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THE CHROMIUM-OXYGEN-HYDROGEN EQUILIBRIUM IN LIQUID IRON

By

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ABSTRACT

Chromium is one of the most important alloying elements used in steel. The knowledge of its behavior in molten iron has long been desired. Data obtained in industrial operating furnaces involve many variables, and have been of little help in establishing equilibria relationships. The present investigation has been undertaken to study the fundamental physico-chemical behavior of chromium in liquid iron under various oxidizing and reducing conditions.

To avoid contamination with foreign oxides, chromite and chromic oxide crucibles have been used as containers. A slip-casting method for the manufacture of crucibles from chromic oxide has been successfully developed. The firing was done at 1430° C in a graphite crucible in a high frequency induction furnace, followed by heating to 1500° C in a globar tube furnace to remove the carbon. It has been found impossible to get good results by firing in air. The removal of carbon is necessary because it causes excessive porosity of the ingot.

During the course of the equilibrium investigation, more than 100 experimental heats have been made at 1595° C $\pm$ 5° in a high frequency induction furnace under water vapor - hydrogen atmospheres of known compositions. The charge consisted of mixtures of electrolytic iron and electrolytic chromium. Due to film formation on the surface of the melt, equilibria could not be reached from the high chromium side. Some heats, however, have been made with the composition of the charges virtually in equilibrium with the gas compositions to assure that equi-

libria have been attained. The range of chromium concentration studied was from 0 to 21.4 percent, and that of the ratio of water vapor and hydrogen in the gas mixture from 1.00 to 0.025.

The apparatus for adjusting the gas composition has been carefully tested and found to be satisfactory. A special furnace head of pyrex glass with molten Wood's metal seal has been designed and constructed. A preheater of platinum wire has been used to avoid thermal diffusion of the gas mixture. The results of preliminary runs on the hydrogen-oxygen equilibrium in liquid iron have been checked with previous reports of other investigators.

Non-metallic crusts have been found in many of the ingots. There were two varieties. By microscopic and X-ray diffraction methods one has been identified as the iron chromite, $FeO \cdot Cr_2O_3$, found in ingots containing less than 5 percent of chromium, and the other the chromic oxide, Cr_2O_3, found in ingots containing more than 7 percent of chromium. From these facts and the study of the equilibrium data, it has been established that iron chromite, or chromic oxide, is the stable solid phase in equilibrium with the liquid iron phase and the water vapor - hydrogen gas phase, when the concentration of chromium in the liquid iron is under or above 5.5 percent and the water vapor - hydrogen ratio is above or below 0.07 respectively.

It has been confirmed that iron-chromium alloy in liquid state obeys the ideal solution law; that is, the activity of chromium is always proportional to its concentration, up to at least 21.4 percent of chromium.

The reactions studied and the values obtained for the equilibrium constant and the standard free energy changes at 1595° C are shown below.

(1) When chromite is the stable solid phase:

$$FeO \cdot Cr_2O_3\ (s) + 4H_2\ (g) = 4H_2O\ (g) + Fe\ (l) + 2Cr\ (\text{in Fe})$$

$$K_1 = \left(\frac{P_{H_2O}}{P_{H_2}}\right)^4 (\%\ Cr)^2 = 7.23 \times 10^{-4}$$

$$\Delta F^\circ = 26840 \text{ cal.}$$

(2) When chromic oxide is the stable solid phase:

$$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (\text{in Fe})$$

$$K_2 = \left(\frac{P_{H_2O}}{P_{H_2}}\right)^3 (\%\ Cr)^2 = 1.036 \times 10^{-2}$$

$$\Delta F^\circ = 16960 \text{ cal.}$$

The equilibrium constant of reaction (2) checks very well with that calculated from Maier's equation[34] of free energy change for the reaction

$$Cr_2O_3\ (s) + 3H_2\ (g) = 2Cr\ (s) + 3H_2O\ (g)$$

and Chipman's equation[36] for the reaction

$$Cr\ (s) = Cr\ (\text{in Fe})$$

Using Maier's heat data and the value of standard free energy change obtained in this investigation, it has been possible to derive the free energy equations for the following reactions at the steelmaking temperatures.

$$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (\text{in Fe})$$

$$\Delta F^\circ = 93170 - 40.75T$$

And $2Cr\ (s) + 1\frac{1}{2}\ O_2\ (g) = Cr_2O_3\ (s)$

$$\Delta F^\circ = -265{,}010 + 60.32T$$

$$\Delta H = -265{,}010 \text{ cal.}$$

$$\Delta S = -60.32 \text{ e.u.}$$

The oxygen content in the melt has been found to decrease first and then increase with an increasing chromium content. The minimum oxygen content has been found to be about .029 percent when the chromium content is 6 percent. By defining the activity of oxygen in the melt as equal to the weight percent of oxygen in a pure iron melt in equilibrium with the same gas atmosphere, the activity coefficients, f_o = activity/weight percent, have been calculated and found to decrease very rapidly with increasing chromium content, from 1.00 at 0 percent to 0.13 at 20 percent of chromium. This effect of chromium on the activity of oxygen might be explained by the assumption of dissolved chromium oxide in one form or another. This also shows that chromium can never be a good deoxidizer, and that no reliable equilibrium data could be found accurately from chromium and oxygen analyses.

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I. INTRODUCTION

Chromium was and will continue to be one of the most important alloy elements in modern iron and steel metallurgy. It has been used for the production of heat resisting and acid resisting steels, stainless iron and steels, armor plate steels, tool and magnet steels, structural and engineering steels, and many others.

As the production of steels for special purposes is increased, more and more alloy steels will be produced, both in variety and quantity. Although chromium is not a very expensive material in comparison with other special alloying elements, being used in such vast amount, it is still imperative to have a good recovery in the manufacture of chromium steels, especially of those with high chromium contents.

The presence of residual metals that come from scrap is also a source of much concern. Owing to the use in open hearth charges of alloy steel scraps, basic open hearth steels have been increasing gradually in residual chromium, along with other alloying elements. While copper, nickel and tin are wholly recovered, molybdenum is mostly recovered, and zinc and lead are largely lost, the behavior of vanadium and chromium is so dependent upon operating conditions that no general statement can be made with respect to their recovery. It has been recorded[1-7] that from 1931 to 1938 the residual chromium content of steels made in the United States and Canada varies from as low as 0.006 percent to as high as 0.071 percent, with an average of around 0.03

percent. These and other residual metals may be detrimental or helpful to the finished steel, as the case may be. A report[8] for 1942 from a number of plants making plain carbon steels gives the amount of residual chromium as high as 0.55 percent. This might be occasional, but it does show that it is a serious problem. Under the oxidizing atmosphere of the open hearth, the oxidation and slagging of the chromium would be considerable, and the loss of valuable chromium metal into the useless slag is too regretable. Also, the elimination of chromium in the open hearth for making plain carbon steels is expensive business. Advantage should be taken of the residual alloying elements in the average steel bath. By taking careful account of these residual metals, by special segregation of alloy scraps, and by careful manipulation of the open hearth operation, alloy steels of definite percentage can be made if the necessary supplementary alloys are added.

As the open hearth operation is primarily an oxidation and reduction process, the knowledge of the behavior of chromium dissolved in the molten metal bath towards various oxidizing conditions is necessary to understand the phenomena related to this alloying element, to improve the recovery of the chromium added as ferrochrome, or to control the residual chromium content.

This study is planned to meet this end. The solid phases in equilibrium with the molten metal in varous conditions are to be investigated, and the equilibrium constants of the reaction between chromium and oxygen and other related reactions are to be determined.

II. LITERATURE SURVEY

The data in the literature on the equilibrium relationships of chromium and oxygen in liquid iron with definite solid phases and with gaseous atmospheres of water vapor and hydrogen are almost blank. In 1933, N. Inshakou[12] reported that the behavior of chromium parallels that of manganese. In 1935 and 1936, F. Körber and W. Oelsen[9] and F. Körber[10] reported their results on the study of the behavior of chromium in liquid iron towards acid slags at the temperature range 1600 to 1640° C. In 1938, P. Herasymenko[11] also reported a set of data on the reactions of chromium in the acid open hearth furnace. A. D. Kramarov[20] reported the relation of silicon content with respect to the chromium content in the melt for an acid slag.

Körber and Oelsen[9,10] investigated the reactions between chromium-bearing iron melts and chromium-bearing ferrous oxide, manganous oxide silicates and solid silica. The slagging of the chromium (i.e. the ratio $(\Sigma Cr)_{slag} : [Cr]_{metal}$ was found to be highly dependent on the composition of the steel and of the silicate slag; with rising ferrous oxide in the slag, the ratio increased very much. Higher manganese and silicon contents in the steel caused a lower ferrous oxide content in the slag and also in the steel, and thus opposed the oxidation of the chromium. It was also found that the ratio $[O]_{metal} : (FeO)_{slag}$ was a constant, so long as the chromium content in the melt is not higher than 5 percent at a temperature of 1600 - 1640°. It was

also stated that in acid slags, and consequently also in the silicate inclusions in chromium-bearing steels, chromium, in the presence of the other metals, occurred to only a limited extent as chromium sesquioxide, Cr_2O_3 and principally probably as chromium monoxide, CrO, so long as the inclusions are molten or have solidified as glasses. It was stated that when the slags, and also the inclusions, crystallized, extensive breakdown of the monoxide into sesquioxide and metallic chromium took place. This is, needless to say, a distinctive and invaluable contribution to the study of the behavior of chromium in liquid iron, but since the slag contains various amounts of iron oxide, manganous oxide, and silica, in view of the amphoteric nature of chromium oxides, the form and activity of chromium in the slag is by itself an indeterminate factor, and consequently all the figures can only be considered as approximations, and can only be applied to particular slag compositions. However, some of their data will be used for comparison later in the discussion of the results of this investigation.

Herasymenko[11] studied the reactions of chromium in liquid steel with acid slags from the data of five acid open hearth heats. The concentration in the bath varied within the following ranges: 0.25 - 0.90 percent carbon, 0.65 - 0.70 percent manganese, 0.07 - 0.47 percent silicon, 0.25 - 0.70 percent chromium, and in the slag 30 - 43 percent manganous oxide, 5.5 - 9.0 percent ferrous oxide, 0.8 - 1.9 percent chromous oxide (CrO), 45 - 56 percent silica, and 1.0 - 4.0 percent lime. He computed the chromium content in the slag as chromium monoxide, because, as the author stated, only this oxide can exist in acid slags in equilibrium with the liquid steel. He calculated the equilib-

rium constant as $K = (FeO) \cdot [Cr] / (CrO)$, and found it to be about 1.7, 2.0, 2.4, 3.0 at the temperatures 1500°, 1555°, 1600° and 1640° respectively. As aforesaid, the introduction of silica and other constituents adds to the complexity of the problem and makes the results rather inaccurate.

Kramarov[20] studied the equilibrium in the reduction of silica by chromium, and found that the curve of silicon content versus chromium content in the melt against acid slag showed a quadratic function, and concluded that the reaction representing the equilibrium condition should be

$$2\,[Cr] + SiO_2 = 2CrO + [Si]$$

and found out that the equilibrium constant $K_1 = [Si] / [Cr]^2$ would be approximately 0.9×10^{-5} at 1600 - 1620°. As the others, this work suffers the same indefiniteness. While it has been proved that silica is most probably in excess of its solubility in the slag and thus its activity can be considered as constant, both the solubility and the amount of chromium in the slag are unknown, and therefore the activity of chromium oxide in the slag is a variable. The equilibrium constant $K = [Si]\,(CrO)^2 / [Cr]^2$ should be used instead, if the reaction is assumed to be correct. Apparently his conclusion may not be justified.

Inshakov's original article[12] was not available, and the abstract shows that it is only qualitative, stating that analyses made during heats containing 0.15 - 1 percent chromium showed that the behavior of chromium paralleled that of manganese, the chromium being oxidized at the beginning and reduced at the end of the heat.

When pure chromium and iron are used, the solid phase in equilibrium with the liquid metal has not hitherto been fully investigated.

As Körber and Oelsen said, the slag in equilibrium with the melt containing considerable amounts of silicon, as shown by the inclusions, was probably chromous oxide or silicate. Granting this is true, it might be due to the acidic nature of the silica. In a basic or even a neutral hearth, the state of chromium in the slag phase might be entirely different, due to the amphoteric property of chromium oxides. Of course, the oxygen concentration, or rather the activity of oxygen in the melt, plays an important role in determining which would be the most stable state of the chromium present in the slag. In various reports[13-19], among many others, both chromic oxide and chromite have been assumed and identified in the non-metallic inclusions in ferrochromes and high chromium steels. This also needs more definite proof and clarification of what will happen under various conditions.

The solubility of oxygen in liquid chromium, or in iron-chromium alloys containing a high percentage of chromium, has not hitherto been determined accurately, but Portevin and Castro[16] stated that "it must be considerable, to judge from an experiment which consists in melting and casting pure iron and a 70 percent ferrochromium under the same conditions of energetic oxidation. In the first case, the iron contains very little more than 0.100 - 0.150 percent of oxygen, while in the second case the oxygen content may exceed 1 percent. This solubility must be appreciable even in the solid state, whereas it is still debatable in the case of iron. It may be possible to prepare chromium alloys containing very few inclusions and having percentages of oxygen of the order of 0.150 - 0.200 percent." This statement is debatable since, although the exact experimental condition is not known, the case

may be that under an energetic oxidizing condition, so that the iron will contain 0.100 - 0.150 percent of oxygen, a high chromium iron melt simply cannot remain in equilibrium, and considerable oxidation with the formation of chromium oxide or chromite in one form or another would occur vigorously, with gigantic rate of nuclei formation. Both chromite and chromic oxide are in the solid state at the steelmaking temperature so it is quite possible for these fine solid particles to remain in suspension without conglomeration and separation from the melt, especially if the melt is under agitated condition. But the prediction of Portevin and Castro that chromium might dissolve considerable amounts of oxygen in the solid state might be true, whereas the solubility of oxygen in solid iron is certainly quite small. It seems to be reasonable to expect that the solubility of oxygen in the liquid state would be higher than that in the solid state, and the results found in this work seem to support the view of higher oxygen solubility in chromium-iron alloys, as will be discussed later.

F. Adcock[25], in his careful work on the preparation of pure chromium by electrolysis, found that the electrodeposited chromium always contained considerable amounts of oxide. While no oxide was found to be visible in the microscopic examination of the polished section of the metal as deposited, and no residue was found by dissolving the metal in dilute acid, considerable quantity of oxide was found in metal made by melting the electrodeposited chromium in vacuo, and also the electrodeposited metal heated to 800° C for a short time under a vacuum of 0.002 millimeter pressure. He also showed that the possibility of any

electrolyte being trapped was slight. This seemed to be an evidence for the assumption that oxygen does dissolve to a considerable amount in solid chromium. A microscopic picture of chromium melted with excess of chromic oxide in vacuo showed considerable amount of large dark masses confined almost entirely to crystal boundaries. These might conceivably represent oxide thrown out of solution during the process of solidification, which means that chromium in the liquid state is able to dissolve a considerable amount of its oxide, in one form or another.

III. PLAN OF WORK

Under various oxidizing conditions, what the nature is of the solid phase or phases that will exist in equilibrium with the molten chromium-iron alloy, and also to what extent chromium can remain in solution without being removed by oxidation are the principal questions to be studied. The effects on the oxygen content of the melt are also to be explored.

With the help of controlled water vapor-hydrogen gas mixtures, heats of various chromium contents are to be made, analyzed and studied. In order to eliminate as many variables as possible, crucibles of chromic oxide and chromite are to be used. The relation of the amount of chromium present in the molten iron with respect to the controlled gas mixture and also to the amount of oxygen in the molten iron is to be studied. The following is an outline of the experimental program which has been carried out in order to arrive at answers to these questions.

(1) Manufacture of Chromic Oxide Crucible

Since no chromic oxide crucible is commercially available, it will be manufactured by slip casting from pure chromic oxide and firing.

a. The nature and amount of the dispersing agent, the nature and amount of the deflocculation agent to be used, and the consistency of the slip in order to make satisfactory casting will be studied.

b. The proper firing of the casting will be studied at various temperatures, using various furnaces, to get satisfactory crucible with-

out cracking. Any trace of carbon is to be avoided to assure reasonable soundness of the ingot.

(2) The Apparatus Used

The apparatus is to contain a silica tube with a water-cooled copper coil around it serving as the furnace. The hydrogen from a commercial hydrogen cylinder will be passed through an orifice for the measurement of the flow rate, a tube filled with platinized asbestos heated to 425° C to eliminate the oxygen contamination with the formation of water vapor, a water bath at proper temperature to saturate the gas with water vapor, and three absorption towers put in an accurately controlled thermostat to adjust the temperature and thereby the water vapor content of the gas mixture, and finally into the silica tube through a properly designed head in which a preheater is installed to prevent any thermal diffusion and condensation of the water vapor.

a. The orifice is to be calibrated.

b. The performance of the catalyzer is to be studied by detecting the presence of any trace of oxygen after the passage of hydrogen through the catalyst.

c. The performance of the thermostat is to be studied by determining the moisture contents of the gas with the thermostat set at various temperatures.

d. The temperature-resistance relation of the preheater is to be calculated.

e. The optical pyrometer to be used for the temperature measurement is to be standardized against the melting point of pure iron (1535° C).

(3) Development of Technique

The apparatus should be so arranged and the experimental procedure so adjusted that reliable chromium and oxygen analysis data of the ingot in true equilibrium with particular $H_2O \cdot H_2$ gas mixture at particular temperature can be obtained. The effects due to variations of the rate of flow of the gas, the temperature of the preheater, the length of each heat, and the method of cooling are to be considered. Convenient and satisfactory methods of sampling for oxygen and chromium analysis are to be developed, with proper care to avoid the contamination of nonmetallic crust and the oxidation of the ingot.

(4) Experimental Heats

a. Various heats with different percentages of chromium and oxygen in equilibrium with various $H_2O \cdot H_2$ gas mixtures are to be prepared.

b. Chromium and oxygen analyses are to be made of the ingots so obtained, by standard methods.

c. Microscopic examinations are to be made of the representative heats made under different conditions.

d. X-ray diffraction patterns are to be found of the representative nonmetallic phase in direct contact with the melt.

(5) Interpretation and the Results to be Anticipated

The data obtained in this work will be anticipated to give some clarification of the following problems:

a. The nature of the solid phase in equilibrium with the molten iron with particular chromium and oxygen content, in the absence of interference from all other elements.

b. The reaction or reactions involved in this equilibrium.

c. The equilibrium constant of the reaction or reactions among chromium, oxygen and hydrogen in molten iron.

d. The activity coefficients of chromium and oxygen in the molten iron.

e. The solubility of the chromium oxide dissolved in the molten iron.

IV. APPARATUS

A. Gas System

A diagram of the apparatus is shown in Figure 1. Commercial hydrogen was used. It was taken from the tank (H) through a needle valve, and led to the safety trap (T). The safety trap was filled with mercury up to the level just above the outlet tube of the gas, and then the mercury was covered with about three inches of water. The pressure was thus maintained high enough to prevent bubbling and escaping of the gas through this tube, but low enough to relieve any excess pressure. The water was used to prevent the blowing off of the mercury in the tube, in case of excess tankside pressure, and could be replenished at times.

A bypass (B) with stopcocks was provided so that the hydrogen could be introduced directly from the tank to the furnace when desired.

The flowmeter (F) was used to determine the amount of hydrogen gas passing through the system by measuring the difference in pressures of the hydrogen before and after an orifice in the tube.

The catalytic chamber (C) was used to convert any contaminated oxygen in the commercial hydrogen into water vapor. It was made of a one-inch pyrex glass tube, nine inches long, filled with platinized asbestos, and closed at both ends by rubber stoppers with holes provided for the inlet and outlet glass tubings. This chamber was heated

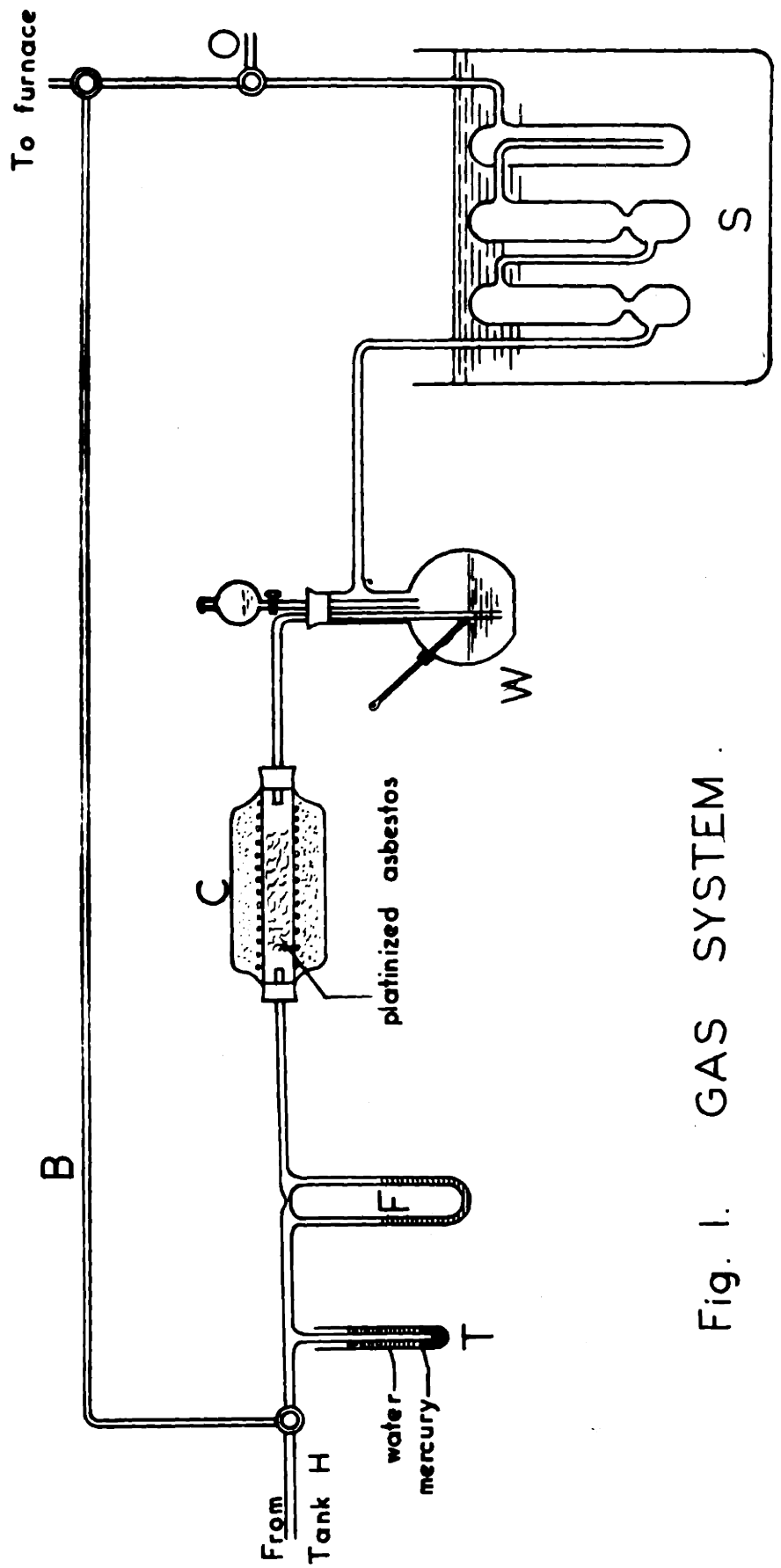


Fig. 1. GAS SYSTEM

by means of electric current through chromel A wire wound around the tube on asbestos paper and covered with asbestos to a thickness of about 3/4 inch. The current, and thus the temperature of the chamber, was adjusted by a variable resistance in series with the heating element. The temperature was kept at 425° C.

The gas then passed through a water bath (W), kept at desired temperature by an auxiliary heating unit, so that the gas was burdened with a proper amount of water vapor before it was introduced into the saturator (S).

All connections beyond the catalytic chamber were of all glass construction, and even before it rubber tubing was used at a minimum. Those beyond the water bath were heated to above 100° C to prevent the condensation of water vapor by means of chromel A wire wound around the tubing and covered with asbestos.

The saturator consisted of three towers as shown in Figure 2, and will be described in section B.

From the saturator the gas passed into the reaction chamber, which is described in section C.

B. The Saturator

The saturator unit was comprised of three glass chambers, as shown in Figure 2, with the first two chambers packed with glass beads and partially filled with water, and the third empty as the entrainment chamber. Each tower has a glass tube with a stopper attached for the purpose of adjusting the amount of water in it. This unit was immersed

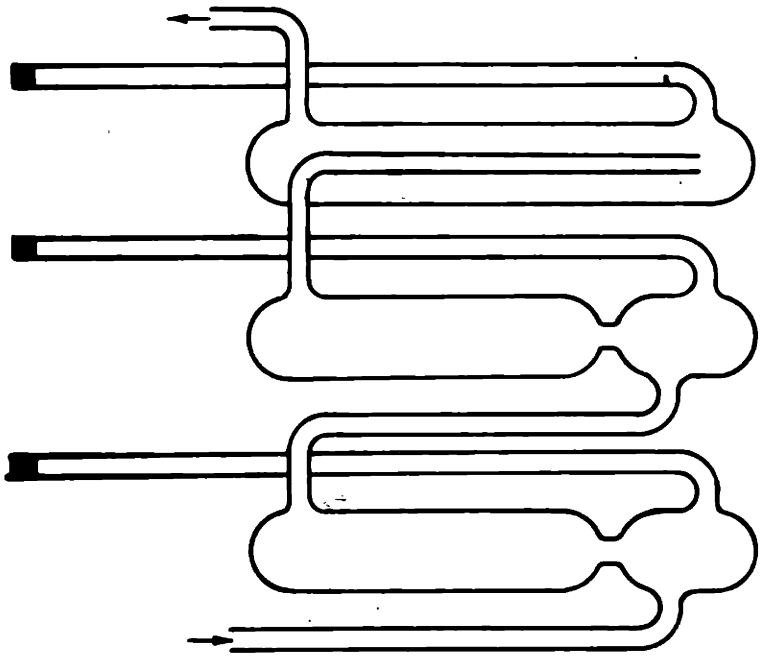


Fig. 2. SATURATOR TOWERS.

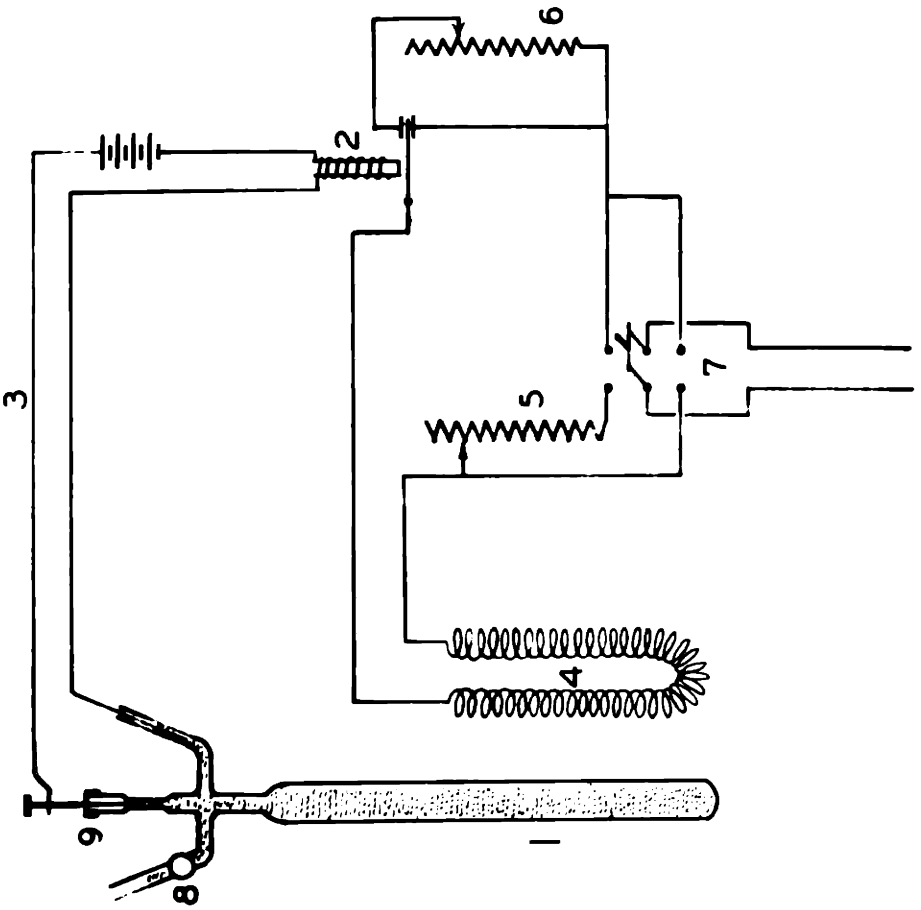


Fig. 3. WIRING DIAGRAM OF THE SATURATOR

in a large water bath, which was covered with a thin layer of oil to cut down the heat loss by evaporation of water. The use of water instead of oil facilitates the adjustment of the saturator temperature, both at the start and during the run. The outside of the drum was insulated with asbestos paper to cut down the heat loss and to insure a more uniform temperature in the bath. The bath was vigorously stirred with a stirrer driven by an electric motor for earlier runs. Later the motor was burnt out due to long service, and since no small motor was immediately available, compressed air was used to stir the bath. It was found to be equally successful, except that the heat loss due to evaporation of water increased, and more current was needed to maintain the bath at the same temperature. The bath was about 17 inches deep and 15 inches in diameter. It was heated by means of a heating coil of nichrome wire immersed in the bath. The wiring diagram is shown in Figure 3. (1) was a thermal regulator containing mercury, whose amount was adjustable through the tube and stopcock (8). (2) was a relay to be actuated by current passing through the thermal regulator when the temperature was high enough so that the mercury level was raised to get into contact with the needle (9), which could be adjusted for its height by means of the screw. When the double throw, double pole switch (7) was thrown downward, the heating coil (4) in the bath would be shorted across a 110 volt line and was used for heating up the bath. To keep the bath at constant temperature, the switch was thrown upward. The resistance (5) was so adjusted that the current passing through the heating coil was just a little higher than needed for the desired temperature of the bath when resistance (6) was shorted,

and a little lower when resistance (6) was thrown into the circuit. Relay (2) acted to throw resistance (6) in or out of the circuit of the heating coil as the temperature of the bath was higher or lower than that desired. The sensitivity of the relay system could be made higher by decreasing resistance (6), whereas a more careful adjustment of resistance (5) was then needed. As the resistance (5) in actual use in the experiment was wound with nichrome wire in steps, no fine adjustment was possible, and consequently resistance (6) had to be larger for certain temperatures and also for low temperatures where a small change of resistance would not be effective enough due to the comparatively high resistance of (5). In actual practice, (6) was disconnected when low bath temperatures were desired. With this arrangement the temperature could be controlled to less than $\pm$ 0.05° C without difficulty and to $\pm$ 0.02° C in certain cases. The thermometer used to measure the temperature and the thermal regulator were placed in the bath near the third tower, fairly far away from both the heating coil and the stirrer.

C. Furnace Set-Up

The furnace set-up is shown in Figure 4. For the first few runs a sand surface quartz tube 18 inches long and two inches in diameter had been used, but later it was found to be permeable by hydrogen at elevated temperatures. As a result, quartz tube with glazed surface of the same dimension was used instead and was found to be successful.

As for the head, in the first 20 runs a brass head with a sight glass of pyrex was used. Later it was found to be always a source of

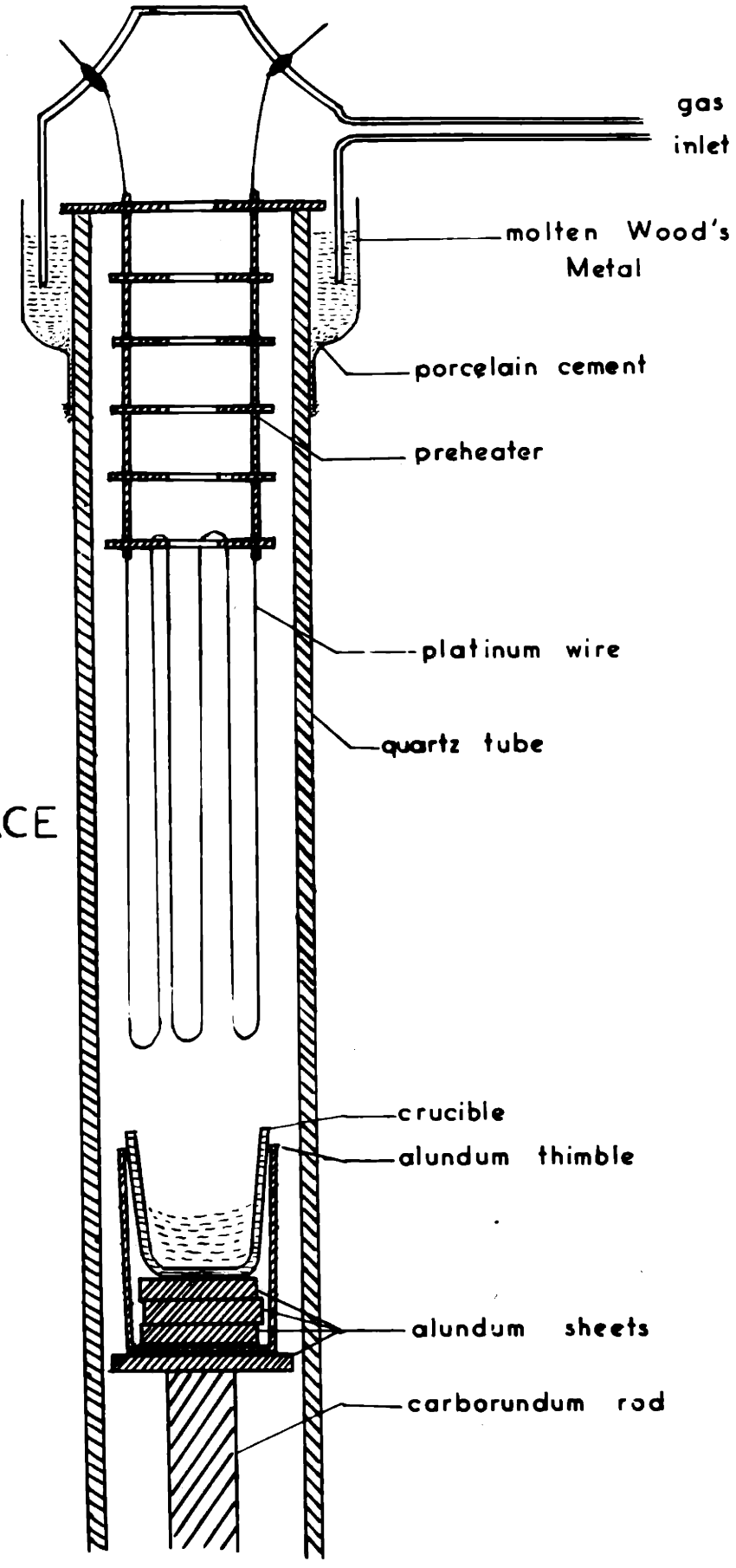


Fig. 4.
THE FURNACE
SET-UP

headaches. Neither porcelain cement nor zinc cement gave good gas-tight seal for the connection between the brass head and the quartz tube as well as that between the head and the inlet tube. Both of these cements were sensitive to temperature changes and liable to have small cracks. It was thought that these cements might work with a water-cooled head, but then water vapor in the gas mixture might condense if the temperature of the water-cooled head were too low. And at best the thermal diffusion of the gas mixture would be exaggerated by the greater temperature gradient within the tube[21,22]. Finally a solution was found by using a pyrex glass head which could be connected directly to the inlet tube. The joint with the quartz tube was made by using a pool of molten Wood's metal (any low fusing alloy might be used), kept molten at all times, as a liquid seal. Copper sheet was bent around and cemented with porcelain cement to the quartz tube to form a container for the molten metal, and nichrome wire was wound outside with asbestos paper insulation to pass electric current to supply the heat needed to keep it molten. Solidification of the metal would certainly crack the pyrex glass head, and overheating of this low fusing metal will cause evaporation and oxidation of the metal, and eventually fogging of the glass head, making the determination of the temperature inaccurate. Several runs had been discarded due to this inaccuracy of temperature reading when both the molten iron and the preheater added to the heating of the Wood's metal, and thus the glass head was fogged.

The preheater will be discussed in section D.

The crucible was rested on two or three alundum sheets in an alundum crucible. This alundum crucible was in turn supported on the top of a carborundum tube, which was placed on a removable transite slide. The alundum sheets were used for heat insulation. When the chromic oxide crucible was supported on the carborundum tube, the crucible would invariably break during the run, probably due to the high heat conductivity of carborundum, and the subsequent high thermal gradient through the thin chromic oxide crucible.

The furnace was completed with an induction coil $2\frac{1}{2}$ inches in diameter, with 12 turns of 3/8 inch copper tubing. The power was supplied by a high frequency converter. About 15 kilowatts were needed for melting, and about nine kilowatts were enough for keeping the metal at 1600° C.

D. The Preheater

In order to cut down the thermal diffusion[21,22] due to the temperature gradient of the gas mixture, a preheater was inserted as shown in Figure 4. Platinum wires of gauge number 30 were used as the heating element, and were supported with a frame of porcelain discs and alundum tubes. The circular porcelain discs with holes for both the alundum tubes and the heating elements were made from high temperature chemical porcelain particularly for this purpose. These were designed to prevent excessive heat radiation to the top part of the furnace set-up where too high a temperature was not desired. Practically it was found necessary to break up the electric circuit used for heating the Wood's metal seal during the actual run to prevent exces-

sive heating and thus evaporation of certain constituents (notably cadmium) of the Wood's metal. The whole frame was supported on the top of the quartz tube with the help of thin alundum tubes, which were cemented to the porcelain discs with porcelain cement in the lower part and bound to each other with iron wire in the upper part. The leads were made of No. 24 platinum wires sealed through the pyrex glass head to prevent any leakage. Stronger wire was used for this part to minimize the amount of heat generated in this part. Direct current was used for the preheater so that the resistance across it could be readily calculated by measuring the voltage across it and the current through it. The temperature of the preheater was estimated by the length of the platinum wire and the resistance change across it. Due to the deterioration of the platinum wire and the non-uniformity of the temperature throughout the preheater, the estimation of its temperature was only an approximation, and its temperature could not be brought much higher than an estimated average temperature of about 1100° C without a rapid breakdown of the platinum wire.

V. CALIBRATION AND TESTING OF THE APPARATUS

A. Calibration of the Flowmeter

The flowmeter was calibrated by passing hydrogen through the whole gas system, and instead of passing into the furnace, was collected over water through the exit, O, in a collecting vessel. The collecting device is shown in Figure 5. The working of the system was as follows. First the collecting vessel, C, was almost filled with water by opening the valve (1) and closing the valves (2) and (3). The pressure from the water tank which was kept at about room temperature would force water into the collecting vessel and expel gas out of it. Care had to be taken not to fill it so that the gas inlet tube would remain above the surface of the water. No water should be let flow into this tube as water in the tube would offer additional resistance to make the gas flow jerky and the flowmeter reading unsteady. Furthermore, the pressure gradient through the whole system would be disturbed. This was not too serious for the calibration of the gas flowmeter; but as this calibration was done simultaneously with the determination of the moisture content of the gas, any increase of the pressure in the saturator tower would decrease the water vapor - hydrogen ratio of the gas mixture. The result would not represent the condition to be expected during an actual heat, which would have the furnace, and thus the third saturator tower, virtually at atmospheric pressure.

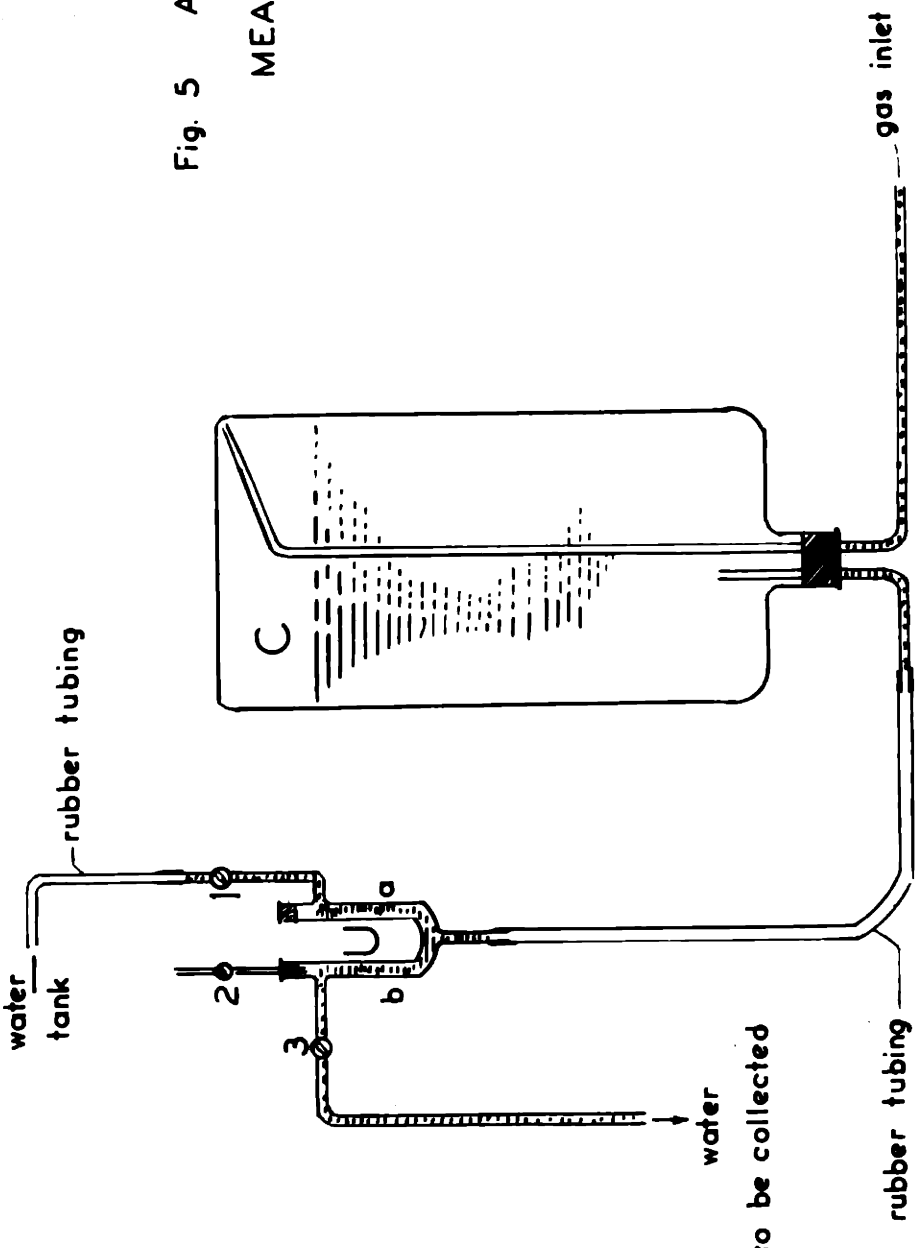
When the collecting vessel was almost full, the valve (1) was closed, the U-tube, U, raised to a point so that the water level in

the side arm (b) was just a little bit lower than the water level in the collecting vessel. Then both valves (2) and (3) were opened. A small amount of water would flow out of the collecting vessel through the U-tube side arm (b) until the water levels were equal, since the gas pressures on both sides were atmospheric.

Now the gas to be determined was led into the collecting vessel. Its pressure was adjusted by lowering the U-tube continuously so that it was always approximately equal to the atmospheric pressure. In this way the pressure gradient of the whole system was maintained close to that during an actual run. Some pressure difference developed due to the resistance of the water flow through the connections, and it was compensated for by lowering the U-tube a little further. Toward the end of the run, though, the two water levels should be kept as closely as possible. At the end, the entering gas current was shut off and the pressure adjusted by letting a very small amount of water flow out of the system so that the water level was just at the bottom of the outlet side tube, and also just equal to that inside the collecting vessel. This was important since otherwise the amount of water expelled would not accurately represent the volume of gas collected.

Finally the volume of gas collected within a certain period of time for a particular reading of the flowmeter was determined by weighing the water expelled from the vessel and dividing with its density. The total volume of gas so obtained was then corrected for the water vapor pressure in the collected gas by multiplying it with a factor (atmospheric pressure minus water vapor tension at water temperature)

Fig. 5 APPARATUS FOR MEASURING AMOUNT OF GAS



divided by the atmospheric pressure. The result was in number of milliliters at atmospheric pressure and approximately room temperature. Dividing with time gave the rate of flow. Since only approximate values are needed for the rate of flow, no attempt had been made to standardize the temperature and pressure, or to make any corrections.

Actually this apparatus was primarily designed for the determination of the moisture content of the gas, otherwise many precautions would be superfluous.

The calibration results are given in Table I and Figure 6.

B. Performance of the Catalytic Chamber

This was done by detecting the presence of any oxygen in the gas mixture as introduced into the furnace. Two methods have been used.

(1) The gas was passed through the gas system and saturated with water vapor in the saturator, which was kept exactly at room temperature. It was then led through a Geissler absorption tube containing alkaline pyrogallol solution to absorb the oxygen. The increase in weight of this absorption tube after passage of a definite amount of gas mixture was supposed to give the amount of oxygen present. Since the gas coming out of the pyrogallol solution would be saturated with water vapor with respect to this solution at room temperature, it was saturated first in the saturator to assure that no water in the absorption tube was carried away by the gas. The data is tabulated in Table II (a). It could be seen that the data did show positive readings of about 0.002 gram in 1000 milliliters of gas. The amount of gas was

TABLE I

Calibration of the Flowmeter

Atmospheric pressure = 761.2 mm.

Temperature of water = 21.6° C

Flowmeter Reading	Total Time Minutes	Weight of Water Grams	Volume ml.	Rate ml/min
2	10	714	715	71.5
17.2	4	1751	1755	438.8
16.6	4	1732	1735	433.8
5.6	10	1747	1751	175.1
5.6	10	1796	1800	180.0
55	2	1904	1908	954.0
7.8	7	1748	1752	250.3
7.8	7	1710	1714	244.9
11.0	5	1633	1636	327.2
11.0	6	1910	1914	319.0
14.3	4	1559	1562	390.5

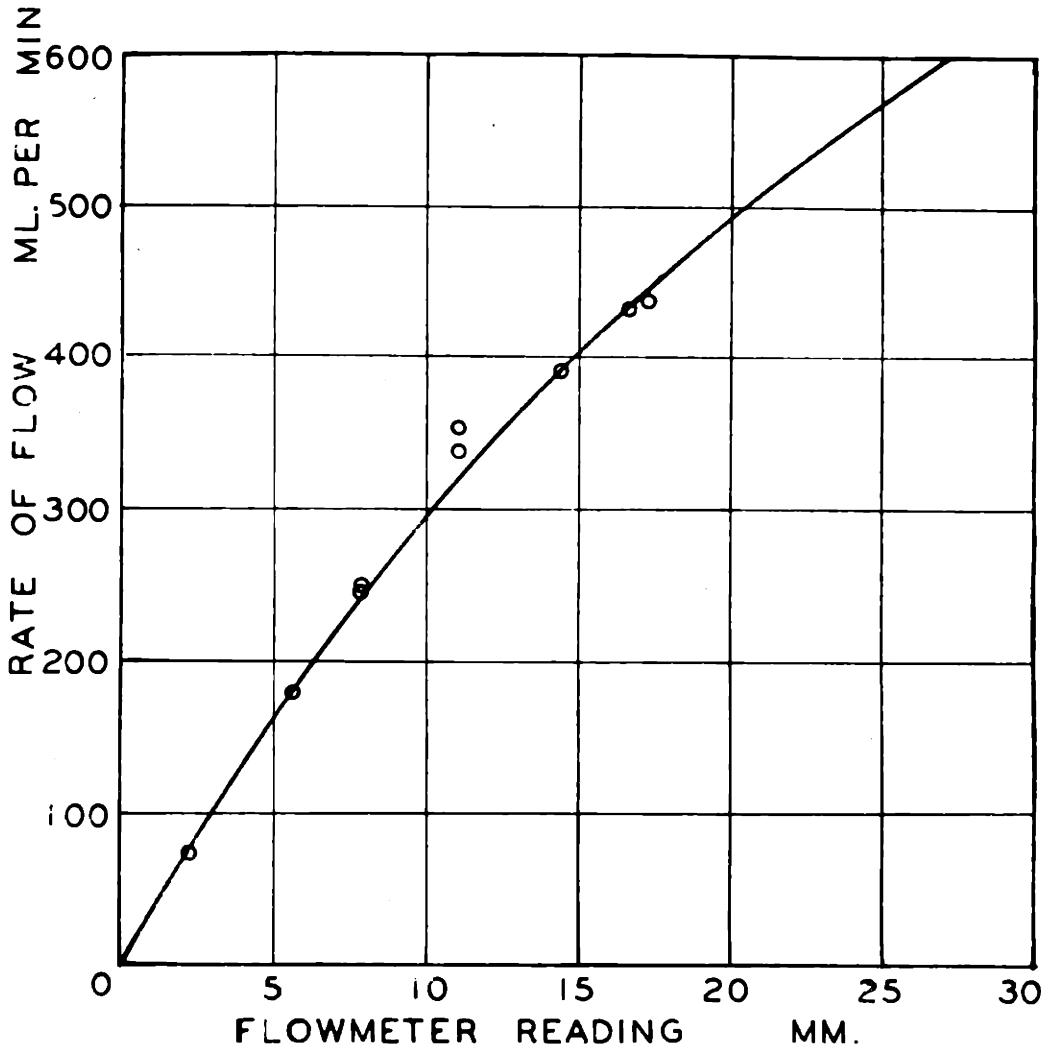


FIGURE 6. Calibration of Flowmeter

measured as described in the calibration of the flowmeter. If it was oxygen, there would be about 0.15 percent by volume. This seemed to be not so small as to be negligible, but it was suspected that since the pyrogallol reagent was a rather concentrated solution of potassium hydroxide, it should exert a much less water vapor tension than pure water and might absorb certain amount of water vapor from the gas. With this in mind, a more complex set-up was devised.

(2) A U-tube filled with phosphorus pentoxide was inserted before the Geissler absorption tube to remove all the water vapor in the gas. Within the absorption system, a ground-in drying tube containing phosphorus pentoxide was also added at the outlet from the Geissler absorption tube to absorb all the water vapor which was taken away from the pyrogallol reagent. The change in weight of the absorption system including the outlet phosphorus pentoxide was determined, as shown in Table II (b). There seemed little doubt left as to the validity of this determination of oxygen content. It is evident that the oxygen present in the system should be negligible, if any.

C. Performance of the Saturator

It was planned that the ratio of the pressure of water vaporto that of hydrogen in the gas mixture was to be calculated from the water vapor tension at the saturator temperature and the atmospheric pressure, with proper correction for non-idealness of the water vapor as shown in Appendix I. As a result, whether saturation was really obtained in the saturator was of utmost importance.

TABLE II

Determination of Oxygen in H_2O-H_2 Gas Mixture

(a) Method (1)

Atmospheric temperature	24.5° C	26° C
Atmospheric pressure	759.1 mm.	754.5 mm.
Saturator temperature	24.45° C	25.50° C
Rate of flow	95 ml./min.	70 ml./min.
Increase in weight of the absorption tube per 1000 ml. of gas	(1) + .0005 gm./l (2) + .0017 (3) + .0028 (4) + .0025 (5) + .0016	(1) .0018 gm./l.

(b) Method (2)

Atmospheric temperature	26.0° C	25.0° C	25.0° C
Atmospheric pressure	759.5 mm.	759.0 mm.	760.2 mm.
Saturator temperature	26.07° C	25.78° C	25.00° C
Rate of flow	75 ml./min.	85 ml./min.	34.3 ml./min.
Increase in weight of the absorption tube per 1000 ml. of gas	(1) -.0007 gm/l	(1) -.0003 gm/l (2) +.0000 (3) +.0002	(1) +.0003 gm/l (2) +.0001 (3) +.0002

The same apparatus used for calibration of the flowmeter was used for the measurement of the amount of dry hydrogen passing through the absorption system.

The absorption system consisted of three glass-stoppered tubes. The first tube (a) was filled with glass wool to remove the major part of the water vapor. Tube (b) was filled with phosphorus pentoxide to remove the last trace of water vapor. The third tube (c) was also filled with phosphorus pentoxide, and was used to prevent any back diffusion of the water vapor from the collecting vessel into the absorption tube (b). As explained later, the gas flow rate was sometimes very low and, consequently, back diffusion was not impossible. Only the increases in weight of tubes (a) and (b) are registered as the amount of water vapor carried in the gas mixture.

All the connections before tube (a) were kept hot in the same way as the main system, by resistance wire.

At first, the whole gas current was passed through the absorption system, and the experimental data are given in Table III (a). However, although extreme care had been taken to adjust the pressure in the collecting vessel as described in the section on the calibration of the flowmeter, there was the possibility that it was not exactly equal to the atmospheric pressure, due to the not-too-fine adjustment and the resistance to water flow in the apparatus. Later, with the main current passing into the furnace with the preheater and Wood's metal seal heated as in an actual run, a small portion of the gas mixture was led out through a side tube by adjusting the pressure in the collecting vessel, C, in Figure 5. In this arrangement, the pressure in the sat-

urator could be assumed as exactly the same as in an actual run, and the ratio of water vapor to hydrogen would show no change. Care had to be taken to remove only a small amount of gas, otherwise the back flow from the furnace would give erratic results.

The results are shown in Table III. It was thought that since the chromium analysis could not be accurate to less than one percent and the accuracy of the oxygen analysis was even worse, the deviation of less than one percent of the gas composition, which might yet be caused by the inaccuracy of the calibration method, would be tolerable. Therefore, the performance of the saturator was assumed to be satisfactory up to 50° C and 430 milliliters per minute rate of hydrogen flow.

The calculation was made with the following equation:

P_A mm. = atmospheric pressure

t° C = room temperature

t_s° C = saturator temperature

W gm. = amount of water expelled

H_2O gm. = amount of moisture absorbed in tubes (a) and (b)

P_t mm. = water vapor pressure at t° C

d_t = density of water at t° C

$\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{measured}$ = molal ratio as determined

$$= \frac{H_2O/18.016}{W \times \frac{.08988}{d_t} \times \frac{P_A - P_t}{P_A} \times \frac{273.1}{273.1 + t} \times \frac{1}{2.016}}$$

TABLE III

Saturator Performance

(a) When the entire gas current was passed through the absorption system.

Rate of Flow ml./min.	Atm. Pres. P mm.	Room Temp. t° C	Water Bath Temp. ° C	Saturator Temp. t_s° C	Water Expelled W gm.	Moisture Absorbed H_2O gm.	$\frac{H_2O}{W}$	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{measured}$	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{calcd.}$
	761.1	23		26.65	1143	0.0286	0.0250	0.0346	0.0359
	769.1	23		27.00	1439	0.0374	0.0260	0.0360	0.0361
	769.1	23		26.80	1319	0.0334	0.0253	0.0350	0.0357
	769.1	23		26.67	1261	0.0311	0.0247	0.0342	0.0354
	765.1	23		27.90	1231	0.0345	0.0280	0.0388	0.0383
130	762.2	24	52.5	35.30	1327	0.0564	0.0425	0.0592	0.0597
130	762.2	24	47.5	35.30	1270	0.0541	0.0426	0.0594	0.0597
250	765.1	21.5	50.0	50.40	1274	0.1292	0.1014	0.1398	0.1406

Table III, continued

(b) When only part of the gas current was passed through the absorption system while the main current passed through the furnace as during an actual run.

Rate of Flow ml./min.	Atm. Pres. P mm.	Room Temp. t° C	Water Bath Temp. ° C	Saturator Temp. t_s° C	Water Expelled W gm.	Moisture Absorbed H_2O gm.	$\frac{H_2O}{W}$	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{measured}$	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{calcd.}$
130	762.2	24	45	35.30	1112	0.0477	0.0428	0.0596	0.0597
325	762.2	24	55	35.30	1346	0.0568	0.0422	0.0588	0.0597
320	762.2	24	48	35.30	1189	0.0502	0.0422	0.0588	0.0597
250	763.1	21.5	70	50.50	1294	0.1332	0.1029	0.1415	0.1416
250	763.1	21.5	65	50.40	1302	0.1332	0.1024	0.1409	0.1406
250	763.1	21.5	45	50.45	1120	0.1149	0.1026	0.1411	0.1411
430	763.1	21.5	45	48.75	1305	0.1204	0.0923	0.1270	0.1280
430	763.1	21.5	50	48.80	1178	0.1093	0.0928	0.1277	0.1289

$$= 1.246 d_t \left(\frac{H_2O}{W}\right) \times \frac{P_A}{P_A - P_t} \times \frac{t + 273.1}{273.1}$$

$$\frac{P_{H_2O}}{P_{H_2}}_{\text{calcd.}} = \text{molal ratio as calculated}$$

$$= \frac{P_{t_s}}{P_A - P_{t_s}} \times \left(\frac{P_i}{P}\right)$$

D. Temperature Measurement

A Leeds and Northrup disappearing filament type optical pyrometer was used for temperature measurement. To eliminate the error introduced due to the liquid iron being not a black body, and also the absorption of part of the radiation by the glass, the optical pyrometer was calibrated by observing the melting point of electrolytic iron in a magnesia or alundum crucible under a gas of dry hydrogen. It was observed that the melting point was 1336° C. The deviation from this figure has never been greater than two degrees in various determinations. The melting point of electrolytic iron was taken to be 1535° C. The equation[23] used was

$$\frac{1}{T} - \frac{1}{T_A} = K$$

where T is the actual temperature in degrees absolute, T_A the observed temperature also in degrees absolute, and K a constant for all practical purposes, when all the conditions were standardized and the emissivity of the observed substances did not change too much.

The calculation gave the value K = - .0000684. This value was used throughout the whole work.

VI. MANUFACTURE OF CHROMIC OXIDE CRUCIBLES

In order to get good equilibrium constant data, the activity of the chromium oxide in the solid phase should be made as constant as possible. Any contamination of the solid phase by the introduction of foreign oxides would tend to alter the situation and make the activity a variable through the formation of solid solution or compound.

The best crucible to be used should be composed of the same compound that would come naturally into equilibrium with the liquid iron under the conditions to be studied. Chromic oxide, Cr_2O_3, seemed to be one of the best materials that could be used. As no commercial product was available, efforts have been made to manufacture it.

Tamped crucibles when used to melt high purity iron in a high frequency induction furnace have the objection of contamination of the melt by particles detached from the walls of the crucible. Therefore, slip-casting seemed to be a better method of manufacturing satisfactory thin-walled crucibles with smooth inner surfaces.

The principle is simple. The slip consists of an aqueous suspension of fine chromic oxide particles, and when it is poured into a plaster of paris mold, the water is removed by absorption into the plaster leaving the chromic oxide particles deposited into a shape determined by the mold. When solid, the casting may be removed, dried and fired.

A. Preparation of the Slip

Three lots of chromic oxide have been used, all of technical grade. Number 1 was bought from the Baker Chemical Company, lot number 10441. It was of dark green color and settled in water rather easily. Number 2 was bought from Merck and Company. It was light green in color and seemed to be not easy to be wetted with water. It tended to float on the surface of water in a thin layer, and if forced down under water by agitation, small air bubbles were always trapped and were difficult to remove. Number 3 was also obtained from the Baker Chemical Company and was lot number 5944. Its appearance was different from number 1, being light green in color and settling not so readily in water as the number 1.

All three were very fine material, leaving practically no residue on a 100 mesh sieve, but their slip-forming properties were quite different from one another. Number 2 was the most plastic, while number 1 was the least. Slip made of number 1 material showed not enough plasticity. It was thin and castings made of it cracked in the molds. No satisfactory castings could be obtained. Slips made of materials numbers 2 and 3 were sticky and rubbery, and contained numerous small air bubbles, and the castings were soft and weak and stuck tightly to the mold. Very few good castings could be successfully removed from the mold. Even these had their inner surfaces scarry due to small air bubbles which did not escape by any means.

Absolute alcohol and some other organic liquids were tried without much improvement. However, crucibles which cast well and which could be dried and fired without cracking finally were obtained by using a

mixture of materials and developing its plasticity by digesting with water and by the use of hydrochloric acid.

A mixture of 70 percent by weight of number 1 material, and 30 percent of number 2, or one of 50 percent number 1 and 50 percent of number 3, was found satisfactory. The mixture was digested in an excess of water for more than 2 days with occasional agitation. Then it was let settle, the superfluous liquid was decanted off, and about one-half percent of concentrated hydrochloric acid was added. The mixture was stirred gently without introducing air bubbles. The desired consistency was about that of thick cream. Water was added if it was too thick. The slip was then ready for use. It could be stored for several days, but stirring would be necessary before the mixture could be used.

B. Preparation of Molds and Castings

The molds were made of plaster of paris. Approximately 4 parts byweight of plaster of paris were stirred into 3 parts of water. The preferred schedule was to sprinkle the powder into water and let it settle without agitation. This would omit later jarring necessary to eliminate air bubbles. Finally it was gently stirred and poured into a cardboard cylinder in which was put a tapered brass mandrel that was covered with a thin film of vaseline. After about 30 minutes, the plaster of paris set and gave a mold with its inner surface smooth and free from gas pockets or mechanical defects. The mandrel was removed, the cardboard shell was stripped, and the mold air-dried for several

days. It was then ready for use. Sometimes it was found necessary to clean traces of vaseline from the inner surface lest the absorption of water during casting should be uneven.

It was found that when the material was very plastic and the slip was sticky and rubbery, it was better to use molds as dry as possible to make the absorption of water from the slip possible and to avoid the adherence of the casting to the mold. On the other hand, if the material was not too plastic and the slip rather thin, it would be better to use molds somewhat moist so that the absorption was not too rapid. For the aforesaid mixture, both could be used satisfactorily.

To make the castings, the slip was poured into the mold without splashing or entrapping air. Water was immediately absorbed by the mold. The liquid level was maintained by additions of slip until the film of solidified material reached the desired thickness. The residual liquid slip was then poured out. The time required varied greatly with the plasticity of the material, consistency and acidity of the slip and the condition of the plaster mold. Within one-quarter of an hour, shrinkage cracks began to appear at the junction of the top of the crucible and the wall of the mold. After about one hour the crucibles would be dry enough to stand gentle handling, and could be removed easily from the mold. The crucibles were air-dried for one day, dried at 105° C for another day, and then fired. The dimensions of the crucible decreased a little before removal from the mold, but drying affects it but little. Castings of various sizes had been made, and it was found that the linear shrinkage during casting and drying was about 6 percent, while that during firing was about 11 percent, varying with the compo-

sition and consistency of the slip as well as the temperature of the firing.

Crucibles used in this investigation were cast about 4.2 centimeters in diameter and 4.5 centimeters in height. The fired crucible was about 3.5 centimeters in diameter and 3.7 centimeters in height.

C. Firing of the Crucible

This has been one of the thorny problems in this work. Chromium forms a large number of oxides with variable valences. No definite information was available with respect to the stability of these oxides under different conditions.

First it was thought firing in air might be possible. A furnace with globar rods as the heating elements was used. The heating was rather slow, taking about 8 hours to reach a temperature of 1500° C. The crucibles became dark-colored, showed no shrinkage, and were very friable. X-ray diffraction pattern showed no change of the position of the lines from those of chromic oxide, but it did show spotty type of pattern, which could be interpreted as due to recrystallization. These crucibles had no strength and could not be used.

Temperature was thought to be not high enough, and gas-fired furnaces were used to fire the crucibles up to 1650° C. One of the furnaces used was small, lined with chromite, and the temperature could be brought up to 1650° C in about 4 hours, while the other was a large catenary-type furnace, lined with number 80 heavy duty firebrick, and the temperature could only be raised very slowly. Two days were norm-

ally needed for the firing. Both were unsuccessful, with the resulting crucibles about the same as those obtained in the globar rod furnace. The atmosphere was not controlled, but it was doubtless more reducing than that in the globar rod furnace.

Then a high frequency furnace with a graphite crucible as the heating element, the same as that used by Marshall[24] for the firing of magnesia crucibles, was used. At a temperature of 1600° C, the crucibles were obviously reduced. Passing nitrogen through the graphite crucible retarded the reduction, but it could not be stopped. As the presence of any chromium carbide was highly undesirable, although the chromic oxide crucibles so fired were hard and strong, it was thought not to be the real solution of this problem. The shrinkage was always very high.

Next the firing was tried in vacuo, using graphite crucible as heating element heated with a high frequency current. Magnesia was used to separate the graphite from the chromic oxide crucible. Due to the reaction in the furnace, it was found to be not quite possible to maintain high vacuum in the furnace. Very few of the fired chromic oxide crucibles were satisfactory and reasonably strong. Many, however, developed cracks, and some showed a thin brownish yellow film, the composition of which was not determined because the amount was so small that the chromic oxide attached to it was always prominent in quantity. Besides, crucibles that could be fired in the available high vacuum furnaces were not big enough to be used in the equilibrium heats. This attempt was given up.

The solution found to be relatively satisfactory was to fire it in the graphite crucible with high frequency electric current to a temperature not higher than 1430° C. This temperature limit was important lest reaction should proceed more rapidly and the carbon absorbed be very hard to remove. The chromic oxide crucibles should be well shielded with alundum cylinders and sheets so that there would be no possibility of any direct contact between the graphite and the chromic oxide. Introduction of commercial nitrogen seemed to do little good. The crucibles so fired had a shrinkage of about 11 percent, and were reasonably hard and strong and dark-colored. Firing at temperatures below 1400° C did not give crucibles strong enough to be used, while the shrinkage was low and the color light. However, the crucibles obtained by firing at 1430° C contained some carbon, which was finally burned out by heating in air in a globar tube furnace for more than 2 hours at a temperature higher than 1500° C. This did not change the appearance of the product. Chemical analysis and an X-ray diffraction pattern did not show the presence of any compound other than the chromic oxide. This did not exclude the possibility of the formation of small amounts of other oxides or carbides, but did show that Cr_2O_3 was the principal constituent of the finished crucible.

The crucibles so obtained might still contain some carbon since the ingots made in these crucibles were mostly somewhat porous, while ingots of the same materials made in alundum or magnesia crucibles were invariably sound.

VII. EXPERIMENTAL WORK

A. Technique

The electrolytic iron was cleaned, pickled, washed and dried to remove any attached dust particles which may contain some carbon. Pieces with smooth surfaces would give better results since there would be less probability of introduction of carbon, which would help to make the ingot porous. A weighed amount was charged into the crucible in such a manner that the upper part would not get in touch with the crucible and, consequently, would drop down when the lower part was melted. This was to minimize the probability of arching of the charge during the melting stage. Calculated amount of previously pickled and dried electrolytic chromium was charged at the same time.

The saturator and the water bath were brought to the desired temperature, which was usually a little bit higher than that expected to give equilibrium condition. The whole system was flushed out with hydrogen for about three-quarters of an hour. The saturator was by-passed most of the time to prevent high water-vapor pressure in the gas, and the resultant condensation of water at the cooler parts of the furnace. The catalyzer chamber was kept hot during the run.

For the high chromium heats, it was more advisable to melt it under hydrogen since water vapor tended to form a solid oxide film around the chromium metal, and thus prolong the time needed for melting. So the preheater was started and the high frequency current was turned on. Since chromium has a higher melting point than iron, pieces of chromium would float on the surface of the melt for quite a while. Yet it was

not advisable to bring the temperature higher than necessary, since more chromium oxide would then be dissolved from the crucible, and later manipulations would become more difficult. After the charge was melted, the hydrogen was led to pass through the water bath and the saturator.

For the low chromium heats, it was found to be necessary to melt under the desired gas mixture, since chromic oxide dissolved rather readily under hydrogen atmosphere, the chromium content was thence higher than needed, and it would be impossible to bring it down to the desired amount without disturbing the equilibrium condition, as will be explained in a later paragraph. For heats with chromium content less than one percent, no chromium was charged, and for those with chromium less than 0.2 percent, small calculated amounts of ferric oxide were charged with the electrolytic iron. After the furnace was well flushed with hydrogen, the preheater was started to bring the upper part of the furnace to a fairly high temperature. Then the hydrogen gas was led through the water bath and the saturator before entering the furnace. After about 15 minutes, the high frequency current was turned on to melt the charge.

After the charge was melted, it should be brought to the desired temperature, in this work 1595° C, as soon as possible. After reaction for a few minutes with the desired gas mixture, solid particles began to appear floating on the melt. These would accumulate first around the rim, and grow toward the center. This was the indication that under such a gas mixture the melt was too high in its chromium content. This

film grew rapidly, except in the case of very low chromium or very low oxygen content, and would cover the whole melt. Since this was a solid film, it would stay on the surface without exposing the liquid metal any more. Even though the pyrometer reading due to the high emissivity of the solid film was corrected accordingly, it could hardly represent the temperature of the melt because the heat loss to the surroundings was so great, and this solid film was so insulative to heat that the temperature of the surface would be greatly affected by the thickness of the solid film. Besides, the reaction between the molten metal bath and the gas would be completely blocked, and the desired equilibrium condition would never be attained. While raising the temperature of the melt even higher was not desirable, the temperature of the saturator had to be lowered. As it took time to get the gas composition in the furnace corresponding to that in the saturator, and also to have the formation of the solid film noticeable, the temperature of the saturator was lowered in steps of from one to two degrees instead of continuously. Yet it would be practically impossible to remove the solid film which had covered the whole melt and thus prevent the transference of oxygen from the melt to the gas, which was necessary before any solid oxide could be dissolved. Dry hydrogen was usually needed in that case, although more chromium would be introduced into the melt. Better procedure would be to lower the saturator temperature before the whole surface was covered; but in most cases the effect of the lowering of the saturator temperature was too slow to be effective, and dry hydrogen had to be resorted to. After a few trials, a condition would be ob-

tained that no solid film was formed, or better that only some isolated solid particles floated around the rim without growing inward.

It was assumed that the equilibrium condition was approached. Keeping everything unchanged for one more hour was supposed to be enough for the attainment of the equilibrium.

At the end, the preheater was turned off first, and then the high frequency current. A strong current of hydrogen was used to cool the melt rapidly, which was kept in its position. The solidification was rather rapid, always within fifteen seconds.

The above technique was found to be the most successful and was used for the last 20 heats. In the earlier heats, however, a charge with chromium content less than required was melted and kept at proper temperature in contact with the desired gas mixture for various lengths of time. It was thought that equilibrium should be approached from both the high chromium and the low chromium sides, but practically no reliable data could be obtained from the high chromium side, due to the formation of the solid film, although it was possible to determine whether a certain melt was on the high chromium side or not.

It was observed that a melt with four percent chromium could be obtained from a pure iron charge by keeping it for only about one hour at 1600° C. From this it could be concluded that the solution of chromic oxide was not a slow process and that equilibrium could be reached within a reasonable length of time if the chromium amount charged was not too low. With this in mind, it seemed that although almost all the data were obtained from the lower side, they could be counted on to represent the true equilibrium conditions.

The ingots always adhered to the chromic oxide crucibles, while they could be separated easily from the chromite crucibles. After grinding off all the non-metallic substances, including the crust found around the ingots as described later, the ingots were analyzed for their chromium and oxygen contents. Samples for oxygen analysis were usually cut with a cut-off wheel or a hacksaw into pie sections. Pickling and grinding were used to clean the surface, and the analyses were done by regular vacuum fusion methods. Samples for chromium analysis were prepared by cutting through the vertical cross-section on a shaper. The chips were cleaned with acetone and analyzed by the regular potassium persulphate method.

The oxygen value for each ingot was always chosen as an average of the duplicates of the lower values. When only one lower value was obtained, with all other values higher, it was chosen on the basis that occlusion of particles of non-metallic crust, such as that shown later in Figure 8, would make the analysis results erroneous and higher than actual values, and hence the lower values were considered to be much more reliable than the higher ones.

B. Experiments and Data

From a total of about 120 trials, 76 ingots were made. The others were discarded during the run due to various troubles such as the failure of some part of the apparatus, fogging of the sight glass, breaking of the crucible, bridging of the charge, covering of the whole surface with solid film, and so forth.

The first two series of heats were made in magnesia and alundum crucibles for comparison with published data and thus to ascertain the overall performance of the assembled apparatus. It could be seen from the data (Tables IV and V) that the performance could be considered as satisfactory, with the exception of heats numbers 1 and 2 which were made with the brass head for the furnace, and leakage was highly probable. These data were entirely compatible with the data of Chipman and Fontana[26].

The third series were made in chromic oxide crucibles. Heats numbers 101 to 125 were made with the brass head, and leakage was probable. Heats 151 - 170 were made without any leakage, but the equilibrium was approached from the low chromium side and, since no information was available, the starting charge might be far from equilibrium and the results could be used only with careful consideration. Among these heats, several would be plotted along with later heats, while others have been discarded.

It was during this time that in many of the ingots, crusts containing considerable amounts of non-metallic substances in the matrix of metallic substances were observed. These crusts were metallic in appearance after rough grinding, and could not be distinguished from the metal at that time. Fine grinding, or better polishing, however, would show the crusts to be darker in color and also less shiny than metal. During the grinding of various ingots, streaks of two different colors, brown and green, could be observed easily, and seemed to be dependent on the chromium percentage of the heat. The solid films

formed occasionally during the heat also showed two different varieties by color, brown and green, the former in low chromium heats while the latter were in high chromium ones. These will be discussed in detail later in the section on the identification of the solid phase in equilibrium with the melt. Heats 171 to 189 were made according to the best procedure as described. These were supposed to be quite reliable. However, for heats 178 and 179, it was suspected that, since the charge was not high in oxygen content, too much chromium was dissolved during the melting operation, with the result that the ingots were somewhat higher in chromium and lower in oxygen than those in actual equilibrium with the gas mixture used. Due to the small amount of chromium present in the melt, it was thought to be quite probable that the film formation process was too slow to be noticed. As a result, the ingot remained to be a little high in chromium and low in oxygen.

The fourth series was made in commercial chromite crucibles after burning out the carbon at 1500° C. These crucibles were found to be rather impure, containing magnesium and aluminum among other elements. It was thought that these impurities together with iron oxides would be insignificant in their effects on the equilibrium data only if they were mixtures instead of solid solutions with the iron chromite. An X-ray diffraction picture did show the shifting of the lines from what had been obtained by Clark, Ally and Badger[27]. The data were calculated and compared in Table IV. It could be seen that the values of d were generally low, which indicated that the chromite did contain some impurities in solid solution, the amount of which cannot be estimated by chemical analysis.

Figure 7 is a picture showing the appearances of the crucibles used and the ingots obtained. The upper row from right to left shows (1) the dried but not fired chromic oxide crucible, (2) the fired chromic oxide crucible, and (3) an unsound ingot with the upper part of the ingot remaining intact. This ingot is a typical one listed as porous in Table VI. The lower row from right to left shows the chromite crucible (1) before and (2) after the heat, and (3) a sound ingot.

All the observations and data of these heats are summarized in Tables V and VI.

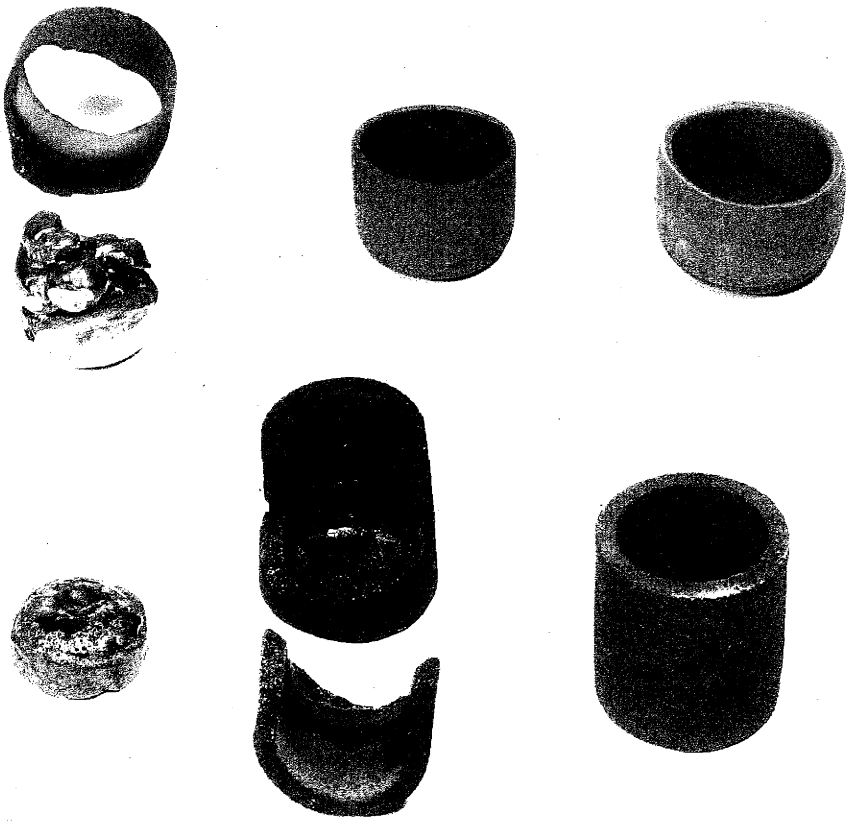


FIGURE 7. Chromic Oxide and Chromite Crucibles and the Ingots.

TABLE IV

X-ray Data for Chromite Crucible

Co Radiation: No filter. λ_α = 1.787 Å λ_β = 1.617 Å

Intensity	Corrected Angle	d_α	d_β	Clark's Data for $FeCr_2O_4$ d	Intensity
vvw	11.23	4.587		4.82	2
vw	18.16	2.866		2.95	4
vvw	19.28	(2.706)	2.45		
s	21.39	2.451		2.52	10
vvw	22.30	2.355		2.40	1
vvvw	23.42	(2.248)	2.038		
w	25.96	2.041		2.080	4
vvw	30.99	(1.736)	1.571		
vvvw	32.28	1.673		1.700	3
w	34.65	1.572		1.606	8
s	38.17	1.446		1.475	9
vvw	45.47	1.253		1.274	4
vvw	48.99	1.184	1.072	1.204	½
vvvw	51.09	1.148		1.167	½
vvw	54.28	1.100		1.116	1
w	56.44	1.072		1.080	4
vw	60.18	1.030		1.045	2
w	69.95	0.951		0.966	3
w	76.25	0.920		0.934	½

Notes:

d_α is calculated from λ_α

d_β is calculated from λ_β

$FeCr_2O_4$ data from Clark, Ally and Badger[27]

s = strong; w = weak; v = very

TABLE V

Experimental Conditions of the Heats

Heat No.	% Cr Charged	Atm. Pres. mm.	Saturator Temp. ° C	$\frac{P_{H_2O}}{P_{H_2}}$	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Metal Temp. ° C	Time Hrs.	Rate of Gas Flow ml./min.	Preheater	Remarks
A. Magnesia Crucible										
1[1]	0	761.3	29.67	0.0428	0.0429	1586	2.2	330	Yes	
2[1]	0	766.4	29.60	0.0423	0.0424	1588	1.0	390	Yes	
3	0	760.0	44.58	0.1020	0.1023	1592	1.6	290	Yes	
4	0	761.0	40.80	0.0821	0.0823	1594	1.5	310	Yes	
B. Alundum Crucible										
24	0	769.0	29.55	0.0420	0.0421	1592	0.75	380	Yes	
25	7.4	764.8	41.28	0.0839	0.0841	1655	1.5	300	No	
26	0	760.1	79.20	0.8258	0.833	1597	1.6	420	No	Crucible broken
27	0	760.3	48.08	0.1243	0.1247	1596	1.4	480	Yes	
C. Chromic Oxide Crucible										
107[1]	6.7	763.7	67.32	0.374	0.377	1595	2	420	Yes	Surface covered up
110[1]	5.9	761.6	35.50	0.0604	0.0605	1653	2.2	750	Yes	
111[1]	4.1	764.9	34.80	0.0577	0.0578	1628	1.7	560	Yes	
112[1]	1.0	760.9	41.87	0.0873	0.0875	1653	2	420	Yes	

Table V, C. Chromic Oxide Crucible, continued

Heat No.	% Cr Charged	Atm. Pres. mm.	Saturator Temp. ° C	$\frac{P_{H_2O}}{P_{H_2}}$	$\left(\frac{P_{H_2O}}{P_{H_2O}}\right)$ corr.	Metal Temp. ° C	Time Hrs.	Rate of Gas Flow ml./min.	Preheater	Remarks
113[1]	0.5	760.9	43.10	0.0936	0.0939	1661			Yes	Data rough[3]
114[1]	0	758.6	44.45	0.1015	0.1018	1661	2.5	800	Yes	Part covered
115[1]	4.8	759.7	32.38	0.0504	0.0505	1596	1.3	830	Yes	
116[1]	0	759.3	47.26	0.1183	0.1187	1598	2.0	730	Yes	
117[1]	1.0	761.1	42.00	0.0879	0.0881	1599	1.5	630	Yes	
118[1]	0	760.0	48.90	0.1302	0.1307	1597	1.7	710	Yes	
119[1]	0	760.7	47.31	0.1189	0.1193	1595	1.2	650	Yes	
120[1]	0	753.7	40.25	0.0804	0.0806	1605	1.8	490	Yes	
121[1]	0	762.6	40.30	0.0796	0.0798	1596	1.3	320	Yes	
122[1]	0	752.6	32.94	0.0523	0.0524	1594	1.3	350	Yes	
123[1]	0	751.1	37.40	0.0684	0.0685	1595	1.3	300	Yes	
124[1]	0	751.1	51.40	0.1520	0.1526	1597	1.0	300	Yes	
125[1]	4.7	753.5	28.80	0.0410	0.0411	1596	1.2	390	Yes	
131	8.1	760.1	40.85	0.0824	0.0826	1653	2.3	300	Yes	Part covered, brown needles
132	5.5	756.7	40.89	0.0830	0.0832	1603	1.7	350	Yes	Brown needles
133	3.6	760.9	41.00	0.0830	0.0832	1603	1.6	300	Yes	
134	0	766.0	48.40	0.1255	0.1259	1598	2.0	240	Yes	
135	2.9	764.9	41.60	0.0855	0.0857	1598	1.5	500	Yes	

Table V, C. Chromic Oxide Crucible, continued

Heat No.	% Cr Charged	Atm. Pres. mm.	Saturator Temp. ° C	$\frac{P_{H_2O}}{P_{H_2}}$	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Metal Temp. ° C	Time Hrs.	Rate of Gas Flow ml./min.	Preheater	Remarks
136	11.8	763.5	31.49	0.0475	0.0476	1599	2.2	340	Yes	
138	5.9	755.4	39.45	0.0766	0.0768	1650	2.0	340	No	Part covered
139	3.9	755.8	41.02	0.0837	0.0839	1596	2.0	260	Yes	
140	1.3	759.3	47.28	0.1190	0.1193	1596	1.6	320	Yes	
141	3.0	761.6	35.80	0.0614	0.0615	1594	1.7	280	No	
142	3.3	761.6	36.00	0.0622	0.0623	1598	1.0	430	Yes	
143	3.5	763.0	36.90	0.0654	0.0655	1597	2.0	350	Part[2]	
144	3.1	765.4	34.20	0.0556	0.0557	1597	1.0	400	Yes	
151	2.4	756.5	41.23	0.0847	0.0849	1597	1.4	390	Yes	
153	0	761.9	31.56	0.0478	0.0479	1600?	1.0	370	Yes	Some fogging
155	0	754.0	33.00	0.0527	0.0528	1596	2.0	320	No	Some bridging
156	0	756.9	39.00	0.0744	0.0746	1607	2.0	250	No	Some bridging
158	0	755.0	38.96	0.0745	0.0747	1595	2.0	260	Yes	
159	2.5	759.5	39.00	0.0742	0.0744	1602	1.2	330	Yes	
160	3.1	759.8	36.03	0.0624	0.0625	1598	2.0	320	Yes	
161	5.0	761.0	36.04	0.0624	0.0625	1598	2.0	300	Yes	

Table V, C. Chromic Oxide Crucible, continued

Heat No.	% Cr Charged	Atm. Pres. mm.	Saturator Temp. ° C	P_{H_2O}/P_{H_2}	$\left(P_{H_2O}/P_{H_2}\right)$ corr.	Metal Temp. ° C	Time Hrs.	Rate of Gas Flow ml./min.	Preheater	Remarks
162	4.3	756.0	36.02	0.0627	0.0628	1601	1.6	330	Yes	Partly covered
165	0	764.5	44.68	0.1019	0.1022	1599	2.5	360	Yes	
168	0	763.5	42.28	0.0890	0.0892	1600	1.2	300	No	
169	0	763.5	50.80	0.1443	0.1449	1600	1.2	380	Yes	Bridging
170	0	762.9	50.67	0.1440	0.1446	1597	1.6	320	Yes	
171	9.9	759.9	22.70	0.0280	0.0280	1602	2.5	340	Yes	
172	8.0	759.9	22.50	0.0276	0.0276	1596	2.0	330	Yes	
174	8.6	762.4	46.90	0.1159	0.1162	1594	1.7	350	Yes	
175	0	760.5	50.09	0.1393	0.1398	1598	3.2	340	Yes	
176	0	751.6	57.82	0.2185	0.2196	1598	2.1	480	Yes	
177	0	751.6	59.91	0.2466	0.2479	1598	1.6	410	Yes	All covered
178	0	766.3	64.63	0.3169	0.3189	1595	1.1	440	Yes	Partly covered
179	0	766.3	67.62	0.3792	0.3818	1596	1.4	480	Yes	Partly covered
180	6.0	752.3	35.67	0.0618	0.0619	1597	2.0	350	Yes	Partly covered
181	10.0	752.3	30.27	0.0447	0.0448	1596	1.2	410	Yes	
182	15.0	751.6	26.40	0.0356	0.0356	1594	2.2	410	Yes	
183	20.1	762.8	22.74	0.0280	0.0280	1594	2.3	400	Yes	Green needle on surface

Table V, C. Chromic Oxide Crucible, continued

Heat No.	% Cr Charged	Atm. Pres. mm.	Saturator Temp. ° C	$\frac{P_{H_2O}}{P_{H_2}}$	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Metal Temp. ° C	Time Hrs.	Rate of Gas Flow ml./min.	Preheater	Remarks
184	9.8	760.6	30.89	0.0461	0.0462	1595	1.5	400	Yes	
185	7.4	760.6	30.89	0.0460	0.0461	1598	1.5	400	Yes	
186	5.0	759.4	35.06	0.0590	0.0591	1596	1.2	450	Yes	
187	3.3	769.5	41.05	0.0823	0.0825	1598	1.6	390	Yes	
188	12.7	772.1	27.70	0.0388	0.0389	1594	1.1	390	Yes	
189	21.4	763.1	21.40	0.0257	0.0257	1593	1.1	350	Yes	
D.	Chromite Crucible									
202[4]	0	752.9	46.90	0.1176	0.1180	1595	1.0	310	Yes	
203	0	753.8	78.25	0.7816	0.789	1595	2.4	410	Part[2]	
204	0	771.2	82.26	1.023	1.033	1595	1.6	390	Part[2]	
205	4.2	766.9	41.50	0.0847	0.0849	1597	1.0	410	Yes	
206	3.2	764.5	44.51	0.1009	0.1012	1597	2.4	410	Yes	

Notes:

1. Heats made with brass head, and leakage probable.
2. Preheater broke during the run.
3. Temperatures unable to be kept constant.
4. Chromite crucibles always showed some reaction, and for this one (No. 202) it was thought that equilibrium with the gas was not attained.

TABLE VI

Data Sheet

Heat No.	Metal Temp. ° C	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Chromium Analysis %	Oxygen Analysis, % Data	Chosen Value	Condition of Ingots Porosity	Crust	Remarks
A. Magnesia Crucible								
1[1]	1586	0.0429		.0165		Sound		
2[1]	1588	0.0424		.0157, .0153		Sound		
3	1592	0.1023		.0246	0.0246	Sound		
4	1594	0.0823		.0200, .0201	0.0200	Sound		
B. Alundum Crucible								
24	1592	0.0421		.0100, .0090 .0116	0.0102	Sound		
25	1655	0.0841				Sound		
26	1597	0.833		.224, .199		Porous		Crucible broken
27	1596	0.1247		.029, .031 .030	0.030	Sound		
C. Chromic Oxide Crucible								
107[1]	1595	0.377	7.42					
110[1]	1653	0.0605	6.68					
111[1]	1628	0.0578	7.08					

Table VI, C. Chromic Oxide Crucible

Heat No.	Metal Temp. ° C	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Chromium Analysis %	Oxygen Analysis, % Data	Oxygen Analysis, % Chosen Value	Condition of Ingots Porosity	Condition of Ingots Crust	Remarks
112[1]	1653	0.0875	3.88					
113[1]	1661	0.0939	3.70					
114[1]	1661	0.1018	3.25					
115[1]	1596	0.0505	5.71					
116[1]	1598	0.1187	2.04					
117[1]	1599	0.0881	2.70					
118[1]	1597	0.1307	1.77	.114		Porous		
119[1]	1595	0.1193	1.95	.043, .042	0.042	Fair		
120[1]	1605	0.0806	2.80	.037, .039	0.038	Porous		
121[1]	1596	0.0798	2.02	.051, .059 .044	0.044	Porous		
122[1]	1594	0.0524	2.47	.043, .047	0.044	Very porous		
123[1]	1595	0.0685	2.23	.043, .039 .041	0.040	Porous		
124[1]	1597	0.1526	0.96	.051, .053	0.052	Fair		
125[1]	1596	0.0411	5.09	.035, .035 .035	0.035	Sound		
131	1653	0.0826	9.25	.068, .083		Fair	G[2], thick	
132	1603	0.0832	6.09	.068, .058		Porous	G (?)[3]	Brown needles on surface

Table VI, C. Chromic Oxide Crucible

Heat No.	Metal Temp. ° C	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Chromium Analysis %	Oxygen Analysis, % Data	Chosen Value	Condition of Ingots Porosity	Crust	Remarks
133	1603	0.0852	5.71	.046, .036 .038	0.037	Very porous		
134	1598	0.1259	2.50	.165, .038 .041	0.039	Porous	B[2]	
135	1598	0.0857	4.37	.061, .034 .026	0.030	Fair	B	
136	1599	0.0476	11.90	.106, .104		Porous	G	
138	1650	0.0768	6.71	.076, .085		Fair	B and G[4]	
139	1596	0.0839	3.99	.034, .036	0.035	Sound		
140	1596	0.1193	2.27	.051, .043	0.043	Porous	B	
141	1594	0.0615	4.56	.026, .028	0.027	Fair	B	
142	1598	0.0623	6.73	.046, .049	0.047	Sound	G(?)[3]	
143	1597	0.0655	5.05	.040, .057	0.040	Porous	B and G[4]	
144	1597	0.0557		>.2500		Porous	G	
151	1597	0.0849	4.40	.088, .052		Porous		
153	1600?	0.0479	3.92	.034, .037	0.035	Porous	B	Some fogging
155	1596	0.0528	4.06	.034, .031	0.032	Sound	B	
156	1607	0.0746				Porous		
158	1595	0.0747	3.89	.044, .042	0.042	Sound		

Table VI, C. Chromic Oxide Crucible

Heat No.	Metal Temp. ° C	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Chromium Analysis %	Oxygen Analysis, % Data	Chosen Value	Condition of Ingots Porosity	Crust	Remarks
159	1602	0.0744	4.27	.033, .045	0.033	Sound		
160	1598	0.0625	4.11	.031, .031	0.031	Sound		
161	1598	0.0625	6.28	.048, .040 .051, .052	0.040	Fair		
162	1601	0.0628	4.89	.028, .028	0.028	Fair		
165	1599	0.1022	3.28	.036, .057 .052	0.037	Porous		
168	1600	0.0892	2.81	.036, .035	0.035	Sound	B thick	
169	1600	0.1449	2.30	.089, .084, .093, .080	0.082	Sound	B	Bridging
170	1597	0.1446	1.73	.046, .049	0.047	Fair		
171	1602	0.0280				Very Porous	G thick	Green needle on surface
172	1596	0.0276	8.90	.038, .039, .034, .029	0.034	Fair	G thick	Green needle on surface
174	1594	0.1162				Fair	B thick	
175	1598	0.1398	1.55	.040, .043 .049	0.041	Sound		
176	1598	0.2196	0.85	.051, .050	0.050	Sound		
177	1598?	0.2479	0.47	.047, .048	0.047	Sound	B	Surface covered with brown film
178	1595	0.3189	0.38	.065, .064	0.065	Sound		
179	1596	0.3818	0.27	.076, .074 .078	0.075	Sound		
180	1597	0.0619	7.21	.057, .061, .031, .045	0.031	Fair	G	

Table VI, C. Chromic Oxide Crucible

Heat No.	Metal Temp. ° C	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ corr.	Chromium Analysis %	Oxygen Analysis, % Data	Chosen Value	Condition of Ingots Porosity	Crust	Remarks
181	1596	0.0448	9.98	.032, .029	0.031	Porous		Green needle on surface
182	1594	0.0356				Porous	G	
183	1594	0.0280	19.30	.055, .049 .051	0.050	Sound		Green needles on surface
184	1595	0.0462	10.70	.047, .042 .062	0.042	Porous	G	
185	1598	0.0461	8.29	.039, .036, .043, .036	0.036	Sound	G	
186	1596	0.0591	5.81	.031, .030, .031, .031	0.031	Sound		
187	1598	0.0825	4.45	.039, .036, .041, .032	0.033	Fair	B	
188	1594	0.0389	15.13	.042, .053, .061, .047	0.044	Porous	G	
189	1593	0.0257	21.40	.076, .057	0.057	Porous	G	
D. Chromite Crucible								
202	1595	0.1180	0.37	.065, .060	0.062	Porous		
203	1595	0.789	0.41	.174, .173	0.174	Sound		
204	1595	1.033	0.30	.182, .190 .214, .186	0.184	Fair		
205	1597	0.0849	3.79	.030, .030	0.030	Sound		
206	1597	0.1012	2.73	.037, .032, .039, .033	0.033	Sound		

Table VI, continued

Notes:

1. Heats that might have leakage.
2. "G" means crust that gave green streak. "B" means crust that gave brown streak.
3. "G (?)" means that the streak color looked like green, but not distinct.
4. "B and G" means that green crust was found around the corner of the bottom of the ingot, while brown one was found at the bottom and the sides. This might well be explained by the difference in temperature at the various positions.

All the data lacking for crusts are due either to failure to record properly, or to the fact that the crust was so thin it could hardly be distinguished from the crucible itself.

VIII. IDENTIFICATION OF THE SOLID PHASE

According to the phase rule, this system consisted of four components, iron, chromium, oxygen and hydrogen, and three degrees of freedom, the temperature, the pressure and the composition of the gas phase, so that only three phases could be present in equilibrium with each other. Now that there were already a gas phase and a liquid phase, only one solid phase (or another liquid phase) could exist. The nature of this solid phase is very important to an equilibrium study and was carefully studied.

When a solid phase, in this case the chromic oxide crucible, was introduced into this system, it might remain as such, if it were the stable solid phase under those conditions, or it might dissolve continuously into the molten metal with the precipitation of a new phase from the molten metal, also continuously. If nothing else came into this picture, the reaction would continue to proceed until one of the phases disappeared which might be, in this study, the complete solution of the crucible or the complete solidification of the molten metal, and no equilibrium could be obtained before this final stage. Fortunately chromic oxide was the stable solid phase for the high chromium heats studied, and iron chromite, $FeO \cdot Cr_2O_3$, was the stable solid phase for the low chromium heats, as would be proved later. Naturally there was no problem for the high chromium heats. Whereas for the low chromium heats, the precipitated chromite, together with the molten metal,

formed a crust at the bottom of the melt which adhered to the crucible without floating up as slag. This blocked further reaction between the molten metal and the crucible, and the result would be about the same as if the melt were done in a chromite crucible.

Three different substances were in direct contact with the melt and their natures have been studied: (a) the crust as described earlier, which was composed of non-metallic substances in a metallic matrix, and was quite high in its content of non-metallic substances; (b) the non-metallic inclusions in the metal, which were present only in small amounts, and most of which might have been precipitated during cooling and might not, therefore, be the solid phase in equilibrium with the melt at the studied temperature; and (c) the crystals, usually needles, observed on the surface of the melt which were practically free from metal, but which might be produced by the vaporization and condensation of the metal and the oxidation of the condensed metal by the gas, and which might be produced at a slightly lower temperature than the melt.

A. Microscopic Examination

Many of the ingots were cut, and both the crusts around the ingot and the non-metallic inclusions in the metal were studied under the microscope. A few of the typical ones are shown in Figures 8 - 21. Figures 9 - 17 show the appearance of the crusts, and Figures 18 - 21 those of the non-metallic inclusions.

Figure 8 shows one of the non-metallic clusters inside the metal ingot, Heat 185. More like this have been found in ingot 189. These,

no doubt, led to high results of the oxygen analysis and could be used to explain why some of the oxygen data were extraordinarily high. It had been observed that these clusters always contained non-metallic substances of the green variety, and occurred only in those ingots where crusts of the green variety were found.

Figures 9 - 13 show the appearance of the crusts of the brown variety under the microscope. These were easily polished. The tendency to pit was small. The particles were medium gray under white reflected light, and showed some bright red internal reflection under dark field illumination. They seemed to be fairly rounded and tended to grow into a network with the particles joining together. They did not exhibit high relief. They were almost opaque under the polarized reflected light. These observations seemed to correspond exactly with what had been observed by other investigators[14,16] for the inclusion of "chromite". However, many black spots were observed which, for most cases, were embodied in the light colored phases and which had not been able to be removed by careful polishing. These black spots increased in number as the chromium content in the metal increased. Some were observed as pitting, but some of them were suspected to be chromic oxide surrounded by chromite.

Figures 14 - 17 show the appearance of the non-metallic crusts of the green variety. In contrast to the brown variety, they were not easily polished, always tending to pit. They were light gray in color under white reflected light. They exhibited rather high relief, and their boundaries were defined by a furrow, which appeared dark in re-

flected and bright in dark field illumination. The particles seemed to be more irregular than the brown variety, and tend to remain as single particles rather than joining together. These seemed to be what is described[14,16] as chromic oxide, with the exception that these particles did not exhibit green color under dark field illumination nor anisotropic characteristics under polarized light, and instead seemed to be opaque under those circumstances.

Etching with an acid permanganate reagent attacked many of the metal ingots very rapidly and offered no opportunity for comparison.

Figure 18 shows crystalline inclusions in the ingot number 169, which had a low chromium content, and Figure 19, those in the ingot number 188, which had a high chromium content. They seemed to be very similar in appearance, but as Portevin and Castro[16] pointed out, octahedron and rhombohedron sections might, in fact, be very similar in appearance, and the shapes of the plane sections are not sufficient to identify their crystal systems. Both were opaque under dark field illumination, and have not been identified.

Figure 20 shows some small inclusions in ingot 180. These looked more likely to be the green variety than the brown. Figure 21 shows some inclusions in the form of globules besides those similar to Figure 20. They were opaque and their nature unknown.

FIGURE 8. Heat No. 185. 500X
Cr 8.29% - O .036%

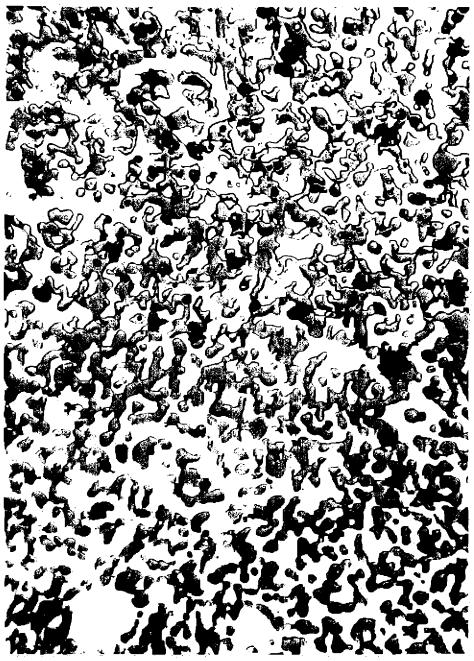


FIGURE 9. Heat No. 187. 100X
Cr 4.45% - O .032%

FIGURE 10. Heat No. 187. 500X
Cr 4.45% - O .032%

FIGURE 11. Heat No. 187. 500X
Cr 4.45% - O .032%

FIGURE 12. Heat No. 140. 100X
Cr 2.27% - O .043%

FIGURE 13. Heat No. 143. 500X
Cr 5.05% - O .040%

FIGURE 14. Heat No. 183. 100X
Cr 19.30% - O .050%

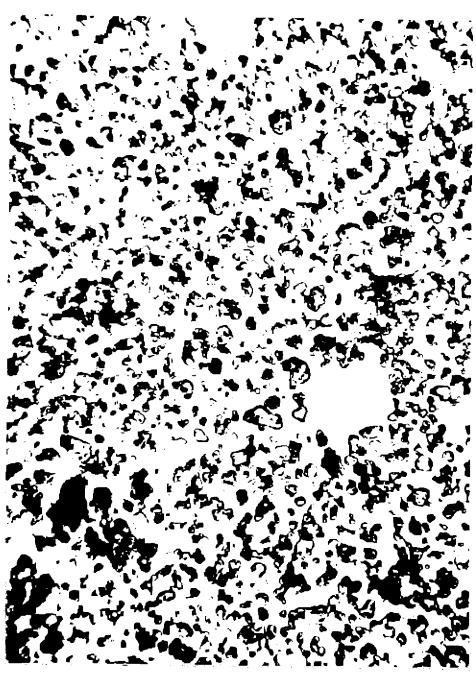


FIGURE 15. Heat No. 180. 100X
Cr 7.21% - O .031%

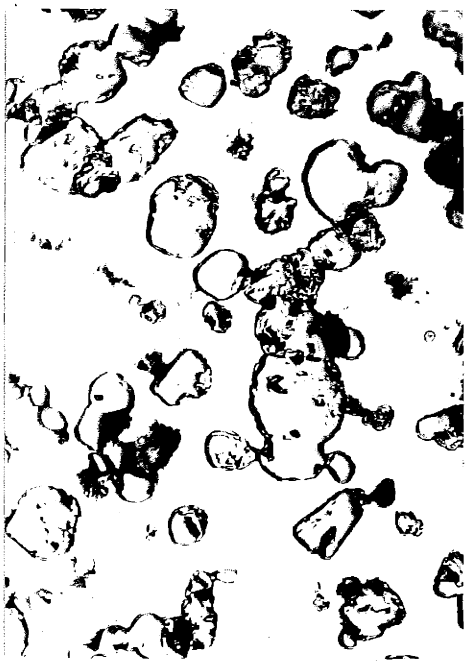


FIGURE 16. Heat No. 180. 500X
Cr 7.21% - O .031%

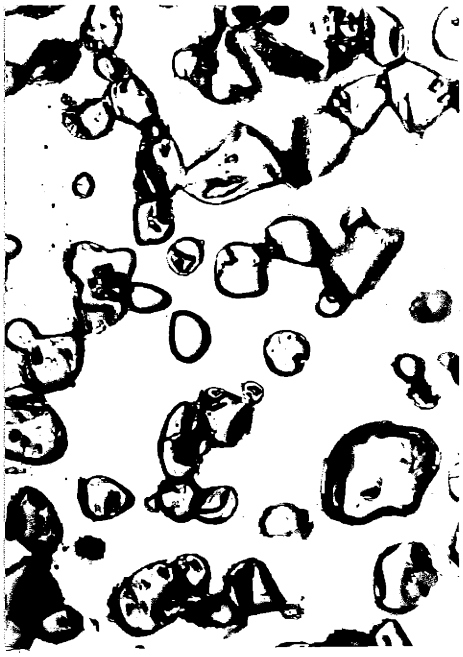
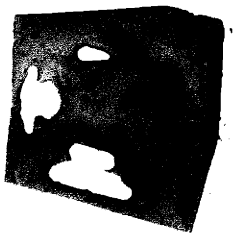


FIGURE 17. Heat No. 189. 500X
Cr 21.40% - O .057%



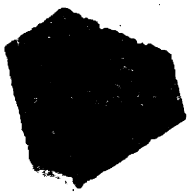


FIGURE 18. Heat No. 169. 500X
Cr 2.30% - O .084%

FIGURE 19. Heat No. 188. 500X
Cr 15.13% - O .045%

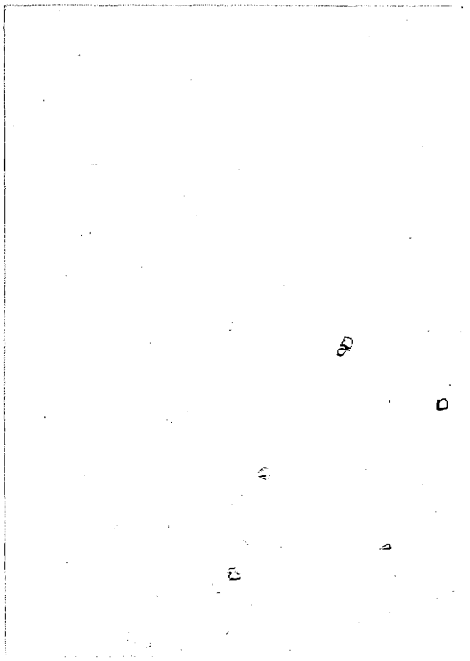


FIGURE 20. Heat No. 180. 100X
Cr 7.21% - O .031%

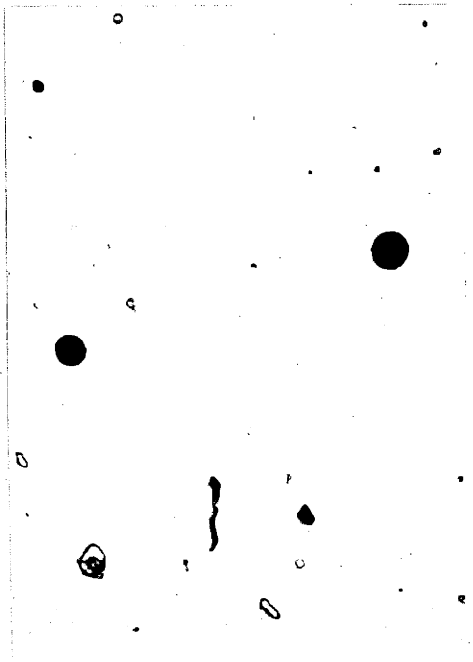


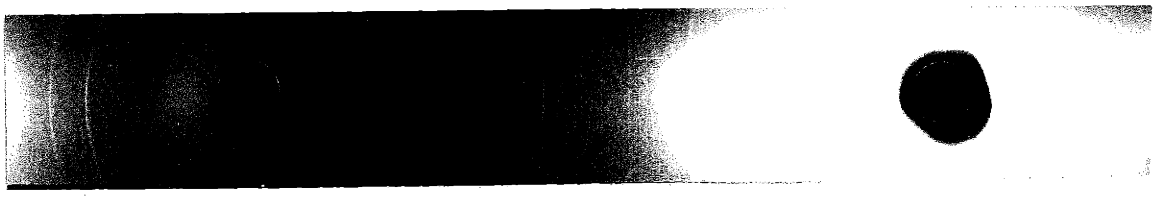
FIGURE 21. Heat No. 183. 500X
Cr 19.30% - O .050%

B. X-ray Examination

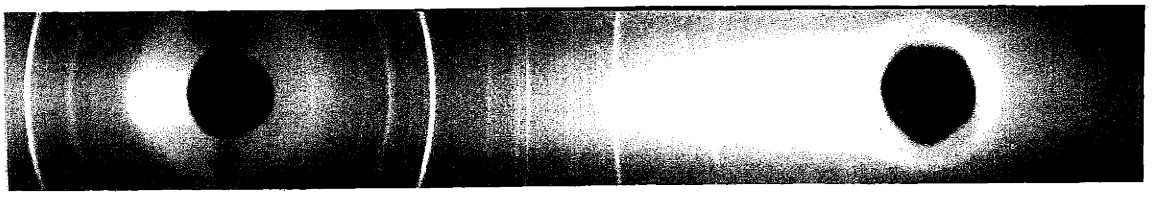
As the microscopic examination was not very conclusive in determining the nature of these solid phases, X-ray diffraction was resorted to. The true inclusions were too small in amount and could be separated from the metal only with difficulty; they were not examined.

Filings of the crust of the brown variety were examined with the result that the iron lines were so predominant that the other lines were too obscure. In order to separate most of the iron from the mixture so that it would be more concentrated in the non-metallic phase, the iodine treatment for oxide inclusions as described by Cunningham and Price[28] was used. The essential part was to dissolve the metallic iron in a ferrous iodide solution with the addition of ammonium citrate, which did not dissolve the oxides. The residue after five hours of digesting at 0° C was filtered and washed. The X-ray diffraction photograph of the residue from ingot 140 is shown in Figure 22, and the measurement tabulated in Table VII. The comparison with the published data proves that there is a good check with those of chromite, considering the inaccuracy of the measurement of the lines on a Debye-Scherrer picture, especially for the very faint lines.

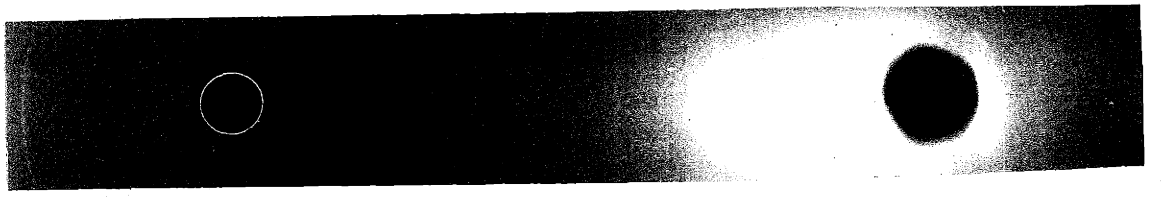
Figure 22 also shows the X-ray photographs of the chromite crucible, the crust of Heat 182 of the green variety, and the green needles which appeared as surface condensate of Heat 181. Table VIII gives the measurements and comparison of the lines for the crust of Heat 182, and Table IX those for the surface condensate of Heat 181. It could be seen that the last two consisted of mixtures of iron and chromic oxide, Cr_2O_3, with more iron for the crust.



a. Chromite Crucible



b. Crust, Heat No. 140 (brown variety)



c. Crust, Heat No. 182 (green variety)

d. Surface Condensate, Heat No. 181 (green)

FIGURE 22. X-ray Diffraction Photograms

TABLE VII

X-ray Diffraction Pattern of Heat No. 140 Crust

Residue After Iodine Treatment

Co Radiation: λ_α = 1.787 Å λ_β = 1.617 Å No Filter

Measured				Fe		$FeO \cdot Cr_2O_3$	
Corr. Angle	d_α	d_β	Intensity	d	Intensity	d	Intensity
10.98	4.69		vw			4.82	0.2
17.82	2.92		vvw			2.95	0.4
19.46	(2.68)	2.43	vvvw				
20.93	2.50		w			2.52	1.0
23.92	(2.20)	2.00	vvw				
25.24	2.10		vvw			2.08	0.4
26.45	2.01		vs	2.01	1.00		
32.74	1.65		vvvw			1.70	0.3
33.64	1.613		vw			1.606	0.8
37.60	1.464		vw			1.475	0.9
38.84	1.425		w	1.428	0.15		
44.38	1.277		vvvw			1.274	0.4
50.00	1.166		s	1.166	0.38		
61.96	1.012		w	1.010	0.10		
68.40	0.961		vvvw			0.966	0.3

Notes:

d_α = d calculated from λ_α ; d_β = d calculated from λ_β
v = very; w = weak; s = strong
Fe data from A. S. T. M. X-ray diffraction data cards No. 3399.
$FeO \cdot Cr_2O_3$ data from Clark, Ally and Badger (27).

TABLE VIII

X-ray Diffraction Pattern of Heat No. 182 Bottom Crust

Co Radiation: λ_{α} = 1.787 Å No Filter

Measured			Fe		Cr_2O_3	
Corr. Angle	d	Intensity	d	Intensity	d	Intensity
20.60	2.54	vw			2.67	0.70
21.71	2.415	vw			2.47	0.70
26.51	2.001	s	2.01	1.00		
29.85	1.795	vvw			1.81	0.45
32.80	1.649	w			1.67	1.00
38.95	1.421	w	1.428	0.15	1.432	0.45
50.07	1.165	s	1.166	0.38		
55.13	1.089	vvw			1.087	0.12
58.73	1.045	vvw			1.041	0.10
61.93	1.013	w	1.010	0.10		
71.00	0.945	vvvw			0.946	0.06

Notes:

Fe data from A. S. T. M. X-ray data card No. 3399.

Cr_2O_3 data from A. S. T. M. X-ray data card No. 3667.

TABLE IX

X-ray Diffraction Pattern of Heat No. 181 Surface Condensate

Co Radiation: λ_{α} = 1.787 Å No Filter

Measured			Fe		Cr_2O_3	
Corr. Angle	d	Intensity	d	Intensity	d	Intensity
14.50	3.57	vvw			3.62	0.45
19.82	2.64	w			2.67	0.70
21.49	2.44	w			2.47	0.70
24.47	2.16	vvw			2.17	0.30
26.36	2.015	s	2.01	1.00	2.03	0.04
29.78	1.800	vw			1.81	0.45
32.50	1.663	w			1.67	1.00
34.90	1.562	vvw			1.58	0.06
37.77	1.460	vw			1.465	0.30
38.82	1.426	w	1.428	0.15	1.432	0.45
43.86	1.290	vvvw			1.294	0.16
46.14	1.239	vvvw			1.236	0.06
49.77	1.170	w	1.166	0.38	1.172	0.05
51.46	1.141	vvvw			1.148	0.06
52.77	1.122	vvw			1.123	0.06
55.48	1.085	vvw			1.087	0.12
59.06	1.041	vvw			1.041	0.10
61.73	1.016	vvvw	1.010	0.10		
71.19	0.943	w			0.946	0.06
72.61	0.937	vw				

Notes: Fe data from A.S.T.M. X-ray data card No. 3399.
Cr_2O_3 data from A.S.T.M. X-ray data card No. 3667.

Since chromium did exhibit some fluorescent radiation, using cobalt as the target, the films were somewhat fogged, and the measurements less accurate. However, the data left no doubt as to the identification of these crusts; that is, the brown variety as chromite and the green variety as chromic oxide. Other substances might occur in the solid phase as solid solutions, but if the assumption that the solubility was limited was true, the activity of the solid phase could be considered as constant and equal to that of solid chromite or chromic oxide.

C. Discussion

From the above observations, it could be concluded that there were two different varieties of crusts, the brown chromite and the green chromic oxide. Since for all these ingots chromic oxide crucibles were used, this left no doubt that chromite was the reaction product and should be the stable solid phase under certain conditions, one of which was the low chromium content. The highest one where the presence of chromite could still be assured was ingot heat number 143 with a chromium content of 5.05 percent. On the other hand, chromic oxide crust could be assured in ingot heat number 180 with chromium content of 7.21 percent. In ingot number 186 containing 5.81 percent chromium, it seemed to contain a very thin chromite crust, but the result was very doubtful. The presence of both the green and the brown variety in one ingot, as number 143, seemed to be due to incompleteness of the reaction between iron and chromic oxide.

It was tried to obtain chromic oxide crust without using chromic oxide crucible so that it could be ascertained that the chromic oxide found was really precipitated from the ingot, and thus proved to be the stable solid phase. This attempt was not successful. First a chromite crucible with not too high a chromium content was used, but the chromite acted differently from the chromic oxide in that it did not dissolve readily, and practically no crust could be found. Next a heat with a high chromium charge was made in an alundum crucible with a gas mixture high in water vapor content which was beyond the equilibrium point. The result was that (Heat 25) the entire surface was covered with a film rapidly, which could be removed only by raising the temperature or lowering the water vapor content of the gas, and that no crust could be found. Yet from the color of the film formed it looked rather certain it was of the green variety, that is, chromic oxide variety.

It seemed quite safe to say that the critical chromium content, above which chromium oxide was stable and below which chromite was stable, was between 5 and 7 percent.

It should be emphasized that the above statement is only true when the oxygen in the metal is just in equilibrium with the stable non-metallic phase. If oxygen is in much excess, the precipitation of both chromite and chromic oxide would be possible. As observed in the case of Heat 174 where chromite was formed from a high chromium melt, it seemed that chromite might be precipitated more rapidly than chromic oxide due to either the rate of nuclei formation or the rate

of growth. This might be one of the explanations of why chromite inclusions were so often found in ferrochromiums and high chromium steels.

As both chromite and chromic oxide are considerably lighter than iron (5.09 for specific gravity of chromite and 5.21 for chromic oxide), they were expected to float on the surface of molten iron. On the contrary, they were often found at the bottom as crusts, which could be explained best by the fact that the crusts adhered to the crucible wall. It was postulated that, owing to the porous nature of the crucible, the liquid iron might creep into the interstices of the crucible wall to form a crust within which the solid particles were not free to move away. In this way the contact surface between metal and crucible was tremendously increased, and the reaction between metal and solid phase promoted. The facts that the chromic oxide crucibles always adhered to the ingots and could be removed only by grinding, while the alundum crucibles and the chromite crucibles could be separated easily from the ingots, supported this explanation too. As the crusts were first formed, they were composed of chromic oxide principally, but as time went on and when conditions were favorable to the formation of chromite, reaction proceeded on the surfaces of the particles with the result that some of the chromic oxide particles might be occluded without further reaction with the melt. If the conditions were favorable to chromic oxide formation, the crust will remain as such without reaction. This was considered as the reason why chromic oxide crusts remained in particles and chromite crusts tended to become a network. The strong eddy current in the melt would also tend to round these par-

ticles up by colliding against each other, like the action of water on small pebbles. That explained why the particles were more or less rounded. While chromic oxide is much harder than chromite, it could be conceived that the effects on chromite particles would be much greater than those on chromic oxide particles. The strong eddy current in the melt would also tend to carry these particles upward to the surface, thus explaining the occasional appearance of clusters of non-metallic substances in the metal. While chromite crusts always tended to grow into a network, the tearing down of a part of these chromite particles would be more difficult, and that was why no cluster of chromite was found in the metal.

As this postulation could be used successfully to explain all the observed phenomena, the hypothesis that the non-metallic particles in the crust constitute the stable solid phase in equilibrium with the melt during the process and were not produced otherwise, could be established. Chromite and chromic oxide are the stable solid phases for low and high chromium melts respectively.

As for the non-metallic inclusions in the metal, the most probable explanation was that most of them were produced during the solidification process. At that stage, the equilibrium constants might drop so low that the precipitation of both solid phases would be possible. As explained earlier, in such cases which phase appeared first would depend more on physical reasons than equilibrium conditions, and could not be used as a criterion for the stability of the solid phase at higher temperatures. Besides, the identification was not conclusive

in such cases, and it seems unwise to count heavily on these observations.

The observations on the surface film and surface condensate were very incomplete, but those available did show a good check with those based on the crusts.

IX. PRESENTATION OF THE EQUILIBRIUM DATA

A. Sources of Error

Before the data are calculated and discussed, it is necessary to consider the possible sources of error in various heats and to study the reliability of the data obtained.

(1) Temperature Measurement. The reading and calibration of the pyrometer were quite satisfactory, and could be duplicated within two degrees. However, as the method of correction presumed that the emissivities of the molten metals of various heats were constant and equal to that of the pure iron, it was possible to introduce some error. No attempt was made to determine the emissivity of the various alloys. As pointed out by Goller[30], the chromium iron alloy would have a higher emissivity than iron. Although his data could not be used in this investigation because other alloying elements were present in the materials he used, it is quite possible that a higher chromium alloy would have a higher emissivity. If this were true, the actual temperature of the high chromium heats would be lower than the corrected temperature as listed in the table.

As for the individual runs, the temperature control for the earlier runs was not very good, and in some cases it had been compelled to go somewhat higher than desired, as listed in the table. Heats 108, 109, 174 and 177 had the metal surface covered with solid film; 137, 153, 158 and 159 showed some fogging on the sight glass due to various reasons; and 169 and 156 bridged badly. For these heats, the temperature measure-

ments might be erroneous. With these exceptions, it was thought that the temperatures were accurate to at least plus or minus 5° C, provided that there was no change in emissivity. It was found to be quite possible to hold the temperature constant to within plus or minus five degrees during an experiment.

(2) Gas Composition. From the data obtained in the testing of the saturator, it was evident that the calculated gas composition did represent the actual gas composition up to at least 50° C. Table X gives the oxygen analysis in iron melted under definite gas composition. The result was very good, and checked very well with the data of Chipman and Fontana[26], which gave the value 3.95 at 1600° F, and the equation of Chipman and Samarin[29], which gave 4.1 at 1595° C for the ratio $K_o = (\frac{P_{H_2O}}{P_{H_2}}) / [O]$. The average value obtained in these heats was 4.15, which will be used in later calculations. This also indicated that the performance of the saturator was excellent, provided the amount of water in the towers and the temperature of the water bath were well adjusted as well as the temperature of the saturator. In case of very high moisture content in the gas, the deviation might be higher but, for those cases, the chromium analyses were also not too accurate, and the data could not be considered very good anyway.

(3) Chromium Analysis and the Equilibrium. The results of chromium analyses checked very well normally. As an estimation, it could be said that for those samples with more than 10 percent chromium, the maximum deviation of single values from the average is ± 0.10 percent; for those around 5 percent, ± 0.06 percent; for those around 1 percent,

TABLE X

Oxygen Activity with Respect to Gas Composition at 1595° C

Heat No.	Crucible Used	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{corr.}$	[O] Analysis	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)/[O]$	Remarks
1	MgO	0.0429	0.0165	2.60	Leak ?
2	MgO	0.0424	0.0155	2.73	Leak ?
3	MgO	0.1023	0.0246	4.16	Single [O] value
4	MgO	0.0823	0.020	4.11	
24	Al_2O_3	0.0421	0.010	4.21	
26	Al_2O_3	0.8258	0.199	4.15	Single [O] value
27	Al_2O_3	0.1243	0.030	4.14	

± 0.03 percent; and for those around 0.3 percent, ± 0.02 percent. As the method used was standard, there seemed to leave little doubt about the validity of the results of these analyses.

As for the equilibrium, since the reaction involved the absorption or evolution of considerable amount of oxygen from or to the gas, and since the transference of gas between liquid and gas was a slow process, the equilibrium condition was more difficult to be attained than in the case where no alloying element and only relatively small amount of oxygen was involved, unless the amounts of chromium and oxygen in the charge were about equal to those needed in the final equilibrium condition. The solution of solid chromic oxide into the metal was fairly rapid, as exhibited by the rapid increase of chromium content in certain heats.

For the high chromium heats more change in chromium concentration was generally needed for the same change of (P_{H_2O}/P_{H_2}). To dissolve more chromium from the crucible, oxygen was also dissolved into the metal to make the melt high in oxygen activity with respect to the gas concentration. This oxygen had to be transferred from the melt to the gas before more chromium could be dissolved. This was a slow process. The effect might not be noticeable for low chromium heats, where the amounts of chromium and oxygen involved were small, but might be significant for high chromium heats. If this was the case, the ingot would be higher in oxygen but lower in chromium than what it should be under equilibrium conditions.

On the other hand, for low chromium heats, oxygen which existed in the melt was generally lower than that corresponding to the gas com-

position. As chromic oxide dissolved readily, it would be dissolved to such an extent that the chromium content was too high for the particular gas composition before enough oxygen had been transferred from the gas, and the melt would be high in chromium but low in oxygen with respect to the gas. Prolonged heating might produce a solid film on the surface of the melt but, since the chromium content was low, the formation of the solid film would be very slow and might not be noticeable within a short time. The consequence would be to get an ingot which was high in chromium and low in oxygen than it should be. The oxygen analyses of Heats 178, 179, 203 and 204 were low, and might be explained by the above reasoning, although in the case of number 204 the solubility of ferrous oxide might limit the amount of oxygen that could be analyzed in the ingot. For heats 203 and 204, there was also the possibility that the gas composition did not correspond to the value calculated.

Besides, in some heats, the amounts of chromite produced were not enough to block the reaction between the melts and the chromic oxide crucibles. In those cases the solution of the chromic oxide and the precipitation of the chromite would proceed simultaneously, and it could be conceivable that the chromium contents of the melts would be intermediate between those corresponding to the chromic oxide equilibrium and those to the chromite equilibrium, depending on the relative rate of these two reactions. Heats 170 and 176 could be cited as examples belonging to this case.

From the above reasoning, it could be said that the chromium content in the ingot tended to be high for low chromium heats and low for

high chromium heats. Therefore, more weight was put on lower chromium data for the low chromium heats, and on higher chromium data for the high chromium ones.

This deviation from the true equilibrium was aggravated when the chromium content in the charge was far away from the equilibrium chromium content, and decreased when proper charge was made. On this basis the later runs, Heats 171 - 189, and 203 - 206, would give better data than the earlier runs where the charges were determined by mere guesses.

(4) Oxygen Analysis. As has been discussed in the above section, oxygen analyses tended to be lower in low chromium heats and higher in high chromium heats than what they should be under equilibrium conditions, due to the heats being short of true equilibrium conditions.

However, unlike the chromium analyses, the oxygen analyses exhibited other complexities by themselves. The chief difficulty encountered was the complete removal of the crusts from the samples. This could be done by prolonged grinding, and it was advisable to do the last grinding on sand paper (number 1, or better number 0) so the presence of any crust could be easily recognized by the difference in luster from the metal itself. This had been done for most of the samples analyzed, with special care exercised in the last twenty heats, 171 - 189 and 203 - 206. As stated before, the lower values of the oxygen analyses of a single heat were considered as better representatives than the higher ones.

In several other cases, especially for high chromium heats, as in Heats 180 and 189, clusters of the non-metallic crusts were found in the ingot. Doubtless this would lead to some extraordinary high values of oxygen in the metal. This was impossible to remove completely, which

was evidenced by the fact that it had been impossible to obtain check data on four oxygen samples which had been analyzed for each of these heats. In such cases, the lowest value was chosen as the best value that could be obtained.

On the other hand, loss of oxygen might occur during the cooling and solidification process through (1) settling of non-metallic substances formed during cooling, and (2) evolution of gas. Since all the non-metallic substances possible to be precipitated in these alloys during cooling were in solid state at the steelmaking temperature, their coalescence and settling should be very slow, and might not be able to be accomplished in such a short time as twenty seconds. The absence of noticeable amount of non-metallic substance on the surface of the solidified ingot, and the presence of clusters of non-metallic crusts, which had a size much larger than the newly-formed non-metallic inclusions, in some of the ingots lent support to this assumption; and it would not be far from fact to say that the loss of oxygen (and also some chromium) through the removal of the non-metallic inclusions was negligible. Nevertheless, the loss of oxygen through evolution of gas might be considerable, as indicated by the bad porosity of some of the ingots. Despite the attempts to reduce the porosity by removing all the carbon in the charge and crucible, many ingots were still obtained porous, especially for the high chromium ones. This porosity might have two contradictory effects on the oxygen analysis. One was the loss of oxygen through formation of carbon monoxide or other gas, and the other was to occlude more of the crust into the ingot by stirring. Needless to say, the larger surface produced by porosity offered more

chances to be oxidized and thus show higher oxygen content. This effect, however, had been reduced by keeping all the ingots in a dessicator and by processing without quenching in water. As a conclusion, the effect of porosity was different in different cases and could not be considered as a whole. It could only be said that oxygen data of sound ingots should be more reliable than those of the porous ones, although good results can still be obtained from the porous ingots.

B. Interpretation of the Data

(1) Chromium and the Water Vapor - Hydrogen Gas Mixtures. When chromite is the stable solid phase, the reaction involved in the system would be

$$FeO \cdot Cr_2O_3\ (s) + 4H_2\ (g) = 4H_2O\ (g) + Fe\ (l) + 2Cr\ (\text{in Fe})$$

where (s) denotes solid state, (g) gas state, and (l) liquid state. Assuming that $FeO \cdot Cr_2O_3$ is a pure solid phase, that the activity of iron is a constant, which is true only when the amount of solute in the molten iron is insignificant, and which may be considered as approximately true in this case with the amount of chromium less than 5.5 percent, and that the activity of chromium is proportional to its weight percent, the equilibrium constant for this reaction would be

$$K_1 = \left(\frac{P_{H_2O}}{P_{H_2}}\right)^4 (\%\ Cr)^2$$

Similarly when chromic oxide is the stable solid phase, the reaction and the equilibrium constant would be

$$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (\text{in Fe})$$

$$K_2 = \left(\frac{P_{H_2O}}{P_{H_2}}\right)^3 (\%\ Cr)^2$$

In this reaction no iron is involved, and thus its activity could be changed to a greater extent without affecting the constancy of the constant K_2.

The data are plotted in Figure 23, and also in Figure 24, in logarithmic scale.

Now if all the assumptions are true, K_1 is a constant when the stable solid phase is chromite, then

$$K_1' = (K_1)^{\frac{1}{4}} = \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\% \text{ Cr})^{\frac{1}{2}}$$

should also be a constant. Or

$$\log\left(\frac{P_{H_2O}}{P_{H_2}}\right) = \log K_1' - \tfrac{1}{2} \log (\% \text{ Cr})$$

Thus, in Figure 24, a straight line should be possible to be drawn with a slope of $-\frac{1}{2}$ to represent all the points pertaining to this part.

Similarly, when the solid phase is chromic oxide

$$K_2' = (K_2)^{1/3} = \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\% \text{ Cr})^{2/3}$$

$$\log\left(\frac{P_{H_2O}}{P_{H_2}}\right) = \log K_2' - 2/3 \log (\% \text{ Cr})$$

and the straight line should have a slope of -2/3.

Considering the possible experimental errors, two straight lines are drawn in Figure 24 with their proper slopes, and almost all of the experimental points do fall on these two lines beautifully. These justify all the assumptions made in deriving the expression for the equilibrium constants.

The equilibrium constants as defined can be read directly from the lines as

$$K_1' = 0.164 \text{ at } 1595 \pm 5^\circ \text{ C}$$

$$K_2' = 0.218 \text{ at } 1595 \pm 5^\circ \text{ C}$$

The critical point, where chromite and chromic oxide can coexist, is found to be (% Cr) = 5.5 percent and $(P_{H_2O}/P_{H_2}) = 0.07$. And

$$K_1 = (K_1')^4 = 7.23 \times 10^{-4}$$

$$K_2 = (K_2')^3 = 1.036 \times 10^{-2}$$

The standard free energy would be

$$FeO \cdot Cr_2O_3\ (s) + 4H_2\ (g) = 4H_2O\ (g) + Fe\ (l) + 2Cr\ (\text{in Fe})$$

$$\Delta F^\circ_{1595^\circ C} = -RT \ln K_1$$

$$= -5.75 \times 1868 \times \log (7.23 \times 10^{-4})$$

$$= 26840 \text{ cal.} \qquad (1)$$

$$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (\text{in Fe})$$

$$\Delta F^\circ_{1595^\circ C} = -4.575 \times 1868 \times \log K_2$$

$$= 16960 \text{ cal.} \qquad (2)$$

With the help of the equation

$$O\ (\text{in Fe}) + H_2\ (g) = H_2O\ (g)$$

$$K = \left(\frac{P_{H_2O}}{P_{H_2}}\right) \cdot \frac{1}{(\%\ O)} = 4.15$$

$$\Delta F^\circ_{1595^\circ C} = -4.575 \times 1868 \times 0.6180$$

$$= -5282 \text{ cal.} \qquad (3)$$

Subtracting (2) and (3) from (1), we obtain

$$FeO \cdot Cr_2O_3\ (s) = Fe\ (l) + O\ (\text{in Fe}) + Cr_2O_3\ (s)$$

$$\Delta F^\circ_{1595^\circ C} = 15160 \text{ cal.} \qquad (4)$$

where O (in Fe) should be expressed in its activity rather than concentration, as shown in the next section. Or, with the help of the equation

$$FeO\ (\text{in Fe}) + H_2\ (g) = H_2O\ (g) + Fe\ (l)$$

$$K = \left(\frac{P_{H_2O}}{P_{H_2}}\right) \cdot \frac{1}{(\%\ FeO)} = 4.15 \times \frac{16}{71.84}$$

$$= 0.924 \qquad (5)$$

$$\Delta F^{\circ}_{1595^{\circ}C} = -4.575 \times 1868 \times (-.0342) = 292 \text{ cal}$$

Subtracting (2) and (5) from (1), we obtain

$$FeO \cdot Cr_2O_3 \text{ (s)} = FeO \text{ (in Fe)} + Cr_2O_3 \text{ (s)}$$

$$\Delta F^{\circ}_{1595^{\circ}C} = 9590 \text{ cal.} \qquad (6)$$

According to Taylor and Chipman's equation[36]

$$FeO \text{ (l)} = Fe \text{ (l)} + O \text{ (in Fe)}$$

$$\log \% O = -\frac{6320}{T} + 2.734$$

$$= -0.649 \text{ at } 1595^{\circ} C$$

$$\Delta F^{\circ}_{1595^{\circ}C} = 5546 \text{ cal.} \qquad (7)$$

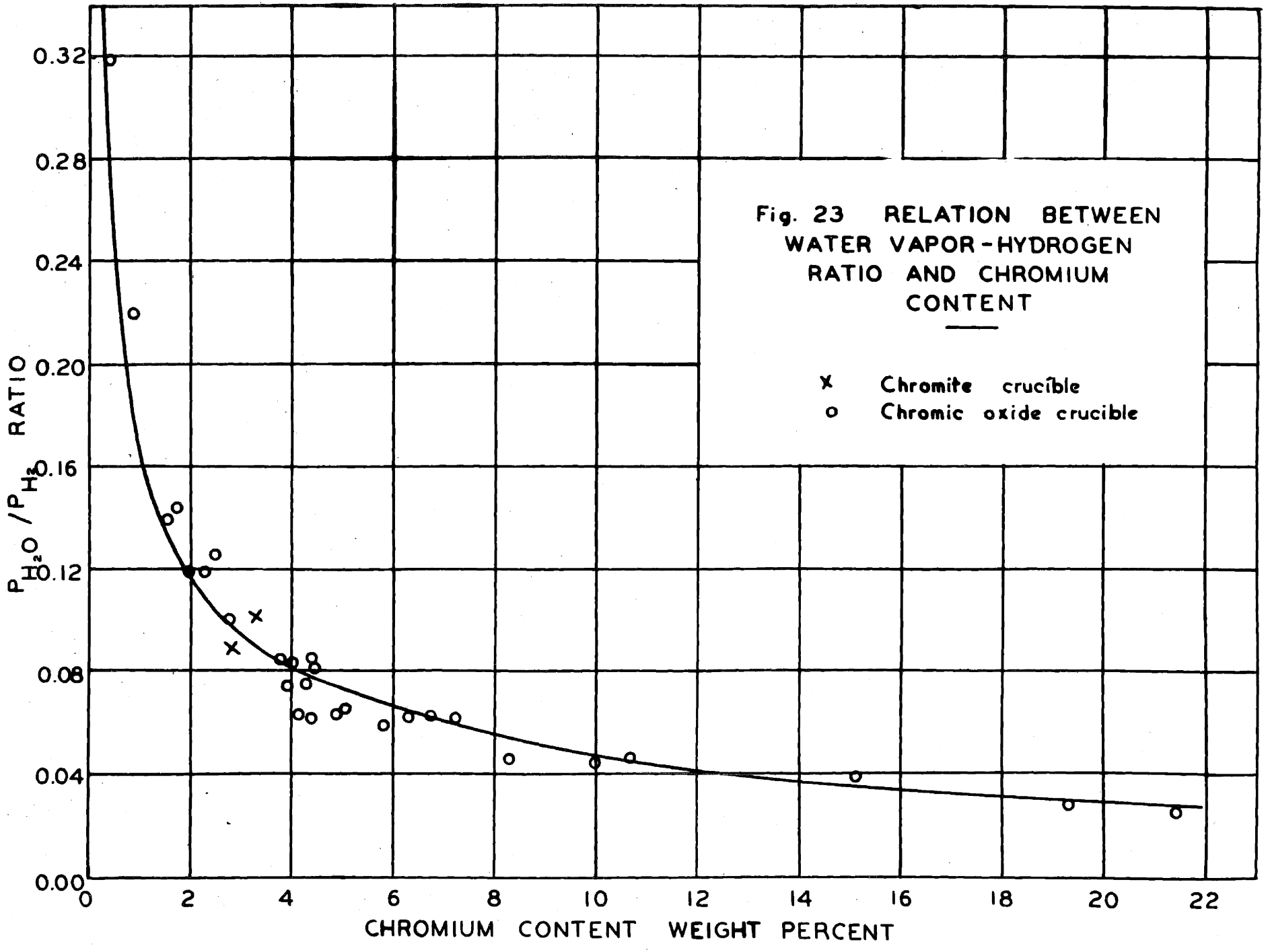
Combining (4) and (7)

$$FeO \cdot Cr_2O_3 \text{ (s)} = FeO \text{ (l)} + Cr_2O_3 \text{ (s)}$$

$$\Delta F^{\circ}_{1595^{\circ}C} = 9610 \text{ cal.} \qquad (8)$$

which means that the reaction always tends to proceed toward the formation of chromite.

(2) Oxygen in the Melt. It has been well proved[26,29] that the activity of oxygen is directly proportional to its concentration in pure iron melts. However, in the case of iron alloys, the situation might be different. Let us define the activity of oxygen in any melt as equal to the concentration of oxygen in pure iron which would exert the same oxygen pressure or, in other words, which would remain in equilibrium with the same H_2O–H_2 gas mixture. Now we have already established the relationship between the oxygen concentration in pure iron and the H_2O–H_2 gas mixture as $(P_{H_2O}/P_{H_2}) = 4.15$ (% O), which can be used to calculate the activity of oxygen of the various heats, as tabulated in Table XI as a_o. The activity coefficient f_o, which is defined as the ratio between activity and actual concentration, is also


0.32
0.28
0.24
0.20
0.16
0.12
0.08
0.04
0.00
P_{H_2O}/P_{H_2} RATIO
0
2
4
6
8
10
12
14
16
18
20
22
CHROMIUM CONTENT WEIGHT PERCENT
Fig. 23 RELATION BETWEEN WATER VAPOR-HYDROGEN RATIO AND CHROMIUM CONTENT
x Chromite crucible
o Chromic oxide crucible

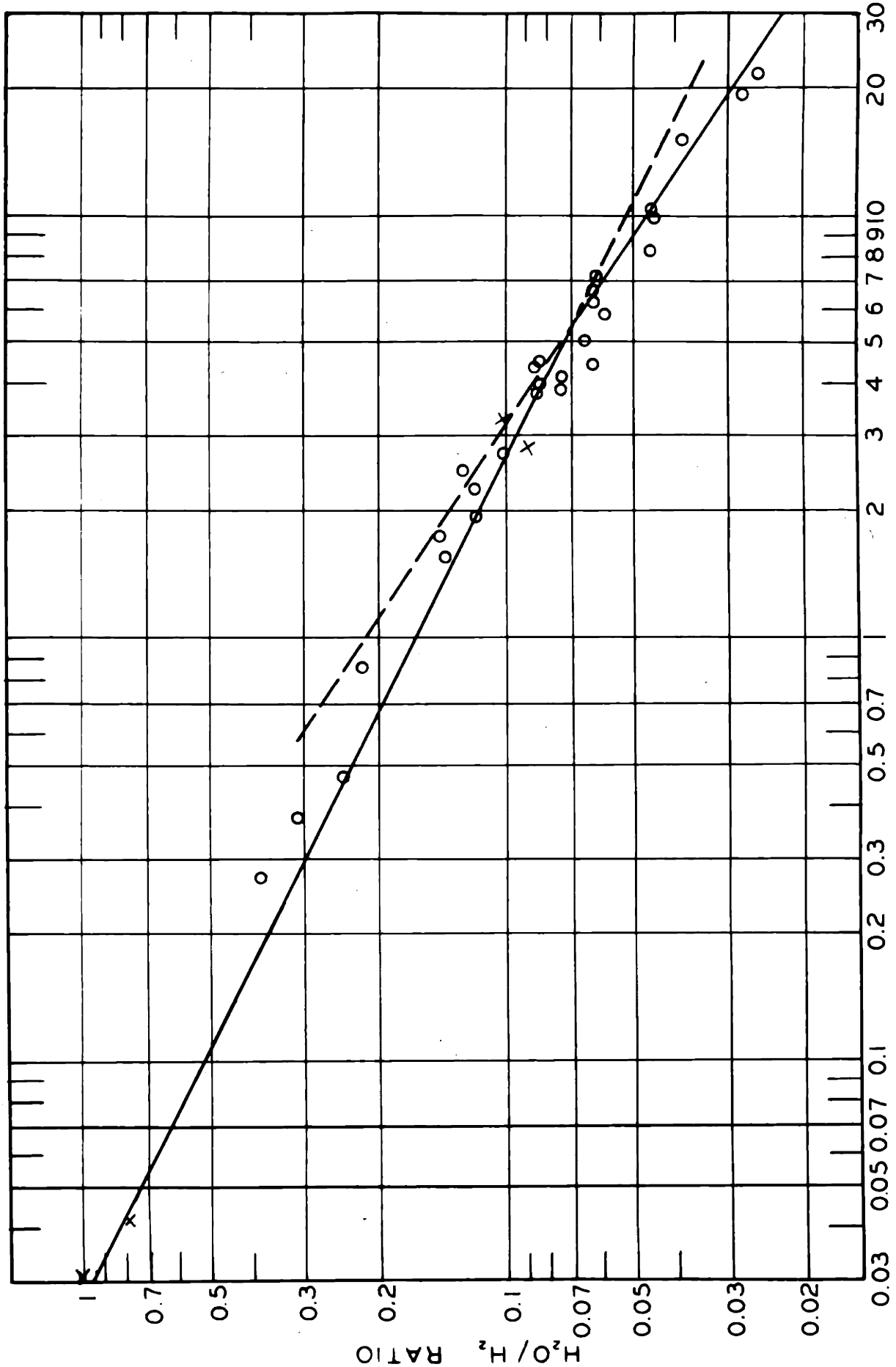


FIGURE 24. Relation Between Water Vapor - Hydrogen Ratio and Chromium Content of the Melt, in Logarithmic Scale.

tabulated in Table XI and plotted against the chromium concentration in Figure 26. It is obvious that the activity coefficient of oxygen drops rapidly as the chromium concentration increases. As stated in section (1), the activity of chromium is almost directly proportional to its concentration, and no serious effect is introduced in using its concentration instead of its activity, or mol fraction.

Using a_o for the activity of oxygen in the melt, the results of section (1) could be converted as follows:

$$FeO\cdot Cr_2O_3\ (s) + 4H_2\ (g) = 4H_2O\ (g) + Fe\ (l) + 2Cr\ (\text{in Fe})$$

$$K_1 = (\%\ Cr)^2 \left(\frac{P_{H_2O}}{P_{H_2}}\right)^4 = 7.23 \times 10^{-4}$$

$$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (\text{in Fe})$$

$$K_2 = (\%\ Cr)^2 \left(\frac{P_{H_2O}}{P_{H_2}}\right)^3 = 1.036 \times 10^{-2}$$

As shown in the section on gas composition,

$$H_2\ (g) + O\ (\text{in Fe}) = H_2O\ (g), K_o = \left(\frac{P_{H_2O}}{P_{H_2}}\right)/a_o = 4.15$$

Therefore,

$$FeO\cdot Cr_2O_3\ (s) = 4\ O\ (\text{in Fe}) + Fe\ (l) + 2Cr\ (\text{in Fe})$$

$$K_3 = (\%\ Cr)^2\ a_o^4 = \frac{K_1}{K_o^4} = 2.44 \times 10^{-6}$$

And

$$Cr_2O_3\ (s) = 3\ O\ (\text{in Fe}) + 2Cr\ (\text{in Fe})$$

$$K_4 = (\%\ Cr)^2\ a_o^3 = \frac{K_2}{K_o^3} = 1.45 \times 10^{-4}$$

The above equations are valid only when the activities of oxygen are used, while relationships involving the actual concentrations are also desired. In order to explain the discrepancy between the activity and concentration of oxygen, and to find the relationship between chromium and oxygen concentration, the following assumptions and calculations are made.

It is assumed that oxygen in the iron-chromium alloy can exist in three forms: as free oxygen, O_f; in the form of FeO, O_{Fe}; and in the form of Cr_xO_y, O_{Cr}, where x and y may be any small whole number, most probably x = y = 1 or x = 2, y = 3.

$$O_{total} = O_f + O_{Fe} + O_{Cr}$$

Let S be the amount of free oxygen dissolved in the alloy when (P_{H_2O}/P_{H_2}) = 1, S_{Fe} that in pure iron, and S_{Cr} that in pure chromium. Now if S changes linearly with the composition, then $S = S_{Fe}$ (% Fe)/100 + S_{Cr} (% Cr)/100, and if the free oxygen is monoatomic in the melt,

$$O_f = S \cdot \left(\frac{P_{H_2O}}{P_{H_2}}\right) = \left[\frac{S_{Fe}}{100}\,(\%\ Fe) + \frac{S_{Cr}}{100}\,(\%\ Cr)\right]\left(\frac{P_{H_2O}}{P_{H_2}}\right)$$

and

$$O_{Fe} = k_{Fe}\,(\%\ Fe)\left(\frac{P_{H_2O}}{P_{H_2}}\right)$$

$$O_{Cr} = k_{Cr}\,(\%\ Cr)^x\left(\frac{P_{H_2O}}{P_{H_2}}\right)^y$$

Therefore,

$$O_{total} = \left[\frac{S_{Fe}}{100}\,(\%\ Fe) + \frac{S_{Cr}}{100}\,(\%\ Cr)\right]\left(\frac{P_{H_2O}}{P_{H_2}}\right) + k_{Fe}\,(\%\ Fe)\left(\frac{P_{H_2O}}{P_{H_2}}\right) + k_{Cr}\,(\%\ Cr)^x\left(\frac{P_{H_2O}}{P_{H_2}}\right)^y$$

$$= \left(\frac{S_{Fe}}{100} + k_{Fe}\right) \cdot \left(\frac{P_{H_2O}}{P_{H_2}}\right) \cdot (\%\ Fe) + \left[\frac{S_{Cr}}{100} + k_{Cr}\,(\%\ Cr)^{x-1}\left(\frac{P_{H_2O}}{P_{H_2}}\right)^{y-1}\right] \cdot (\%\ Cr)\left(\frac{P_{H_2O}}{P_{H_2}}\right)$$

In pure iron, (% Cr) = 0, (% Fe) = 100, thus

$$O_{total} = \left(\frac{S_{Fe}}{100} + k_{Fe}\right) \cdot \left(\frac{P_{H_2O}}{P_{H_2}}\right) \cdot 100$$

We know in such case, $O_{total} = \left(\frac{P_{H_2O}}{P_{H_2}}\right) / 4.15$ at the particular temperature, so

$$\left(\frac{S_{Fe}}{100} + k_{Fe}\right) = 0.00241$$

Thus for any iron -chromium alloy

$$O_{total} = 0.00241\left(\frac{P_{H_2O}}{P_{H_2}}\right)\cdot(\%\ Fe) + \left[\frac{S_{Cr}}{100} + k_{Cr}\ (\%\ Cr)^{x-1}\left(\frac{P_{H_2O}}{P_{H_2}}\right)^{y-1}\right] \cdot(\%\ Cr)\left(\frac{P_{H_2O}}{P_{H_2}}\right)$$

If we introduce a new function defined as

$$U = \left[O_{total} - 0.00241\left(\frac{P_{H_2O}}{P_{H_2}}\right)\ (\%\ Fe)\right] / (\%\ Cr)\left(\frac{P_{H_2O}}{P_{H2}}\right)$$

then

$$U = \frac{S_{Cr}}{100} + k_{Cr}\ (\%\ Cr)^{x-1}\left(\frac{P_{H_2O}}{P_{H_2}}\right)^{y-1}$$

Now let us discuss the various cases of different values of x and y.

(a) When all oxygen in the melt associated with chromium is free oxygen, that is, $k_{Cr} = 0$, then U should always be a constant.

(b) When $x = y = 1$, that is, oxygen is partly dissolved in the form of CrO, U should also be a constant, independent of either the gas composition or the chromium content.

(c) When $x = 2$, $y = 3$, that is, oxygen is dissolved partly in the form of Cr_2O_3, then

$$U = \frac{S_{Cr}}{100} + k_{Cr}\ (\%\ Cr)\left(\frac{P_{H_2O}}{P_{H_2}}\right)^{2}$$

In the low chromium heats, where $(\%\ Cr)^2\ (P_{H_2O}/P_{H_2})^4$ is a constant, U should also be a constant, and in the high chromium heats, where $(\%\ Cr)^2\ (P_{H_2O}/P_{H_2})^3$ is a constant, U will be a linear function of $(P_{H_2O}\ /\ P_{H_2})^{\frac{1}{2}}$, with a positive slope.

(d) When $x = 1$, $y > 1$, since k_{Cr} is always positive, U should be a function of $(P_{H_2O}\ /\ P_{H_2})$ and always increase with $(P_{H_2O}\ /\ P_{H_2})$.

(e) When $x > 1$, $y = 1$, U should be a function of (% Cr) and always increase with (% Cr). And U should be a linear function of

(% Cr), $(\% Cr)^2$, ... , when x is equal to 2, 3, ... respectively. Other combinations are considered to be not quite probable under the given conditions.

The calculation of U involves a difference of two not too accurate figures, the oxygen analysis and the oxygen activity, and is not precise by its nature. It is, therefore, determined that only the best data, which were obtained by the best practice in the later runs, Heats 180 - 189, and 205 - 206, are to be used. The calculations are tabulated in Table XII, and the graphs plotted in Figures 27 - 29. It is obvious that U is in no way a constant; it decreases with (P_{H_2O} / P_{H_2}) but increases with (% Cr). This cancels all the possibilities of cases (a), (b), (c) and (d), and leaves only the possibility of case (e) and others which are not quite probable.

In Figure 29, when U is plotted against $(\% Cr)^2$, an excellent straight line relationship can be obtained and expressed in mathematical form as

$$U = 0.031 + 1.36 \times 10^{-4} (\% Cr)^2$$

The three points lying high above the line might be due to high oxygen analysis.

This result indicates that part of the oxygen is dissolved in the form of Cr_3O, or in other words, the concept of Cr_3O in the melt explained the data best. It is true that the data are not quite adequate enough to make the explanation conclusive, and further investigations are needed to establish this concept definitely.

Based on this equation, the total oxygen content in the melt would be

$$O_{total} = 0.00241 \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\%\ Fe) + \left[0.031 + 1.36 \times 10^{-4}\ (\%\ Cr)^2\right] (\%\ Cr) \left(\frac{P_{H_2O}}{P_{H_2}}\right)$$

From this equation and the equilibrium constants

$$K_1' = \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\%\ Cr)^{\frac{1}{2}} = 0.164 \text{ for low Cr heats}$$

$$K_2' = \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\%\ Cr)^{2/3} = 0.218 \text{ for high Cr heats}$$

the oxygen solubilities in various iron-chromium alloys are calculated and plotted against chromium contents in Figure 25, as compared with the actual analysis results. It is obvious that there is a good check, considering the accuracy of the oxygen analysis.

The activity coefficient, f_o, which is defined as $0.241\ \frac{P_{H_2O}}{P_{H_2}}\ /O_{total}$ can also be expressed as

$$1/f = \frac{(\%\ Fe)}{100} + \frac{1}{.241}\left[0.031 + 1.36 \times 10^{-4}\ (\%\ Cr)^2\right](\%\ Cr)$$

$$= 1 - \frac{(\%\ Cr)}{100} + \left[0.129 + 5.64 \times 10^{-4}\ (\%\ Cr)^2\right](\%\ Cr)$$

$$= 1 + 0.119\ (\%\ Cr) + 5.64 \times 10^{-4}\ (\%\ Cr)^3$$

The value of f_o's are calculated and plotted against chromium concentration in Figure 26, in comparison with the experimental data. Here, as the error in oxygen analysis is magnified, the data do not check very well. Since the occlusion of non-metallic substances may give rise to too high oxygen analyses which would correspond to too low activity coefficients, it is reasonable to expect the theoretical curve to pass through the higher values of activity coefficients found experimentally.

The assumption that the activity of chromium is directly proportional to its concentration, however, should be reconsidered if part of the chromium dissolved is in the form of some kind of oxide. From

the above equation, the amount of oxygen in the form of Cr_3O is

$$O_{Cr_3O} = 1.36 \times 10^{-4} \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\% Cr)^3$$

Thus the amount of chromium in the form of Cr_3O would be

$$Cr_{Cr_3O} = \frac{3 \times 52}{16} \times 1.36 \times 10^{-4} \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\% Cr)^3$$
$$= 1.33 \times 10^{-3} \left(\frac{P_{H_2O}}{P_{H_2}}\right) (\% Cr)^3$$

This would be 0.062 percent, and 0.31 percent, when (% Cr) is equal to 10 and 20 percent respectively. These are insignificant in comparison with the total amount of chromium present, and the assumption is justified.

There is another possibility that two or more different oxides of chromium might be present in the melt, but there has been no success in explaining the oxygen concentration with two simpler oxides, and the concept of Cr_3O seems to be the most simple but adequate explanation. Of course, this concept as outlined above can still be considered as one of a combination of two oxides, Cr_3O and CrO, since the free oxygen as defined cannot be distinguished mathematically from the oxygen in the form of CrO, which is also true in the case of FeO.

TABLE XI

Activity and Activity Coefficient of Oxygen

Heat No.	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$	% O	% Cr	$a_o = \frac{1}{4.15}\left(\frac{P_{H_2O}}{P_{H_2}}\right)$	$f_o = \frac{a_o}{O}$
119	0.1193	0.042	1.95	0.0288	0.69
134	0.1259	0.039	2.50	0.0303	0.78
135	0.0857	0.030	4.37	0.0206	0.69
139	0.0839	0.035	3.99	0.0202	0.58

Table XI, continued

Heat No.	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$	% O	% Cr	$a_o = \frac{1}{4.15}\left(\frac{P_{H_2O}}{P_{H_2}}\right)$	$f_o = \frac{a_o}{O}$
140	0.1193	0.043	2.27	0.0288	0.67
141	0.0615	0.027	4.36	0.0148	0.55
142	0.0623	0.047	6.73	0.0150	0.32
143	0.0655	0.040	5.05	0.0158	0.40
158	0.0747	0.042	3.89	0.0180	0.43
159	0.0744	0.033	4.27	0.0179	0.54
160	0.0625	0.031	4.11	0.0150	0.48
161	0.0625	0.040	6.28	0.0150	0.38
162	0.0628	0.028	4.89	0.0151	0.54
165	0.1022	0.037	3.28	0.0246	0.67
168	0.0892	0.035	2.81	0.0215	0.61
170	0.1446	0.047	1.73	0.0349	0.74
175	0.1398	0.041	1.55	0.0337	0.82
176	0.2196	0.050	0.85	0.053	1.06
178	0.3189	0.065	0.38	0.077	1.18
179	0.3818	0.075	0.27	0.092	1.22
180	0.0619	0.031	7.21	0.0149	0.48
181	0.0448	0.031	9.98	0.0108	0.35
183	0.0280	0.050	19.30	0.00674	0.135
184	0.0462	0.042	10.70	0.0111	0.264
185	0.0461	0.036	8.29	0.0111	0.31
186	0.0591	0.031	5.81	0.0142	0.46
187	0.0825	0.033	4.45	0.0199	0.60

Table XI, continued

Heat No.	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$	% O	% Cr	$a_o = \frac{1}{4.15}\left(\frac{P_{H_2O}}{P_{H_2}}\right)$	$f_o = \frac{a_o}{O}$
188	0.0389	0.044	15.13	0.0094	0.213
189	0.0257	0.057	21.40	0.0062	0.109
203	0.789	0.174	0.041	0.190	1.09
205	0.0849	0.030	3.79	0.0204	0.68
206	0.1012	0.033	2.73	0.0244	0.74

TABLE XII

Calculation of the Function U

Heat No.	$\left(\frac{P_{H_2O}}{P_{H_2}}\right)$	% Cr	% O	U
180	0.0619	7.21	0.031	0.0385
181	0.0448	9.98	0.031	0.0475
183	0.0280	19.30	0.050	0.0826
184	0.0462	10.70	0.042	0.0650
185	0.0461	8.29	0.036	0.0675
186	0.0591	5.81	0.031	0.0510
187	0.0825	4.45	0.033	0.0380
188	0.0389	15.13	0.044	0.0611
189	0.0257	21.40	0.057	0.0947
205	0.0849	3.79	0.030	0.0324
206	0.1012	2.73	0.033	0.0334

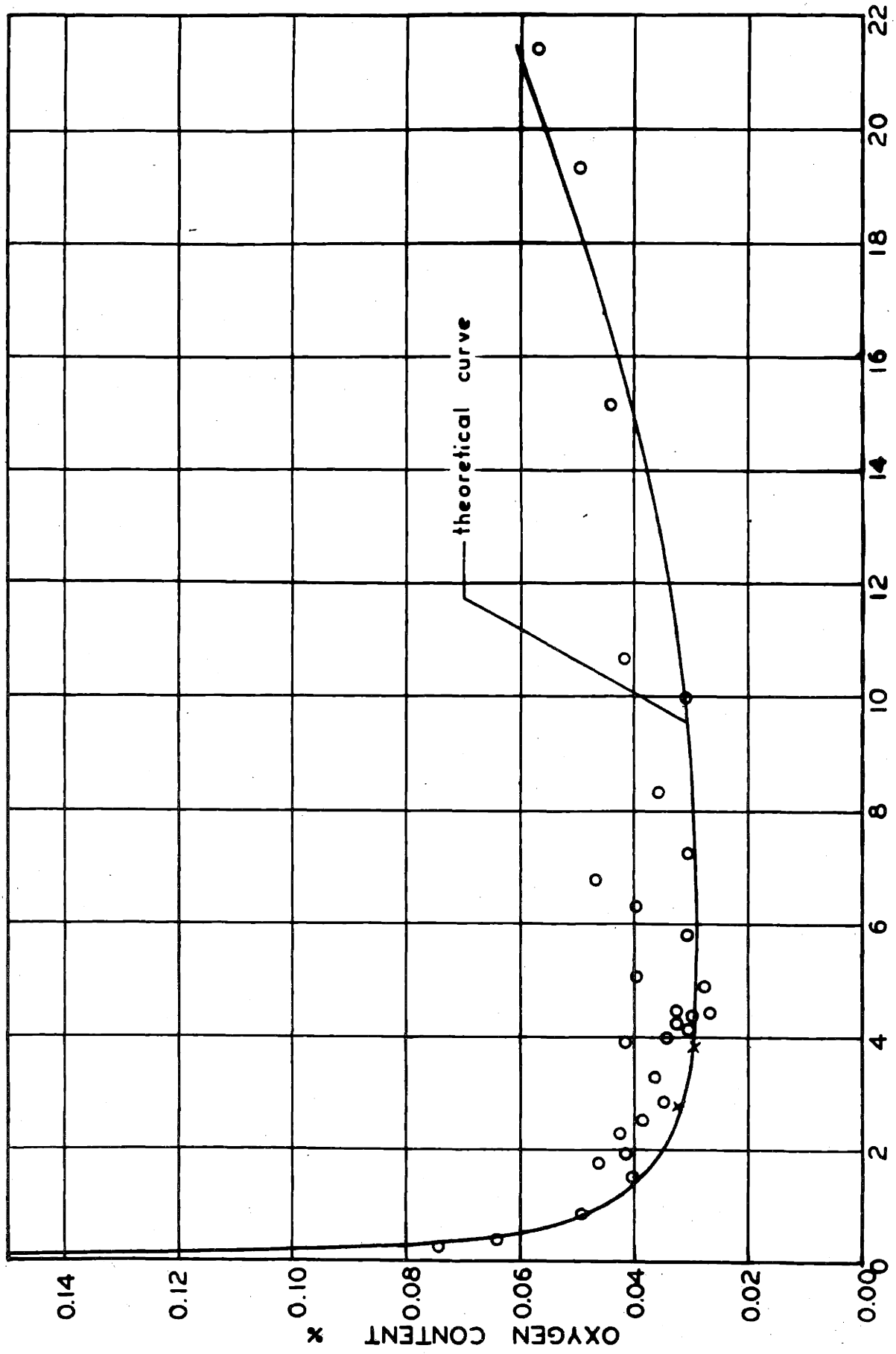


FIGURE 25. Effect of Chromium on Oxygen Solubility

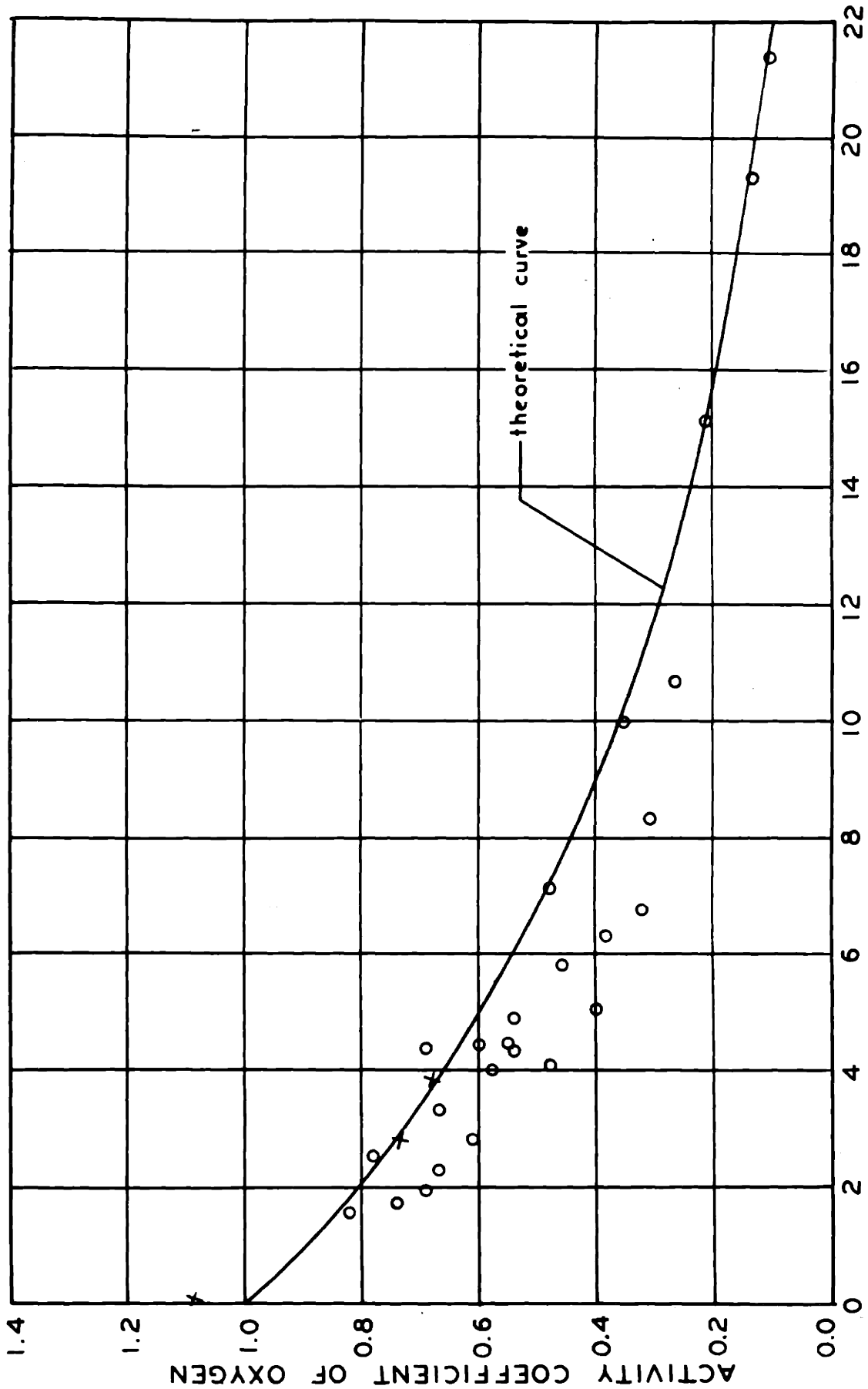


FIGURE 26. Effect of Chromium on the Activity Coefficient of Oxygen

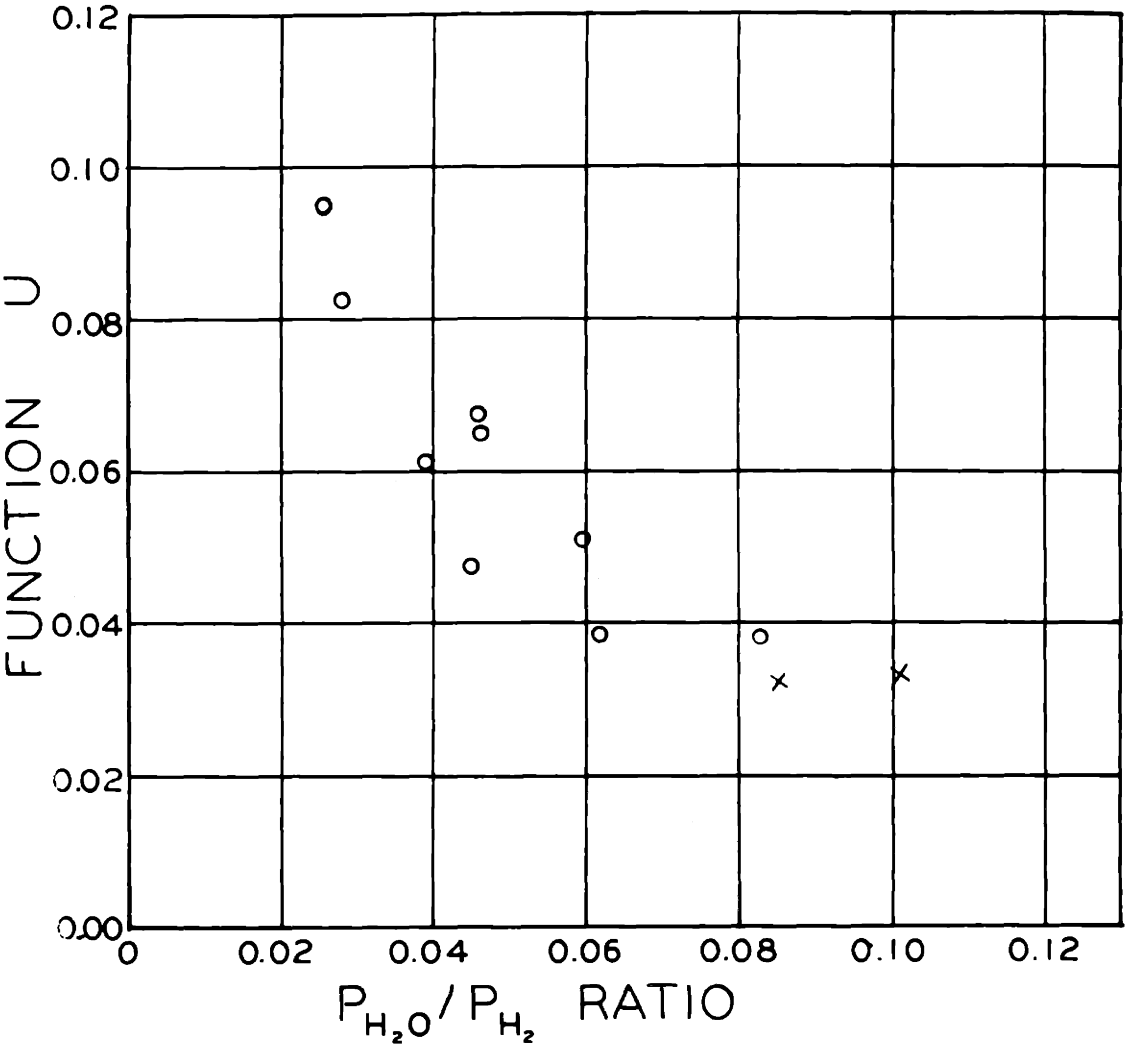


FIGURE 27. Relation of Function U and Water Vapor - Hydrogen Ratio

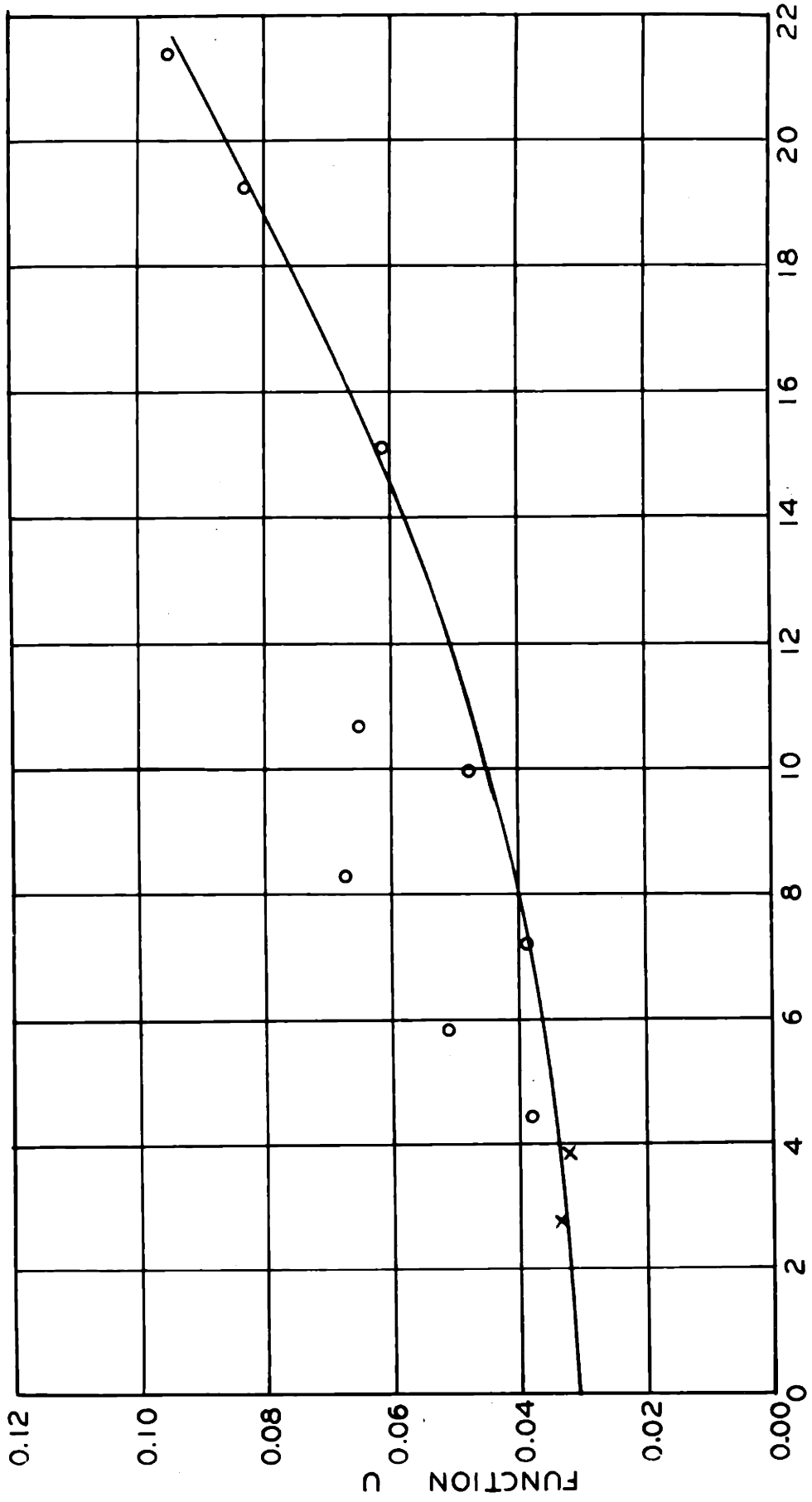


FIGURE 28. Relation of Function U and Chromium Content

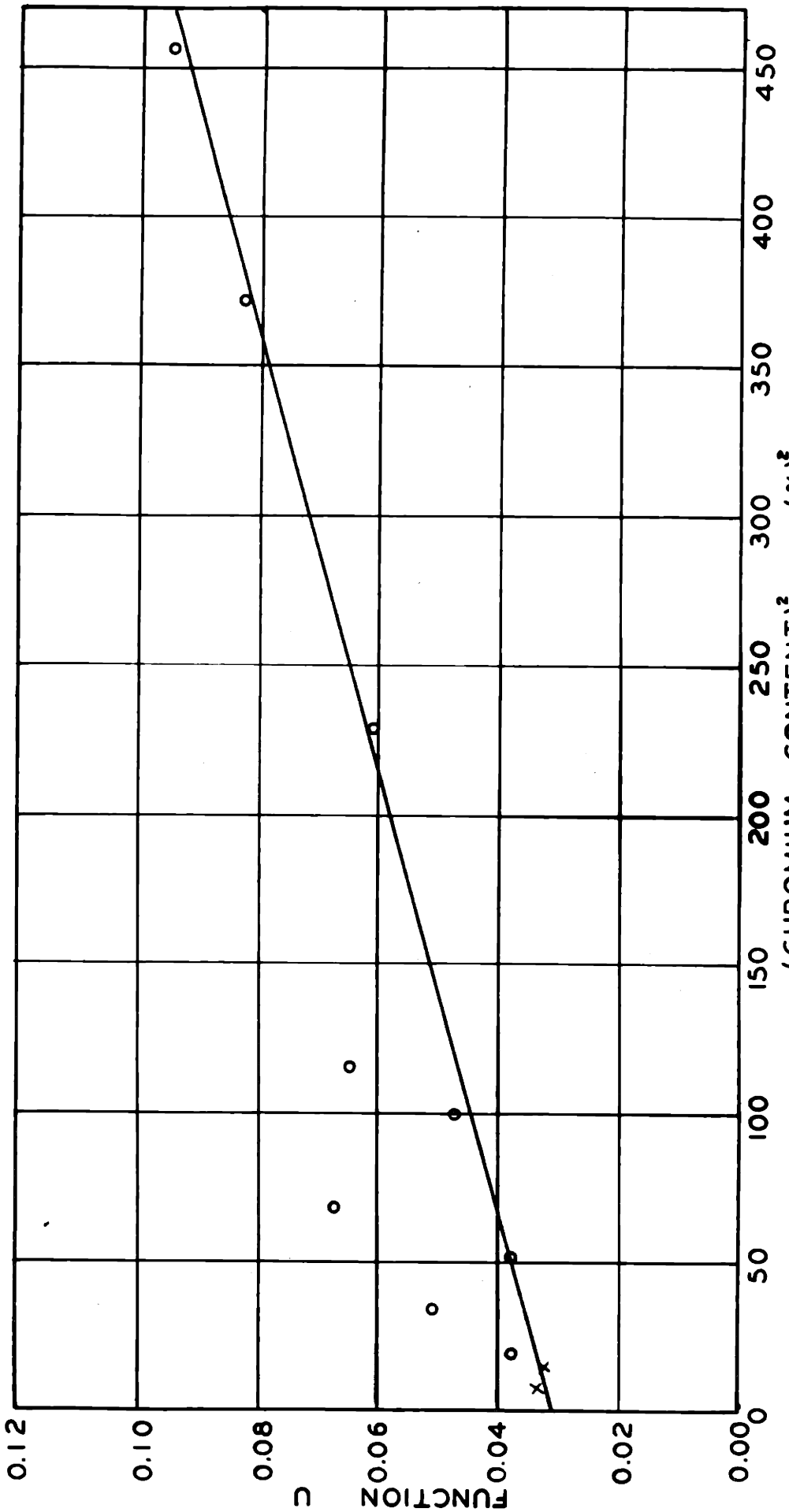


FIGURE 29. Relation of Function U and Square of Chromium Content

C. Comparison with Low Temperature Equilibrium Data

As stated in the review of literature, all previous data at higher temperatures were carried out in acid slags[10,11,20]. It seemed to be quite conclusive that the chromium in the slag acts like chromous compound. This seems to be not true where there is no silica present, as shown in this investigation. Therefore, there is no way to make any comparison with these data.

Results have been reported[31,32,33,35] on the low temperature oxidation of chromium with H_2O-H_2 gas mixture.

$$\frac{1}{3} Cr_2O_3 (s) + H_2 = H_2O + \frac{2}{3} Cr (s)$$

$$K_s = \left(\frac{P_{H_2O}}{P_{H_2}}\right)$$

Granat[35] claimed the intermediate stage of CrO, but as Maier[34] pointed out that Granat obtained only four "equilibrium" points through which he drew two lines, one representing the reduction of Cr_2O_3 to metal and the other the reduction of CrO to metal, and that the amount of water weighed in the experimental determination at 1000° was 0.0006 gram, such evidence seems to be quite doubtful.

By plotting the values of log K_s against 1/T° K in Figure 30, a very good straight line can be obtained passing through almost all the experimental points by Wartenberg and Aoyama[31], Grube and Flad[33], and three of the four points of Granat[35]. This line can best be expressed by the equation

$$\log K_s = -\frac{7020}{T} + 2.036$$

$$\Delta F^\circ = -RT \ln K = -4.575T \left(-\frac{7020}{T} + 2.036\right)$$

$$= 32120 - 9.315T$$

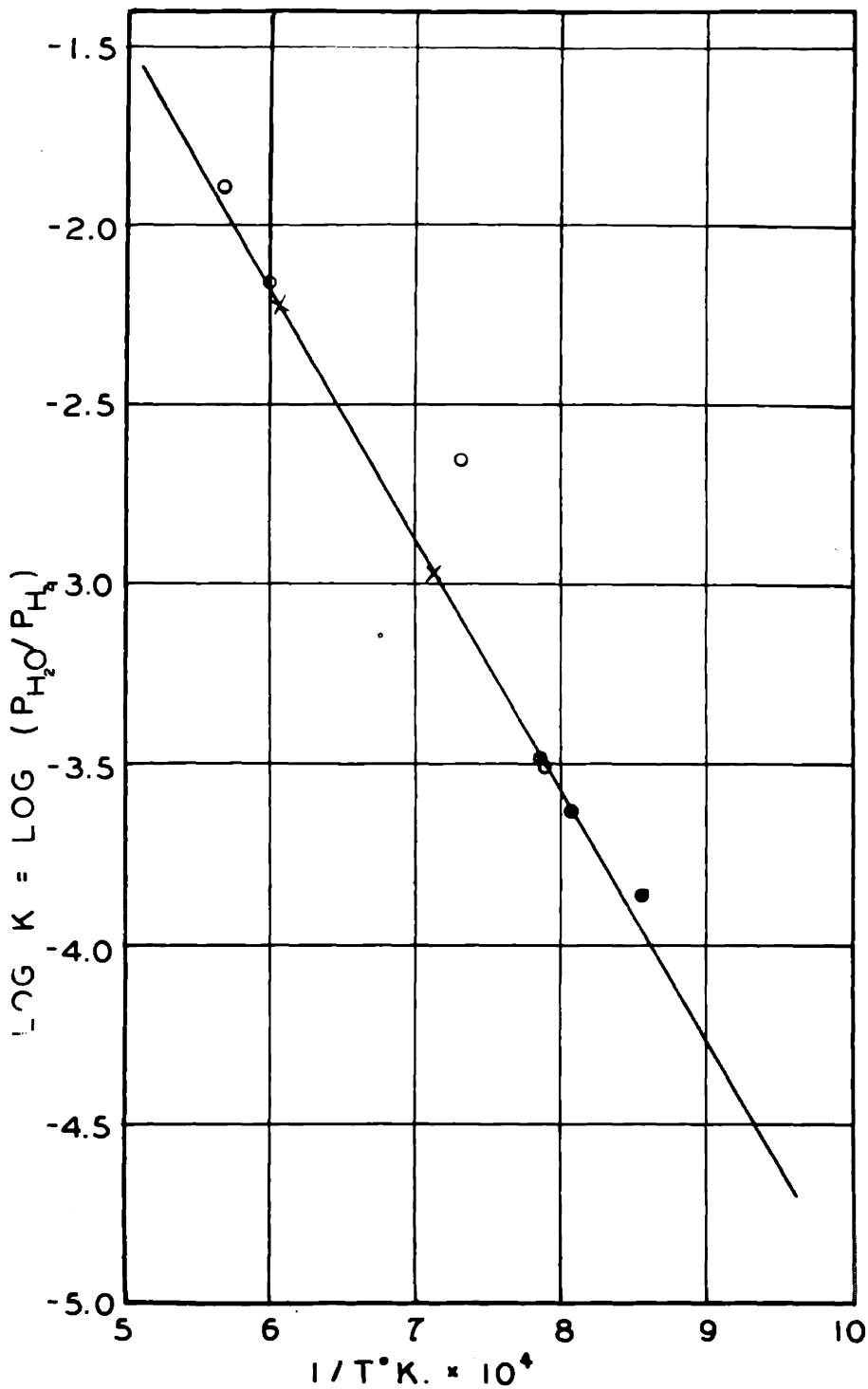


FIGURE 30. Effect of Temperature on the Equilibrium Constant of the Reaction Cr_2O_3 (s) + $3H_2$ (g) = $3H_2O$ (g) + 2Cr (s)

× Wartenberg and Aoyama

• Grube and Flad

○ Granat

for the reaction

$$\frac{1}{3} Cr_2O_3 (s) + H_2 = H_2O + \frac{2}{3} Cr (s)$$

We do not know the free energy change during fusion of chromium. According to Chipman[36], we can assume that

$$Cr (s) = Cr (\text{in Fe})$$

$$\Delta F^\circ = 4350 - 11.11T$$

Thus for $\frac{1}{3} Cr_2O_3 (s) + H_2 = H_2O + \frac{2}{3} Cr (\text{in Fe})$

$$\Delta F^\circ = 32120 - 9.315T + \frac{2}{3} (4350 - 11.11T)$$

$$= 35020 - 16.72T$$

At 1868° K $\Delta F^\circ = 3790$ cal.

$$\log K_2' = - 3790 / (4.575 \times 1868)$$

$$= - 0.444$$

$$K_2' = 0.36$$

This is somewhat higher compared with the value 0.218 obtained in this investigation, but they are of correct magnitude.

Thermodynamically, Maier[34] gave the standard free energy equation for the reaction

$$Cr_2O_3 (s) + 3H_2 (g) = 2Cr (s) + 3H_2O (g)$$

as $$\frac{\Delta F^\circ}{T} = 99.39 \times \frac{1000}{T} + 13.78 \ln T - 4.84 \times 10^{-3} T + 0.46 \times 10^{-6} T^2 - 123.16$$

And thus for the reaction

$$\frac{1}{3} Cr_2O_3 (s) + H_2 (g) = \frac{2}{3} Cr (\text{in Fe}) + H_2O (g)$$

$$\frac{\Delta F^\circ}{T} = 36.03 \times \frac{1000}{T} + 4.593 \ln T - 1.613 \times 10^{-3} T + 0.153 \times 10^{-6} T^2 - 48.46$$

At 1595° C

$$\log K_2' = - 0.648$$

$$K_2' = \left(\frac{P_{H_2O}}{P_{H_2}}\right) (Cr)^{2/3} = 0.225$$

This is almost identical with the value 0.218 obtained in this investigation.

Such an excellent check could not be considered as purely incidental, and it should be admitted that the heat data used by Maier were well chosen.

Now let us use his heat data and calculate the temperature coefficient of free energy change at steelmaking temperatures.

It has been shown from data of this investigation that for the reactions

$$Cr_2O_3 \text{ (s)} + 3H_2 \text{ (g)} = 3H_2O \text{ (g)} + 2Cr \text{ (in Fe)}$$

$$\Delta F^\circ_{1595°C} = 16960 \text{ cal.}$$

$$Cr \text{ (s)} = Cr \text{ (in Fe)}$$

$$\Delta F^\circ_{1595°C} = 4350 - 11.11 \times 1868$$

$$= - 16,400 \text{ cal.}$$

Thus $Cr_2O_3 \text{ (s)} + 3H_2 \text{ (g)} = 3H_2O \text{ (g)} + 2Cr \text{ (s)}$

$$\Delta F^\circ_{1595°C} = 49,760 \text{ cal.}$$

Assuming that Maier's heat data are correct, then his equation for ΔH would be $\Delta H = 99390 - 13.78T + 4.84 \times 10^{-3}T^2 - 0.927 \times 10^{-6}T^3$

At 1600° C $\Delta H = 84,470$

From the familiar equation

$$\Delta F^\circ = \Delta H - T\Delta S$$

we can calculate $\Delta S = \frac{1}{T} (\Delta H - \Delta F) = \frac{1}{1868} (84470 - 49760)$

$$= 18.53 \text{ at } 1595° \text{ C}$$

At steelmaking temperatures, we can assume that ΔH and ΔS do not change very much; therefore,

$$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (s)$$

$$\Delta F^\circ = 84470 - 18.53T$$

and $$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (\text{in Fe})$$

$$\Delta F^\circ = 93170 - 40.75T$$

And since[36]

$$H_2\ (g) + \tfrac{1}{2}\ O_2\ (g) = H_2O\ (g)$$

$$\Delta F^\circ = -\ 60180 + 13.93T$$

Thus $$2Cr\ (s) + 1\tfrac{1}{2}\ O_2\ (g) = Cr_2O_3\ (s)$$

$$\Delta F^\circ = -\ 265{,}010 + 60.32T$$

This gives the heat of formation of chromic oxide as 265,010 cal. and change of entropy as -60.3 at steelmaking temperatures, and should be used to replace the older values given on page 492 in the "Basic Open Hearth Steelmaking"[36].

X. SUMMARY OF WORK DONE

The equilibria between solutions of chromium and oxygen in liquid iron and gaseous atmospheres of H_2O and H_2 have been studied over a chromium range of 0 - 21.4 percent at 1595° C.

The stable solid phase in equilibrium with liquid iron containing less than 5.5 percent of chromium has been established as iron chromite, and that in equilibrium with liquid iron containing more than 5.5 percent of chromium as chromic oxide. Equilbrium constants have been determined for the following equations:

$$FeO \cdot Cr_2O_3\ (s) + 4H_2\ (g) = 4H_2O\ (g) + Fe\ (l) + 2Cr\ (\text{in Fe})$$

$$K_1 = \left(\frac{P_{H_2O}}{P_{H_2}}\right)^4 (\%\ Cr)^2 = 7.23 \times 10^{-4}$$

$$Cr_2O_3\ (s) + 3H_2\ (g) = 3H_2O\ (g) + 2Cr\ (\text{in Fe})$$

$$K_2 = \left(\frac{P_{H_2O}}{P_{H_2}}\right)^3 (\%\ Cr)^2 = 1.036 \times 10^{-2}$$

The activity of chromium was found to be directly proportional to its concentration, while the activity of oxygen was found to decrease rapidly with increasing chromium content. The activity coefficients, defined as activity/percent of oxygen were calculated, and are shown to be a function of the chromium content.

A method for the manufacture of chromic oxide crucible is described.

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BIOGRAPHICAL NOTE

The author was born on November 17, 1912 at Wangkiang, Anhwei, China, and is a Chinese citizen. He attended the Nankai Middle School at Tientsin. He entered the National Tsinghua University at Peiping in September 1931, and graduated in June 1935 with the Bachelor of Science degree in Chemistry.

He worked in the Tangshan Works of the Cheehsin Cement Company of Tientsin as assistant chemist for one and one-half years. In December 1936 he transferred to the Kiangnan Cement Company of Nanking, where he worked as assistant chemist in charge of the laboratory, and held this position until November 1937 when Nanking was occupied by the Japanese army. Following one of the great migrations of history, he travelled through most of West China, and worked successively in the provincial government of Kansu, the Northwestern Institute of Scientific Education, and finally the Research Institute of Chemistry of the Academia Sinica, where he worked from December 1939 to July 1941. It was in this period that he began his metallurgical work.

In September 1941, receiving the National Tsinghua University Fellowship for studying abroad, he came to the United States and registered at the Massachusetts Institute of Technology for graduate work.

In June 1945 he submitted a thesis entitled "The Chromium-Oxygen-Hydrogen Equilibrium in Liquid Iron" in partial fulfillment of the requirements for the degree of Doctor of Science.

The author is a member of the Chinese Chemical Society and a member of the Chinese Institute of Engineers. He is a member of the Sigma Xi Society.

He was co-author with Peter P. T. Sah of a paper entitled "β-Naphthyl Hydrazine as a Reagent for the Identification of Aldehydes and Ketones", published in the Journal of the Chinese Chemical Society, volume IV, page 62 (1936); also co-author with T. Y. Chang and C. P. Lo of a paper entitled "Miscibility of the Thermally Treated Castor Oil with Mineral Oils", published in the Journal of Chemical Engineers of China, volume 7, page 11 (1940).

APPENDIX I

IDEAL GAS CORRECTION FOR WATER VAPOR

While the hydrogen gas can be considered as ideal gas both at 1600° and ordinary temperature, the water vapor is not so, especially when the water vapor pressure is comparatively high at ordinary temperatures. What we obtain by calculation from the total pressure and the saturator temperature would be the ratio of pressure of water vapor to that of hydrogen at that particular saturator temperature. In order to get the ratio of pressures at furnace temperature, where both gases can be considered as ideal, and the pressure ratio would be virtually equal to the molar ratio, a correction factor should be applied.

The calculation of the correction factor is as follows:

Let $\left(\frac{P_{H_2O}}{P_{H_2}}\right)$ be the ratio of pressures of water vapor to hydrogen at saturator temperature

P_i be the water vapor pressure if it is ideal at temperature T° K

P be actual water vapor pressure at T° K

u be the specific volume of water vapor at T° K

R be the gas constant

$P_i = nRT/V = RT/18.016u$

$R = 82.06 \times 760 = 62366$ cc.-mm.

$\therefore P_i = 3462\ (T/u)$

and

$$\left(\frac{P_{H_2O}}{P_{H_2}}\right)_{\text{corrected}} = \left(\frac{P_{H_2O}}{P_{H_2}}\right) \times \frac{P_i}{P}$$

TABLE XIII

Ideal Gas Correction for Water Vapor

t° C	T° K	u	$\therefore P_i$	P	$\therefore P_i/P$
20	293.1	57824	17.549	17.535	1.0008
30	303.1	32922	31.875	31.824	1.0016
40	313.1	19543	55.465	55.32	1.0026
50	323.1	12045	92.87	92.51	1.0039
60	333.1	7678	150.2	149.4	1.0053
70	343.1	5046	235.4	233.7	1.0073
80	353.1	3409	358.6	355.1	1.0098
90	363.1	2362	532.2	525.8	1.0122

Sources of data:

u - Landolt-Bornstein Physik-Chem. Tabellen, Eg. III, c., page 2421 (1936)

P - International Critical Table