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The equilibrium of the reaction ZN + CO₂ = ZNO + CO

Clarence Ware Burkhart

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THE EQUILIBRIUM OF THE REACTION ZN + CO_2 = ZNO + CO.

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Clarence Ware Burkhart

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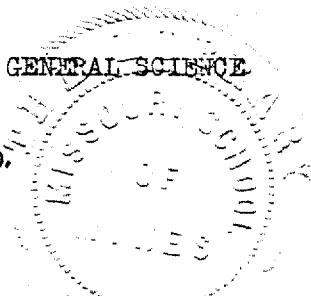ROLLA MO.

1922

Approved By _Chas. f. Clayton_ .

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INTRODUCTION.

Many attempts have been made in the last twenty years to smelt zinc ores in the electric furnace. The disadvantages of the present retort process have been discussed so often that they need not be dwelt upon here. The principle ones are, the low thermal efficiency of the retort furnace, low metal recoveries, small smelting units necessary, short life of the retorts and the difficulty of treating impure and low grade ores.

Electric smelting offers remedies for most of these difficulties, but has other disadvantages. One of the principle causes of failure of the earlier attempts to smelt zinc ores electrically, was the fact that the greater part of the zinc produced condensed as zinc dust or blue powder, instead of as liquid spelter. In recent years this trouble has been overcome by some investigators, and the factors involved are better understood than formerly. Much of the physical and chemical data required for a full understanding of the problem are still lacking.

The causes of poor condensation lie partly in the smelting conditions in the furnace and partly in the design of the condenser itself. Blue powder may be classed as physical blue powder if caused by improper physical conditions of condensation and chemical blue

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powder, if caused by impurities present in the mixture of gases and zinc vapor during condensation.

Physical blue powder is due mainly to poor condenser design, for example improper ratioof condensing surface to volume, or improper temperature regulation. A complete explanation of the physical aspect of condensation would require a discussion of the effects of surface tension, diffusion, viscosity, vapor tension, adhesion cohesion and capillary attraction. The inter-related effect of all these forces is not very well understood at the present time.

Chemical blue powder consists of minute globules of zinc, which have been coated with zinc oxide, sulphide or other similar foreign substance, which prevents the globules coalescing and joining the main body of the liquid zinc. It is largely due to conditions which give rise to impurities in the zinc vapor, which in turn form the inhibitive coatings on the zinc globules. Some of these impurities which give rise to the formation of blue powder are, water vapor, carbon dioxide, sulphur vapor or its gaseous compounds, sulphur dioxide, sulphur trioxide or carbon disulphide. Fine dust carried over with the zinc vapor is also an important cause of blue powder formation.

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The Effect of Carbon Dioxide in Blue Powder Formation.

One of the most important causes of the formation of chemical blue powder is carbon dioxide. This when present in more than small percentages causes oxidation according to the following equation. $Zn + CO_2 = Zno + CO$.

In a retort there is formed continuously a certain amount of carbon dioxide gas according to the equations. $Zno + CO = Zn + CO_2$. and $Zno + C = Zn + CO$., but due to the fact that there is always an excess of reduction material this carbon dioxide is partly decomposed. The carbon dioxide reacts with the carbon of the fuel as follows. $CO_2 + C = 2CO$. and at the temperature of the retort this reaction is very near complete, and since the evolution of the carbon dioxide is very uniform there is time for the above reaction to proceed.

Reduction in an electric furnace of the arc, or buried arc type, is more rapid than in a retort and in the immediate vicinity of the electrodes the reaction is violent and large amounts of carbon dioxide are produced in these spaces. This rapid evolution of carbon dioxide gas makes the chances for its decomposition less probable, and the result is that a greater amount of this gas enters the condenser with the zinc vapor than in the retort process.

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Carbon dioxide is also produced in the cooler parts of the furnace due to reduction of metals by carbon and carbon monoxide and at these low temperature carbon dioxide does not react with carbon to produce carbon monoxide. The percent of carbon dioxide gas present in retort smelting as taken from several sources is 1%, while that present in electric furnace smelting is very likely to be more than 1%.

Study of the Equilibrium of the Reaction. $Zn + CO2 = Zno + CO.$

The reaction $Zn + CO2 = Zno + CO.$ is reversible. Because of its importance in the metallurgical condensation of zinc, it is desirable to know the exact equilibrium of the reaction. The present study was undertaken with this end in view.

It has been well known for many years that the reaction goes from left to right at the temperature of condensation, if carbon dioxide is present in more than small percentages. The exact percentage of the carbon dioxide that can be present without causing oxidation of the zinc, however has not been accurately determined.

C. H. Fulton has drawn a curve(Trans. Am. Inst. Min.&Met. Eng. Vol. IX pg.260)showing that a temperature of 500 degrees C requires that 5% of carbon dioxide must be present before oxidation of thezinc takes place and a temperature of 750 degrees C requires

2% of carbon dioxide. This curve is based upon only a few scattered determinations and for this reason cannot be taken as definite. It is not an equilibrium curve in the physical chemical sense, as it does not take into consideration the varying percentages of zinc vapor present in the gases at the different temperatures. It is intended, however, to represent the actual conditions obtaining in a practical zinc condenser.

Some Theoretical Considerations

The equilibrium conditions for this reaction at any definite temperature are represented by the equation, $\frac{Conc.CO_2 \times Conc.Zn}{Conc.ZnO \times Conc.CO} = K.$

This constant K varies with the temperature. The reaction from left to right is exothermic, $Zn + CO_2 = ZnO + CO + 16760$ calories. According to the principle of Le Chatelier and Braun, this indicates that K must increase as the temperature rises, or zinc and zinc oxide concentrations being constant, the carbon dioxide that can be present without oxidation of the zinc taking place is greater at higher temperatures than at lower ones.

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INVESTIGATIONS

Outline of Experimental Work

An attempt was made to determine the equilibrium for the reaction $ZnO + CO = Zn + CO_2$ approaching from both sides of the equation. Considering this equation from left to right the task was to determine the percentage of carbon monoxide in a mixture of carbon dioxide and carbon monoxide necessary to reduce the zinc oxide at various temperatures. On the other hand considering the reaction from right to left, it was necessary to determine the amounts of carbon dioxide that would oxidize zinc in the presence of carbon monoxide at various temperatures. The actual equilibrium is expressed by the equation, $K = \dfrac{\text{Conc. Zn Vapor} \times \text{Conc. } CO_2}{\text{Conc. } CO}$. It therefore follows that the concentration of the zinc vapor in the gases during the tests must be taken into consideration in any calculations made or any conclusions drawn in regard to the equilibrium.

Description of Apparatus.

Figure 1 shows the apparatus used in the preparation and in the washing of the gases, also the supply bottle used for storage of the gas mixtures. The carbon dioxide was generated in an ordinary Kipp generator (A) from limestone and hydrochloric acid, then passed through

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bottle (I) containing a strong solution of sodium carbonate to remove traces of acid, then passed into the supply bottle (D).

Carbon monoxide was prepared in two different ways, one was by the reduction of carbon dioxide by the use of carbon at a bright red heat.(Note) and the other was by dropping 85% formic acid on hot concentrated sulphuric in generator (B). The reaction is as follows. H-COOH $=$ H2O $/$ CO. The carbon monoxide prepared by either method was washed by passing through a solution of pyrogallic acid bottle (2) to remove oxygen, and by passing through strong caustic solution bottle (3) to remove carbod dioxide. Small percentages of carbon dioxide were desired in the gas, with the exception of a few tests when nearly pure carbon monoxide was desired, but it was found most convenient to prepare the carbon monoxide fairly pure and add the proper amount of carbon dioxide to it in the container(D).

Figure (2) represents the purification train, combustion furnace and tube. With the proper mixture of gases in the supply bottle it was necessary to purify them before entering the combustion tube where the reactions took place. This was accomplished by passing the gases over stick phosphorus in bottle (4) to remove oxygen, and by passing through strong sodium carbonate solutions Note. Tis method is described in detail further on.

bottles (5) and (6), to remove traces of acids and fumes. Moisture was taken out of the gases by passing through tubes (7)and (8), containing respectively, calcium chloride and phosphorus pentoxide. In order to insure the absence of oxygen a spiral of copper (9) was placed in the combustion tube in front of the boat, which contained either the zinc or zinc oxide. During the tests the copper was heated to a good red.

(E) is the furnace, a three unit electrical heated type purchased from the Denver Fire Clay Co., in which the combustion tubes (F) were heated. The samples of zinc or zinc oxide were contained in alundum boats (IO). (II) is a water seal, which served as a means of estimating the rate of flow of the gas through the combustion tube. These combustion tubes were made of fused pyrex glass $\frac{5}{4}$" by 4' and would withstand a temperature of 800 degrees C without softening.

The gas analysis apparatus is the kind as described by Burrel and Siebert in Bureau of Mines Bulletin#42 pg. 42. This apparatus consists of five absorption pipettes, one combustion pipette, for the determination of hydrogen and one pipette which serves as a nitrogen container. The manipulation of this apparatus

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is easy and excellent results can be obtained on mixtures of gases
containing carbon dioxide, carbon monoxide, methane, ethane, ethylene,
oxygen, hydrogen and nitrogen.

Preparation of Carbon Monoxide by the Furnace Method.

At first it was thought advisable to prepare this gas by
passing carbon dioxide through charcoal at a bright red heat, about
1100 or 1200 degrees C, in order to insure a gas as free as possible
from impurities. Figure (3) is a curve showing the percentage
decomposition of carbon dioxide by carbon at various temperatures
and pressures. The reaction is. $CO_2 + C = 2CO$. In the actual preparation
of the gas a temperature of about 1000 degrees C was used in all
cases; any small amounts of carbon dioxide remaining were removed
in the washing bottles.

The furnace used for this work was the Fulton gran- annular
resistance type (C). The reduction material was either charcoal or
graphite (4). The use of charcoal was not satisfactory because of the
presence of much volatile matter, which had to be removed before
collection of the gas could be started. It was also found impossible
to remove all of the hydrogen from the charcoal. The manipulation is
as follows. A $\frac{3}{4}$" silica or porcelain tube containing a bed of charcoal
about 6" in length was placed in the furnace, heated to about 1000

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degrees C and the carbon dioxide passed through slowly. The carbon dioxide coming in contact with the charcoal was converted into carbon monoxide, which was washed as already described and passed into the supply bottle. As stated above gas prepared from charcoal was not satisfactory and for this reason graphite was used. This gave a good clean gas, but this method proved to be very annoying and expensive, as the silica or porcelain tubes would inherently crystallize and crack at the points where the highest temperatures were maintained. The use of the furnace was abandoned and the carbon monoxide used in the latter part of the work was prepared by the formic acid, sulphuric acid method.

Experimental Work and Results.

The first work undertaken was a study of the equilibrium of the equation, $ZnO + CO \rightleftharpoons Zn + CO_2$ approaching from left to right. The general plan followed was to determine the amount of carbon dioxide, in the presence of carbon monoxide, necessary to prevent reduction of the zinc oxide. The tests were carried out as follows. About .5 gram of the zinc oxide was weighed out into an alundum boat and placed in the combustion tube in the furnace. The gas was allowed to pass slowly through the tube and when all of the air

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had been displaced, the heat was turned on and held for one hour after the desired temperature had been reached. The combustion tube was then examined under the microscope for evidences of metallic zinc, reduced from the zinc oxide.

It was found that a slight amount of reduction took place, even with as high as 60% of carbon dioxide present in the gas mixture. This is explained theoretically as follows; the equilibrium constant is expressed by the constant $K = \dfrac{CO \times ZnO}{CO_2 \times Zn}$ hence if zinc vapor is present in small amounts only, as is the case in these experiments, carbon dioxide can be present in large percents without preventing reduction. Since the zinc vapor concentration is unknown this method of experimentation did not enable us to calculate the value of K.

These experiments however show one important point and that is that there is some reduction in mixtures of the two gases even when high percentages of carbon dioxide are present . The results of these experiments are given in tabulated form on the following page.

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TABLE I.

Percent CO_2	Temperature ^{0} C.	Remarks.
6.3	755	Considerable Reduction.
17.3	749	"
22.4	767	"
22.6	595	Slight Reduction.
30.5	755	"
33.0	757	"
52.8	752	"
70.7	753	"
94.0	753	"

Experiments With Metallic Zinc.

        This part of the work was undertaken in order to reach the equilibrium of the equation $ZnO + CO = Zn + CO_2$. approaching from the right hand side. In the early experiments in this connection tests were made using small percentages of carbon dioxide in carbon monoxide and passing over pure stick zinc at different temperatures. In all cases oxidation was noticed in the cooler portions of the tube. This could not be called oxidation at the temperature taken, because it was a reaction between the zinc vapor and the carbon dioxide gas at temperatures lower than that of the vapors immediately above the zinc. As a result of this condition it was decided to make a series of tests, noting in particular the nature of the deposit, if any, in the region of highest temperature, that observed. Conclusions were to be drawn as follows; if zinc oxide was present in the immediate region of the zinc, the effect was to be called oxidation, and if no zinc was present , the effect was to be recorder as oxidation. When oxidation did not occur there was usually evidence of bright zinc in the hot portion of the tube.

        A great number of tests were made under these conditions, using from 3-9% of carbon dioxide in carbon monoxide between the

temperatures 600 and 800 degrees C. The manipulation was the same as described above for zinc oxide, the temperature being held for one hour and two litres of the gas were passed over the zinc. The boat contained about 20 grams of zinc for each test. In all cases there was volatilized sufficient zinc to saturate the gases with zinc vapor at the given temperature. The results are plptted and the curve is shown in figure (4). This curve shows in general that,in mixtures of gases saturated with zinc vapor between the above temperatures, increasing percentages of carbon dioxide require increasing temperatures to prevent oxidation.

CONCLUSIONS.

A brief summary of the conclusions drawn, from the results of this investigation are as follows.

I. In a mixture of carbon dioxide and carbon monoxide, at 750^0 C. zinc oxide is considerably reduced, when the percentage of carbon dioxide present is low.

There is a slight reduction even when the percentage of carbon dioxide is high.

II. In a mixture of carbon dioxide and carbon monoxide, in which the percentage of carbon monoxide varies from 3 to 9%, and between the temperatures of 600^0 and 900^0 C., oxidation varies inversely as the temperature, the gases being saturated with zinc vapor.

III. The effect of the gas mixture upon metallic zinc, depends largely upon the concentration of zinc vapor in the gases.

Remarks.

The work with metallic zinc is being continued and all determinations that gave doubtful results will be repeated, in order to determine the slope of the curve more definitely.

In the gas mixtures used there was always some nitrogen present and also a trace of hydrogen, but the effect of these upon the results of the determinations was considered negligible.
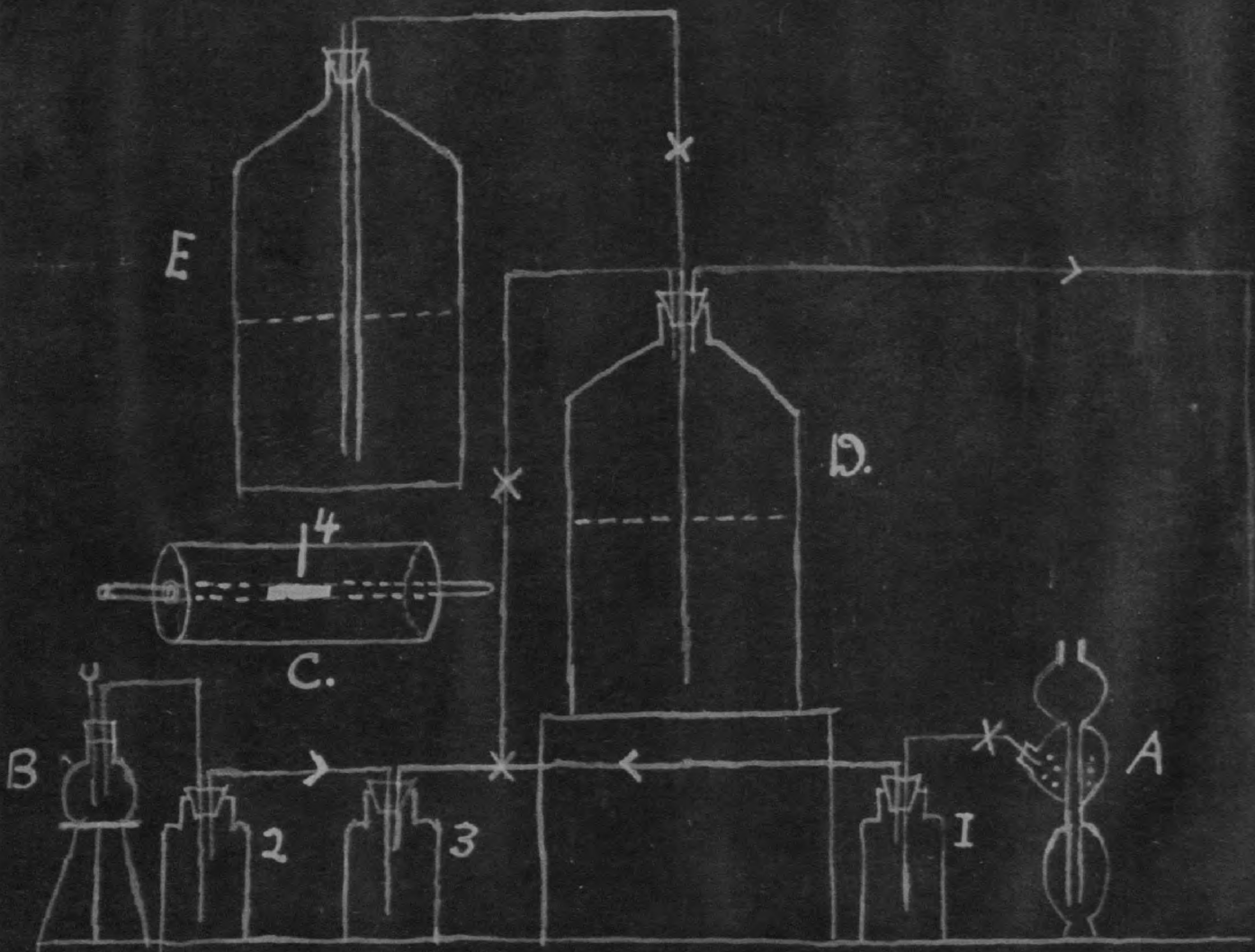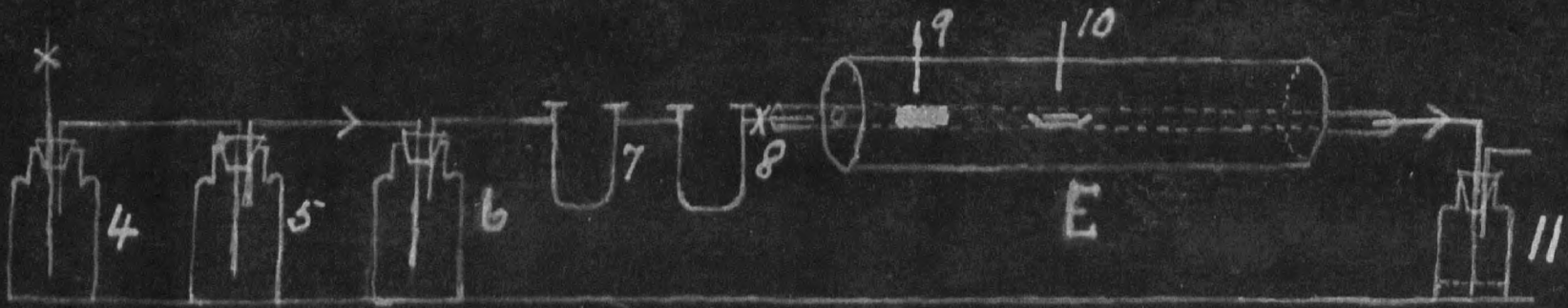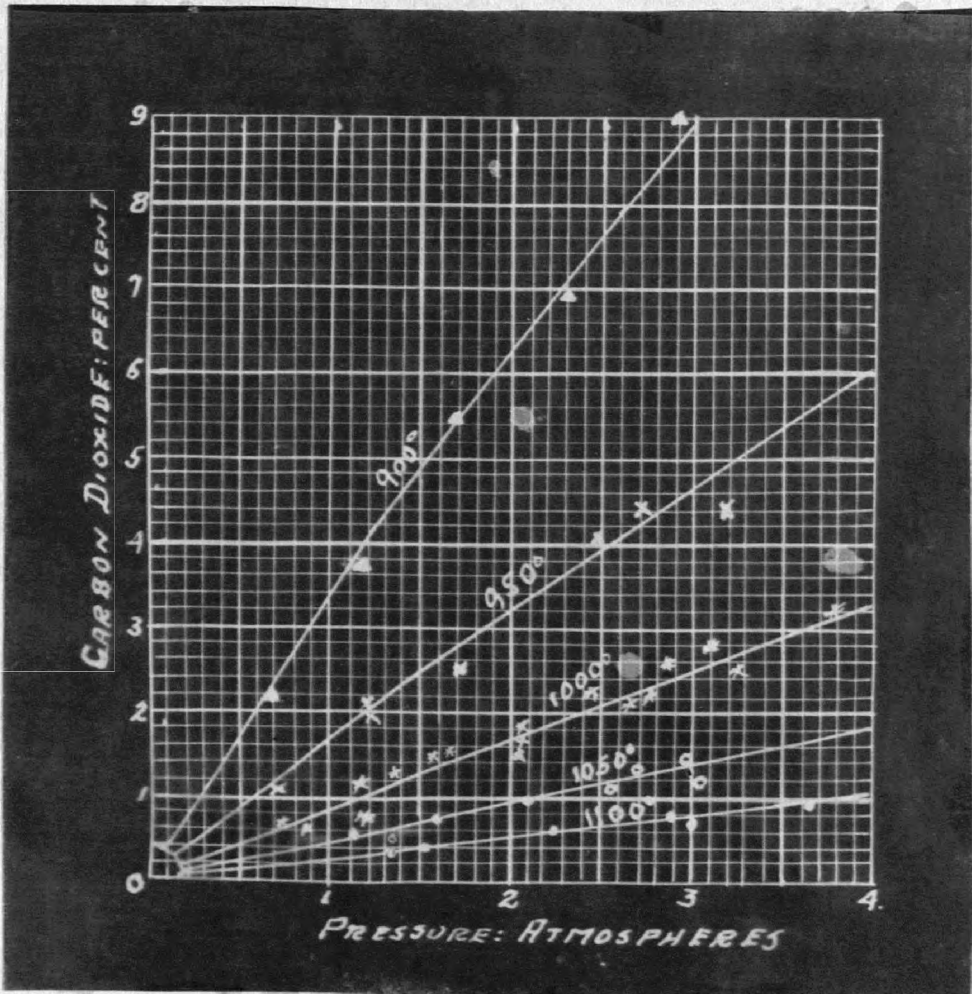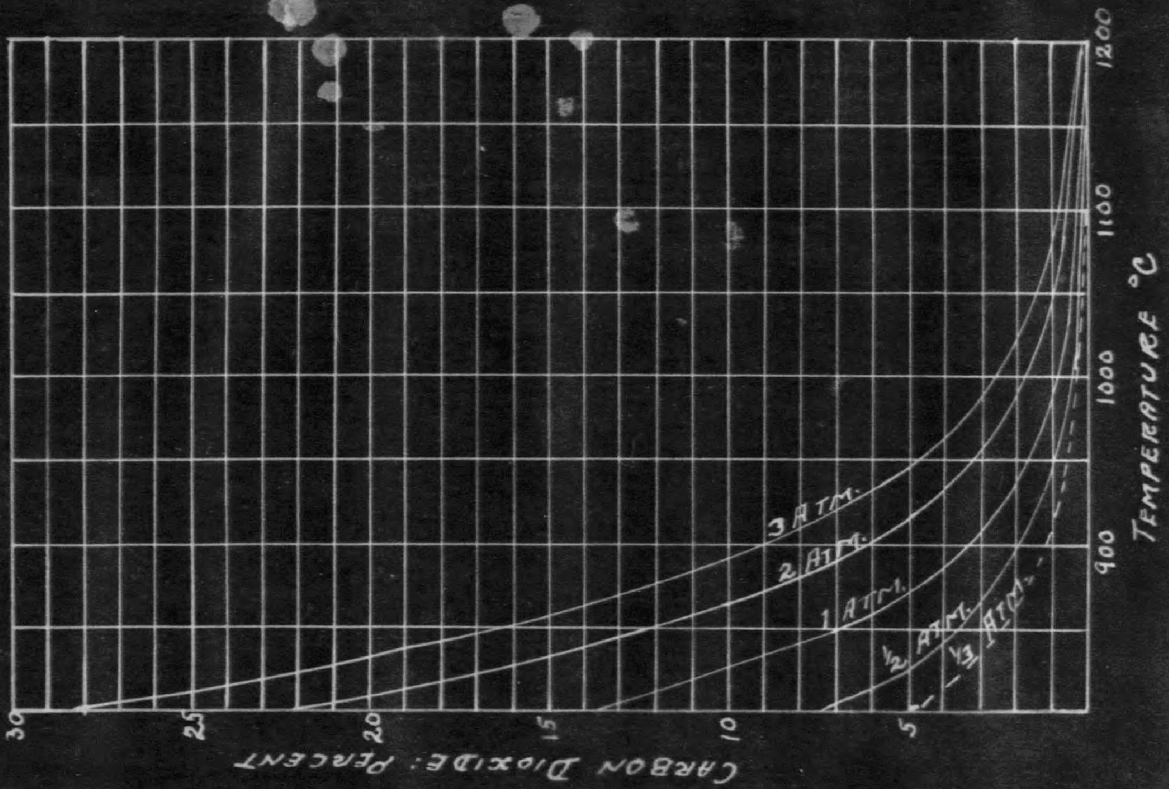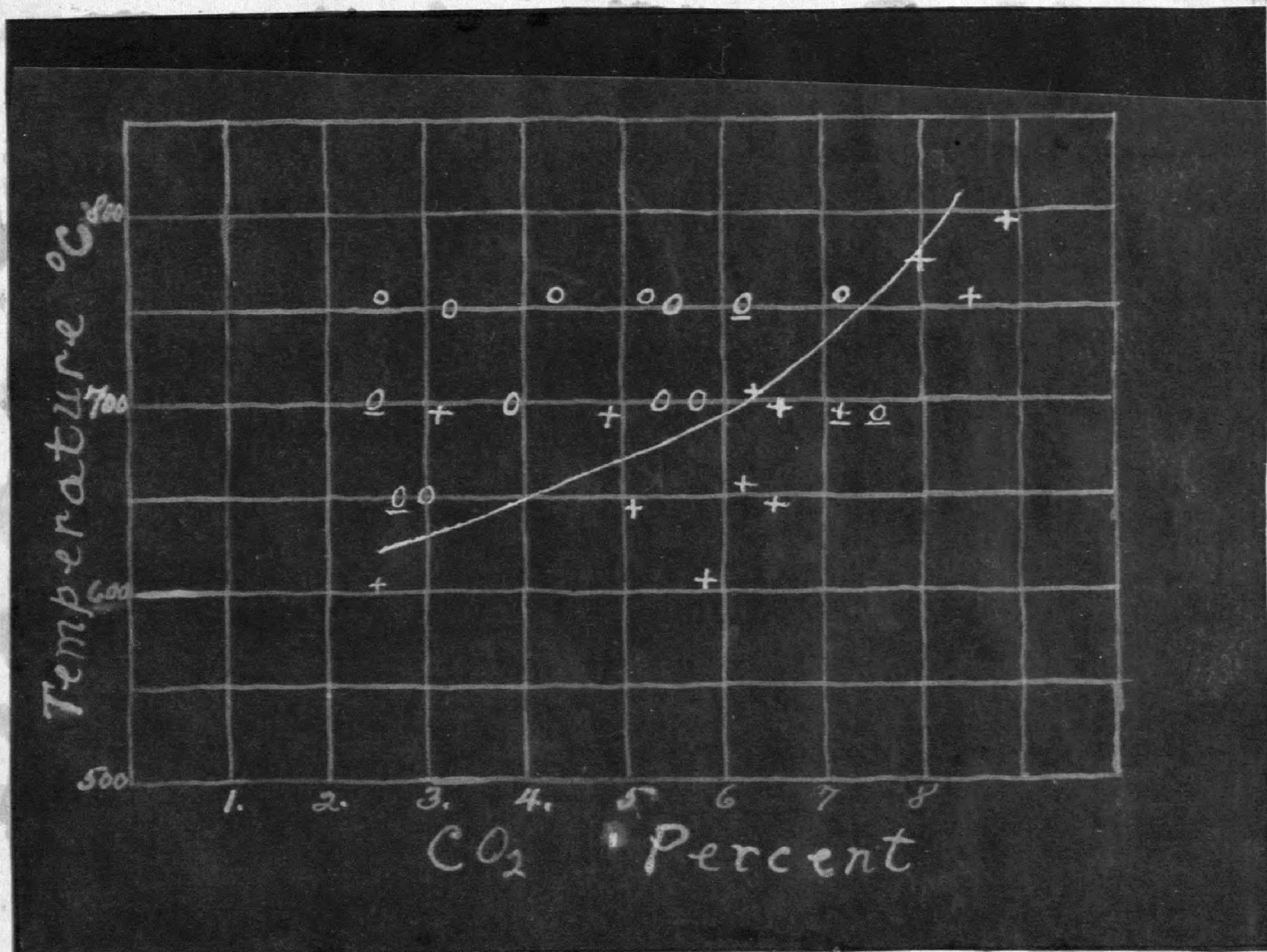
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Figure I.

I6.

Figure 2.

Figure 3.

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Figure 4.

<u>Note</u>
O indicates bright zinc.
+ indicates oxidation.
O doubtful probably no oxidation.
± doubtful probably oxidation.

I9.

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