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A STUDY OF THE REDUCTION OF ZINC OXIDE BY  
HYDROGEN AND METHANE.

BY

FRED A. WEIRICH....

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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 CHEMICAL ENGINEERING

Rolla, Mo.

1926

Approved by \_\_\_\_\_  
Associate Professor of Chemistry

*W. D. Turner*  
*Head Dept. Chem.*

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(1)  
A STUDY OF THE REDUCTION OF ZINC OXIDE BY  
HYDROGEN AND METHANE.

I. A Brief Review Of Previous Work

(1).Introduction.

The successful reduction of zinc ores and the condensation of its vapor has been a slow but steady climb. The difficulty in the extraction of zinc is due to certain inherent properties in the zinc itself. Zinc reduction, as carried out in the present retort method, probably requires the most exact control of any successful method of metal production today. This is evidenced by the necessary continued use of employing small units which are susceptible to very careful control and in which the various conditions of the reactions are practically identical in each case.

As the essential features of the retort process have not been and probably will not be changed, future development of this process must depend upon modifications of the present process, rather than upon radical changes. These modifications may be made by: reducing the labor, lengthening the life of the retort, reducing the cost of producing the cost of the ore for reduction, and studying the internal mechanism of the process, with regard to temperature, concentration of the vapors, and rate of reduction and condensation.

(2)

The net result of the present process is summed up in the statement coke and ore produce gas and zinc, or that carbon and zinc oxide produce carbon monoxide and zinc. Different metallurgists offer divers explanations of the actual steps in this reaction, but the net result in each case; and, if equilibrium is obtained, a condition in which all the partial reactions contributing to the net result are proceeding at a uniform rate, then the various explanations proposing the sequence of reactions are reconciled, since there is actually no sequence but a simultaneous procedure of all.

(2). The  $H_2 + ZnO \rightleftharpoons Zn + H_2O$  reaction

Experimentation with this equilibrium is difficult due to the fact that there is such a small amount of water vapor in equilibrium with hydrogen and oxygen. O.C.Ralston (bib. 1) believes that such experimentation would be unprofitable because the constants of the equilibrium may be calculated with far greater accuracy than actual experiments would show.

The reduction by hydrogen is interesting because it plays a small part in actual reductions where water vapor is present, but plays its largest part in the reduction by methane or by natural gas. R.S.Dean and three others (bib. 2) found that by reducing zinc oxide with hydrogen, the gas became nearly saturated with zinc

(3)

vapors at  $650^{\circ}\text{C}$ ., its partial pressure being reached with 2.9 % zinc. They obtained complete condensation of the vapor, however, with only 2 % zinc vapor in the gas. Upon calculating the constants for the hydrogen-zinc oxide equilibrium, it has been shown that a given quantity of hydrogen-above  $830^{\circ}\text{C}$ .- will reduce more zinc oxide than the same volume of carbon monoxide; but that below  $830^{\circ}\text{C}$ , a given concentration of water vapor will oxidize zinc more readily than the same concentration of carbon dioxide. It follows then, that the hydrogen assists in the reduction but increases the tendency to oxidize in condensation.

Dr. C.H.Fulton (bib. 3) found that the reduction by hydrogen began at a much lower temperature than when carbon was used as the reducing agent. In his experiments the reduction by hydrogen began before a high enough temperature was reached to start the carbon reduction. Experiments carried on by Deville (bib. 4) showed that in the reduction by hydrogen, equilibrium demands an increasing concentration of hydrogen with an increase in temperature.

(3). The Methane-zinc oxide reaction.

In connection with the study of gaseous reduction metallic oxides, Fay and his collaborators (bib. 5) demonstrated that reduction of zinc oxide by methane

(4)

took place at a temperature as low as 152-59<sup>0</sup>C. A cold mirror was placed at the outlet of their reducing apparatus and the water vapor showed as a haze on the mirror.

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## II. Investigations

### (1). Purpose of the Investigation

The purpose of the investigation was to make a study of the reduction of zinc oxide by hydrogen and methane and to study the conditions for the most efficient condensation of the zinc vapor.

There are five equilibria to be considered:

#### (a). Zinc oxide with zinc and oxygen.

This reaction will take place and equilibrium will be quickly established at high retort temperatures. The percent of the net charge present at any moment as zinc and oxygen, however is small. In order to get decomposition of the zinc oxide, therefore, the equilibrium must be disturbed by introduction of a reducing agent to combine with and remove the oxygen.

#### (b). Carbon monoxide with carbon dioxide and carbon.

At zero degrees the percent of carbon dioxide is negligible. At 1,000<sup>0</sup>C the amount has increased to 8 per cent and will play a part in the reoxidation of the zinc vapor. This reaction reaches equilibrium rather slowly compared to some of the other reactions and it is pos-

sible to condense the zinc <sup>5.</sup> before the concentration of carbon dioxide has become high enough to be detrimental.

(c). The carbon dioxide with carbon monoxide and oxygen.

Since the total quantity of carbon dioxide is small and since this reaction is at equilibrium when only a small percent is in the form of carbon monoxide and oxygen, the total of oxygen from this source is very small.

The two previous reactions, (b) and (c) are summed up in the reaction



As there is also some carbon dioxide present so that there will be some of each of the four gases present when the final equilibrium is reached.

(d). Water vapor with hydrogen and oxygen.

This reaction comes quickly to equilibrium with a small amount of hydrogen and oxygen formed. If the water vapor is removed from the region of condensation, the equilibrium is kept unbalanced. In actual reduction with hydrogen complete equilibrium is probably not reached.

(e). Methane with carbon and hydrogen.

Below 850°C this reaction comes to an equilibrium in which methane is the main component of the resulting gas. Above this temperature the equilibrium is displaced to the right. The fact that with methane passing over

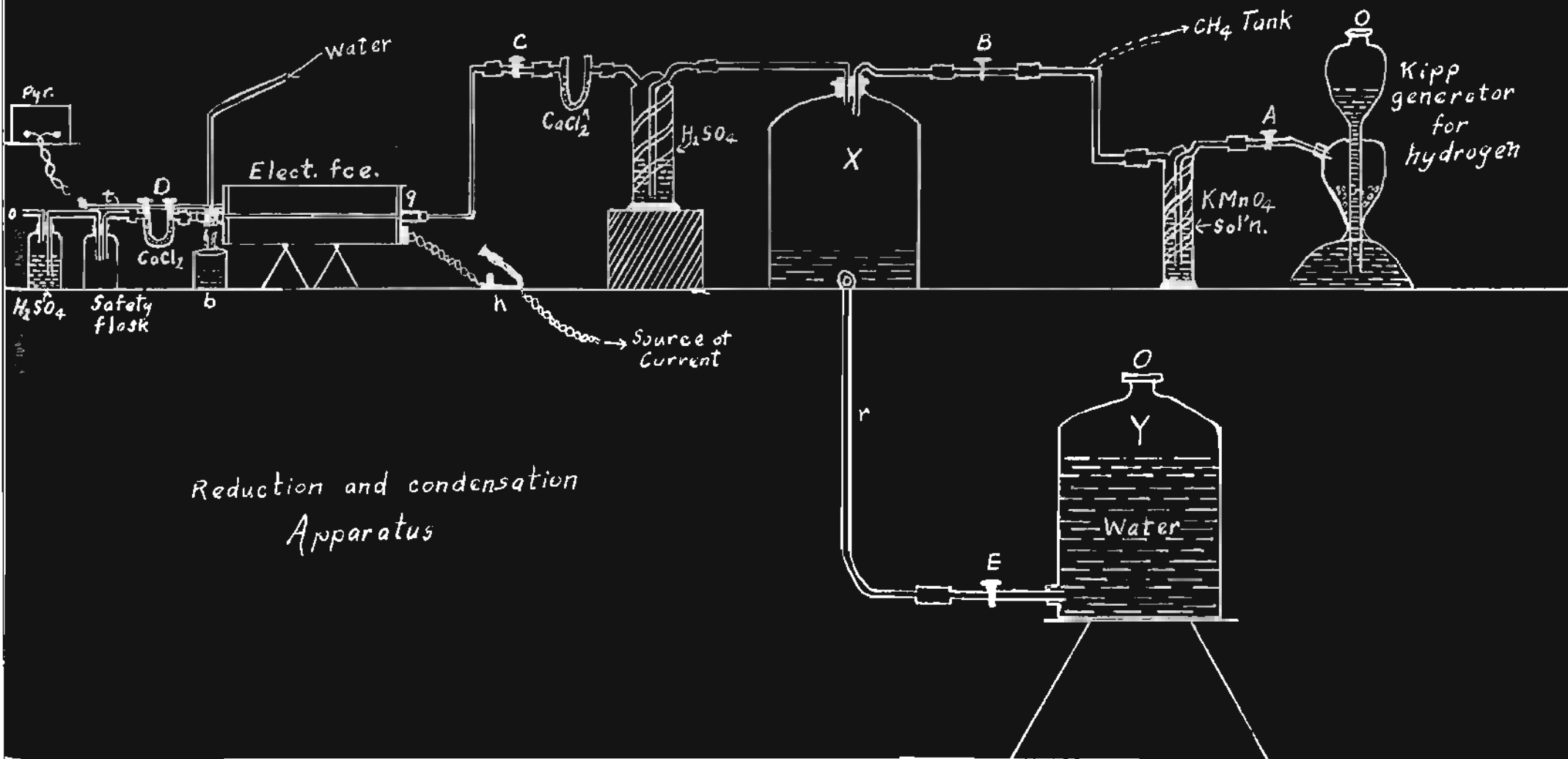


zinc oxide at  $1,000^{\circ}\text{C}$  in which the main products are zinc and carbon, shows that at or above this temperature the presence of carbon deposits indicate that there is sufficient dissociation to give a concentration of hydrogen such as will react with the zinc oxide to produce water and metallic zinc.

(2). Description of the Apparatus.<sup>7</sup>

The bottle Y was raised above the bottle X and the pet-cocks E, C, and D were opened, A and B being closed. The top of the bottle Y was open to the atmosphere so that the water ran by gravity into the bottle X. When the level of the water had almost reached the top of the bottle X, pet-cock E was closed and A and B opened. (Note: At this point the boat containing the zinc oxide was inserted in the furnace, the apparatus being disconnected at the U-tube D, so that the apparatus would not have to be reopened after the system had been cleared of air). The hydrogen was then passed thru the system until all the air was eliminated. The bottle Y was then lowered, the pet-cocks C and D closed, and the pet-cock E opened. When the bottle X was filled with hydrogen, pet-cocks A, B, and E were closed and the bottle Y again elevated above the bottle X. By regulating the pet-cocks E, C, and D the gas could be made to flow thru the furnace at a uniform rate.

The hydrogen coming from the Kipp generator was first passed thru a potassium permanganate solution to remove any hydrochloric acid gas which might be carried over by the hydrogen. In order that no water vapor would be carried thru the furnace by the hydrogen, it was first passed thru a strong solution of sulfuric acid and then thru a U-tube containing calcium chloride. The water vapor formed by the reaction of hydrogen upon the



Reduction and condensation  
Apparatus

10 a



PHOTOGRAPH OF APPARATUS  
RESEARCH LABORATORY

zinc oxide was held by the calcium chloride at D. A bottle containing sulfuric acid was connected to the outlet of the furnace thru a safety bottle, in order that the apparatus may be air-tight. A region for sudden cooling of the vapors was provided just outside of the furnace at the outlet end of the tube and consisted of a small piece of cloth, one inch wide, which was wrapped around the quartz tube and upon which cold water dripped constantly during each run.

A tube of fused quartz was used for the experiments. The maximum temperature of the furnace is  $1,000^{\circ}\text{C}$ . A pyrometer was used to read the temperatures. The electric circuit was opened or closed by means of the key k, and regulated by means of a rheostat.

The bottle X was graduated so that the amount of gas sent thru the system could be noted.

The cloth around the quartz tube served the double purpose of keeping the rubber stopper at the end of the tube burning as well as providing a cooling zone for the condensation of the zinc vapor.

### (3). Experimental procedure:

Preliminary runs were made with hydrogen, using one gram samples of 100 mesh Baker's analyzed zinc oxide. The hydrogen was first passed thru slowly, the temperature being raised 50 degrees in each succeeding run. The hydrogen was then passed thru quickly and the

10.

difference in condensation noted. The amounts of water vapor and zinc formed in each run were calculated from the known amount of zinc oxide that was volatilized from the boat. These results are not quantitative because there was a certain amount of zinc oxide sublimed from the boat and condensed on the tube.

The runs designated 'a' are the slow runs in which one tenth of a liter of hydrogen was passed over the zinc oxide per minute. Eight liters were passed over the zinc oxide, making the length of the run eighty minutes. The runs designated (b) were the rapid runs, in which one liter was passed per minute over the zinc oxide, making a total of eight minutes for the eight liters.

The experiments with methane were similar to those with hydrogen except for the following differences: One half gram samples were used; in the slow runs, methane was passed over the zinc oxide at the rate of .06 liters per minute for a period of thirty minutes. During the rapid reduction, methane was passed over the zinc oxide at the rate of .26 liters per minute for a period of thirty minutes.

(4). Tabulation of the data.

a<sub>1</sub> Reduction by hydrogen.

| Run no. | Temp.              | ZnO left, gms. | Water, gms. | Zn, gms. |
|---------|--------------------|----------------|-------------|----------|
| 1a.     | 500 <sup>0</sup> C | 1.0990         | 0.0000      | 0.0000   |
| 1b      | 500                | 1.0000         | 0.0000      | 0.0000   |
| 2a      | 550                | 0.9965         | 0.0008      | 0.0028   |
| 2b      | 550                | 0.9976         | 0.0007      | 0.0021   |
| 3a      | 600                | 0.9840         | 0.0035      | 0.0129   |
| 3b      | 600                | 0.9954         | 0.0010      | 0.0037   |
| 4a      | 650                | 0.9578         | 0.0099      | 0.0364   |
| 4b      | 650                | 0.9761         | 0.0052      | 0.0192   |
| 5a      | 700                | 0.8906         | 0.0242      | 0.0877   |
| 5b      | 700                | 0.9570         | 0.0095      | 0.0345   |
| 6a      | 750                | 0.7288         | 0.0602      | 0.2179   |
| 6b      | 750                | 0.9208         | 0.0175      | 0.0636   |
| 7a      | 800                | 0.4951         | 0.1116      | 0.4057   |
| 7b      | 800                | 0.8110         | 0.0418      | 0.1518   |
| 8a      | 850                | 0.2376         | 0.1686      | 0.6125   |
| 8b      | 850                | 0.6449         | 0.0785      | 0.2847   |
| 9a      | 900                | 0.0008         | 0.2209      | 0.8028   |
| 9b      | 900                | 0.4283         | 0.1264      | 0.4593   |
| 10a     | 950                | 0.0000         | 0.2212      | 0.8034   |
| 10b     | 950                | 0.1981         | 0.1773      | 0.6443   |
| 11a     | 1000               | 0.0000         | 0.2212      | 0.8034   |
| 11b     | 1000               | 0.0004         | 0.2210      | 0.8031   |

a<sub>2</sub> Detailed description of results.

- 1a. No zinc formed
- 1b. No zinc Formed
- 2a. A light brown deposit on the tube and on the front of the boat.
- 2b. A dark brown deposit on the front of the boat with a very light blue haze deposited on the tube above boat.
- 3a. Light yellow deposit in the boat, on the front of which was a light layer of blue powder.
- 3b. No yellow deposit but a trace of blue powder on the boat.
- 4a. Blue powder formed but no metallic zinc.
- 4b. Very small crystals of metallic zinc were formed on the front of the alundum boat.
- 5a. No metallic zinc formed; only blue powder.
- 5b. Small, bright globules of metallic zinc condensed on the tube, but the majority of the condensate was blue powder.
- 6a. Only blue powder formed.
- 6b. About the same amount of metallic zinc formed as in the previous run.
- 7a. Metallic zinc showed up for the first time with slow condensation. Sublimed zinc oxide was deposited for the first time on the tube.



13.

7b. Front end of boat covered with pure, metallic zinc.

Altho less zinc oxide was volatilized than in the previous run, a much larger percentage of zinc was formed.

8a. About fifty percent metallic zinc and fifty percent blue powder were formed .

8b. Over fifty percent metallic zinc formed. It was found on the front of the boat and on the tube in front of the boat.

9a. No globules of zinc was formed but about fifty percent of the condensate was made up of crystals of zinc and zinc of a massive variety.

9b. Much larger crystals of zinc found than at any previous run. Less blue powder.

10a. There seems to be a certain order in which the various condensates place themselves. The metallic zinc is found in each case nearest the boat and the blue powder in front of this. If any zinc oxide sublimes, it is found in front of the blue powder.

10b. Majority of deposit was zinc in the form of crystals.

11a. For the first time in a slow run over fifty percent of the deposit on the tube was metallic zinc. However, more zinc oxide sublimed than ever before.

11b. The deposit on the interior of the tube was the same as the last run except that there was less zinc oxide sublimed and condensed on the tube.

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b<sub>1</sub> and b<sub>2</sub>. Reduction by methane and detailed description.

(1). Slow reduction and condensation.

Run.

1. Temp., 600°C. A fine deposit of zinc oxide was deposited near the outlet of the boat.
2. Temp., 650°C. Larger amount of zinc oxide sublimed.
3. Temp., 700°C. Same condition as above except the amount of zinc oxide condensed on the tube was greater.
4. Temp., 750°C. No trace of blue powder or metallic zinc. Sublimed zinc oxide the only product.
5. Temp., 800°C. The contents of the boat were gray. A deposit of yellow powder was formed in front of the boat and in front of this a deposit of sublimed zinc oxide.
6. Temp., 850°C. The boat was covered with a fine layer of carbon and a very small amount of metallic zinc was found on the front of the boat. The contents of the boat were gray. A small quantity of blue powder was deposited in front of the boat.

Between this deposit and the boat were a few crystals of metallic zinc.

7. Temp.,  $900^{\circ}\text{C}$ . A larger amount of carbon was formed this time. It is this that is turning the boat black at each run and causing the contents of the boat to assume a gray appearance. Some metallic zinc was condensed in front of the boat and in front of this zinc was a deposit of blue powder containing a few globules of metallic zinc. The zinc deposited immediately in front of the boat was a mixture of globules and crystals.
8. Temp.,  $950^{\circ}\text{C}$ . Contents of the boat were a mixture of zinc oxide and carbon, with more carbon than before. In front of the boat were condensed mirror bright globules of zinc and in front of this, blue powder. Immediately behind the boat was a small deposit of zinc globules and behind this some blue powder.
9. Temp.,  $1,000^{\circ}\text{C}$ . Only carbon remained in the boat. Carbon was also deposited at either end of the boat in the quartz tube. In front of the carbon was deposited a mixture of globules and flat pieces of metallic zinc. Blue powder was formed in front of the metallic zinc.

(2). Rapid reduction and condensation,

Run.

1. Temp., 600<sup>0</sup>C. No volatilization of zinc oxide.
2. Temp., 650<sup>0</sup>C. No indication that there was any reduction of zinc oxide. The reason for the absence of volatilization in the rapid reduction may be due to a slightly lower temperature in the quartz tube on account of the more rapid passage of the methane.
3. Temp., 700<sup>0</sup>C. A very small amount of zinc oxide was volatilized from the boat and deposited near the front end of the quartz tube.
4. Temp., 750<sup>0</sup>C. First traces of reduction. Along with the blue powder that was condensed, was a layer of sublimed zinc oxide.
5. Temp., 800<sup>0</sup>C. Metallic zinc was produced and condensed in front of the boat. The contents of the boat were a mixture of zinc oxide and carbon, which gave a gray color. Blue powder was found in front of the metallic zinc but no zinc oxide was sublimed during this run.
6. Temp., 850<sup>0</sup>C. The boat was black and the contents of the boat a dark gray. At the top of the tube in front of the boat were condensed small, bright,

globules of metallic zinc; in front of this, blue powder; and in front of this, sublimed zinc oxide. Zinc oxide was also found behind the boat.

7. Temp., 900°C. Less blue powder and more metallic zinc. Contents of boat black from the carbon. Deposits of sublimed zinc oxide were found behind the boat and near the front of the tube.
8. Temp., 950°C. Boat black and contents of boat black. Much larger globules of metallic zinc were formed than in the previous run. At the top of the tube in front of the metallic zinc was a deposit of blue powder. Immediately below this deposit was a narrow strip of sublimed zinc oxide.
9. Temp., 1,000°C. The only contents of the boat were spongy masses of carbon. Immediately in front and behind the boat was deposited the same variety of spongy carbon. In front of the carbon, at the top of the tube, was a deposit of bright globules of metallic zinc; while in front of this was a mixture of metallic zinc and blue powder. Pure blue powder was deposited in front of this.

### III. Discussion of results.

#### (1). Reduction by hydrogen.

The blue powder formed in the process was al-  
found just beyond the metallic zinc. This is proba-  
bly due to two causes:

- a. At the higher temperatures there is but slight tendency for reoxidation of the zinc by the water vapor.
- b. There is a rather high viscosity of zinc at the lower temperatures, preventing it from coalescing until superficial oxidation has taken place.

#### (2). Reduction by methane.

It is possible to secure reduction of zinc oxide with methane, but in general, to obtain the same results as with hydrogen, higher temperatures are necessary.

Above  $900^{\circ}\text{C}$ ., carbon was deposited on the tube on both sides of the boat and was always the product nearest the boat. This is due to the fact that at any given instant there was contained in the region of the boat the four substances, carbon, hydrogen, oxygen, and zinc; and that the carbon, being non-volatile was deposited first. The tendency for the

hydrogen to unite with the oxygen at this temperature and pass off as water vapor, left the zinc free to deposit as such when it reached a region in the tube where it would no longer be volatile. The deposits of carbon and metallic zinc were quite distinct from each other.

(3). Conclusion.

Under the best conditions obtained the condensate contained about seventy five percent metallic zinc. This was obtained by a rapid stream of excess gas above the boiling point of zinc, with condensation at as low a temperature as possible.

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