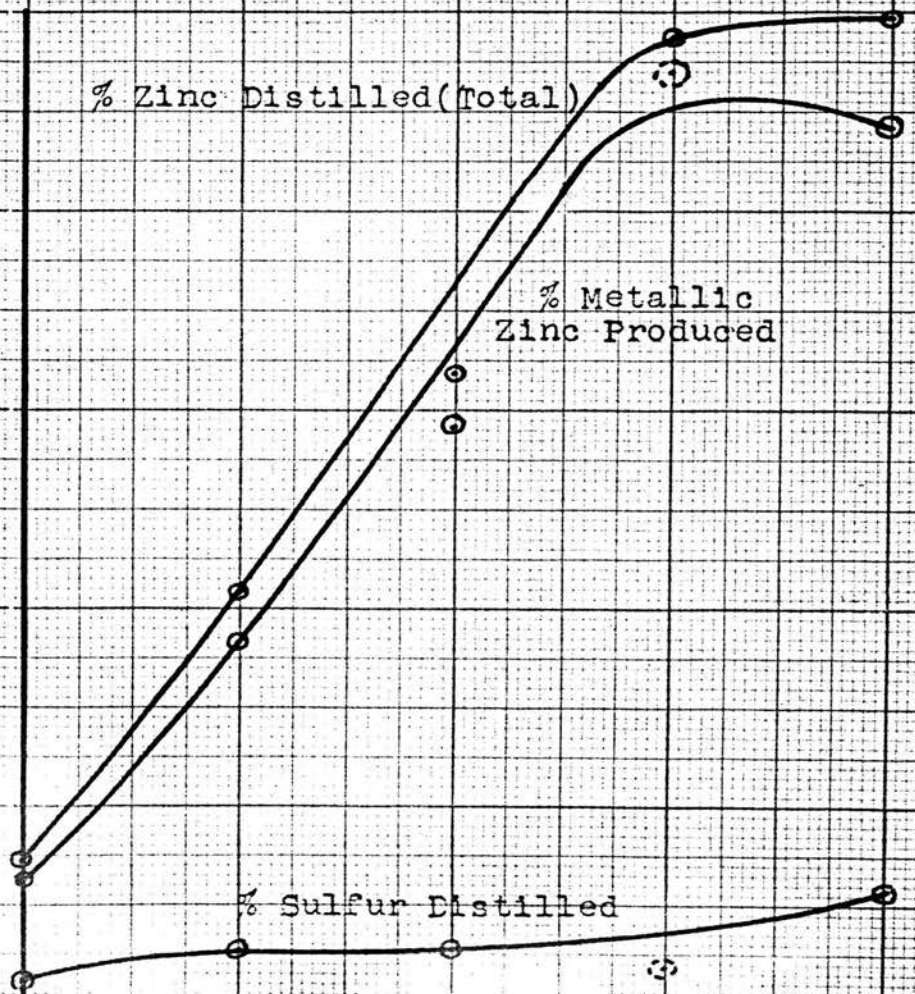
% by Weight
Distilled from Charge

% Zinc Distilled (Total)

% Metallic
Zinc Produced

% Sulfur Distilled

800 350 900 950 1000
Reaction Temperature-°C



reduction of zinc sulfide somewhere between 950 and 1000.

Additional runs were made using various reaction times and temperatures to give a more complete picture of the reduction process and its dependence upon these two factors. The condensed data together with pertinent data from previous Tables is given in Table VII. The purpose of plotting the data as shown in Figure 14 is to present the results of the reduction of zinc sulfide by iron in such a manner as to show the effect of reaction time for a complete series of runs. It is seen that for reductions made at 800 and 850 the percent zinc recovered never approaches an appreciable value regardless of the reaction time chosen; whereas, the percent sulfur distilled gradually decreases the purity of the zinc metal when the time exceeds six hours. On the other hand, reductions performed at 900 are greatly influenced by the time at temperature as indicated by an increase in recovery of total zinc from 20 percent for one-half hour to 73.7 percent for nine hours. The 950-degree curve includes only a range from three to nine hours, and there is some doubt as to the exactness of the portion between 4.5 and nine hours, particularly for the six-hour period, but it is assumed that the trend is approximately correct as shown. The percent total zinc increases rapidly from 77.8 to a maximum of 99.3 percent. The percent metallic zinc also increases in a rapid manner, but then the curve decreases in slope because of an increase in the amount of sulfur distilled as zinc sulfide after a comparatively long time at temperature. It appears that the reduction by iron reached its maximum after approximately six hours, and that the additional increase in total zinc was mostly the result of the sublimation of unreduced zinc sulfide. The reaction took place most readily at 1000, but the purity of the zinc decreased considerably as

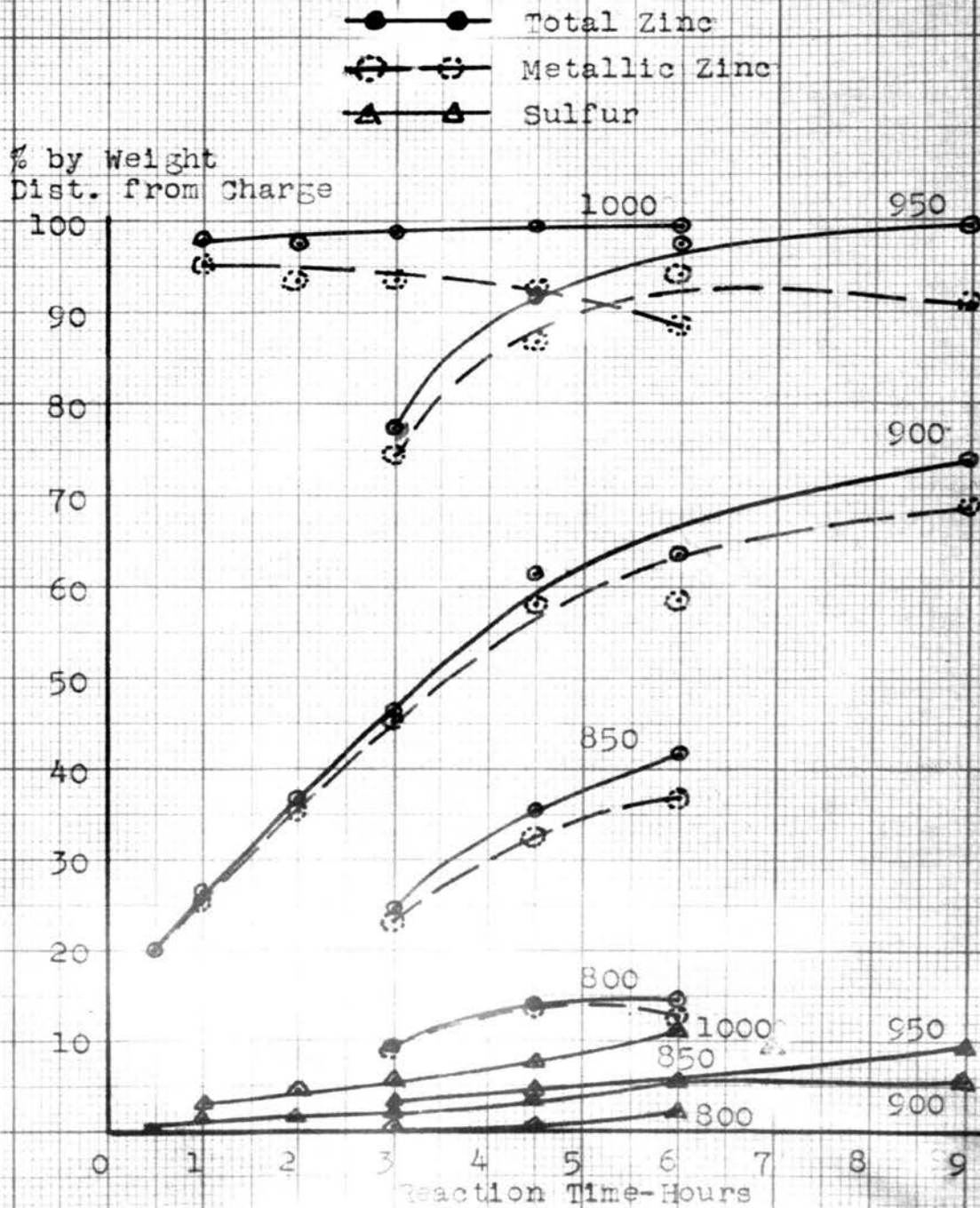
TABLE VII

ZnS + 2Fe Reduction: Reaction Time and Temperature Varied

| <u>Temp °C</u> | <u>Time Hrs.</u> | <u>% Zinc Distilled (Total)</u> | <u>% Zinc Metal Produced</u> | <u>% Sulfur Distilled</u> |
|--------------------|----------------------|-------------------------------------|----------------------------------|-------------------------------|
| 800 | 3 | 9.4 | 9.1 | 0.4 |
| | 4.5 | 14.0 | 13.3 | 0.8 |
| | 6 | 14.6 | 12.7 | 2.1 |
| 850 | 3 | 24.8 | 23.1 | 2.0 |
| | 4.5 | 35.6 | 32.6 | 3.2 |
| | 6 | 41.8 | 36.8 | 5.4 |
| 900 | 0.5 | 20.0 | 19.9 | 0.2 |
| | 1 | 26.4 | 25.2 | 1.3 |
| | 2 | 36.9 | 35.4 | 1.5 |
| | 3 | 46.7 | 45.1 | 1.9 |
| | 4.5 | 61.5 | 58.1 | 4.2 |
| | 6 | 63.7 | 58.5 | 5.5 |
| | 9 | 73.7 | 68.7 | 5.3 |
| 950 | 3 | 77.3 | 74.8 | 2.9 |
| | 4.5 | 91.4 | 86.9 | 4.8 |
| | 6 | 97.6 | (94.0) | (3.9) |
| | 9 | 99.3 | 91.0 | 9.1 |
| 1000 | 1 | 98.0 | 95.5 | 3.0 |
| | 2 | 97.4 | 93.4 | 4.3 |
| | 3 | 98.9 | 93.7 | 5.6 |
| | 4.5 | 99.3 | 92.8 | 7.6 |
| | 6 | 99.3 | 88.3 | 11.4 |

Figure 14

ZnS + 2Fe Reduction
Reaction Time Varied



the time at temperature was lengthened.

From the foregoing discussion it seems that the most satisfactory combination of time and temperature for the reduction of zinc sulfide by iron under reduced pressure is 1000°C for one hour at temperature.

B. Effect of Crucible Shape on the Rate of Vapor Flow

All of the runs discussed previously were made using a Morgan Battersea crucible whose sides were tapered to give the shape of a truncated cone to the crucible. When this crucible was placed on the supporting ring in the furnace, there was a clearance of about one thirty-secondth of an inch between the crucible and the inner surface of the graphite tube. To determine the effect, if any, of the crucible shape on the rate of flow of the vapor phase from the crucible to the cold region of the condensing portion of the graphite tube, a cylindrical alundum crucible was substituted for the Morgan crucible, and a reduction was made by iron at 900° for 4.5 hours. The clearance in the latter case was about one fourth of an inch between the crucible and the graphite tube. The following data show the similarity of results obtained.

| <u>Crucible</u> | <u>Shape</u> | <u>% Weight Loss</u> | <u>% Zn Dist. Total</u> | <u>% S Dist.</u> | <u>% Zn Metal Produced</u> |
|-----------------|----------------|----------------------|-------------------------|------------------|----------------------------|
| Morgan | Truncated cone | 19.6 | 61.5 | 4.2 | 94.2 |
| Alundum | Cylindrical | 17.8 | 59.1 | 2.3 | 96.3 |

The above data show such close agreement that the slight variations in the results between the two types of crucibles was most likely caused by experimental errors and not by a difference in crucible shape. Thus it may be concluded that the Morgan crucible with its relatively small clearance did not retard the rate of vapor flow any more than did the alundum

crucible which had a relatively large clearance between the crucible and the graphite tube.

C. Effect of Compacting on the Reduction by Iron

In all of the previous work performed by Gross and Warrington, Liu, and the author the charge was always briquetted prior to charging it to the furnace, the purpose being to bring about a maximum degree of intimate contact between the particles of iron and zinc sulfide. To determine the effect of compacting on the reduction process, two loosely packed charges were run at 900° for 4.5 and 6 hours at temperature. Contrary to the theory that the greater the intimacy of contact the greater the reduction efficiency, the results showed that for 4.5 hours a 75.0 percent total zinc recovery was obtained as compared to only 61.5 percent for a similar charge which had been briquetted under 1000 psi. And for the 6-hour period the recovery was increased from 63.7 to 80.9 percent. The relative amounts of sulfur that distilled over remained in the same ratio as before.

Apparently the advantages gained by compacting the charge are nullified by fusion of the surface of the briquet, preventing the free escape of zinc vapor formed within the briquet, and resulting in a displacement of the equilibrium to the left. This condition is analogous to the early stage of bloating of fireclay bricks during their firing operation in that surface fusion causes an entrapment of gases within the bricks. When the residue from the 6-hour run was removed from the furnace, it was noticed that the loosely-packed charge had shrunk to about two-thirds of its original size to form a porous compact that was more easily ground for analysis than a similar briquetted charge.

D. Effect of Heating Zinc Sulfide Under a Reduced Pressure

To determine the extent of sublimation of zinc sulfide when heated under a reduced pressure, a ten-gram charge was held for 4.5 hours at 900°C and at 40 microns pressure. When the graphite tubes were removed and examined, three distinct zones of condensates were found: (1) a thin white layer of about one-half inch in length located eight inches below the crucible, (2) a two and one-half inch zone of thin yellow condensate below the first layer, and (3) a three-fourth inch layer of thin grey deposit about three inches below the second deposit. In all probability the uppermost region consisted of zinc sulfide that was deposited by sublimation. The other two zones resembled sulfur and metallic zinc in appearance, but it is not certain whether these two products were produced during this run or whether they resulted from the deposition of residual material that had been present from previous runs. The thinness of the latter two layers causes an uncertainty as to their actual composition; the color of a condensate will vary with its change in thickness.

A weight loss of 17.9 percent included the values of 22.5 and 15.9 percent for the percent total zinc and the percent sulfur distilled, respectively. A calculated value of 4.9 percent was obtained for the percent zinc produced as metal, but the validity of this figure is doubtful in that the decomposition of zinc sulfide is negligible at 900°C. The latter value most probably was the result of an error in chemical analysis.

The significant point derived from performing this one run is that the recovery of zinc at the temperature in question is dependent not only on the reduction of zinc sulfide by iron but upon the sublimation of zinc sulfide as well. Consequently, at 900°C iron may be responsible for the majority of the total zinc distilled, but the remainder is due to the

sublimation of unreduced zinc sulfide, the latter being the most undesirable feature of the entire vacuum reduction process.

E. Appearance and Analysis of Typical Condensates

At the lower reaction temperatures the condensate consisted of a thin metallic-grey deposit of loosely compacted granular material, suggesting a direct condensation from the vapor to the solid state. As the reaction temperature was increased, the relative thickness of the deposit increased and its physical characteristics improved. At the higher temperatures the deposit was more dense, showing both granular and sheet products. The extraction of a deposit from the graphite tube in sheet form suggested that the vapor condensed first to a liquid and then to a solid. In most instances the sheet was extremely brittle and would crumble to small fragments when scraped from the tube; whereas, in some cases it was possible to remove the sheet as such because of its plastic nature. In general, the higher the temperature, the better the physical properties of the condensate.

The results for each run were based on an analysis of the residue from which the amounts of material that were distilled could be found by taking the difference between the original and final analyses for zinc and sulfur. This method indicated that a certain amount of zinc and sulfur was lost from the charge, but it did not indicate where the two substances were most prevalent in the condensate. For this reason several typical condensates were analyzed to determine the extent of contamination by sulfur. It was found that the chosen condensates were much purer than one would expect from the data reported for the amount of sulfur distilled. For example, the condensate produced after 4.5 hours at 900 analyzed 95.5 percent zinc and only 0.072 percent sulfur, the balance

consisting of graphite picked up during the removal of the condensate from the tube. Table IV reported a 4.2 percent distillation of sulfur. A similar analysis for the run at 1000° for 4.5 hours showed 97.0 percent zinc and 0.095 percent sulfur content in the condensate; whereas, Table IV reported 7.2 percent sulfur distilled. The explanation for this higher purity is that the zinc sulfide that distilled was relatively sparse in comparison to the amount of zinc metal produced, and the former condensed as a very thin layer over a wide region above the zone occupied by the bulk of the condensate, making its removal impossible. Hence, in removing the bulk of the condensate, the author obtained a condensate much purer than the purity indicated by the analysis of the residue.

II. Reduction of Zinc Sulfide by Iron and Carbon

To determine the effect of carbon added to a charge of iron and zinc sulfide a series of runs were made using a normal charge of $ZnS + 2Fe$ to which a quantity of carbon as lamp or oil black was added. The data in Table VIII and curves in Figure 15 indicate that the reduction with added carbon was more pronounced between 800 and 950 than were previous runs for 4.5 hours in which carbon was not used. Above 950 there was no noticeable difference in the results. It is not altogether certain why carbon improves the reduction at these lower temperatures. One theory is that the carbon combines with sulfur to form carbon bisulfide which enters the gaseous phase, resulting in the production of metallic zinc. This would assume that the following reactions take place:

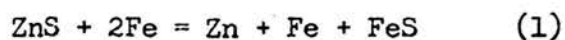


TABLE VIII

ZnS + 2Fe + Carbon¹ Reduction: Reaction Time - 4.5 Hours

| Temp °C | Gms. Sample | Gms. Residue | Gms. Loss | Gms. Zinc in | | | % Zn Dist. |
|------------|----------------|-----------------|--------------|--------------|---------|-------|---------------|
| | | | | Sample | Residue | Loss | |
| 800 | 14.125 | 12.545 | 1.680 | 4.194 | 2.760 | 1.434 | 34.1 |
| 850 | 14.122 | 11.809 | 2.313 | 4.194 | 2.078 | 2.116 | 50.4 |
| 900 | 14.136 | 10.773 | 3.363 | 4.194 | 1.045 | 3.149 | 75.1 |
| 950 | 14.122 | 9.911 | 4.211 | 4.194 | 0.297 | 3.897 | 92.9 |
| 1000 | 14.139 | 9.592 | 4.547 | 4.194 | 0.043 | 4.151 | 99.1 |

| Temp °C | Gms. Sulfur in | | | % S Dist. | % Zn Dist. as Metal | % Zn Metal Produced |
|------------|----------------|---------|-------|--------------|------------------------|------------------------|
| | Sample | Residue | Loss | | | |
| 800 | 1.938 | 1.898 | 0.048 | 2.0 | 94.2 | 32.3 |
| 850 | 1.938 | 1.912 | 0.026 | 1.3 | 97.8 | 49.3 |
| 900 | 1.938 | 1.903 | 0.035 | 1.8 | 98.0 | 73.5 |
| 950 | 1.938 | 1.848 | 0.090 | 4.6 | 95.1 | 88.6 |
| 1000 | 1.938 | 1.813 | 0.125 | 6.5 | 93.8 | 93.0 |

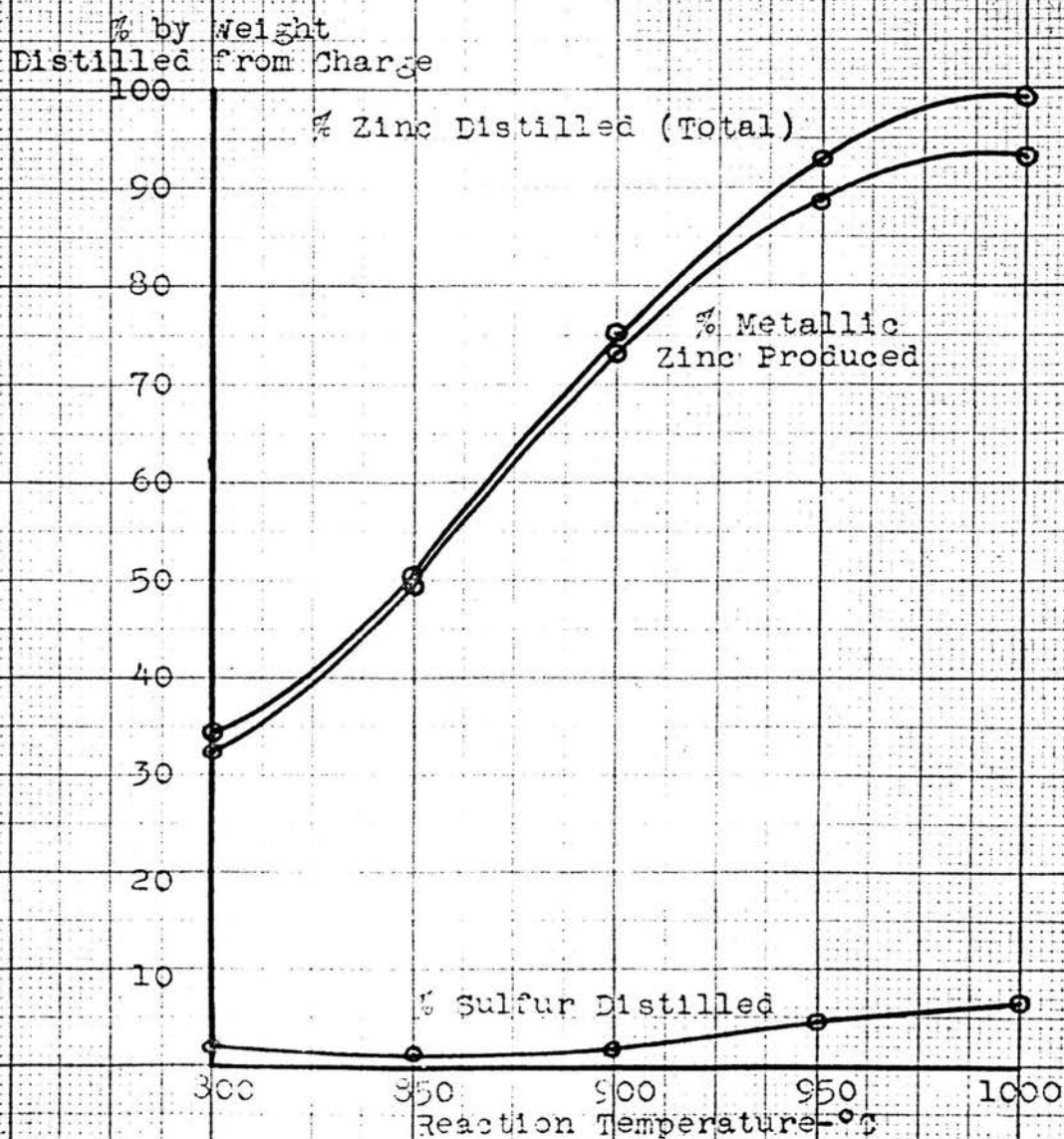
| Temp °C | Pressure microns Hg |
|------------|------------------------|
| 800 | 40 |
| 850 | 35 |
| 900 | 35 |
| 950 | 40 |
| 1000 | 40 |

¹Carbon used in form of lamp- or oil-black

Figure 15

$ZnS + 2Fe + C^1$ Reduction
Reaction Time Constant: 4.5 Hours

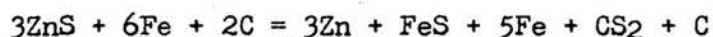
¹as Carbon black - Lamp or Oil



According to Scortecci⁽²⁴⁾ the second reaction starts at about 800 and

(24) Scortecci, A., and Scortecci, M. A., A New Process for Direct Reduction of Iron Pyrites, Metal Progress, Vol. 60, No. 4, pp. 72-75, Oct. 1951.

is complete at about 1800°C. The rate of the reaction is not known, but it may be assumed that the amount of carbon bisulfide formed between 800 and 950 is not large; that only a small amount of the FeS is reduced by carbon in this temperature range. Due to a lack of sufficient data the effect of carbon cannot be fully explained, but perhaps one effect may be expressed by combining the two preceding equations as follows:



The use of lamp black caused a considerable pressure fluctuation during heating to temperature. Instead of maintaining a constant temperature during the fluctuation period until the original vacuum was restored, the heating cycle was not interrupted; however, the recommended practice requiring that the diffusion pump be turned off when the forepressure exceeded 100 microns was followed. In summarizing the behavior of the system, it may be said that the higher the reaction temperature, the lower temperature of initial fluctuation, the greater the maximum fluctuation, the lesser the time to reach this maximum, and the shorter the time required to restore the original vacuum. Had no more work been performed on this reduction process, it could have been concluded that the pressure increase was due to two causes: (1) the formation of carbon bisulfide according to the foregoing equations, and (2) the distillation of certain volatile impurities present in the carbon.

An additional run was made to determine the effect of using pure graphite instead of lamp or oil black in the charge, thus eliminating the

second cause for the pressure increase as given above. The data given in Table IX give a comparison of the results obtained by using the two forms of carbon at 900°C and for 4.5 hours.

TABLE IX

Comparison of Results for the Reduction
of Zinc Sulfide Using Carbon as Graphite
and Lamp or Oil Black

| <u>Carbon</u> | <u>% Zn Dist. Total</u> | <u>% Zn Dist. as Metal</u> | <u>% Zn Metal Produced</u> | <u>% S Dist.</u> |
|----------------------|-----------------------------|--------------------------------|--------------------------------|----------------------|
| Lamp or Oil Black | 75.1 | 98.0 | 73.5 | 1.8 |
| Graphite | 80.3 | 98.2 | 87.8 | 1.7 |

Table IX shows that there was no substantial difference in the results obtained when graphite was substituted for lamp black. The main difference was that there was no noticeable pressure increase during the heating cycle when graphite was used. In view of this fact the previous statement might well be modified to say that carbon bisulfide could be a product of the reaction, but the amount produced was very small and was not detected by pressure variations during the experiment.

Another run was made to determine the effect, if any, of graphite alone on the reduction of zinc sulfide at 900°C for 4.5 hours. 31.7 percent of the zinc in the charge was distilled, of which 33.8 percent was distilled as metal, or 8.6 percent metallic zinc was produced. Although the analysis of the residue indicated that 24.6 percent sulfur had been distilled from the charge, presumably by the sublimation of zinc sulfide and by the formation of carbon bisulfide, this was not what happened actually. An examination of the bottom of the crucible after removing the

residue showed a thin hard crust of yellowish material which resembled sulfur. This crust could not be removed by scraping nor could it be removed by heating in an oxidizing flame from a Fisher burner, proving that the material was zinc sulfide and not sulfur.

Although it was not possible to determine whether part of the sulfur distilled over as carbon bisulfide, it was found that a fraction of the condensate has the appearance of sulfur. About eight inches below the crucible a relatively thick layer of bright yellow condensate was found which closely resembled the material that adhered to the bottom of the crucible. Directly below this yellow layer there was a thin grey deposit of zinc powder. It is believed that the value 8.9 percent is too high for the percent metallic zinc produced because this calculation depended upon the accuracy of the sulfur analysis, which was questionable in view of what has been said.

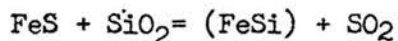
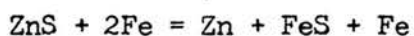
As the reaction temperature was increased, the condensate that was scraped from the lower region of the graphite tube changed in appearance from a loose powder to a compact sheet. For example, after 4.5 hours at 800 the condensate was removed as a silvery metallic powder; whereas, at 950 the condensate existed partly as a loose grey powder and partly as a thin metallic sheet which could be rolled for storage. No analyses were made on any of the condensates produced by the iron and carbon reduction method.

III. Reduction of Zinc Sulfide by Iron and Silica

After completing the series of runs using iron and carbon as the reducing agents, it was brought to the attention of the author that perhaps some other substance similar to carbon would prove effective in reducing zinc sulfide. For this reason one run was tried using silica in place of

carbon. The results of this run showed a weight loss of 17.9 percent, which compared favorably with the value obtained by using iron alone; 60.2 percent total zinc distilled at the chosen reaction temperature of 900 and for 4.5 hours; a sulfur loss of 0.2 percent; and 60.0 percent zinc distilled as metal. The condensate was not unusual in appearance. From the foregoing results it is seen that with the exception of the low sulfur loss there was no benefit derived from using silica.

Speculating on the possible reactions which could have occurred during the reduction process, two equations seem to be the best possibilities.



The first equation is the fundamental equation upon which the usual reduction of zinc sulfide by iron is based. The second equation may have occurred to some extent, but there is no evidence in its favor. On the contrary, it is not likely that the second reaction was in operation because the data showed an unusually low sulfur loss which would rule out the formation of sulfur dioxide. There was no apparent advantage in using silica in addition to iron in the charge.

IV. Reduction of Zinc Sulfide by Iron and Steel Wool

On the recommendations made by Liu in his thesis and by Dr. Schlechten during a conference several runs were tried to study the effect of steel wool on the efficiency of the reduction of zinc sulfide by iron. A normal charge of zinc sulfide and iron was prepared in the usual manner and then steel wool was firmly packed over the top of the crucible to act as a filter for the retention of sulfur. A complete tabulation of the results is given in Table X and is presented graphically in Fig. 16.

TABLE X

ZnS + 2Fe + Steel Wool Reduction: Reaction Time = 4.5 Hours

| Temp °C | Gms. | | | Gms. Zinc in | | | % Zn Dist. |
|------------|--------|---------|-------|--------------|---------|-------|---------------|
| | Sample | Residue | Loss | Sample | Residue | Loss | |
| 900 | 13.068 | 10.645 | 2.423 | 4.175 | 1.775 | 2.400 | 57.5 |
| 950 | 13.111 | 9.881 | 3.230 | 4.193 | 1.087 | 3.106 | 74.1 |
| 1000 | 13.100 | 8.905 | 4.095 | 4.189 | 0.098 | 4.091 | 97.6 |

| Temp °C | Gms. Sulfur in | | | % S Dist. | % Zn Dist. as Metal | % Zn Metal Produced |
|------------|----------------|---------|-------|--------------|------------------------|------------------------|
| | Sample | Residue | Loss | | | |
| 900 | 1.930 | 1.840 | 0.090 | 4.7 | 92.2 | 53.1 |
| 950 | 1.937 | (1.945) | --- | --- | ---- | ---- |
| 1000 | 1.935 | 1.825 | 0.110 | 5.7 | 94.7 | 92.2 |

| Temp °C | Gms. Steel Wool | | | % S Final | Gms. S. in Steel Wool | | |
|------------|-----------------|-------|-------|--------------|-----------------------|--------|--------|
| | Initial | Final | Gain | | Initial | Final | Gain |
| 900 | 3.024 | 3.027 | 0.003 | 0.573 | 0.0009 | 0.0173 | 0.0164 |
| 950 | 3.711 | 3.774 | 0.063 | 0.577 | 0.0011 | 0.0217 | 0.0206 |
| 1000 | 3.570 | 3.631 | 0.061 | 1.782 | 0.0011 | 0.0644 | 0.0633 |

Analysis of Steel Wool (Original) = 0.032% Sulfur

| Temp °C | Gms. Sulfur To Condenser | Gms. Zn as ZnS | Gms. Zn as Metal | % Zn Dist. as Metal |
|------------|-----------------------------|-------------------|---------------------|------------------------|
| 900 | 0.074 | 0.150 | 2.250 | 93.7 |
| 950 | --- | --- | --- | ---- |
| 1000 | 0.047 | 0.096 | 3.995 | 97.8 |

| Temp °C | % Zn Metal Produced | Vacuum microns Hg |
|------------|------------------------|----------------------|
| 900 | 54.0 | 40 |
| 950 | ---- | 40 |
| 1000 | 95.5 | 40 |

Figure 16

ZnS + 2Fe + Steel Wool Reduction
Reaction Time Constant: 4.5 Hours

Uncorrected

Corrected for Sulfur
Pick-Up by Steel Wool

% by Weight
Distilled from Charge

100

90

80

70

60

50

40

30

20

10

% Zinc Distilled (Total)

% Zinc
metal Produced

% Sulfur Distilled

800

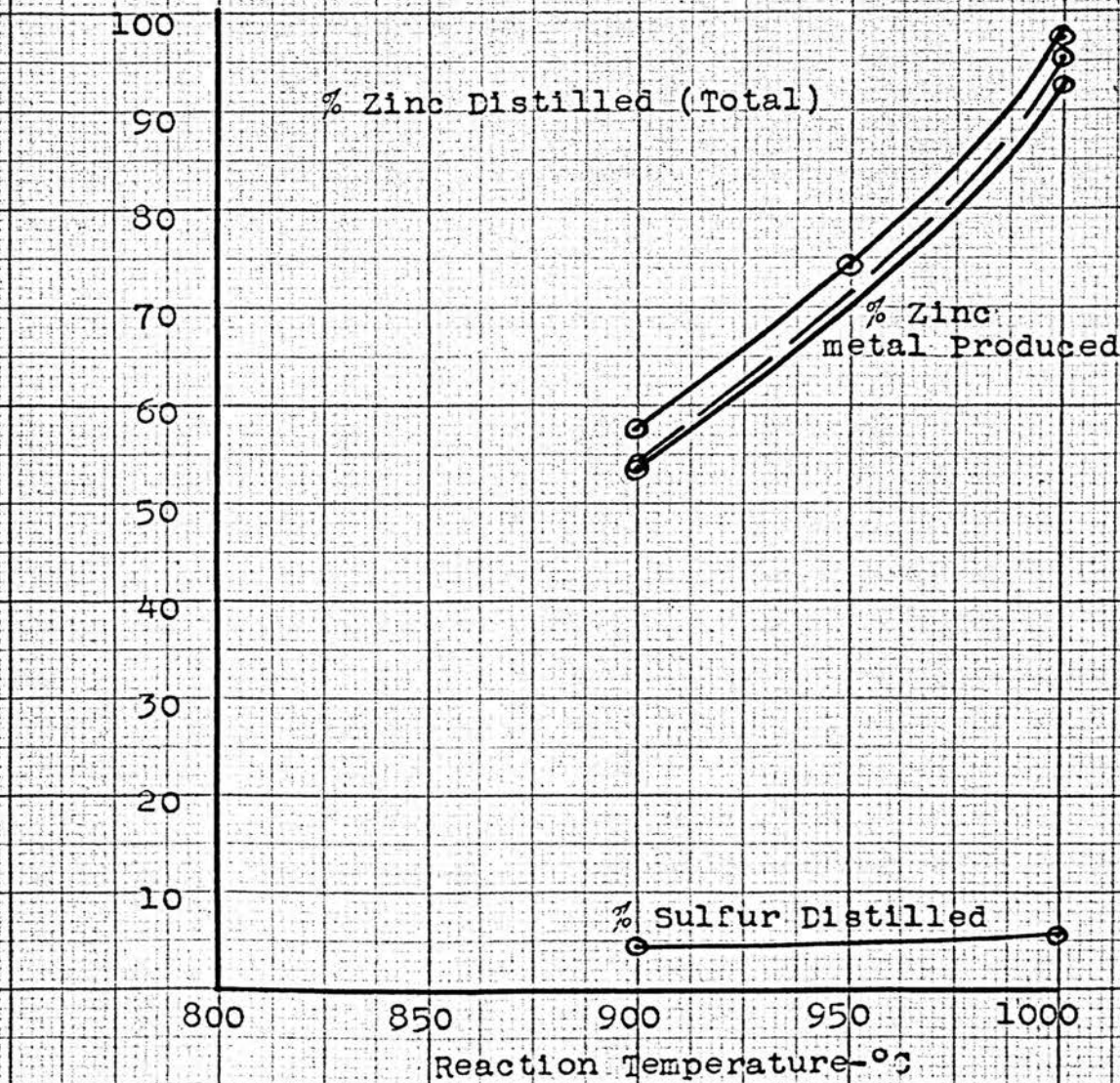
850

900

950

1000

Reaction Temperature-°C



The condensate showed no evidence of improvement, but the steel wool had a brownish discoloration after each run, indicating that a portion of the zinc sulfide was reduced during sublimation to form FeS in the filter. There was a little difficulty in selecting a truly representative sample of the steel wool, but it is believed that the results showed a definite advantage in using the steel wool filter, especially for the run made at 1000°C. In this case the yield showed an increase of 3.3 percent over the percent zinc metal produced without correcting for the sulfur retained in the steel wool. Apparently the filtering action was almost negligible at 900 in that very little sulfur was found by chemical analysis.

The percent sulfur picked up by the steel wool increased from 17.8 at 900 to 57.7 percent at 1000°C. The greater part of this increase could be attributed to an increase in the amount of zinc sulfide distilled at the higher temperature.

V. Reduction of Zinc Sulfide by Calcium Oxide and Carbon

The purpose of performing this experiment was merely to check the data reported by Liu in his work, and for this reason only one run was made. Appendix IV shows the calculations for the charge. A reaction temperature of 1000°C and a time of 4.5 hours at temperature were chosen to duplicate the conditions used by Liu. A study of Table XI shows that a very close agreement exists between the two investigators with regard to the percent total zinc distilled, but not for the percent sulfur distilled.

The author obtained a higher value for the percent sulfur retained in the charge than did Liu, resulting in a higher sulfur-to-zinc ratio.

Liu stated that the possible reaction is given by the equation

TABLE XI

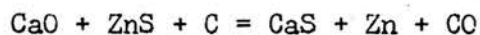
Reduction of Zinc Sulfide
by Calcium Oxide and Carbon

1000°C - 4.5 Hours

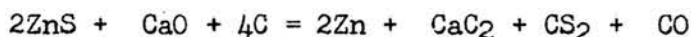
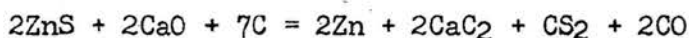
| <u>Investigator</u> | <u>Gms. Sample</u> | | <u>Gms. Residue</u> | | <u>Gms. Zinc in</u> | |
|---------------------|--------------------|-------------|---------------------|-------------|---------------------|----------------|
| | <u>Sample</u> | <u>Loss</u> | <u>Sample</u> | <u>Loss</u> | <u>Sample</u> | <u>Residue</u> |
| Liu | 18.080 | 12.473 | 5.607 | 7.14 | 3.955 | 3.19 |
| Langston | 14.190 | 8.601 | 5.589 | 6.039 | 1.875 | 4.164 |

| <u>Sample</u> | <u>Gms. Sulfur in</u> | | <u>% Zinc Dist.</u> | <u>% S Dist.</u> | <u>% Zn Dist. as Metal</u> | <u>% Zn Metal Produced</u> |
|---------------|-----------------------|-------------|---------------------|------------------|----------------------------|----------------------------|
| | <u>Residue</u> | <u>Loss</u> | | | | |
| 3.50 | 1.65 | 1.85 | 68.3 | 52.8 | (see following note) | |
| 2.790 | 2.036 | 0.754 | 68.2 | 27.0 | 63.2 | 43.6 |

(Note: Liu reported that 3.19 gms. zinc and 1.85 gms. sulfur were distilled. By calculations it was found that 3.76 gms. zinc would be as zinc sulfide, but this is more than the total amount of zinc distilled.)



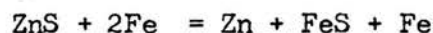
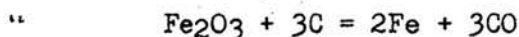
Brown and Oesterle said that the reaction has two possible equations



Regardless of which one of the three equations governs the reaction, it was found that the reduction was not very satisfactory using calcium oxide and carbon; however, a very metallic sheet was obtained from this run.

VI. Reduction of Zinc Sulfide by Iron Oxide and Carbon

An unsuccessful attempt was made to reduce zinc sulfide by a mixture of iron oxide and carbon. It was believed that the reduction could be carried out according to the reactions



The charge was heated to 650°C where it was held for two hours in an attempt to reduce the iron oxide by carbon. The diffusion pump was purposely left off during this initial reaction period. While heating from 290 to 650 the pressure increased from 50 to 220 microns indicating two possibilities: (1) volatile material was being driven out of the carbon, or (2) the first reaction was proceeding as anticipated. At the end of the two-hour period at 650 the diffusion pump was turned on and the temperature was raised to 900 and held for three more hours. A second fluctuation in pressure occurred at about 800, requiring that the diffusion pump be turned off until the vacuum was restored once again.

The residue was a porous mass which had lost very little zinc sulfide as evidenced by a low weight loss. The condensate was a spongy bluish deposit which bore no resemblance to any previous condensates. This

was probably blue powder and not zinc metal owing to the large amount of the residue because of the unsatisfactory nature of the condensate and the comparatively low weight loss.

VI. Redistillation of Zinc Condensates

In each of the preceding discussions concerning the effect of various reducing agents on the reduction of zinc sulfide, the governing principles were that the nonvolatile matter was concentrated in the residue and the volatile constituents were concentrated in the condenser. This depended upon the existence of a substantial difference in the effective vapor pressures of the materials in question. And it was mentioned that zinc sulfide sublimed to increase the total amount of zinc distilled but decreased the overall purity of the metallic zinc produced. An attempt was made to purify the contaminated zinc condensates by applying the principle that two volatile constituents can be separated from each other by virtue of a difference in their rates of evaporation and condensation temperatures. Since zinc sulfide has a higher temperature of condensation and a much slower rate of evaporation than does pure zinc, it was thought that an effective separation could be brought about merely by heating the impure zinc condensates under a reduced pressure to a temperature slightly above the boiling point of pure zinc. Theoretically, pure zinc could be produced in this manner; any zinc sulfide which should happen to sublime would be deposited within a zone above the region for the deposition of pure zinc.

Several experiments were performed to verify the above statements, using a composite charge of zinc condensates that had been produced during previous $\text{ZnS} + 2\text{Fe}$ reductions. A charge of approximately three grams was heated under a pressure of about 40 microns to some temperature

TABLE XII

Redistillation of Zinc Condensates

| Temp-°C | 400 | 500 | 550 | 600 |
|------------------|---------|---------|---------|---------|
| Vacuum-microns | 45 | 45 | 40 | 40 |
| Wt. Charge-gms. | 3.007 | 3.024 | 3.059 | 3.011 |
| Wt. Residue-gms. | 2.804 | 1.157 | 0.018 | 0.004 |
| Wt. Loss-gms. | 0.203 | 1.876 | 3.041 | 3.007 |
| % Wt. Loss | 6.4 | 61.6 | 99.4 | 99.8 |
| Wt. Zinc/gm. | | | | |
| Charge | 0.912 | 0.912 | 0.912 | 0.912 |
| Residue | 0.915 | 0.808 | ----- | ----- |
| Upper Cond. | ----- | 0.880 | ----- | 0.615 |
| Lower Cond. | 0.508 | 0.904 | 0.948 | 0.915 |
| Wt. Sulfur/gm. | | | | |
| Charge | 0.00083 | 0.00083 | 0.00083 | 0.00083 |
| Residue | 0.00052 | 0.00123 | ----- | ----- |
| Upper Cond. | ----- | 0.0227 | ----- | ----- |
| Lower Cond. | ----- | 0.00087 | 0.00135 | 0.00160 |
| Ratio: S to Zn | | | | |
| Charge | 0.00091 | 0.00091 | 0.00091 | 0.00091 |
| Residue | 0.00057 | 0.00152 | ----- | ----- |
| Upper Cond. | ----- | 0.0258 | ----- | ----- |
| Lower Cond. | ----- | 0.00092 | 0.00143 | 0.00175 |

(Note: (---) indicates insufficient quantity of material for sample or for analysis.)

between 400 and 600°C for one-half hour. The results of this series of runs are shown in Table XII.

An upper and a lower condensate were extracted whenever possible, the division between the two depending upon the amount and the appearance of each.

The most outstanding shortcoming of this experiment was that the percent sulfur in the composite was too small to show a substantial change, if any, in the sulfur content of the composite, the residue, and the condensate(s). In repetition to what has been said previously, the condensates produced by the $ZnS + 2Fe$ reduction were generally found to be concentrated within a certain region of the graphite tube, and it so happened that this region consisted almost entirely of metallic zinc as proven by chemical analysis. Although sulfur was distilled in varying amounts as zinc sulfide, it was condensed as a thin layer over a wide region of the graphite tube, making its removal impractical. Therefore, the total amount of sulfur distilled was reduced to a very small value in the extracted condensate because of the manner of extraction. Had it been possible to recover all of the condensate produced, then perhaps the composite would have contained sufficient sulfur to give the data for the redistillation experiments some meaning. Consequently, it is rather difficult to draw any conclusions from the data given in Table XII other than to say that there seems to be no improvement in the purity of the zinc produced by this method.

In the review of the literature it was mentioned that St. Clair and Spendlove of the Bureau of Mines reported a rapid rate of distillation of zinc at 500°C under reduced pressure. The effect of the rate of evaporation of zinc on the amount of zinc condensate produced was proven

to be an important consideration during the performance of this inconclusive series of runs. It was thought that a larger sample should be used instead of the former three-gram charge to secure a proportionally greater quantity of condensate for examination and analysis. Therefore, a ten-gram charge was heated for one hour as before at 550°C. Instead of a 99.4 percent weight loss corresponding to the amount lost by the three-gram sample, the ten-gram charge lost only 71.7 percent. Obviously the rate of evaporation was too slow to allow a proportional loss of charge by distillation for the one-hour period. The reaction time was increased to two hours and the weight loss of 99.4 percent was obtained. This redistillation process did not improve the nature of the condensate as desired.

Conclusions

The direct reduction of zinc sulfide by iron under vacuum with the equipment and procedure described previously was most satisfactory for a period of one hour at a temperature of one hour. Investigations could not be made at higher temperatures because of the type of equipment used. An increase in the length of time at this temperature was not beneficial in that it resulted in an increase in the amount of sulfur transferred from the crucible to the condensate without any appreciable gain in the reduction. The rate of zinc distillation decreased rapidly as the reaction temperature was decreased from 950°C. Experimental results showed that the Morgan crucible with its relatively close tolerance did not retard the rate of vapor flow any more than did the alundum crucible with its relatively large clearance between the crucible and the inner wall of the graphite tube. A loosely-packed charge gave a higher recovery of zinc than did a charge that had been compacted in a press under 1000 psi. The total recovery of zinc was not only dependent upon the reduction of zinc sulfide by the reducing agent as desired but also upon the sublimation of unreduced zinc sulfide, which caused a decrease in the percent zinc metal produced by this process.

With regard to the nature of the condensate, the higher the reaction temperature, the more superior were the physical properties. Chemical analyses of typical condensates showed that the condensates were of a far greater purity than the values given by the analyses of their residues and by the subsequent calculations of the condensates.

The use of lamp black and iron as a reducing combination increased the recovery of zinc by approximately 20 percent over the amount produced by iron alone between 800 and 900°C. There was no appreciable difference

in the amount of zinc distilled as metal at each temperature using carbon added to the $ZnS + 2Fe$ charge. The substitution of graphite for lamp black produced the same results as did the lamp black.

When silica and iron were used as the reducing agents, the results were the same as for a charge consisting of iron alone as the reducing agent.

Steel wool placed on top of the charge of iron and zinc sulfide acted as a filter to retard the sublimation of zinc sulfide during the reduction process. The percent zinc metal produced increased from 92.2 to 95.5 percent and the percent zinc distilled as metal increased from 94.7 to 97.8, all values representing a reaction temperature of $1000^{\circ}C$ for a 4.5-hour period. The filter was found to be ineffective in picking up sulfur at $900^{\circ}C$.

The reduction of zinc sulfide by iron oxide and carbon was wholly unsuccessful in that only a very small amount of total zinc was obtained which bore a resemblance to blue powder.

The redistillation of a composite sample of the zinc condensates produced by the iron reduction process did not improve the nature of the metallic condensates chemically or physically.

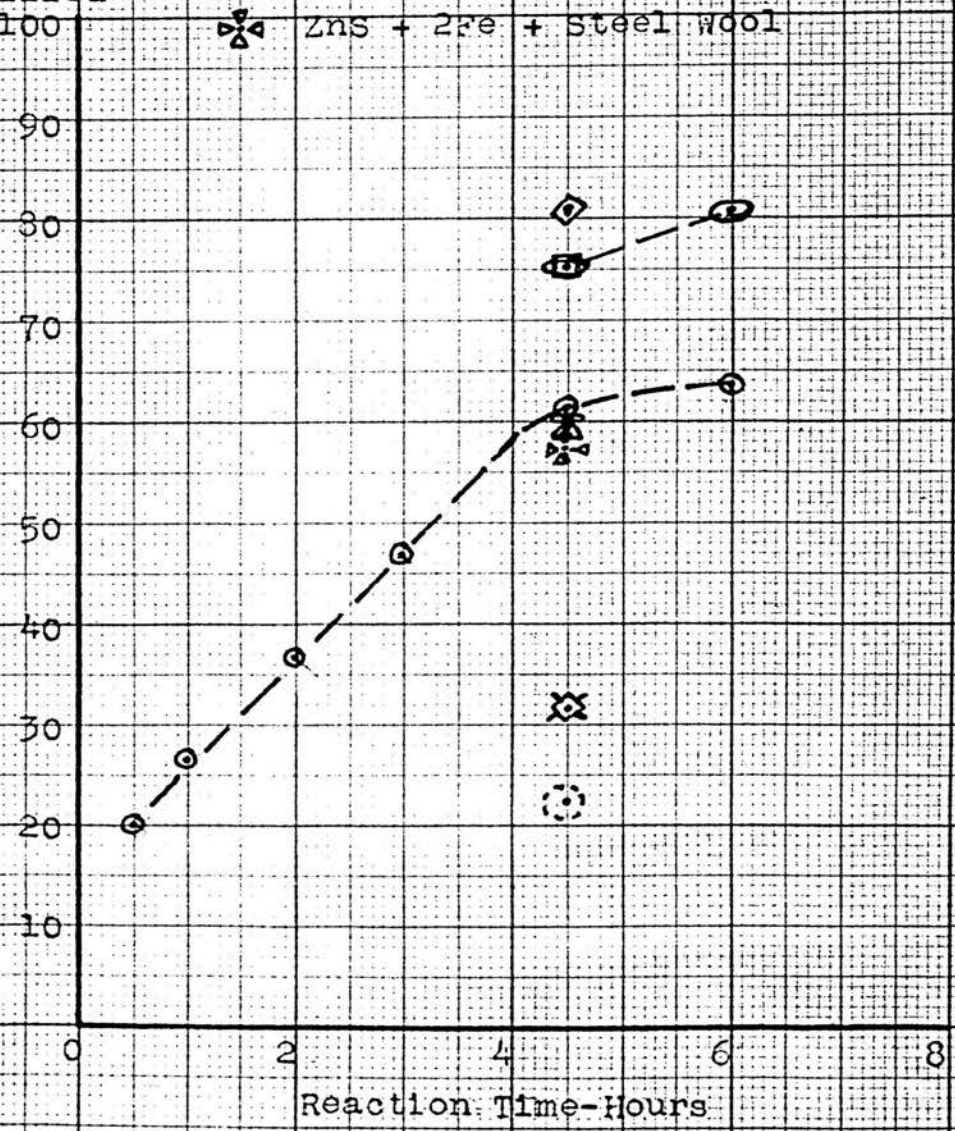
Figure 17 shows a comparison of the effectiveness of the various agents for the reduction of zinc sulfide.

Figure 17
Comparison of Results for the
Reduction of ZnS by Various Reducing Agents

Reaction Temperature - 900°C

- ZnS + 2Fe-Morgan Crucible
- △ ZnS + 2Fe-Alundum Crucible
- ZnS + 2Fe + Lamp Black
- ◇ ZnS + 2Fe + Graphite
- ✦ ZnS + 2Fe + Silica
- ⊖ ZnS + 2Fe-Loose Charge
- ⊙ ZnS Alone
- ⊗ ZnS + Graphite
- ⊠ ZnS + 2Fe + Steel Wool

% Total
Zinc
Distilled



Summary

A study was made of the reduction of zinc sulfide under vacuum by such reducing agents as iron, iron and carbon, iron and silica, iron and a steel wool filter, iron oxide and carbon, and calcium oxide and carbon. The most successful process was that involving the use of a charge of $\text{ZnS} + 2\text{Fe}$ at 1000°C for one hour which produced a 98.0 percent total recovery of zinc and 95.5 percent zinc distilled as metal. The use of steel wool in a subsequent experiment proved to be effective in increasing the percent zinc distilled as metal from 94.7 to 97.8 percent by the reduction of sublimed zinc sulfide.

An attempt to improve the zinc condensates obtained from the iron reduction process by a differential distillation of a composite charge was wholly unsuccessful in that no purification was obtained and the condensate could not be produced in the form of a metallic sheet.

The success of this method for the production of zinc seems possible from a purely scientific viewpoint; however, its adaptation to a commercial scale of production would involve a number of economic aspects.

APPENDIX I

Raw Materials

Zinc Sulfide - Fisher - Technical-grade powder
Iron - Fisher - Electrolytic (pure) powder
Carbon - Fisher - Lamp or Oil Black powder
Steel Wool - American Steel Wool Mfg. Co. - Common household
Iron Oxide - Mallinkrodt - Technical-grade powder
Silica - Source unknown - White granular
Graphite - Discarded arc furnace electrode - Powdered
Calcium Oxide - Baker - Commercially pure lump, Ig. loss = 1%

APPENDIX II

Analytical ProceduresZINC

1. Weigh 0.200 to 0.500 grams sample into a 400 ml. beaker.
2. Add 5 ml. HNO_3 plus a small amount of KClO_3 to decompose sulfur.
3. When violent reaction subsides, place on hot plate and evaporate to dryness.
4. Cool, add 5 ml. cold water, 5 ml. HCl , and 10 ml. H_2SO_4 .
5. Evaporate to strong white fumes.
6. Cool, add 20 ml. cold water and heat to dissolve soluble salts.
7. Cool, add NH_4OH to alkalinity and heat to coagulate ppt.
8. Filter on fast paper, wash once with hot water.
9. Sluice $\text{Fe}(\text{OH})_3$ off filter paper, add 5 ml. HCl , neutralize with NH_4OH , heat to coagulate, and filter into original beaker.
10. Neutralize filtrate with HCl plus 5 ml. excess.
11. Dilute to 200 ml. with hot water and heat nearly to boiling.
12. Titrate hot with $\text{K}_4\text{Fe}(\text{CN})_6$ solution using UNO_3 outside indicator.
Split solution repeatedly during titration to avoid overtitrating.
Deduct 0.2 ml. from burette reading to allow for blank.

Calculations:

$$\frac{(\text{burette reading} - 0.2 \text{ ml.})}{\text{weight sample}} \times \text{gms Zn/ml. solution} = \text{gms Zinc per gm sample}$$

SULFUR

1. To 0.500 grams sample in a 400 ml. beaker add 10 ml. HNO_3 and a small amount of KClO_3 to decompose sulfur.
2. When violent reaction subsides, place on hot plate and evaporate to dryness.
3. Add 10 ml. HCl and evaporate to dryness.
4. Add 3 ml. HCl , 5 gms. NH_4Cl , and 50 ml. water and heat to boiling.
(At this point two alternate methods are used.)
- 5¹ Filter on fast paper, wash 6 times with boiling water.
- 6¹ Heat filtrate nearly to boiling, add 20 ml. hot BaCl_2 solution, cover, boil, allow ppt. to settle in beaker while on hot plate.
- 7¹ Filter hot on slow paper, wash 6 times with boiling water.
- 8¹ Ignite residue, cool in dessicator, weigh as BaSO_4 and convert to sulfur.

(For samples high in iron proceed from 4 above as follows:)

- 5² Neutralize with NH_4OH and heat to boiling to coagulate ppt.
- 6² Filter on fast paper, wash once with hot water.
- 7² Neutralize filtrate with HCl plus 10 ml. in excess.
- 8² Heat to boiling and proceed with 6¹ above.

Calculations:

$$\frac{\text{Weight BaSO}_4 \times 0.1374}{\text{weight sample}} = \text{weight sulfur/gm sample}$$

APPENDIX III

Operational Data Recorded During Typical Runs

Run No. L-26
 Date 12 June 1951
 Reaction Temperature 900°C
 Reaction Time at Temperature 3 Hours
 Charge ZnS + 2Fe

Log

| <u>Time</u> | <u>Temperature</u> | <u>Vacuum</u> | <u>Remarks</u> |
|-------------|--------------------|---------------|------------------------------|
| 1210 | 42°C | --- microns | Mech. pump on, valve closed. |
| 1220 | 42 | --- | Chge., valve opened. |
| 1245 | 42 | 100 | Diff. pump on. |
| 1252 | 42 | 25 | 10 amps. to fce. |
| 1300 | 120 | 25 | |
| 1308 | 150 | 25 | |
| 1217 | 200 | 25 | |
| 1331 | 260 | 25 | |
| 1342 | 300 | 25 | |
| 1358 | 350 | 25 | |
| 1417 | 400 | 25 | 20 amps. to fce. |
| 1420 | 450 | 25 | |
| 1422 | 500 | 25 | |
| 1425 | 560 | 25 | |
| 1427 | 600 | 25 | |
| 1430 | 650 | 25 | |
| 1433 | 700 | 25 | |

| <u>Time</u> | <u>Temperature</u> | <u>Vacuum</u> | <u>Remarks</u> |
|-------------|--------------------|---------------|--|
| 1436 | 750 | 25 | |
| 1439 | 800 | 25 | |
| 1442 | 850 | 25 | |
| 1447 | 900 | 25 | Reaction temp. reached, fce set at 15 amps. |
| 1747 | 900 | 25 | Reaction time complete, fce. off. |

Run No. L-37
Date 12 July 1951
Reaction Temperature 900°C
Reaction Time at Temperature 4.5 Hours
Charge ZnS + 2Fe + Carbon

Log

| <u>Time</u> | <u>Temperature</u> | <u>Vacuum</u> | <u>Remarks</u> |
|-------------|--------------------|---------------|----------------------------------|
| 1003 | 30°C | ---microns | Mech. pump on, valved closed. |
| 1115 | 30 | --- | Chge., valve opened. |
| 1240 | 30 | 75 | Diff. pump on. |
| 1350 | 30 | 40 | 10 amps. to fce. |
| 1602 | 405 | 40 | 20 amps. to fce. |
| 1622 | 760 | 35-60 | Initial pressure varia- tion. |
| 1624 | 800 | 30-75 | |
| 1626 | 840 | 50-110 | |
| 1627 | 850 | 100-125 | |
| 1629 | 865 | 160-290 | Diff. pump off. |
| 1630 | 880 | 400 | |

| <u>Time</u> | <u>Temperature</u> | <u>Vacuum</u> | <u>Remarks</u> |
|-------------|--------------------|---------------|--|
| 1632 | 900 | 500 | Reaction temperature reached. Fce. set at 17.5 amps. |
| 1634 | 900 | 600 | |
| 1700 | 900 | 155 | |
| 1717 | 900 | 100 | Diff. pump on. |
| 1727 | 900 | 33 | |
| 2102 | 900 | 35 | Reaction time complete. Fce. off. |

Run No. L-43
Date 20 July 1951
Reaction Temperature 900°C
Reaction Time at Temperature 4.5 Hours
Charge ZnS + 2Fe + Graphite

Log

| <u>Time</u> | <u>Temperature</u> | <u>Vacuum</u> | <u>Remarks</u> |
|-------------|--------------------|---------------|--|
| 0915 | 55°C | ---microns | Mech. pump on, valve closed. |
| 0930 | 55 | 500 | Chge., valve opened. |
| 0945 | 50 | 100 | Diff. pump on. |
| 0955 | 50 | 45 | 10 amps. to fce. |
| 1200 | 400 | 43 | 20 amps. to fce. |
| 1230 | 900 | 42 | Reaction temperature reached. 17.5 amps. to fce. |
| 1700 | 900 | 42 | Reaction time complete. Fce. off. |

Run No. L-52
Date 3 October 1951
Reaction Temperature 550°C

Reaction Time at Temperature 1 Hour

Charge No. 1 Composite

Log

| <u>Time</u> | <u>Temperature</u> | <u>Vacuum</u> | <u>Remarks</u> |
|-------------|--------------------|---------------|--------------------------------------|
| 1000 | 40°C | ---microns | Mech. pump on, valve closed. |
| 1010 | 40 | --- | Chge., valve opened. |
| 1050 | 40 | 95 | Diff. pump on |
| 1100 | 40 | 40 | 10 amps. to fce. |
| 1310 | 405 | 40 | 15 amps. to fce. |
| 1327 | 550 | 40 | Reaction temperature reached. |
| 1427 | 550 | 40 | Reaction time complete. Fce. off. |

APPENDIX IV

Calculations

I. Calculation of Charge

A. ZnS + 2Fe

$$(65.38 + 32.06) + 2(55.84) = 209.12$$

$$\% \text{ Zn} = 65.38/209.12 = 31.50\%$$

$$\% \text{ S} = 32.06/20.912 = 15.25$$

$$\% \text{ Fe} = 111.68/209.12 = \underline{53.25}$$

100.00%

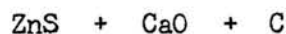
Desired: a 13.116 gm. charge

$$13.116 \times 0.5325 = 6.984 \text{ gms. Fe}$$

13.116 gms. charge

6.984 gms. Fe

6.132 gms. ZnS

B. ZnS + CaO + C

$$97.44 + 56.08 + 12.01 = 165.53 \text{ gms.}$$

$$58.86 + 33.88 + 7.26 = 100.00\%$$

$$\text{Zn} = 39.49\%$$

$$\text{S} = 19.37$$

$$\text{Ca} = 24.20$$

$$\text{O} = 9.68$$

$$\text{C} = \underline{7.26}$$

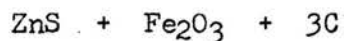
100.00%

$$\text{S/Zn} = 19.37/39.49 = 0.491$$

On the basis of a 15-gm. charge, the following amounts of materials are needed:

$$8.829 \text{ gms. ZnS} + 5.082 \text{ gms. CaO} + 1.089 \text{ gms. C} = 15.000 \text{ gms.}$$

C. ZnS + Fe₂O₃ + 3C



$$97.44 + 159.70 + 36.03 = 293.17$$

$$33.1 + 54.6 + 12.3 = 100.00\%$$

On the basis of a 10-gm. charge the following amounts of material are needed:

$$\text{ZnS} = 3.310 \text{ gms.}$$

$$\text{Fe}_2\text{O}_3 = 5.460$$

$$\text{C} = \underline{1.230}$$

$$10.000 \text{ gms.}$$

II. Sample Calculation of Zinc Metal Produced

Example: 1-28

Charge: ZnS + 2Fe

Assume: All S distilled and condensed as ZnS

$$\text{Wt. Zn in sample} = 4.189 \text{ gms.}$$

$$\text{Wt. Zn distilled} = 2.577 \text{ gms.}$$

$$\text{Wt. S in sample} = 0.074 \text{ gms.}$$

$$\text{Zn as ZnS} = \text{Wt S} \times \frac{\text{ZnS}}{\text{S}} = 0.074 \times \frac{65}{32} = 0.150 \text{ gms.}$$

$$2.577 \text{ gms. Zn distilled (total)}$$

$$\underline{0.150 \text{ gms. Zn as ZnS}}$$

$$2.427 \text{ gms. Zn as metal}$$

$$\frac{2.577}{4.189} \times 100 = 61.5\% \text{ Zn distilled (total)}$$

$$\frac{2.427}{2.577} \times 100 = 94.2\% \text{ Zn distilled as metal}$$

$$\frac{2.427}{4.189} \times 100 = \underline{58.1\% \text{ Zn metal produced}}$$

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