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## THE EQUILIBRIUM BETWEEN CHROMIUM AND OXYGEN IN LIQUID IRON

The thermodynamics of the iron-chromium-oxygen system have been investigated at 1600°C by equilibrating iron-chromium alloys with water/hydrogen mixtures in chromic oxide crucibles. The gas mixtures were bubbled through the molten alloys to avoid thermal diffusion and enable equilibrium to be approached in two directions. Metal samples were quenched in water and subsequently analysed for chromium and oxygen.

The relation between  $\log \frac{P_{H_2O}}{P_{H_2}}$  and  $\log N_{Cr}$  has been considered. The curve obtained can be interpreted either by variations in the activity of chromium in iron-chromium solutions or by equilibrium with oxides of variable chromium-oxygen ratios. The latter requires the assumption of equilibrium with chromous oxide in the composition range 7 - 35% Cr. Separate experiments to prove the existence of such an oxide were unsuccessful. It is therefore considered that iron and chromium do not form ideal solutions as has often been assumed. In a recent publication the same order of variation in activity coefficient has been observed. The actual magnitude of the activity coefficients cannot be compared directly with the ones in the present work as

they are presented on different standard states. The necessary data for conversion from one standard state to the other is shown to be insufficient.

The equilibrium between chromium and oxygen in iron-chromium-oxygen solutions is compared with data from previous investigations. Using the most reliable data on the activity of oxygen in iron, the magnitude of the interaction coefficients,  $f_o^{Cr}$ , has been calculated. From these figures a new value of the interaction parameter  $e_o^{Cr}$  has been found.

Finally the results have been applied to the decarburisation of chrome steels. Using the data on the activity of carbon in iron-chromium-carbon alloys, equilibrium in the system iron-chromium-carbon-oxygen has been discussed.

THE EQUILIBRIUM  
BETWEEN  
CHROMIUM AND OXYGEN  
IN  
LIQUID IRON

Thesis submitted to the  
University of Glasgow  
for the degree of  
Doctor of Philosophy

by

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INTRODUCTION



## INTRODUCTION

Research and development has led to considerable advances in the manufacture of plain carbon steels. The same cannot be said in the case of alloy steel production.

Most alloy steels are, to a greater or lesser extent, based on chromium as the main alloying element. Since chromium forms carbides, to obtain the full benefit of chromium as an alloying element, the carbon must be brought to a very low level. This is done by oxidation and is accompanied by appreciable losses of chromium to the slag. Its recovery is both an expensive and time-consuming process. During the oxidising stage, equilibria between iron, chromium, carbon and oxygen are involved. Data on the iron-carbon-oxygen system, while being incomplete, are considered to be fairly accurate at low carbon levels. The loss of chromium to the slag involves iron-chromium-oxygen equilibria and there are certain anomalies among the available data. Accurate data on this system would therefore be a useful contribution to the theory of alloy steelmaking. From this the chromium distribution between metal and slag for any given carbon concentration can be calculated. The oxidising stage of the process would then be placed on a sounder theoretical basis. The work could then be extended to cover more complex alloy steels.

However, the first requirement is the basic thermodynamic

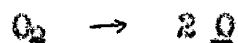
data relating to plain chromium steels and this forms the basis of the present work. The thermodynamic properties of iron-chromium-oxygen alloys have been studied by equilibrating iron-chromium melts with water/hydrogen mixtures, a technique employed with considerable success in previous gas-metal studies.

REVIEW OF LITERATURE

## (1) THE IRON-OXYGEN SYSTEM

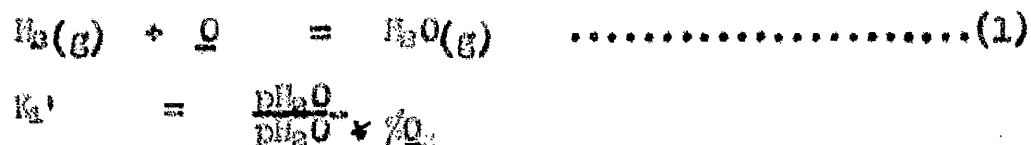
Oxygen dissolves to a limited extent in liquid iron. The iron-oxygen phase diagram (Fig. 1) has been reviewed by Darken and Gurry<sup>1</sup>. Liquid wustite, a compound of variable composition, is the oxide phase in equilibrium with liquid iron-oxygen alloys. The solubility of oxygen in iron increases with temperature. If a melt is rapidly quenched from a high temperature, this oxygen is retained in the metal. If the rate of cooling is somewhat slower, wustite separates out and the oxygen concentration will fall to the monotectic composition, which corresponds to 0.16 per cent oxygen.

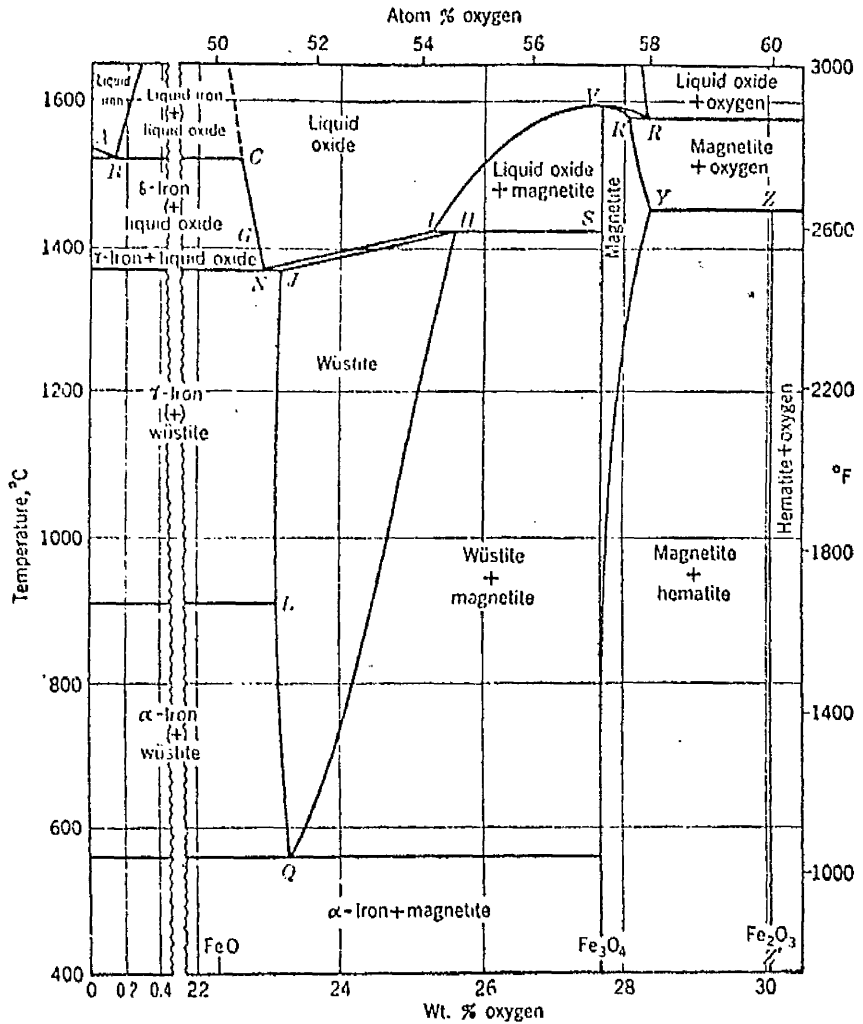
In view of the pronounced effects of a small quantity of oxygen in steel, it is not surprising that the thermodynamics of oxygen in iron have been extensively studied. Oxygen dissolves in liquid iron according to the equation



To study the thermodynamic properties below saturation, a means of controlling the oxygen potential has to be employed. This can be done by using controlled  $\text{H}_2\text{O}/\text{H}_2$  or  $\text{CO}_2/\text{CO}$  mixtures.

The activity and free energy of oxygen dissolved in liquid iron has most frequently been studied by means of the following reaction:-





Point	°C	% O	$p_{\text{CO}_2}/p_{\text{CO}}$	Point	°C	% O	$p_{\text{CO}_2}/p_{\text{CO}}$	$p_{\text{O}_2}$ (atm)
A.....	1539			Q.....	560	23.26	1.05	
B.....	1528	0.10	0.209	R.....	1583	28.30		1
C.....	1528	22.60	0.209	R'.....	1583	28.07		1
G.....	1400*	22.84	0.263	S.....	1424	27.61	10.2	
H.....	1424	25.60	16.2	V.....	1597	27.64		0.0575
I.....	1424	25.31	16.2	Y.....	1457	28.36		1
J.....	1371	23.16	0.282	Z.....	1457	30.04		1
L.....	911*	23.10	0.447	Z'.....		30.08		
N.....	1371	22.01	0.282					

\* Values for pure iron

FIG. 1. THE IRON-OXYGEN PHASE DIAGRAM.

where the undermentioned symbol  $Q$  represents oxygen dissolved in liquid iron.

In one of the early studies of this reaction by Chipman<sup>2</sup>, a small charge of electrolytic iron, heated by induction, was held in the molten condition at constant temperature for varying times up to a maximum of 2 hours to ensure attainment of equilibrium under a controlled water vapour/hydrogen gas stream. It was allowed to solidify and the oxygen content of the metal determined by vacuum fusion technique. The results, in the main, were confined to low oxygen concentrations and in order to extend the data up to the limiting solubility of oxygen in liquid iron, a further investigation was undertaken by Fontana and Chipman<sup>3</sup>. Their experimental technique differed in two respects from that mentioned above, in that an attempt was made to minimise errors arising from thermal diffusion by preheating the incoming gases. Secondly, some of the heats were quenched in liquid tin or water in an effort to retain, in the metal at room temperature, the high temperature equilibrium oxygen concentration. Using the same technique the effect of temperature on the reaction was studied by Samarin and Chipman<sup>4</sup>.

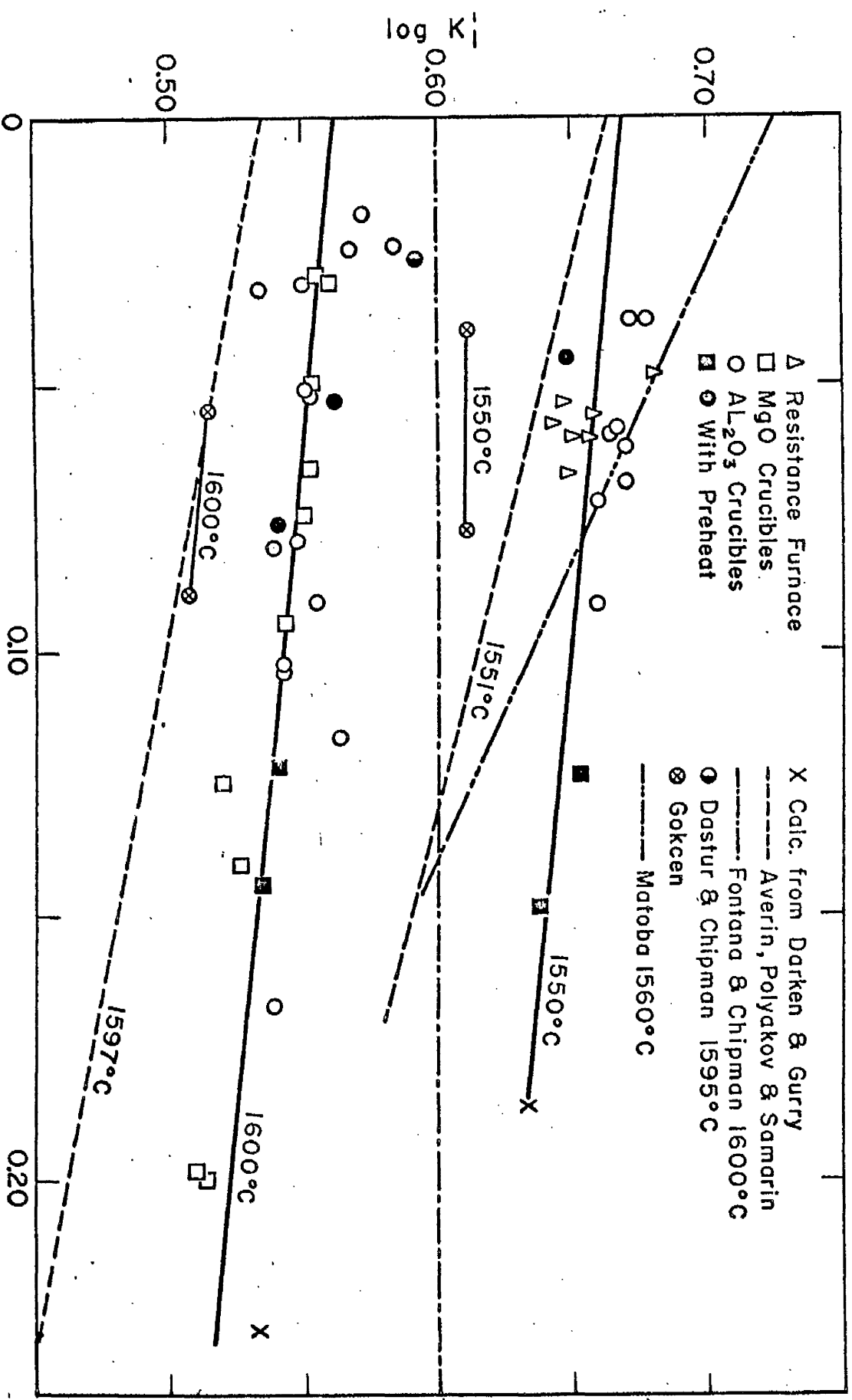
In a later study of reaction [1] by Dastur and Chipman<sup>5</sup> it was stated that errors due to thermal diffusion had been eliminated by the addition of an inert gas, argon, to the water-vapour/hydrogen mixture in the ratio 4 : 1 and then preheating the inlet gases up

to the temperature of the melt. Floridis and Chipman<sup>6</sup> used a similar technique but increased the argon/hydrogen ratio to 6, 1. The results were in fairly good agreement with those obtained from a series of heats made in a resistance furnace in which thermal diffusion was eliminated by bubbling the gas through the molten metal, a technique previously used with considerable success by Gokcen.<sup>7</sup>

Reaction [1] has also been studied by Matoba<sup>8</sup> and Averin et alia<sup>9</sup> and their results together with those obtained from the previously mentioned investigations are summarised in Fig. 2 where  $\log K_1'$  is plotted against weight per cent oxygen.

From Fig. 2 it can be seen that all the investigations, other than those of Fontana and Chipman<sup>3</sup> and Dastur and Chipman<sup>5</sup>, indicate that  $K_1'$  is not a true constant but, in fact, decreases with increasing oxygen concentrations implying that iron-oxygen solutions do not conform precisely to Henry's Law.

At the time of these investigations<sup>3, 4, 5</sup> it was assumed from the work of Tritton and Hanson<sup>10</sup>, Herty and Gaines<sup>11</sup>, and Körber and Oelsen<sup>12</sup> that the monotectic composition in the iron-oxygen system was about 0.21 - 0.22% oxygen. It was thought that there had been no primary wustite present before quenching the melts. However, subsequent<sup>work</sup> by Chipman and Petters<sup>13</sup>, Taylor and Chipman<sup>14</sup>, Sloman<sup>15</sup>, Fischer and von Ende<sup>16</sup> and Gokcen<sup>7</sup> has shown that the maximum solubility of oxygen in iron at its melting-point is about 0.16% oxygen. This discrepancy in the monotectic composition was probably



**FIG. 2.** EFFECT OF OXYGEN CONCENTRATION ON EQUILIBRIUM RATIO,  $K' = \frac{P_{H_2O}}{P_{H_2} [\%O]}$



due to errors in temperature measurement since the earlier workers used optical pyrometers which, under the experimental conditions would give low readings. Despite an attempt by Korber and Oelsen to correct their values by means of emissivity coefficients, it would appear their values are still on the low side.

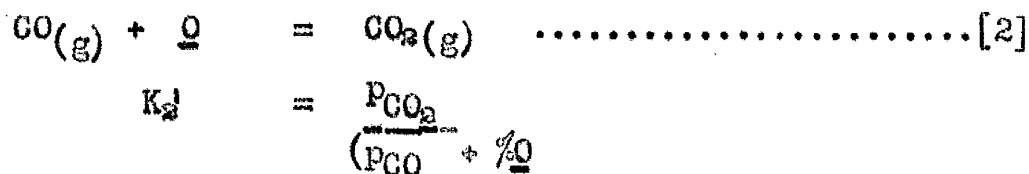
The results obtained by Fontana and Chipman indicated that  $K_1'$  was independent of the oxygen concentration up to about 0.21%. This conclusion was based on the results of a small number of experiments in the range 0.16 - 0.22% oxygen, for which the values of  $K_1'$  were in approximate agreement with those of samples containing less than 0.07% oxygen. It is very likely, therefore, in the light of present knowledge on the monotectic composition, that the values for  $K_1'$  in the range 0.16 to 0.22% were high due to loss of appreciable amounts of primary wustite on freezing, despite the fact that some of the heats were rapidly cooled by quenching in liquid tin or water, since this method induces freezing from the bottom of the melt upwards, which would tend to encourage the separation of primary iron oxide. Unfortunately no heats were made in the range 0.07 to 0.16% oxygen so that the apparent agreement between results obtained for melts containing more than 0.16% O and those containing less than 0.07% may be largely incidental.

On the basis of results obtained by Fontana and Chipman, Chipman and Samarin, and Dastur and Chipman, it was assumed that the activity of oxygen dissolved in liquid iron was directly proportional to  $i$

the concentration. The heats were made over a wide temperature range (1563 - 1760°C). Most of these were at low oxygen (<0.06%) concentrations, well below saturation value, and so there was little likelihood of loss of oxygen on cooling. The few experiments at high oxygen concentrations are now considered unreliable. These data are therefore insufficient to provide convincing proof that  $K_1'$  is constant up to saturation value for oxygen in iron.

In a recent study by Floridis and Chipman the oxygen concentrations ranged up to 0.2% and, at the end of a heat, the melt was lowered into a cooler part of the furnace tube and quenched in a stream of cold helium, a quenching technique first introduced by Gokcen and Chipman<sup>17</sup>. The advantage of this technique is that freezing begins at the top surface and thus assists the "freezing-in" of oxide.

The results obtained by Floridis and Chipman are in fairly good agreement with those of Fontana and Chipman, Dastur and Chipman and Averin et alia at low oxygen concentrations and with those of Matoba in the range 0.07/0.14% oxygen. Two points at high concentrations, attributed to Darken and Gurry<sup>18</sup> were obtained by combining the results of a study of the equilibrium in the system CO - CO<sub>2</sub> - Fe - FeO with solubility data for oxygen in iron to give  $K_2'$  values for the following reaction :-



By means of the known free energies of the gases involved, values of  $K_2'$  may be converted to give values of  $K_1'$  and such values, shown in Fig. 2 agree well with the experimentally determined values of  $K_1'$ . The slope of Floridis and Chipman's line at 1550°C and 1600°C indicates that the activity coefficient of oxygen  $f_{\text{O}_2}$  decreases with increasing oxygen concentration according to the equation

$$\log f_{\text{O}_2} = -0.20 [\% \text{O}_2]$$

In Fig. 2 the intercept on the  $\log K_1'$  axis, i.e. where  $\% \text{O}_2 = 0$  represents the value of the equilibrium constant  $K_1$ .

The effect of temperature on the equilibrium constant as reported by several workers is shown in Fig. 3. Since the data of Floridis and Chipman covered only a narrow temperature range, the temperature effect has been represented by a line drawn parallel to that of Dastur and Chipman. The line is represented by the equation

$$\log K_1 = \frac{7050}{T} - 3.20 \dots\dots\dots [3]$$

$$\Delta G = -32200 + 14.63 T \text{ cal.}$$

Oxygen activities at different  $\frac{\text{H}_2\text{O}}{\text{H}_2}$  ratios can be calculated using equation [3]. Fig. 4 shows these relationships at 1600 and 1700°C. The data at 1600°C is probably the more reliable but errors in either should be relatively small. These lines are used later in calculating the activity of oxygen in iron-chromium-oxygen alloys.

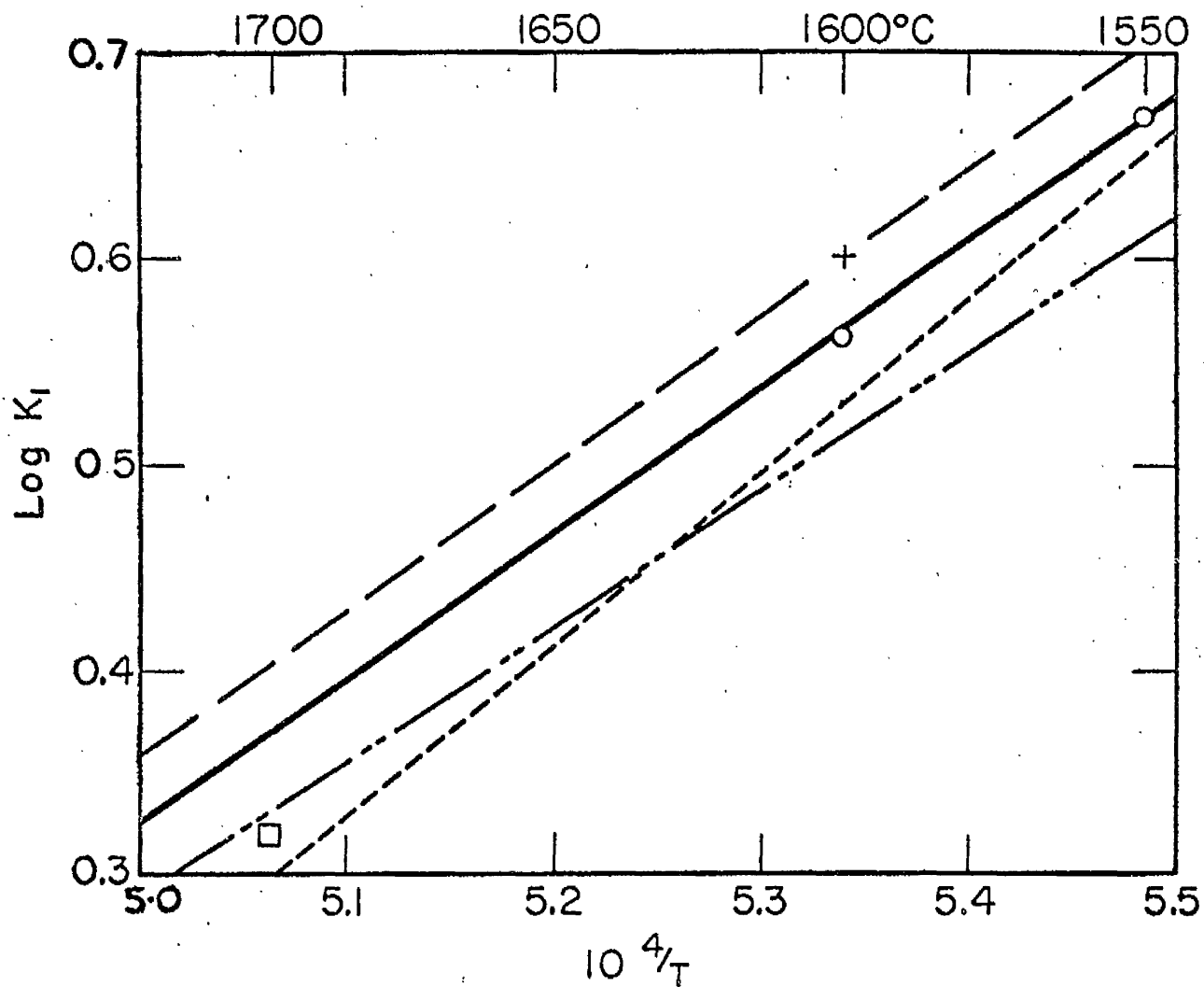


FIG. 3.—EFFECT OF TEMPERATURE ON THE EQUILIBRIUM CONSTANT  $K_1 = \frac{P_{H_2O}}{P_{H_2} \cdot a_o}$

- Floridis and Chipman; + Fontana and Chipman; □ Chipman and Samarin;
- Dastur and Chipman; —·—·—Gokcen;
- Averin, Polyakov and Samarin

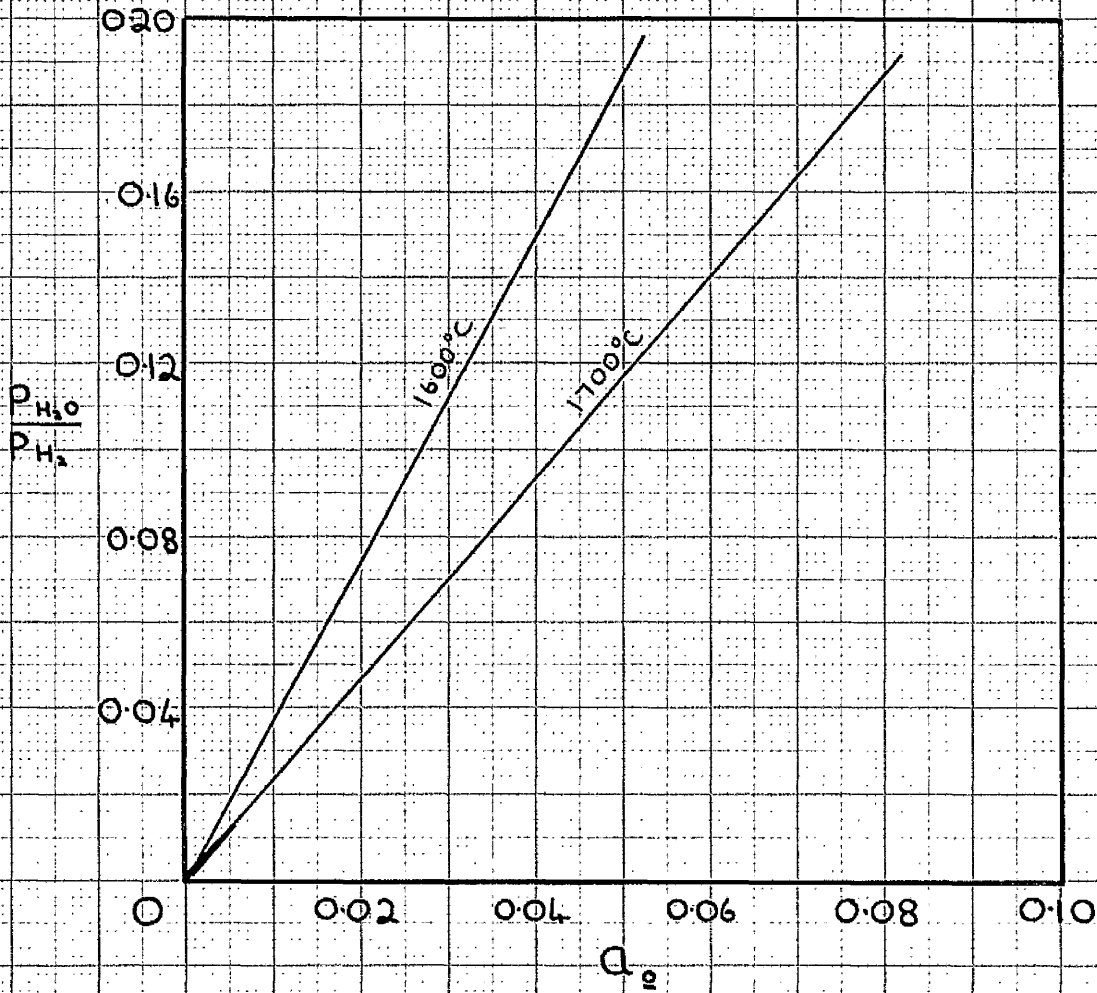
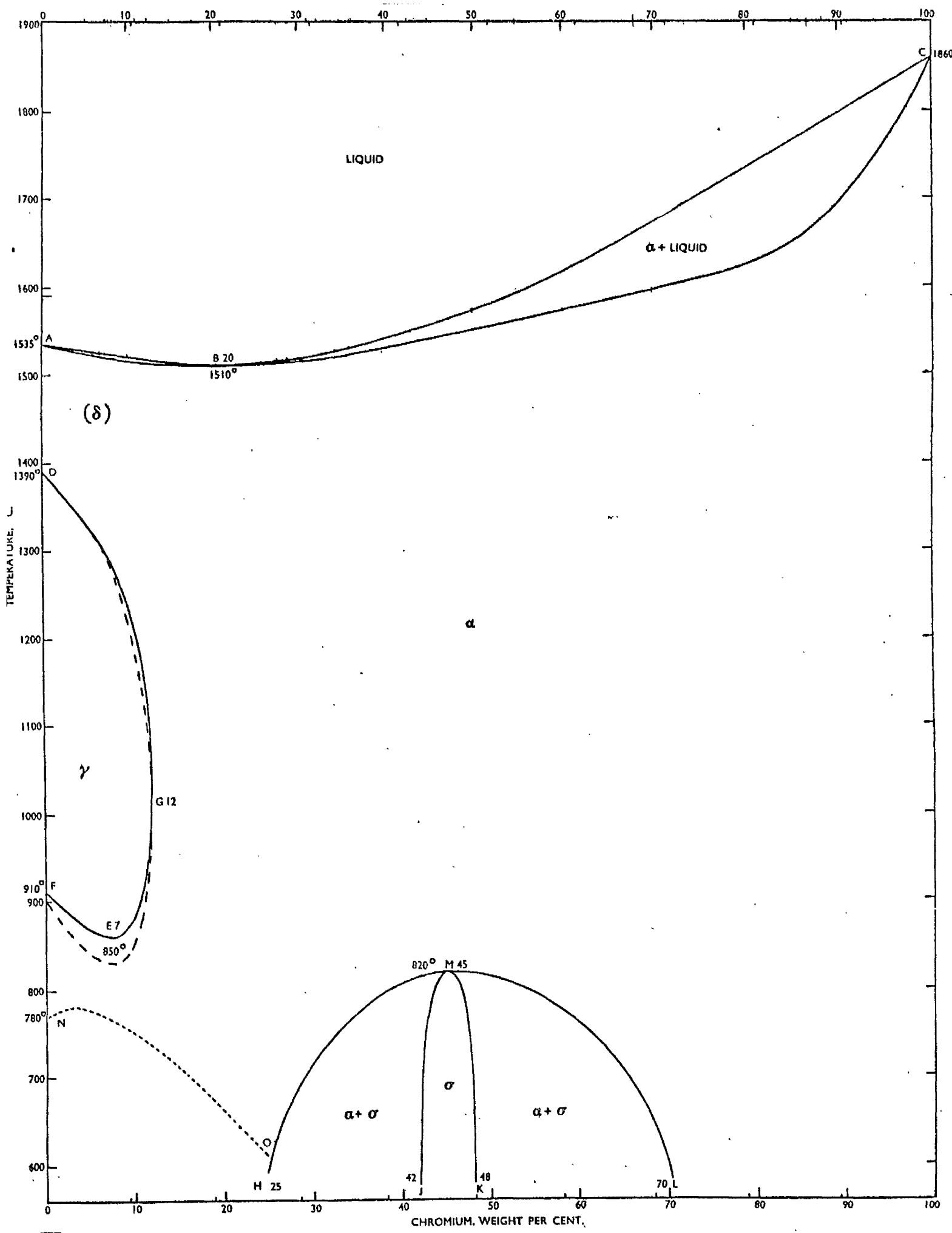


FIG. 4. THE ACTIVITY OF OXYGEN IN IRON  
(FLORIDIS AND CHIPMAN)

(2) THE IRON-CHROMIUM SYSTEM(2) THE IRON-CHROMIUM SYSTEM

There is a lack of concordant data concerning the iron-chromium system both in the solid and liquid states. The phase diagram was first determined experimentally by Adcock<sup>19</sup> and has recently been reviewed by Hellowell. (Fig. 5) From this, and other evidence<sup>20,21</sup> it has been suggested that, in the liquid state, the iron-chromium system follows Raoult's Law. The atomic size and chemical properties of chromium are similar to those of iron. Above 800°C, iron and chromium are miscible in all proportions both in the solid and liquid states. It does therefore seem a reasonable prediction that any departure from ideality would be relatively small.

Two recent studies have been made on the pure iron-chromium liquid system using radioactive tracer techniques. Positive deviations from Raoult's law were reported by Lyubimov and Gromovskaya<sup>22</sup>. A more detailed study of the system has been made by Wada, Kawai and Saito<sup>23</sup> and considerable negative deviations from ideality were reported. In the latter case, iron-chromium alloys, containing chromium<sup>51</sup>, were held at 1630°C in an alumina crucible. After de-gassing, a target was placed in the stream of vapourising atoms and the vapour condensed for 16 minutes. The condensate was analysed for chromium by a counting technique. The ratio of the amount of chromium condensed to the total amount evaporated was considered constant as the same conditions were used for all experiments. No measurements were made to determine the vapour pressure of pure liquid



**FIG. 5.** THE IRON-CHROMIUM PHASE DIAGRAM

chromium due to the high temperature required. From the results it is only possible to calculate the order of variation of activity coefficients. For this reason the results are presented as activity coefficients on the infinite dilution scale ( $f \rightarrow 1$ ,  $N \rightarrow 0$ ). The variation in activity coefficient (Fig. 17) was found to be considerable, a factor of six in the range 0 - 40% chromium. The type of results and their actual magnitude suggest negative deviations from ideality. An attempt is made later to convert these activities into the ideal solution scale.

Chen and Chipman<sup>24</sup> have studied the reaction between chromium and oxygen in liquid iron at 1600°C using  $H_2O/H_2$  mixtures to control the oxygen potential. If the chromium were assumed to behave ideally and the effects of oxygen were negligible, the results indicated that in the range 0 - 5.5% chromium, equilibrium with chromite was established. At higher chromium concentrations, equilibrium with chromic oxide was achieved. Experimental data were rather scattered and the conclusions have since been modified. However, general trends in the data gave no indication that iron and chromium might not behave ideally.

McCabe<sup>25</sup> and co-workers and Kubaschewski and Heymer<sup>26</sup> have measured vapour pressures above solid iron-chromium alloys. McCabe measured weight losses from a Knudsen cell and from this estimated the vapour pressure due to chromium. Kubaschewski also used a Knudsen effusion cell but measured the vapour pressure of chromium using a



radioactive tracer technique. From vapour pressure measurements the activity of chromium was calculated (Fig. 20) . The results of the investigators are in fairly good agreement both showing positive deviations from Raoult's law. McCabe reports a maximum deviation of 19% from ideality whereas from Kubaschewski's data the deviation is about 100%. McCabe has suggested that the deviation will decrease as the solidus temperature is approached and may become a negative deviation in the liquid. As there is a minimum in the iron-chromium phase diagram at 20% Cr it is possible that there will be negative deviations at less than 20% and positive deviations above this figure.

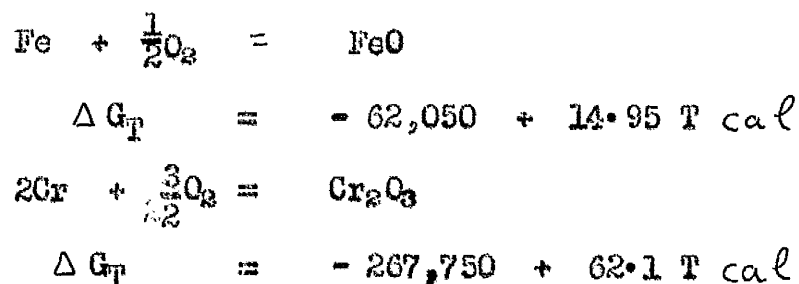
Vintaikin<sup>27</sup> has also measured the activity of chromium in iron in the solid state and large positive deviations from ideality are reported. Only a few experimental points have been determined and, in view of the discrepancy compared with other data, one doubts the reliability. In another investigation of the solid system, Matveyeva and Ivanov<sup>28</sup> have reported negative deviations from ideality.

It is seen that there is conflicting evidence on the thermodynamics of chromium in iron and it was hoped that the present work would shed some light on the subject.

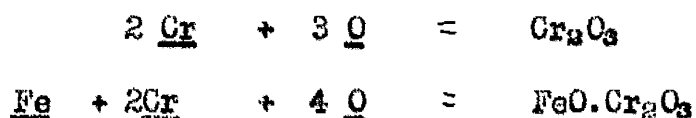
### (3) THE IRON - CHROMIUM - OXYGEN SYSTEM

Chromic oxide is only moderately stable at steelmaking temperatures. Compared with ferrous oxide, temperature has a

pronounced effect on its free energy of formation.



It is not stable enough to make chromium a good de-oxidiser but it is sufficiently stable to lead to the formation of chromic oxide and chromite inclusions in chrome-bearing steels. Studies of inclusion have, for the most part, revealed only these two types. Chen and Chipman<sup>24</sup> studied the equilibria for the following two reactions :



Iron-chromium alloys were melted in chromic oxide or chromite crucibles and the melt brought to equilibrium with a controlled atmosphere of hydrogen and water vapour. High frequency induction heating was used and the temperature was measured by an optical pyrometer, applying an emissivity correction obtained by observing the melting-point of pure iron. The gas was passed into the top of the furnace tube and preheated by suspended platinum wires at 1100°C to cut down thermal diffusion. The gas was not diluted with argon. In view of later work, it is possible that insufficient precautions, against thermal diffusion, were taken and the results may be in error. In nearly all cases, equilibrium was approached by reducing the chromic oxide crucible. Approaching

equilibrium in the opposite direction led to the formation of slag  
 equilibrium in the opposite direction led to the formation of slag  
 which prevented accurate temperature measurement and further reaction  
 between the gas and metal. At the end of a run the preheater and  
 induction heater were switched off and the metal quenched by a strong  
 current of argon. About 15 seconds were normally required before  
 solidification took place. As a melt containing 4% Cr could be  
 obtained from a pure iron charge in one hour, it was concluded that  
 the solution of chromic oxide was not a slow process and equilibrium  
 could be reached in less than two hours.

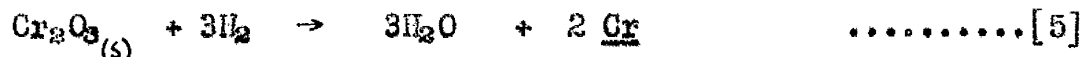
At low chromium concentrations the relevant reaction  
 was considered to be as follows:-



$$K_3 = \left( \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^4 (\% \text{Cr})^2 \quad \gamma_{\text{Cr}} \text{ assumed unity}$$

$$a_{\text{Fe}} = 1$$

At higher chromiums the probable reaction was



$$K_2 = \frac{\left( \frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right)^3}{(\% \text{Cr})^2} \quad \gamma_{\text{Cr}} \text{ assumed unity}$$

The experimental results were plotted on a logarithmic scale when  
 the significance becomes apparent

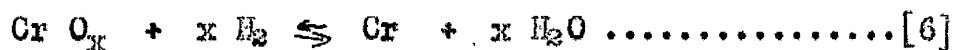
$$\log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = \frac{1}{4} \log K_3 - \frac{1}{2} \log (\% \text{Cr})$$

$$\log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = \frac{1}{3} \log K_2 - \frac{2}{3} \log (\% \text{Cr})$$

If the suggested equilibrium were obtained, a graph showing the variation of  $\log \frac{p_{H_2O}}{p_{H_2}}$  against  $\log (\%Cr)$  should give two intersecting straight lines, having gradients of  $-\frac{1}{2}$  and  $-\frac{2}{3}$  respectively.

As is normal with high temperature research, the data were insufficiently precise to draw two straight lines, a curve would probably have been a better fit. However, there was additional evidence obtained from streak tests in the metallic crusts formed inside the crucibles. There was a change from brown to green in the range 5 - 6% chromium. It was concluded that at 5.5% chromium the anticipated change from chromite to chromic oxide equilibrium occurred. Two straight lines were drawn, having the correct theoretical slopes and intersecting at 5.5% Cr, and were considered to fit the experimental data very well. Despite this, the conclusions were later revised to conform with other equilibria.

Similar  $H_2O/H_2$  investigations, i.e. equilibration of Fe-Cr-O alloys with  $H_2O/H_2$  mixtures, have since been carried out by Linczinski<sup>29</sup> and Samarin<sup>30</sup> and by Turkdogan<sup>30</sup>. The former expressed the equilibrium as a general equation and attempted to evaluate  $x$  experimentally.



$$K_5 = \%Cr \left( \frac{p_{H_2O}}{p_{H_2}} \right)^x$$

$$\log K_5 = \log \% Cr + x \log \frac{p_{H_2O}}{p_{H_2}}$$

$$\log \frac{p_{H_2O}}{p_{H_2}} / \log \% Cr = \frac{-1}{x} + C$$

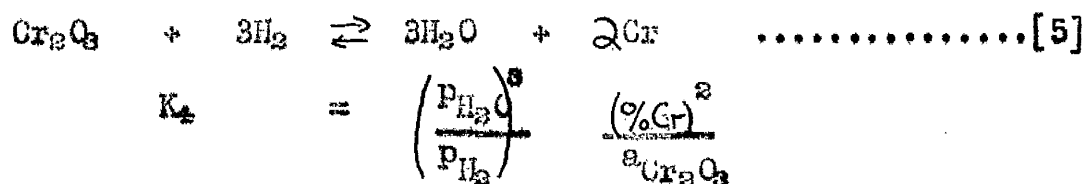
Alumina crucibles were used and equilibrium could only be approached by oxidising chromium out of the metal. Equilibrium was considered to have been reached as soon as an oxide phase appeared on the melt. This is obviously incorrect as, for a particular gas composition, it may have been necessary to oxidise considerable amounts of chromium out of the melt. The results would therefore be expected to be too high in chromium. No experimental details are given and so it is not known whether or not adequate precautions were taken to prevent thermal diffusion. As seen from Fig. 15, where  $\log p \frac{H_2O}{pH_2}$  is plotted against  $N_{Cr}$ , the results are much higher than those of Chen and Chipman. From the form of the logarithmic plot the following conclusions were drawn:

<u>Chromium content</u>	<u>Gradient</u> $\left(\frac{1}{x}\right)$	<u>Oxide phase</u>
0 - 6%	$-\frac{1}{2}$	Chromite
6- 16%	$-\frac{2}{3}$	Chromic oxide
Over 16%	$+\frac{3}{4}$	CrO + Cr <sub>2</sub> O <sub>3</sub>

If free energies of formation of chromite and chromic oxide are calculated from these data (Table 1), the results are far removed from thermal data and those of Chen and Chipman, additional evidence that equilibrium has not been established. The gradient of the line was found to change both in magnitude and sign at 16%Cr. However, as has previously been shown the gradient of the logarithmic plot must be  $-\frac{1}{x}$ . Since  $x > 0$  the slope must always be negative. The positive value obtained by Linczinskii and Samarin must be

incorrect and it is suggested that these experimental points are even further away from equilibrium than the remainder. Though it is possible to explain the observed effects in terms of varying activity coefficients of chromium, these coefficients would be unrealistic and are hence considered impossible.

Turkdogan<sup>30</sup> used the same approach as Linczinski and Samarin. The gas was preheated and diluted with a 4 : 1 ratio of argon to prevent thermal diffusion. Heats were run for 2 hours after the appearance of slag on the melt. Only a small composition range (4 → 12% Cr) was studied. The results lie below those of Chen and Chipman. Comparison of the thermodynamic data obtained from this work with that from other methods also suggests the results are low. The main reaction studied was:-



As in other work, it was assumed that  $a_{\text{Cr}_2\text{O}_3} = 1$ . In this work it is possible that the solid phase contained some alumina in solution and the activity of chromic oxide would be less than unity. This would account for the low chromium contents.

In the three investigations described, it was assumed that chromium in iron behaved ideally. Any changes in gradient in the  $\log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \sim \log \text{Cr}$  plot were ascribed to changes in oxide phase. It should be pointed out that any changes must be such that the gradient becomes more negative. If this were not the case, equilibrium with the metastable oxide would correspond to a lower

free energy level than equilibrium with the stable one. This is a violation of the second law of thermodynamics.

Ignoring that part of Linczinskii and Samarin's work which has been shown to be theoretically unsound, all three investigations have concluded that equilibrium with chromite then chromic oxide is involved. The graphs of  $\log \frac{H_2O}{H_2} \vee \log \% Cr$  have all been drawn having the correct theoretical gradients corresponding to these equilibria. However, the data are all at different levels. Free energy calculations give some indication of the discrepancy between the various data as shown.

TABLE 1

Comparison of thermodynamic data for chromite and chromic oxide

a) Chromite

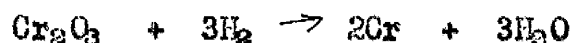
Figures given are for the following reaction at 1600°C



	$\Delta G^\circ_{cal}$	<u>Quoted error</u>
Boericke and Bangert <sup>31</sup>	62535	<u>+ 3000</u>
Chen and Chipman	59660	-
Linczinskii and Samarin	52070	-
Turkdogan	72350	-

b) Chromic Oxide

Figures are given for the following reaction at 1600°C



Elliott and Gleiser <sup>32</sup>	53400	<u>+ 500</u>
Chen and Chipman	49900	-
Linczinskii and Samarin	44000	-
Turkdogan	56200	-

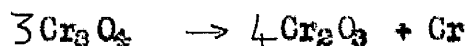
Differences between the various data are such that the various authors may not be justified in drawing the correct theoretical slopes to correspond with the most probable equilibria. Hilty, Forger and Folkman<sup>33</sup> have made an investigation into the phases present in inclusions in iron-chromium oxygen alloys which produced some rather unexpected results. The experimental procedure involved the use of a rotating magnesia crucible. After melting the metal and adjusting the speed of rotation to form a good cup, oxygen was added in the form of ferric oxide. After 20 minutes samples were taken and analysed for chromium and oxygen. The inclusions present in the metal were also examined. After sampling, chromium additions were made to the melt and the bath equilibrated prior to subsequent sampling. Oxygen data were found to be unsatisfactory due to excessive scatter so a modified experimental technique, providing some improvement, was employed. In this case the chromium content was kept constant throughout the experiment and the melt equilibrated at different temperatures.

Inclusions which were isolated electrolytically, were studied at various chromium levels using both microscopic and X-ray diffraction techniques. Polarised light was also used to determine the true transmission colour of the inclusions. Three arbitrary chromium ranges were selected as follows:-



- |                       |             |
|-----------------------|-------------|
| a) Low chromium       | 0 - 3% Cr.  |
| b) Medium chromium    | 3 - 9% Cr.  |
| c) High chromium      | 9 - 25% Cr. |
| d) Very high chromium | Over 25%    |

The low chromium samples all contained chromite. X-ray examination revealed only the presence of the cubic spinel structure having a constant axial ratio. In the medium range all inclusions were of the chromite type but the axial ratio was variable. This was stated as being due to distortion of the cubic structure by replacement of iron by chromium in chromite. In the last two chromium ranges all inclusions contained some red crystalline material which gave an approximate analysis, corresponding to  $\text{Cr}_3\text{O}_4$ . Larger amounts of chromic oxide were also found but these were thought to have come from the disproportionation of  $\text{Cr}_3\text{O}_4$



$\text{Cr}_3\text{O}_4$  inclusions were all found to contain some iron, replacing the chromium. Since these types of inclusions were found in samples consisting of virtually pure chromium, it has been suggested that chromic oxide is not the stable oxide phase in equilibrium with any Fe-Cr-O alloys. From this, the theoretical slopes of a  $\log \frac{p\text{H}_2\text{O}}{p\text{H}_2}$  v log Cr curve can be calculated. At low chromium concentrations the slope should be  $-\frac{1}{2}$ , above 9% the gradient should be  $-\frac{3}{4}$ . In the intermediate range a gradual change would be expected.

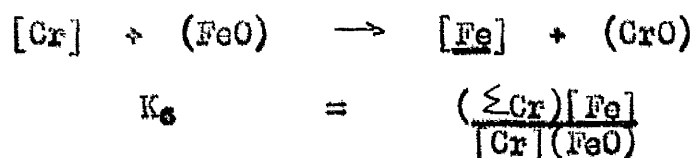
Inclusions in chromium steels have been studied by various workers

and it seems surprising that  $\text{Cr}_3\text{O}_4$  had not been observed earlier. Chen and Chipman found only chromite and chromic oxide inclusions in their samples, which were also quenched from the molten state. Linezinski and Samarin and other workers have reported the same conclusions. In a study of the non-stoichiometry of oxides at high temperatures Kramers and Smith<sup>34</sup> have found only minor deviations from the theoretical composition of chromic oxide. If  $\text{Cr}_3\text{O}_4$  were the stable phase, one would expect a considerable loss of oxygen on prolonged heating of  $\text{Cr}_2\text{O}_3$ . On cooling, either  $\text{Cr}_3\text{O}_4$  would be found or perhaps a mixture of chromium metal and chromic oxide resulting from the disproportionation of  $\text{Cr}_3\text{O}_4$ . Since this was not the case some doubt is cast on the validity of Hilty Forger and Folkman's results. However, in the light of this work, Chipman<sup>35</sup> reviewed the earlier data of Chen and Chipman. The results at low chromium concentrations required little modification to conform with the new work. If the best straight line were drawn through the high chromium results, the gradient corresponded to equilibrium with chromous oxide, not  $\text{Cr}_3\text{O}_4$ . Whilst there are several references concerning the possibility of a CrO phase, evidence is only circumstantial. For example, Zepffe<sup>36</sup> has claimed to have observed blue coloured slags over high chromium melts and attributes this to the presence of CrO. Hilty<sup>37</sup> has postulated that the oxidation of carbon, in the presence of chrome-containing slags, occurs by the following mechanism



Variations of chromium content with carbon were found to fit in well with this mechanism, without any complications regarding thermodynamic activities of carbon and chromium. Dennis and Richardson<sup>38</sup> presented calculations purporting to show that the results could have been predicted from the activities of carbon and chromium and the assumption that chromic oxide was the stable phase.

Similarly, Tesche<sup>39</sup> has considered that chromium may be oxidised out of the melt by the reaction:



Neglecting activity coefficients, a graph showing the relationship between  $\frac{\sum(\text{Cr})}{[\text{Cr}]}$  and (FeO) should give a straight line. This was found to be the case but other workers have not been able to confirm it. (Fig. 16).

In connection with the increased solubility of oxygen in high chromium alloys, the possibility of a soluble chromous oxide has been suggested, even though there is no experimental evidence confirming its existence.

From all the available data, there is considerable doubt concerning the oxide phases in equilibrium with Fe-Cr-O alloys. Recent work has also caused doubt about the ideality of Fe-Cr alloys. For the present investigation it was hoped that these two variables could both be considered in interpreting the results.

(4) Atomic Interactions in Molten Steels

An alloy steel bath is a multicomponent system and so manifold interactions between its components would be expected.

Wagner<sup>40</sup> has derived a simple mathematical treatment which is correct for infinitely dilute solutions. It should be realised that these relationships may not apply for real solutions. However, at the present time, there is no more satisfactory treatment than that derived by Wagner. Chipman<sup>35</sup> has summarised the work briefly as follows:

When a solvent metal 1 contains a number of solute metals 2, 3, 4 etc., the activity coefficient of one of these, for example  $f_2^1$ , may be expressed as a product of each of the other components. Thus in a solution of mole fraction  $x_3, x_4, x_2$  etc.

$$f_2^1 = f_2^2 \times f_2^3 \times f_2^4$$

where  $f_2^2$  is the activity coefficient of 2 in the binary solution of

$$f_2^1 = f_2^2 \times f_2^3 \times f_2^4$$

where  $f_2^2$  is the activity coefficient of 2 in the binary solution of<sup>on</sup> has been derived by Wagner

$$\ln f_2(x_3, x_4) = \ln f_2^0 + x_3 \frac{\partial \ln f_2}{\partial x_3} + x_4 \frac{\partial \ln f_2}{\partial x_4}$$

Derivatives are to be taken for the limiting case of zero concentration of all solutes and higher order terms of a Taylor series neglected.

The term  $\ln f_2^0$  is made zero by taking  $f_2 = 1$  at infinite dilution.

The derivatives are represented by symbols defined as

$$\xi_2^2 = \frac{\partial \ln f_2}{\partial x_2} \quad \xi_2^3 = \frac{\partial \ln f_2}{\partial x_3} \quad \text{etc.}$$

The equation then becomes

$$\ln f_2(x_3, x_4) = x_3 \xi_2^2 + x_4 \xi_2^3 + x_2 \xi_2^4$$

Two methods are in common use for the definition of interaction parameters. When weight percentages are used the parameter is defined as

$$e_2^3 = \frac{\delta \log f_2}{\delta \% 3}$$

If concentrations are expressed as mole fractions the interaction parameter is defined as

$$\xi_2^3 = \frac{\delta \log f_2}{\delta x_3}$$

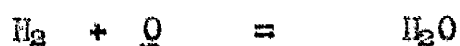
Wagner has also shown that the following simple relationship exists between the effect of a component  $i$  on  $f_j$  and the effect of  $j$  on  $f_i$

$$\xi_i^j = \xi_j^i$$

There are very few cases where there is sufficient data to test the validity of this relationship. The activities of the two components in dilute solutions must be known, independently. Activity data on the Fe-Si-O system are available although one doubts the reliability of some of the data. The activity of silicon in iron is known fairly accurately from distribution experiments between iron and silver. From techniques employing  $H_2O/H_2$  mixtures the effect of silicon on the activity of oxygen can be found. The effect of oxygen on silicon can then be calculated from Wagner's equation and the result compared with the available Fe-Si data. If the data are reliable and the equation holds, oxygen has a considerable effect on the activity of silicon. As silicon is present in greater quantities than oxygen this must be considered extremely doubtful. From present knowledge, it would be safer to conclude that the sign

of the interaction parameter will be the same but perhaps not the magnitude.

Recently, theoretical treatment on interaction parameters has been developed by Samarin, Mtschedlischwili and Averin<sup>41</sup>. In the first case,  $H_2/H_2O$  equilibria in iron, containing an alloying element R, are considered.



$$K = \frac{p_{H_2O}}{p_{H_2}} \cdot \frac{1}{\%O \cdot f_O^R}$$

$$\text{Let } \%O = A N_O$$

$$K = \frac{p_{H_2O}}{p_{H_2}} \cdot \frac{1}{A} \cdot \frac{1}{N_O} \cdot \frac{1}{f_O^R}$$

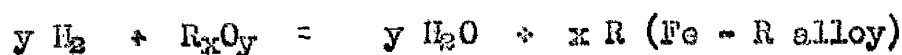
$$\ln K = \ln \frac{p_{H_2O}}{p_{H_2}} - \ln A - \ln N_O - \ln f_O^R$$

$$\frac{\partial \ln \frac{p_{H_2O}}{p_{H_2}}}{\partial N_R} = \frac{\partial N_O}{\partial N_R} + \frac{\partial \ln f_O^R}{\partial N_R}$$

K and A are constants and disappear on differentiation

$$\text{i.e. } \frac{\partial \ln \frac{p_{H_2O}}{p_{H_2}}}{\partial N_R} = \frac{\partial N_O}{\partial N_R} + \epsilon_O^R$$

A similar treatment is then applied to the system containing the oxide  $R_xO_y$



$$K = \left( \frac{p_{H_2O}}{p_{H_2}} \right)^y a^{xR}$$

$$= \left( \frac{p_{H_2O}}{p_{H_2}} \right)^y N_R^x \gamma_R^x$$

Assuming  $\gamma_R = 1$  (ideal solution scale)

$$\ln K = y \ln \frac{p_{H_2O}}{p_{H_2}} + x \ln N_R + x \ln \gamma_R$$

$$\frac{1}{y} \ln K = \ln \frac{p_{H_2O}}{p_{H_2}} + \frac{x}{y} \ln N_R + \frac{x}{y} \ln \gamma_R$$

$$\begin{aligned} \frac{\partial \ln \frac{p_{H_2O}}{p_{H_2}}}{\partial N_R} &= -\frac{x}{y} \times \frac{\partial \ln N_R}{\partial N_R} \\ &= -\frac{x}{y} \frac{1}{N_R} \end{aligned}$$

The two equations can now be equated

$$-\frac{x}{y} \frac{1}{N_R} = \frac{\partial N_o}{\partial N_R} + \epsilon_o^R$$

If the equilibrium oxide composition is known as well as the interaction parameter, the position of the minimum can be calculated. Applying the equation in reverse permits the calculation of the interaction parameter if the minimum is known. It is interesting to note that minima would theoretically be expected in %R - %O<sub>2</sub> curves. In recent years these have been observed for a number of Fe-R-O systems, e.g. Fe-Cr-O, Fe-Si-O, Fe-C-O, Fe-AlO, etc. Samarin used the equation to calculate the minima on the Fe-Cr-O system and compared the results with other experimental data.

TABLE 2

<u>Calculated Value</u>				<u>Experimental Value</u>
$\xi_{\alpha}^{\text{Cr}}$	$e_{\alpha}^{\text{Cr}}$	$\eta_{\alpha}$	$\% \text{Cr}$	$\% \text{Cr}$
6.8	0.011(1)	0.085	8	12(111)
3.7	0.064(11)	0.05	4.5	6(iv)

(1) Chen and Chipman  
(11) Turkdogan

(111) Linczinskii and Samarin  
(iv) Hilby et alia

The minimum concentrations were calculated from the data of Turkdogan and Chen and Chipman. In view of the discrepancies between the data it is not surprising that the minima are widely separated. The experimental values for the position of the minimum are not in good agreement either. The available data are obviously insufficiently accurate to test the validity of the theory. Treating the Fe-Cr-O system in this manner is further complicated due to lack of knowledge on the stable oxide phases and the activity of chromium in iron. Either or both of these difficulties arise in other Fe-R-O systems making the treatment perhaps, only of academic interest. It does, however, give some theoretical justification for the existence of a minimum on R - O curves.

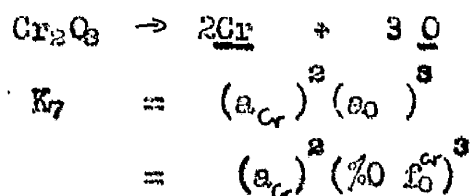
#### (5) Calculation of Interaction Parameters from Experimental Results

The results of various investigators, together with the present work are discussed in detail later. At the same time, the liberty has been taken to revise some of the earlier work in the light



of subsequent knowledge.

Interaction coefficients can be calculated using two different methods and this ought to provide a useful check on the accuracy. Using  $H_2O/H_2$  mixtures, the activity of oxygen in iron has now been fairly well established. For investigations of the Fe-Cr-O system involving the use of  $H_2O/H_2$  mixtures, the interaction coefficient,  $f_O^{Cr}$ , can be calculated directly from the observed oxygen concentration. Interaction coefficients can also be calculated from the free energy data.



The interaction coefficient can be calculated if the following information is available.

- (1) Thermodynamic data on the oxide phase concerned.
- (2) Stable oxide phase at any particular level of chromium activity.
- (3) Activity of chromium in iron.

In view of the doubts about (2) and (3), less error will be involved in using Fe-O data since the nature of the oxide phases and chromium activities are not involved in the calculations. This was the approach used by Chen and Chipman although they used earlier iron-oxygen data, now known to be in error. The value of the parameter, calculated by Chipman was  $e_O^{Cr} = -0.041$ . Turkdogan, using the same method of calculation, found the value to be  $-0.064$ . No oxygen data were given in the published paper by Linczinski and Samarin.

Chipman has presented calculations on Hilty's work and obtained a value of  $-0.041$ . This is not considered to be significant since it involved an estimation of the free energy of formation of  $\text{Cr}_3\text{O}_4$ , a rather dubious phase to be in equilibrium with Fe-Cr-O solutions.

There is, as yet, no accurate value for the interaction parameter  $\xi_0$ . It was hoped that the present work, together with a close examination of previous data, would result in an accurate value for the parameter. The effect of temperature on interaction coefficients is not known although they would be expected to approach unity with increasing temperature, i.e. form "more ideal" solutions. Data at a higher temperature would be useful in confirming this to be the case.

EXPERIMENTAL PROCEDURE

(1) THERMAL DIFFUSION

In any study involving equilibria between gases and solids or liquids, certain precautions must be taken to minimise errors due to thermal diffusion.

In a mixture of gases of different molecular weights, a temperature gradient tends to produce a composition gradient, the less dense gas diffusing towards the hotter region. This phenomenon of thermal diffusion was first predicted by Enskog<sup>42</sup> and observed in 1917 by Chapman and Dootson<sup>43</sup>. It has caused errors in many gas-metal studies. Emmott and Schultz<sup>44</sup> have discussed at length its bearing on the results of measurements of the equilibrium  $H_2O-H_2-Fe-FeO$  by a static method in which errors in the  $\frac{p_{H_2O}}{p_{H_2}}$  ratio could be as great as 40%.

When metal is heated by induction a sharp temperature gradient is set up near the metal surface. Some early studies of the reaction



produced apparent values of  $K_1'$  which are now known to be too high.

A study of the factors affecting thermal diffusion<sup>45</sup> have indicated two possible methods of minimising errors from this course:

(a) Preheating the gas mixture to eliminate as far as possible thermal gradient near the melt surface.

(b) Based on Gillespie's<sup>46</sup> simplified treatment which has shown that thermal separation is diminished by admixture of a gas of high molecular weight.

By this theory the error in

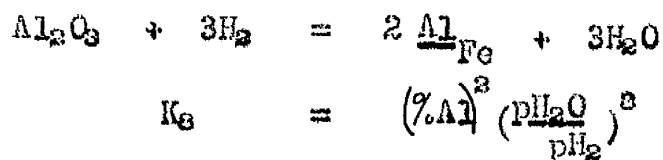
$$\log K_1' \propto \frac{1}{\text{mean square root of M.Wt. of gas mixture}}$$

Experimental evidence has shown that the error is eliminated by adequate preheating and greatly minimised by the addition of a heavy inert gas.

Chen and Chipman<sup>24</sup> used a platinum preheater in their study of the Fe-Cr-O system. The temperature used was roughly 1100°C as, at higher temperatures, rapid break-down of the platinum wire took place. No carrier gas was used. The gas stream was not directed on to the metal and in the light of later work it seems extremely likely that thermal diffusion took place.

In later work by Dastur and Chipman<sup>5</sup> in a study of the Fe-O systems, a much greater degree of preheat was given as well as the addition of argon in the ratio 4/1. Floridis and Chipman<sup>6</sup> used similar conditions as above but used a 6/1 argon/hydrogen ratio.

McLean<sup>27</sup>, in a study of the reaction:-



has used a molybdenum winding on an alumina tube to preheat the inlet gases for which the argon/hydrogen ratio was 6/1. The temperature of the preheater was 1600°C for experiments carried out at 1730°C. Some experiments were done without preheat and the aluminium concentrations were considerably higher indicating that thermal

diffusion had taken place.

Although difficult to perform experimentally, the best way to overcome thermal diffusion is to bubble the reactive gas through the pool of molten metal. Gokeen<sup>7</sup> has used this technique in a study of Fe-O equilibria. After the charge had melted, the liquid metal was pushed up until the bubbling tube immersed approximately 2 mins. in the melt as judged by a manometer. At this time the gases, poured uniformly through the melt but when immersion was much deeper pressure fluctuations were irregular and metal was blown out of the crucible. The technique was also used by Floridis and Chipman to confirm results obtained by the more usual method described earlier.

In the light of previous work it was decided that the safest method of avoiding thermal diffusion was to use the bubbling technique and a wire wound resistance furnace so that the gas received a considerable degree of preheat.

## (2) CRUCIBLES

One of the practical difficulties of high temperature research is to obtain a container which is not attacked yet has no contaminating effect on the equilibria being studied. In gas/metal/oxide studies, the pure oxide would be the most suitable container. There are two such materials which could be used in a study of the Fe-Cr-O system. The first of these is chromic oxide which is obtainable in a pure form and is made in considerable quantities for

use as a pigment in the paint industry. The second is chromite,  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ , which is a common refractory material but, unfortunately, contains several impurities. An attempt was made to produce chromic oxide and chromite crucibles.

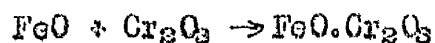
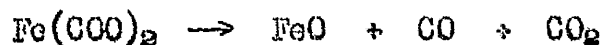
Chromic oxide crucibles were made by a method similar to that suggested by Chen and Chipman. Green chromic oxide was obtained from a commercial source in finely divided form. To assist in making a plastic slip the material was ground in a ball mill for 24 hours. It was then mixed with a 10% hydrochloric acid solution to give a slip of suitable consistency. This was left overnight as conditioning seemed to make the slip-casting operation more productive.

Good plaster of Paris moulds were found to be essential in producing chromic oxide crucibles. Ordinary commercial plaster of Paris was never entirely satisfactory as it was too coarse and the rapid rate of drying caused the crucibles to crack. Finely divided plaster of Paris was used to make moulds for slip-casting. This was added to water and the mixture well stirred until it was of a creamy consistency. The mixture was then poured into a greased mould containing a metal core which was the shape of crucible desired. Once the plaster of Paris had set the metal core and the mould were removed and the plaster mould allowed to air dry for several days. A crucible shape was chosen having a slight taper from top to bottom to make it easier to extract the slip-cast crucibles from the mould.

The crucibles were made by filling the plaster mould with the aqueous slip and when a sufficient thickness of chromic oxide had formed round the walls, the superfluous slip was poured off. The first two or three casts were not normally successful as very rapid drying caused cracking. Thereafter the moulds gave up to a dozen successful casts although they had to be dried intermittently. The moulds were then scrapped as a change in texture slowed down the rate of absorption of water and the crucible collapsed before drying. The crucibles shrunk sufficiently to be easily extracted from the mould.

The chromic oxide crucibles were dried in an air oven at 120°C for two days after which they were fired in a muffle furnace at 1000°C. They were then fired for two hours in air or argon at 1700°C after which they were quite strong and impervious to fluids.

A few chromite crucibles were made but these were seldom used. Pure chromite was made by heating a mixture of ferrous oxalate and chromic oxide, in the correct proportions, to 1200°C in an alloy tube.



The chromite was then crushed for 24 hours in a ball mill and made into crucibles in a similar way to that for chromic oxide crucibles. After drying these were fired at 1600°C in nitrogen for three hours, whereupon they could withstand the attack of metal and small amounts of slag.



To protect the alumina furnace tube from being splashed with metal or slag, the chromic oxide crucibles were held in larger slip-cast alumina crucibles. These were made by grinding fused alumina for 12 hours in a ball mill, afterwards treating it with 10% hydrochloric acid to form the necessary slip material. The crucibles were fired at 1600°C and, while not giving an impermeable surface, they were satisfactory for the purpose required.

### (3) MATERIALS USED IN MELTS

Metal High purity electrolytic iron was used. Several grades of chromium were tried, the most satisfactory being electrolytic lump chromium (Grade A) as supplied by Union Carbide, Ltd. The analyses of the materials used are given below.

	C	S	Si	Fe	O <sub>2</sub>	H <sub>2</sub>	N <sub>2</sub>	Cr
Chromium	.010	.006	.030	.020	.008	.0005	.016	99.90
Iron	.010	.018	.008	99.87	-	-	-	-

To prepare a charge the chromium was broken up and mixed with iron then formed into a pellet. At first this was premelted in an alumina crucible to form a homogeneous alloy. This was later found to be unnecessary and so the pellets were charged straight into the chromic oxide crucible. After the iron had melted, the chromium took only a few minutes to dissolve whence the run could commence.

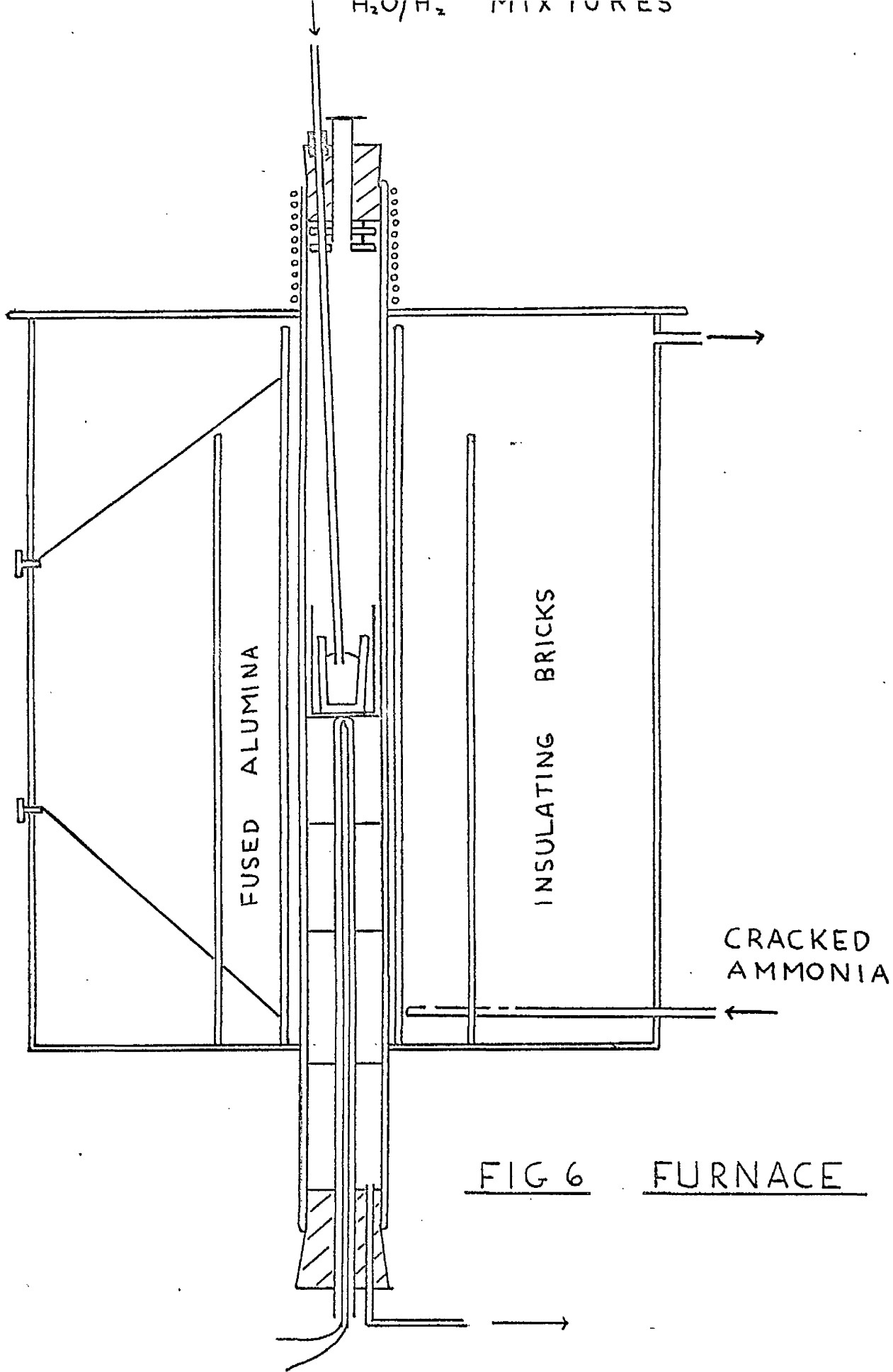
Slag Except in a few preliminary heats, no slag was charged. In some runs slag was formed by oxidation of chromium and iron from the melt.

#### (4) FURNACE AND APPARATUS

In order that a temperature effect for the reaction between chromium and oxygen in iron may be calculated, experiments had to be carried out at least at two temperatures. For greater accuracy it is preferable that these should differ by at least 100°C and so 1600° and 1700°C were the selected temperatures. To attain such temperatures experiments were carried out using a molybdenum wound furnace as shown in Fig. 6.

A 2-inch I.D. recrystallised alumina furnace tube was used being impermeable to gases up to 1800°C. This tube was placed inside an "Alpor" alumina tube which was wound over a length of 16" with 18 gauge molybdenum wire. The hot zone extended over a distance of 2", but 4" above the hot zone, the temperature was only 100°C below operating temperature. This ensured that a considerable degree of preheat was given to the inlet gases.

A molybdenum winding must be kept under a reducing or neutral atmosphere to prevent oxidation and subsequent failure of the wire. The furnace must therefore be reasonably gas-tight to prevent inward leakage of air. An asbestos gasket was placed between the furnace lid and the main body, and the two bolted together. Leaks between the casing and the furnace tube were minimised by packing



thin asbestos rope between the two. Dry cracked ammonia (Fig. 7) was passed into the furnace at a rate of 5 litres per minute. This gave a slight pressure at the outlet end and ensured that cracked ammonia was leaking out of the furnace rather than air leaking in. The winding never failed due to oxidation but on two occasions broke due to embrittlement.

The top end of the alumina furnace tube was, at first, found to be too hot to hold a rubber bung. A 6" water-cooled copper coil was fitted around the tube and radiation shields were bolted on to the underside of the bung. Subsequently, the bung suffered no damage due to overheating. The bung at the top of the furnace held a glass window and a gas-tight brass support in which the thin alumina bubbling tube could be raised or lowered.

The rubber bung at the bottom of the furnace tube, which supported alumina stools and the crucible, was cold enough not to require additional water-cooling.

The temperature was measured using a 5%Rh Pt/20%Rh Pt thermocouple situated under the charge and at the bottom of the hot zone. The E.M.F. developed was measured by a Cambridge Workshop potentiometer. To check that the reading of the thermocouple was the same as the crucible temperature, another thermocouple was suspended from the top of the furnace tube so that the tip was in the middle of the crucible. The difference between the two readings was insignificant

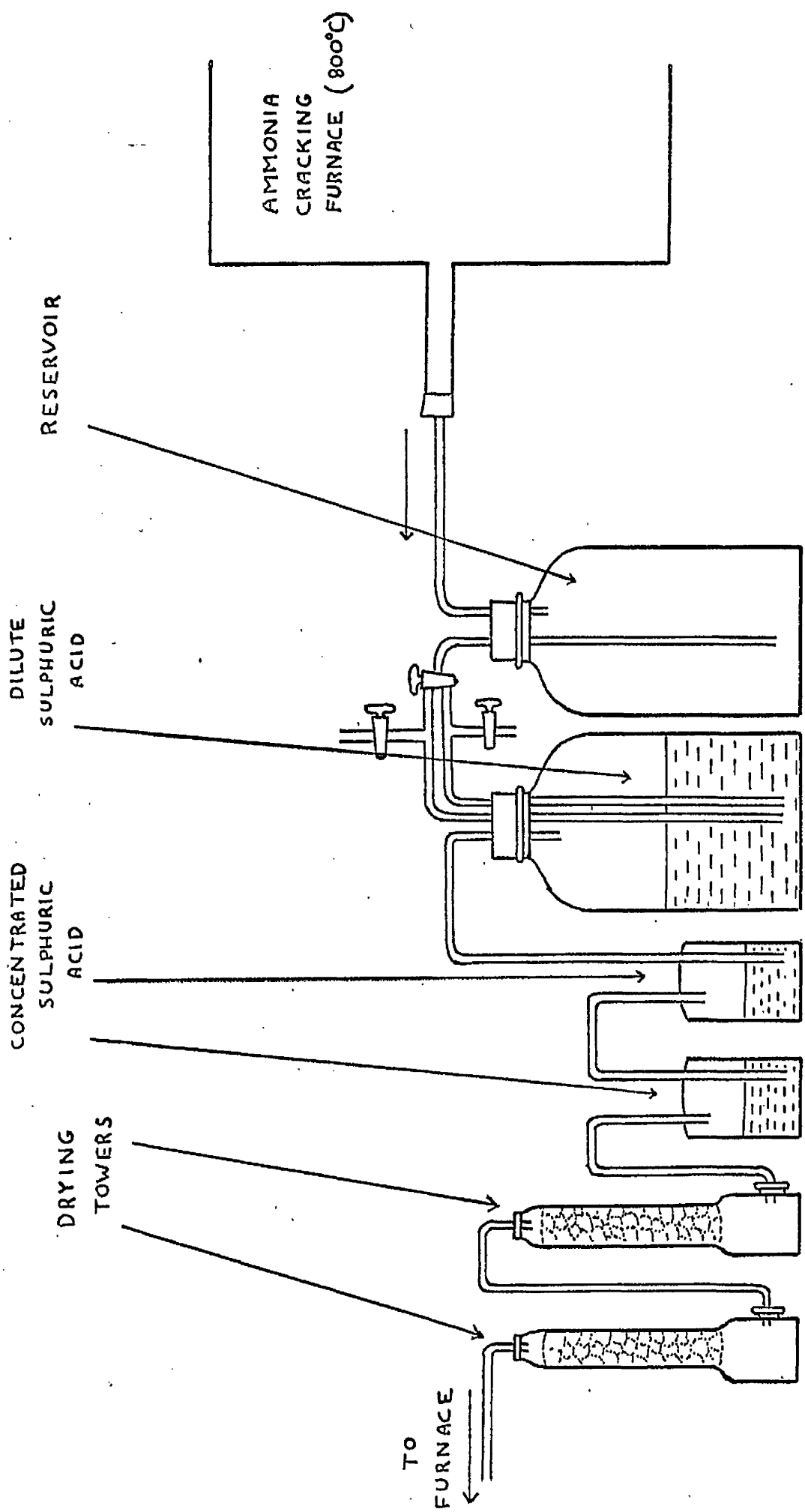


FIG 7 THE AMMONIA CRACKING TRAIN

showing that temperature measurement was reliable. Thermocouples were calibrated against the melting points of gold (1063°C) and palladium (1554°C).

An attempt was made to control automatically the furnace temperature using a controller and 30 ampere mercury relay switch. Since the furnace must be gas-tight, a control thermocouple could not be placed just outside the winding, the practice normally adopted for platinum resistance furnaces. The thermocouple was placed up the inside of the furnace tube. This method proved to be of no avail, the lag between winding and crucible temperatures being too great. Control was no better than  $\pm 40^\circ\text{C}$ . To improve this the mercury switch was by-passed with a low resistance so that the winding current only dropped a few amps when the switch "opened". Even with this modification control was no better than  $\pm 15^\circ\text{C}$  and thereafter the temperature was manually controlled by adjustment of the Variac transformer. Once steady conditions had been obtained, the temperature could be controlled to  $\pm 5^\circ\text{C}$  with only occasional adjustments of the transformer.

The gases passed into the furnace were argon and hydrogen/water mixtures. Argon was dried with magnesium perchlorate before being passed into the furnace. High purity hydrogen was used to avoid contamination of the melt by carbon as hydrocarbons are the chief impurity in commercial hydrogen.

The gas flowmeters were calibrated by passing through hydrogen or argon at a constant rate for a noted time. The volume of gas was measured using a rotary gas meter. During the calibration the pressure drop across a suitable Venturi orifice was recorded. The volume of gas (converted to N.T.P.) in ml./min was then calculated. The experiment was repeated at several different flow rates enabling a calibration curve (pressure drop against flow rate) to be drawn. Separate flowmeters were constructed for hydrogen and argon.

Hydrogen/water ratios were controlled by bubbling hydrogen through flasks containing distilled water (Fig. 8). The saturators were immersed in a large tank (B) containing water. A 500 watt heater (C), together with a toluene regulator (D) and hot wire vacuum switch (E), enabled the water temperature to be controlled to  $\pm 0.1^{\circ}\text{C}$ . The water vapour pressure, and hence the hydrogen/water ratio was varied by altering the water bath temperature. The performance of the saturators (A) was checked by passing through a known volume of hydrogen, the water being absorbed in magnesium perchlorate drying towers. From these weights the water vapour pressure was calculated and found to agree with standard tables.

To observe pressure fluctuations when gas was being bubbled through the molten metal, a small mercury manometer (F) was fitted into the bung of the last saturator.

After leaving the last saturator the gas was carried to the furnace through a heated copper tube to prevent condensation. The copper tube was joined to the alumina tube by a small piece of rubber tubing as it has been suggested that rubber is slightly permeable to water vapour.

For most of the runs distilled water was used in the saturators. However, for high chromium heats, some difficulty was encountered in obtaining a sufficiently low oxygen potential. For this reason, some experiments were carried out using saturated lithium chloride solutions in the saturators. These solutions gave rise to some experimental difficulties as solid lithium chloride precipitated inside the bubbling tubes after a comparatively short time. The tubes were cleaned regularly to ensure that runs would not have to be abandoned through choking of the saturators.

Data on the water vapour pressure of saturated lithium chloride solutions are conflicting. Gokcen<sup>46</sup> has determined the variation of water vapour pressure with temperature. McLean<sup>47</sup> tried to confirm this on several occasions but always found a divergency at higher temperatures. Since the present author used the same grade of lithium chloride as McLean, his curve (Fig. 9) was taken as applicable to the present work.

#### (5) EXPERIMENTAL METHOD

In carrying out a melt, the crucible was charged with 30 gms of iron or iron-chromium alloy and placed in the furnace as shown in Fig. 6. The power was switched on and adjusted so



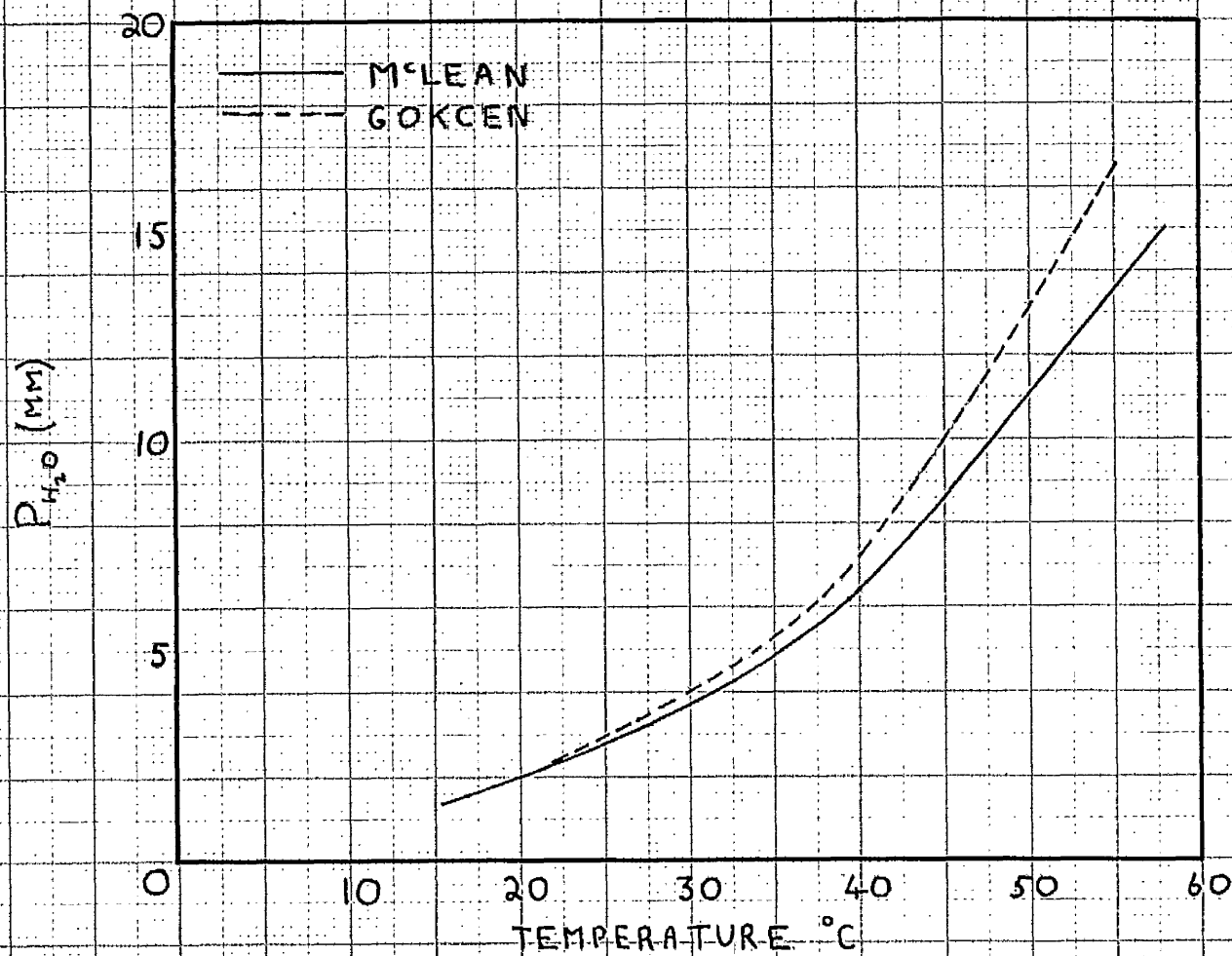


FIG. 9. THE WATER VAPOUR PRESSURE OF SATURATED LITHIUM CHLORIDE SOLUTIONS.

that the operating temperature was reached in 4 to 5 hours. After reaching this temperature, the melt was held for 1 hour to dissolve the chromium and allow the furnace to reach a steady state whereby control of temperature was much easier. Melting out was normally done in argon, but, in the few cases where powdered chromium was used, melting was done in dry hydrogen. The water bath temperature was adjusted early in the day so that the water or solution in the saturators would reach this temperature long before the run was started.

For a number of preliminary runs a 6/1 argon hydrogen mixture was blown on to the top of the metal through a thin (10 mms I.D.) alumina tube. The dead space above the crucible was filled with alumina stools to prevent currents which might aid thermal diffusion. It is always desirable to approach equilibrium in two directions so that equilibrium concentrations can be fixed within certain limits. Thus in some experiments the crucible is reduced by the  $H_2/H_2O$  mixture and in others chromium is oxidised out of the melt to form a slag. Using the blowing technique it was found impossible to oxidise reasonable amounts of chromium out of the melt as a solid film of oxide formed on the surface of the melt and prevented further reaction.

Due to the above limitation, for most of the experiments, a bubbling technique was employed. After melting out, the thin alumina bubbling tube ( 3 mms. I.D ) was pushed down into the metal to a depth

of approximately 5 mm. a guide to this depth being the reading on the small mercury manometer. Using a flow rate of not more than 150 ml. hydrogen per minute, the gas bubbled steadily through the melt, very little being lost through splashing. By this method equilibrium could be approached in both directions as a surface film of slag did not prevent further reaction.

For low chromium alloys, 2% of chromium could be oxidised or reduced in 2 hours, since equilibrium was approached from both sides, this is sufficient as direction of movement is just as important as magnitude. Chen and Chipman regarded 2 hours as being ample time and so a large number of experiments were done for that duration.

At high chromium concentrations (low oxygen potentials) the magnitude of movement was found to be very small. Repeated and very accurate analysis was required to establish the direction in which the reaction had gone. In a few cases, movement was in the opposite direction to that expected. About this time fine chromium powder was being used and this may have contained considerable amounts of oxide causing doubt about the initial composition of the melt. From then onwards, a high grade lump chromium was used but although movement occurred in the expected direction, the magnitude was always small (approximately 0.3% Cr.). This was particularly marked when chromium was being oxidised from the metal and a calculation showed that, at these low oxygen potentials, the available oxygen was only sufficient to oxidise about 0.3% Cr.

from the bath in 2 hours. From this time onwards at low oxygen potentials, runs were carried out for 5 to 6 hours when appreciable movement in either direction was observed.

Before sampling, the bubbling tube was raised out of the melt and the furnace purged with argon. The top bung was then removed and a sample of metal taken by suction into a silica tube using a rubber bulb. Samples were quenched in water, the middle section only being used for analysis.

With chromic oxide crucibles, a crust was formed between the crucible and the metal and it is thought that equilibrium is established between this crust and the metal. A streak test, commonly used by geologists, was used to investigate the oxides present in these crusts. Below 3% chromium the streak was always brown and X-ray examination confirmed the presence of chromite. Above 9% chromium, the streak was always green due to the presence of chromic oxide. The streak tests were inconclusive in the important range between 3 and 9% chromium.

A few melts were made in chromite crucibles, all at low chromium levels but these merely confirmed the results obtained from chromic oxide crucible experiments. This provided added confirmation that equilibrium is established between the crucible crust and the metal. Since chromite and chromite crucibles took much longer to prepare, only a few melts were made in such crucibles.

At a later stage a few experiments were performed to investigate the high temperature oxides of chromium. Chromium and

chromic oxides were mixed up finely in the proportion corresponding to  $\text{CrO}_3$ . This was made into a pellet and placed in a molybdenum crucible. It was held in an argon atmosphere for 4 hours at  $1600^\circ\text{C}$ , then cooled in the furnace, polished and examined metallographically. In another experiment to study the volatility of any lower oxides of chromium, hydrogen was passed over chromic oxide, then through a condenser situated in the cooler part of the furnace tube. A horizontal, platinum wound, furnace was used, the maximum temperature attained being  $1550^\circ\text{C}$ . The apparatus was similar to that used by Ramstad and Richardson<sup>49</sup> in their study of silicon monoxide. In the 3-hour experiment no condensate was obtained.

### (6) ANALYSIS

(a) Chromium Metal samples were analysed for chromium and oxygen. Chromium analyses were carried out by the standard persulphate method, the details being given in "The analysis of Steel and Ferro-Alloys"<sup>50</sup>. The method involved the solution of the metal and subsequent oxidation to dichromate using ammonium persulphate. This was titrated using standard ferrous ammonium sulphate and standard potassium permanganate. At low chromium levels results were reproducible to within  $\pm 0.02\%$  while at high concentrations the accuracy was estimated to be  $\pm 0.06\%$ .

(b) Oxygen The metal was analysed for oxygen using the vacuum fusion method which is the standard method for determining oxygen in steel.

Apparatus The furnace side of the apparatus (Fig. 10) was identical with that described by Murad<sup>51</sup> except a high-speed, 4-stage mercury diffusion pump was used to give a higher vacuum and faster pumping rate.

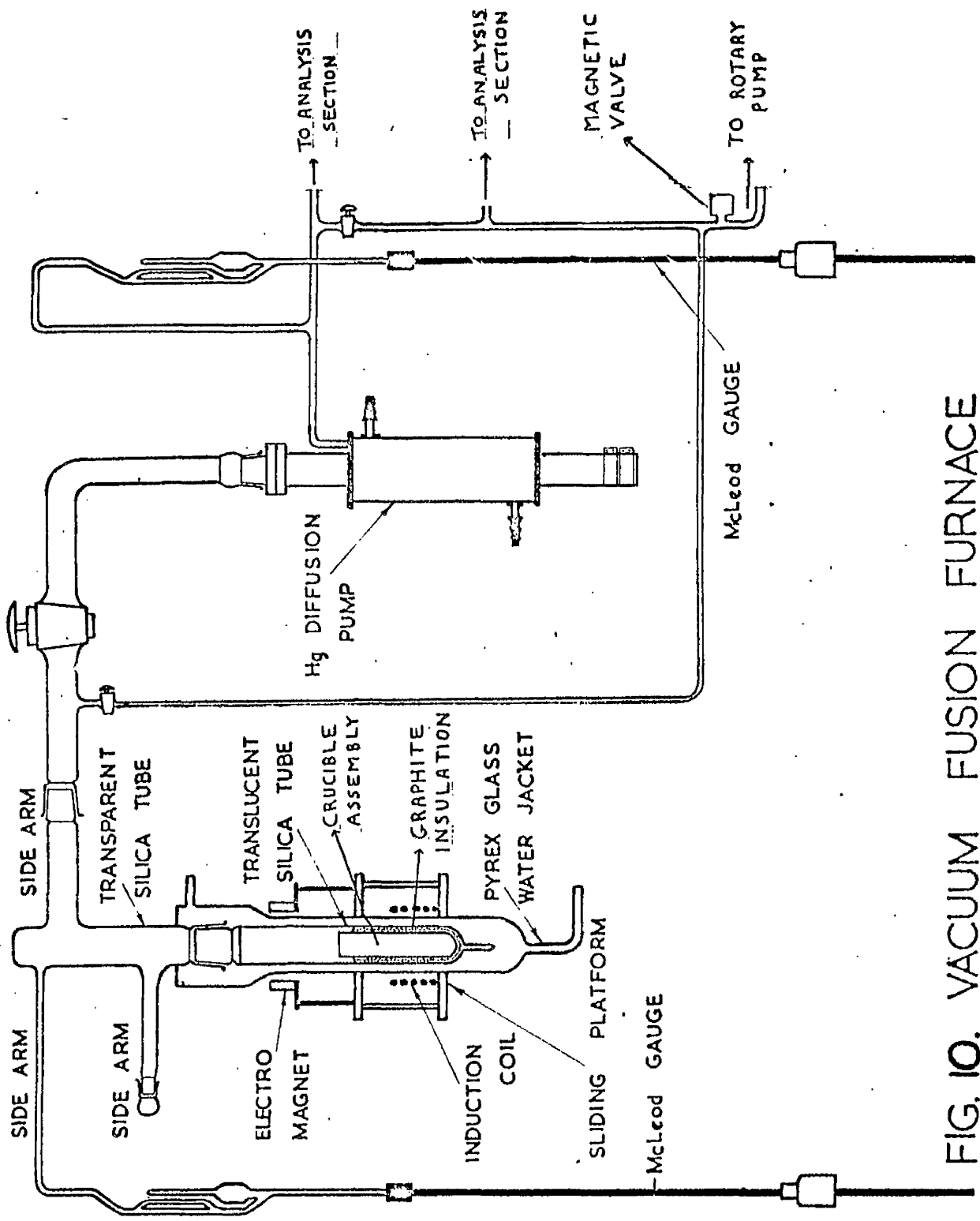
A physical method was used for analysis (Fig. 11). Hydrogen and carbon monoxide were oxidised with copper oxide at 350 - 450°C. The water formed was absorbed in phosphorous pentoxide and the decrease in volume of gas noted. The carbon dioxide was then frozen out using a liquid oxygen trap and the volume again measured. Any remaining gas was assumed to be nitrogen but this was usually negligibly small.

Some difficulty was encountered in finding a suitable oxidiser. Commercial copper oxide was too inactive at the temperature used. Hopcalite was equally unsuitable due to adsorption and subsequent desorption of carbon dioxide. Finally - 200 mesh copper powder was oxidised at a low temperature (250°C - 300°C) and tightly packed in the copper oxide furnace tube. This proved to be a rapid oxidiser and was used in almost all subsequent determinations.

#### Notes on the Technique Employed

(i) Sample preparation. Samples weighing one to three grams were used depending upon the oxygen content expected. These were filed clean then washed in carbon tetrachloride and dried in acetone.

(ii) Graphite. The graphite crucible assembly was packed in high purity - 200 mesh graphite powder. Initially a coarser grade was



**FIG. 10. VACUUM FUSION FURNACE**

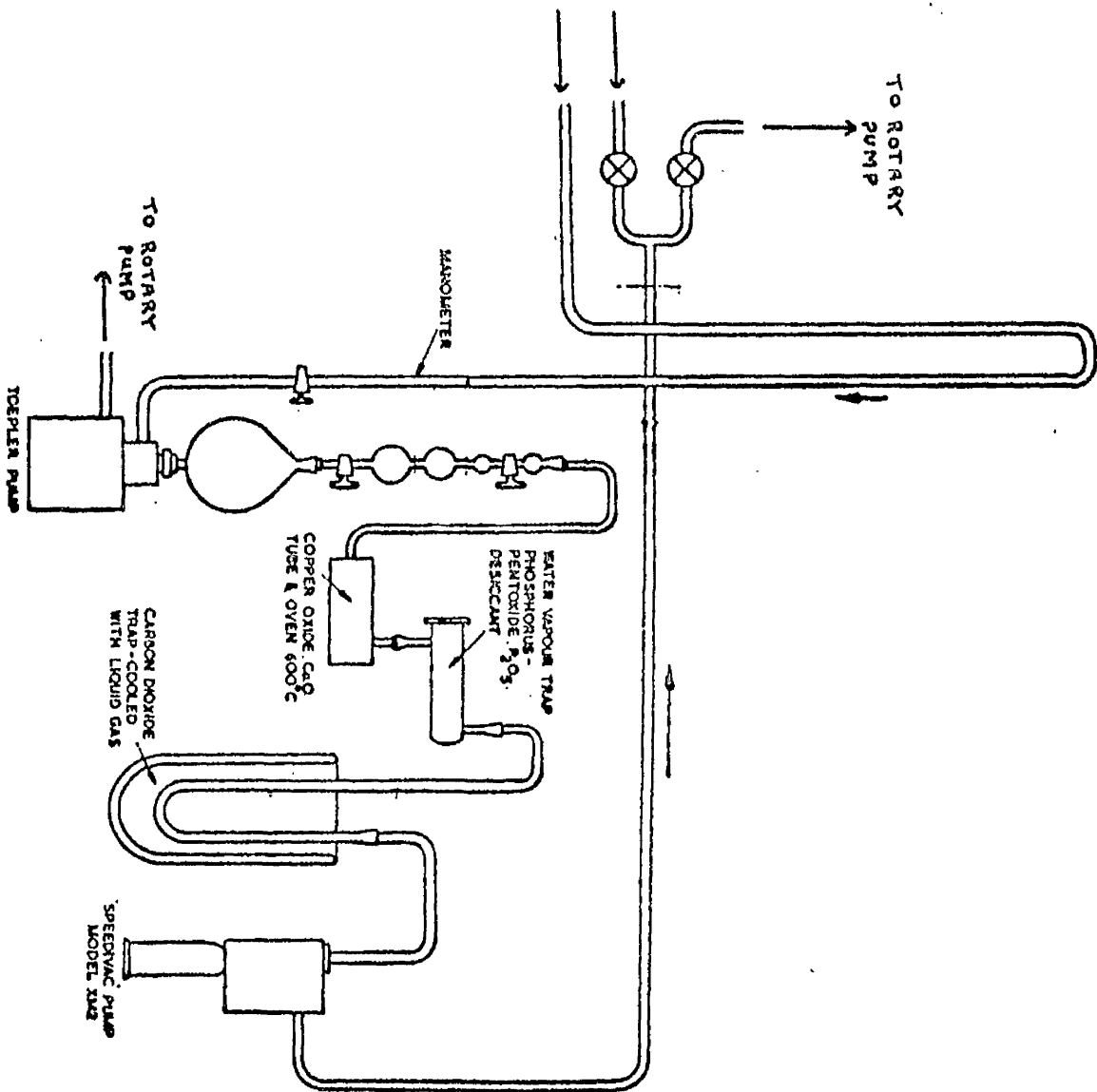


FIG. 11. ANALYSIS SECTION



used but this did not give the necessary insulating properties and hot-spots and irregular blank rates were common.

(iii) Furnace pump-down. The furnace was pumped down using the rotary pump and a magnetic bleeder valve. The time normally required was 10 to 15 minutes. The diffusion pump was by-passed so that if "fluffing" of the graphite powder did occur, it was not necessary to dismantle the pump for cleaning purposes.

(iv) De-gassing. The furnace assembly was heated slowly in the initial stages to avoid graphite "fluffing". At dull red-heat the diffusion pump was brought into operation and the furnace heated rapidly to 2250°C. The furnace assembly was de-gassed for 5 - 7 hours at this temperature to obtain a low blank rate. Higher de-gassing temperatures were tried but gave rise to numerous difficulties. At 2300°C to 2500°C the furnace tube became plated with graphite or some impurity therein and this adsorbed gas from the samples giving low results. Hot spots were common at such temperatures due to sintering and consequent loss of insulating properties of the graphite powder. The graphite lid sometimes welded to the crucible assembly and complete dismantling was needed to remove it. Furthermore the life of the crucible assembly was markedly reduced when very high de-gassing temperatures were employed.

(v) Blank. Blank collections were made in the temperature range 1350°C to 1650°C for approximately  $\frac{1}{2}$  hour. The blank rate was usually in the range 0.03 to 0.06 ccs/hour of which 60 - 70% was carbon monoxide, the remainder being hydrogen. If the fraction

of nitrogen in the blank was appreciable, a leak was suspected.

(vi) A standard sample was analysed first to check that the apparatus was functioning properly. This invariably gave low results yet the second sample gave accurate values. This problem was overcome by adding 4 to 6 gms of Armco iron to form a molten bath. It resulted in more rapid and complete release of gas from the samples to be analysed.

(vii) Operating temperature. The higher the operating temperature the more rapid and complete is the release of gas from the metal. Excessively high temperatures cause film formation on the furnace tube due to volatilisation of iron. This gives rise to low results as the evolved gas is adsorbed by the metal film. Samples dropped at 1600°C gave similar results to those done at 1750°C. Consequently 1600°C was used being the safer operating temperature. Samples known to be high in oxygen were dropped at much lower temperatures to avoid spattering and consequent loss of metal from the bath. After the initial release of gas the temperature was raised to 1600°C.

(viii) Accuracy. For samples low in oxygen (e.g. the standard which contained 0.0105%) the accuracy was  $\pm 0.0005\%$ . Samples in the present work contained from 0.03 to 0.10% oxygen and for these the reproducibility was  $\pm 0.002\%$ . Table 3 gives the details of some other vacuum fusion apparatus as reported in the literature .

TABLE 3

<u>Source</u>	<u>Degassing Temp. °C</u>	<u>Degassing time and min. pressure</u>	<u>Blank Pressure at working temp.</u>	<u>Blank Rate ccs/hr</u>
National Physical Laboratory	2600	2 - $\frac{1}{2}$ hours $2 \times 10^{-6}$ mm Hg	1550-1600 $5 \times 10^{-6}$ mm Hg	0.04
United Steel Co.	2000	2 hours $5 \times 10^{-4}$	1650 $2 \times 10^{-4}$	0.3 - 0.4
Sheffield Univ.	2100	3 hours $1 \times 10^{-4}$	1650 $1 \times 10^{-5}$	0.9
Firth-Brown Research Labs.	2100	2 hours $2 \times 10^{-4}$	1650 $5 \times 10^{-5}$	0.5 - 1
Present work	2250	5 - 7 hours $10^{-6}$	1600 $< 10^{-6}$	0.03 - 0.06

RESULTS

## RESULTS

The analyses of the melts made are shown in Table 4.

Chromium analyses are expressed both as weight and mole fractions.

Oxygen analyses are all quoted as weight per cent. Where several determinations were made the selected value is also tabulated.

For Run numbers 11 to 21, the <sup>gas</sup>/mixture was blown on to the top of the melt, a 6 : 1 argon hydrogen ratio being used to cut down thermal diffusion. For the other experiments the hydrogen/water mixture was bubbled through the melt. Chromic oxide crucibles were used in all cases except Nos. 21, 25, where chromite crucibles were used. In order to study separately the metal-crucible reaction an argon atmosphere was used for Run No. 82.

The gas saturators contained distilled water in all cases except Run Nos. 74 - 81, 83 - 87 where saturated lithium chloride solutions were used.

TABLE 4a

Experimental results at 1600°C.

Gas blown on top of metal

Run No.	Chromium charged		Final chromium		$\frac{P_{H_2O}}{P_{H_2}}$	$\%O_2$
	wt. %	$N_{Cr}$	wt. %	$N_{Cr}$		
11	0	0	2.71	0.0290	0.0805	-
12	0	0	1.88	0.0200	0.0805	-
13	0	0	3.00	0.0321	0.048	-
14	3.83	0.0404	4.42	0.0470	0.0456	-
15	5.67	0.0602	5.42	0.0580	0.047	-
16	5.67	0.0601	5.60	0.0596	0.0456	-
17	5.64	0.0600	5.59	0.0596	0.0515	-
18	7.54	0.0804	7.58	0.0808	0.0485	0.043
19	7.55	0.0804	7.43	0.0792	0.0367	0.045
20	7.50	0.0802	7.90	0.0842	0.0328	-
21 <sup>+</sup>	4.99	0.0533	4.81	0.0512	0.050	0.047

+ Chromite crucible

TABLE 4b

Experimental results at 1600°C

Gas bubbled through metal

Run No.	Chromium charged		Final chromium		$\frac{P_{H_2O}}{P_{H_2}}$	%O
	wt. %	N <sub>Cr</sub>	wt. %	N <sub>Cr</sub>		
23	7.51	0.0803	6.07	0.0649	0.0503	0.040
24	6.90	0.0736	7.65	0.0815	0.0348	0.036
25*	6.90	0.0736	5.88	0.0629	0.050	-
26	6.90	0.0736	9.57	0.1018	0.0297	-
27	2.04	0.0218	3.71	0.0396	0.0643	-
28	4.69	0.0500	4.57	0.0488	0.0643	-
29	4.95	0.0528	4.30	0.0459	0.0787	-
30	8.01	0.0854	7.98	0.0851	0.0416	0.041
31	8.00	0.0853	7.41	0.0790	0.0430	0.0297
32	11.91	0.1266	9.77	0.1038	0.0416	-
33	12.66	0.1346	12.15	0.1292	0.0308	0.037
34	8.48	0.0904	8.23	0.0878	0.0416	-
35	6.10	0.0652	4.68	0.0498	0.077	-
36	0	0	3.07	0.0328	0.077	-
37	2.92	0.0313	4.84	0.0517	0.054	0.035
38	5.94	0.0636	4.56	0.0486	0.0812	0.037
39	4.00	0.0427	4.95	0.0528	0.0423	-
40	7.54	0.0804	7.65	0.0816	0.0337	0.039

TABLE 4b(cont'd)

Run No.	Chromium charged		Final chromium		$\frac{P_{H_2O}}{P_{H_2}}$	%O <sub>2</sub>
	wt. %	N <sub>Cr</sub>	wt. %	N <sub>Cr</sub>		
41	3.00	0.0321	3.86	0.0412	0.0767	-
42	8.00	0.0853	7.84	0.0836	0.0448	-
43	6.01	0.0643	5.75	0.0614	0.0534	0.031
44	11.99	0.1275	11.80	0.1255	0.0341	-
45	10.00	0.1062	9.99	0.1061	0.0268	-
46	14.01	0.1487	13.45	0.1429	0.027	-
47	0	0	0.88	0.0093	0.199	0.056
48	0	0	2.01	0.0201	0.112	0.048
49	3.13	0.0335	1.19	0.0135	0.201	-
50	3.99	0.0426	2.31	0.0247	0.118	-
51	8.72	0.0929	9.34	0.0994	0.0163	-
52	20.00	0.2115	17.90	0.1897	0.0163	0.052
53	14.00	0.1486	12.16	0.1293	0.017	-
54	15.69	0.1664	13.44	0.1428	0.0168	0.038
74 <sup>p</sup>	19.90	0.2104	18.05	0.1913	0.0141	0.047
75 <sup>p</sup>	15.30	0.1620	14.23	0.1510	0.014	0.035
78 <sup>p</sup>	25.00	0.2641	23.80	0.2507	0.01187	0.057
79 <sup>p</sup>	35.00	0.3678	33.46	0.3505	0.01167	0.096
82 <sup>x</sup>	23.00	0.2430	22.22	0.2346	-	0.055



TABLE 4b (contd)

Run No.	Chromium charged		Final chromium		$\frac{P_{H_2O}}{P_{H_2}}$	%O <sub>2</sub>
	Wt. %	N <sub>Cr</sub>	Wt. %	N <sub>Cr</sub>		
83 <sup>φ</sup>	24.00	0.2535	22.96	0.2418	0.01187	0.0678
84 <sup>φ</sup>	20.00	0.2115	20.32	0.2148	0.01184	0.0495
85 <sup>φ</sup>	21.00	0.2217	21.79	0.2300	0.01182	0.055
86 <sup>φ</sup>	14.00	0.1486	17.18	0.1823	0.0144	0.0552
87 <sup>φ</sup>	16.50	0.1751	16.97	0.1802	0.01435	0.0515
88	3.00	0.0321	4.30	0.0459	0.0812	-
89	4.30	0.0459	6.17	0.0660	0.0596	-
90	5.40	0.0577	7.10	0.0758	0.0470	-
91	7.00	0.0747	8.05	0.0858	0.0390	-
92	2.00	0.0214	2.85	0.0304	0.1102	-
93	10.00	0.1062	10.62	0.1130	0.0298	-
94	15.00	0.1590	14.58	0.1546	0.0240	-
95	17.00	0.1805	17.02	0.1807	0.020	-
97	34.20	0.3590	32.50	0.3406	0.011	-
98	31.00	0.3242	30.60	0.3215	0.011	-

+ chromite crucible  
 x argon atmosphere  
 φ LiCl solutions in saturators.

TABLE 4c

Experimental results at 1700°C

Gas bubbled through metal

Run No.	Chromium charged		Final chromium		$\frac{P_{H_2O}}{P_{H_2}}$	%O <sub>2</sub>
	wt. %	N <sub>Cr</sub>	wt. %	N <sub>Cr</sub>		
55	0	0	1.96	0.0210	0.191	0.085
56	0	0	2.74	0.0293	0.145	-
57	2.91	0.0311	1.72	0.0190	0.194	-
58	4.00	0.0427	3.34	0.0357	0.156	0.105
59	2.00	0.0214	4.35	0.0464	0.105	0.0775
60	6.00	0.0642	5.81	0.0621	0.105	0.078
61	5.00	0.0533	5.73	0.0613	0.0756	0.051
62	9.00	0.0959	7.19	0.0767	0.0773	0.079
63	6.00	0.0642	7.26	0.0775	0.0567	-
64	10.00	0.1062	10.20	0.1085	0.0580	0.070
65	8.00	0.0853	9.58	0.1019	0.041	0.066
66	12.50	0.1329	11.91	0.1266	0.0403	0.081
67	12.50	0.1329	10.45	0.112	0.0413	-
68	9.50	0.1010	9.58	0.1019	0.030	-
69	14.00	0.1486	11.52	0.1226	0.0295	0.080
70	12.00	0.1276	11.38	0.1211	0.0227	-

TABLE 4c (contd.)

Run No.	Chromium charged		Final chromium		$\frac{P_{H_2O}}{P_{H_2}}$	%O <sub>2</sub>
	wt. %	N <sub>Cr</sub>	Wt. %	N <sub>Cr</sub>		
71	15.00	0.1590	13.71	0.1455	0.0169	-
72	20.00	0.2115	17.75	0.1882	0.0168	0.099
73	17.00	0.1805	14.78	0.1567	0.0232	0.104
76 <sup>φ</sup>	19.98	0.2113	19.87	0.2112	0.0140	0.095
77 <sup>φ</sup>	15.85	0.1682	16.46	0.1747	0.0140	0.092
80	25.00	0.2641	25.65	0.2715	0.0116	0.157

φ Li Cl solutions in saturators

DISCUSSION

## DISCUSSION

### (1) Phase Equilibria and Chromium Activity

Fig. 12 shows the relation between the corrected  $H_2O/H_2$  ratio and the chromium content of the melt. Initial and final chromium concentrations are plotted to show direction of movement towards equilibrium. In drawing the curve several points have been ignored. Most of these were preliminary results aimed at finding approximate equilibrium concentrations. Experiments were then repeated at the same oxygen potential to determine more accurately the equilibrium value.

In a few experiments (Runs 64 - 74) fine -200 mesh chromium powder was used to make up the iron-chromium alloy. Most of these showed apparent decreases in chromium content when increases were expected. This, as was found later, was due to the presence of large quantities of chromic oxide in the powder and so these results have also been rejected.

Some difficulty was encountered in locating the exact position of the curve at high chromium concentrations. The extrapolation of results obtained with distilled water in the saturators does not agree too well with those determined using saturated lithium chloride solutions. The results from the latter should be reliable as several runs were made to establish equilibrium concentrations. To overlap the  $\frac{P_{H_2O}}{P_{H_2}}$  ratios from lithium chloride

solutions, a few experiments were carried out using cooled distilled water in the saturators. These latter data seemed to agree with the extrapolation of earlier experiments suggesting that there may be a systematic error in results involving lithium chloride solutions. Gokcen and Chipman<sup>65</sup> have encountered certain discrepancies in their work concerning aluminium-oxygen equilibria, extrapolated values to 0% aluminium not agreeing with the data on the iron-oxygen system. For the work involving aluminium, lithium chloride solutions were used whereas distilled water has been used for several independent investigations of the iron-oxygen system. McLean<sup>47</sup> has also found anomalous effects which could be explained on the basis of a higher water vapour pressure of lithium chloride solutions. Thus, three sets of data all indicate a systematic error arising from the use of such solutions. The source of the error, if indeed there be one, is as yet unknown.

Fig. 12 is therefore drawn showing two curves above 12% Cr. - (a) the lower one treating lithium chloride results as correct, (b) treating above results as subject to a systematic error and using the extrapolated curve together with a few experimental points obtained from cooled distilled water experiments.

The curve is shown again in Fig. 13 together with the data of Chen and Chipman<sup>34</sup>. The data are in reasonable agreement up to about 10 mole % chromium. Indeed, in this range, the experimental scatter of results from the two investigations is sufficient to account for the differences shown. However, at

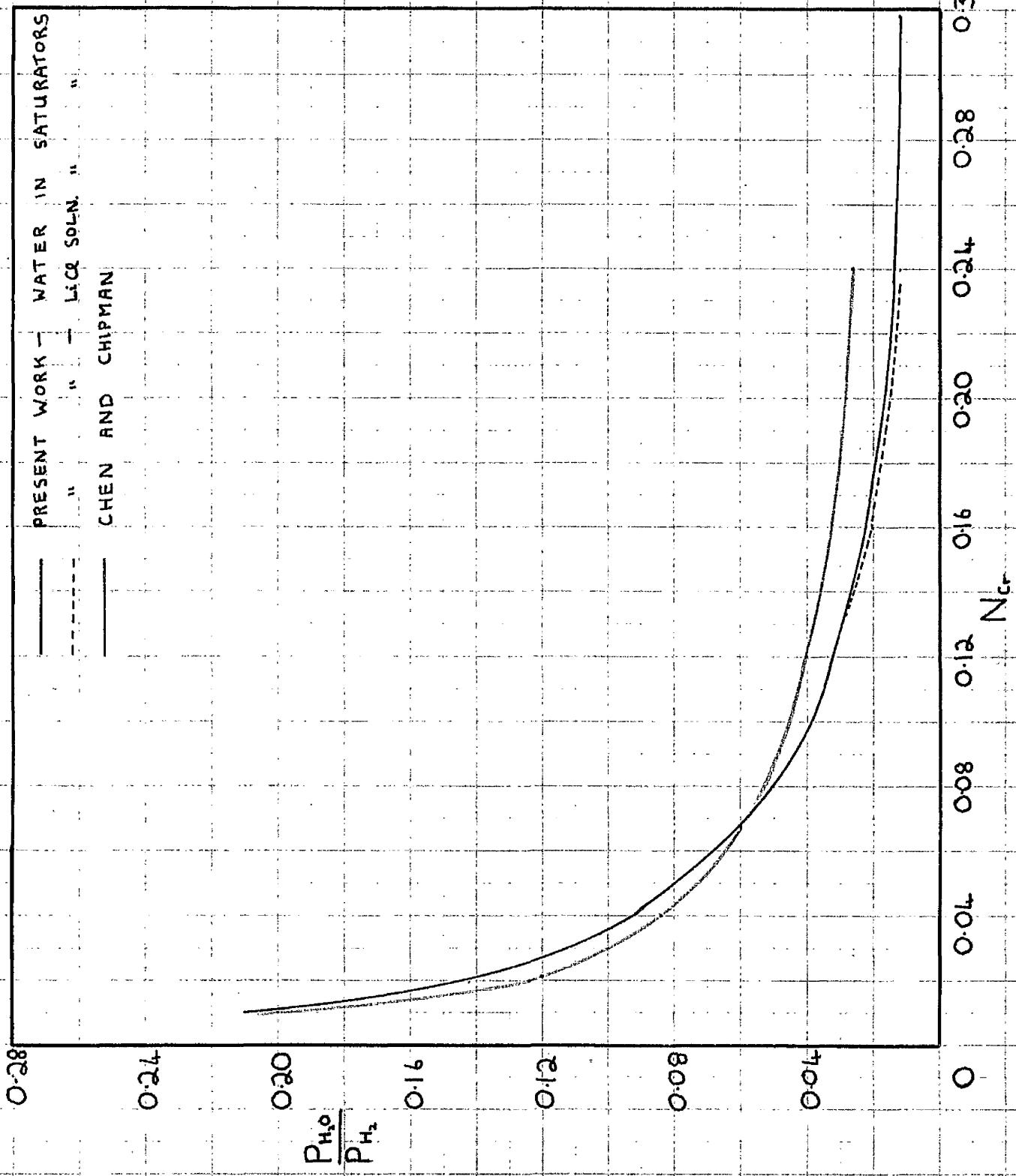


FIG. 13. EFFECT OF OXYGEN POTENTIAL ON THE CHROMIUM CONTENT OF THE MELT (1600°C)

higher chromium contents there is a considerable discrepancy between the two sets of data. As previously mentioned the apparatus used by Chen and Chipman seems prone to errors arising out of thermal diffusion in the gas mixture. If this be the case, the relative error will be greater as the  $H_2O/H_2$  ratio decreases. Diffusion of water vapour away from the reaction zone would give rise to increased chromium contents. It should also be pointed out that between 11 and 22 atomic per cent chromium, Chen and Chipman's curve depends on only three experimental results. Two of these showed virtually no change in chromium content during the experiments and one questions their validity as equilibrium values. Small changes in composition at high chromium contents were also found in the present work. The following calculations shows the approximate change in composition one could reasonably expect in two hours using a gas mixture with a low partial pressure of oxygen.

e.g. Flow rate 150 ml/min

Let  $p_{H_2O} = 10$  mm

Duration of experiment 2 hours

Atmospheric pressure = 760mm

Total  $H_2O$  passed into the furnace will be

$$\frac{150 \times 120 \times 10}{760 \times 22400} \quad \text{g moles}$$

$$= \frac{16 \times 18000}{22400} \times \frac{10}{760} \times \frac{152}{48} \quad \text{g } Cr_2O_3$$

$$\text{i.e.} \quad 16 \times \frac{18000}{22400} \times \frac{10}{760} \times \frac{152}{48} \times \frac{104}{152} \quad \text{g Cr}$$

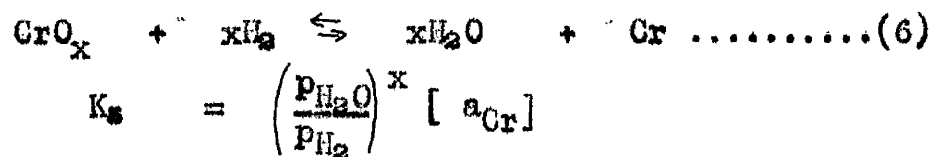
$$= 0.366 \text{ g chromium}$$



This is a change of 1.25 weight % chromium in a 30 g charge. Not all the oxygen will be available for oxidation of chromium. If, for a given chromium content the equilibrium  $\frac{P_{H_2O}}{P_{H_2}}$  corresponds to  $P_{H_2O} = 9$  mm, while that actually being used is 10 mm, only one tenth of the oxygen will be available for oxidation. In this case only 0.125% chromium would be oxidised in a 2 hour experiment. This is considered inadequate and so in the present work, the time was increased considerably when using low water vapour pressures so that a more significant change in composition could be obtained.

Chen and Chipman used double the charge, double the flow rate and experiments usually lasted between one and two hours. A small change in composition would be expected and so several heats should have been made to find each equilibrium point. As it was, at high chromium concentrations only three results were quoted and so it is extremely doubtful if these are equilibrium values.

Little can be learned from Figs. 12 and 13. It is more informative to plot the results on a logarithmic basis. If the oxide phase in equilibrium with the melt has a composition  $CrO_x$



$$\log K_s = \log a_{Cr} + x \log \frac{P_{H_2O}}{P_{H_2}}$$

If Fe-Cr alloys form ideal solutions, a plot of  $\log \frac{P_{H_2O}}{P_{H_2}}$  against

$\log N_{Cr}$  should be a curve having a slope  $-\frac{1}{x}$ , thus providing useful information about the oxide phase in equilibrium with iron-chromium-oxygen melts at different oxygen potentials. Such a graph is shown in Fig. 14. Points are again plotted showing initial and final compositions of the melts, preliminary results being omitted as irrelevant at this stage. There is, again, a discrepancy between the distilled water and lithium chloride solution results.

In Fig. 15, the curve is plotted together with those obtained by Chen and Chipman<sup>24</sup>, Turkdogan<sup>30</sup> and Linczinskii and Samarin<sup>29</sup>. The present results are in reasonable agreement with those of Chen and Chipman but not with those of other workers.

The results of Linczinskii and Samarin are displaced from those of other workers so much that one suspects the reliability of the data. They passed  $H_2O/H_2$  mixtures over the melt, held presumably in an alumina crucible, until an oxide phase appeared. Gas-metal equilibrium was then assumed to have been reached. When the oxide appeared the metal would be saturated with oxygen at the particular chromium level. To achieve gas-metal equilibrium it may well have been necessary to oxidise considerable amounts of chromium from the melt whereas this was not done. The results are so high they would appear to be non-equilibrium values. The same explanation is offered to account for the change in sign of the slope of the curve which has been shown earlier to be impossible on theoretical grounds. If the

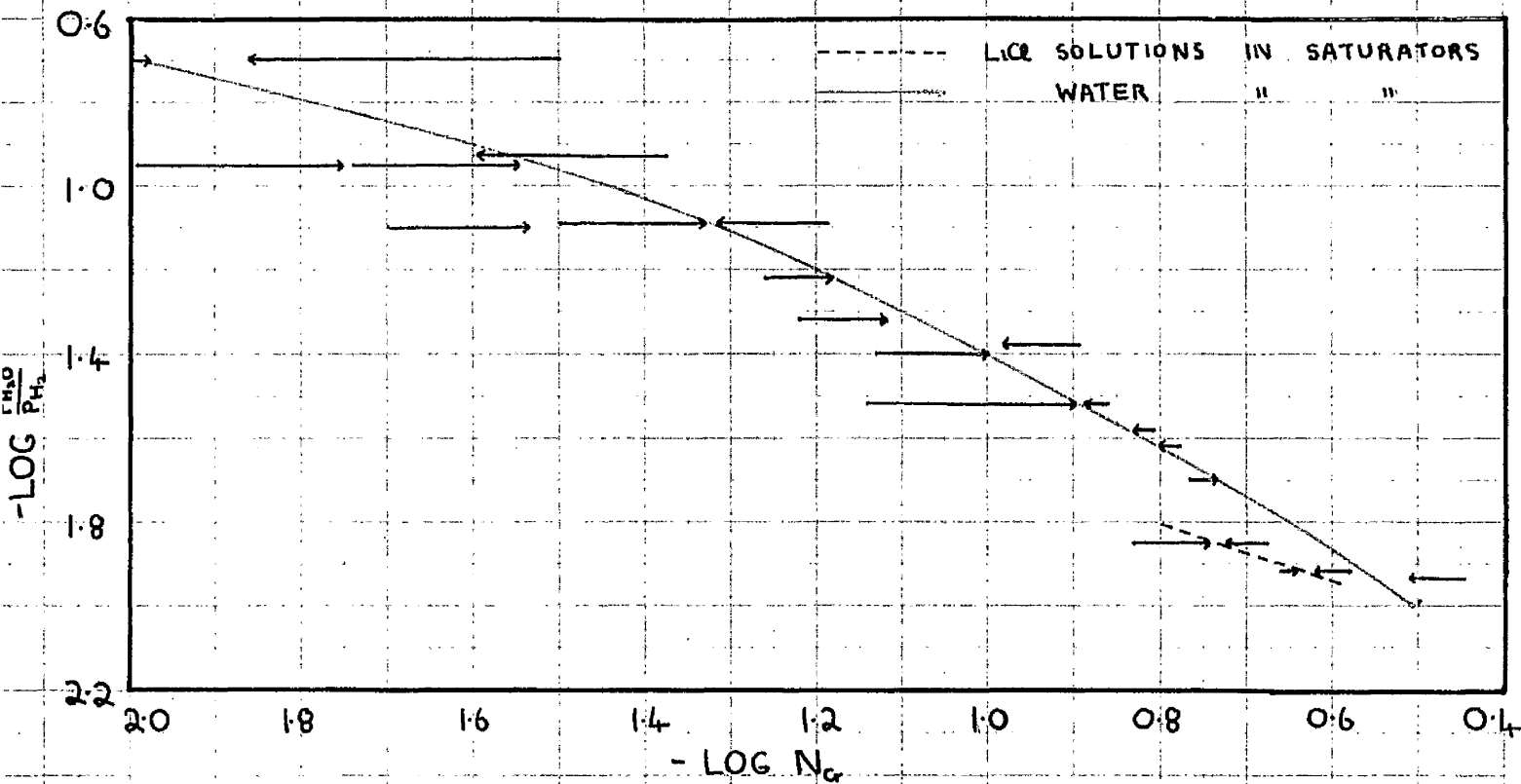


FIG. 14. ESTIMATION OF THE  $\text{LOG} \frac{P_{H_2O}}{P_{H_2}} - \text{LOG} N_G$  CURVE SHOWING RELEVANT EXPERIMENTAL DATA

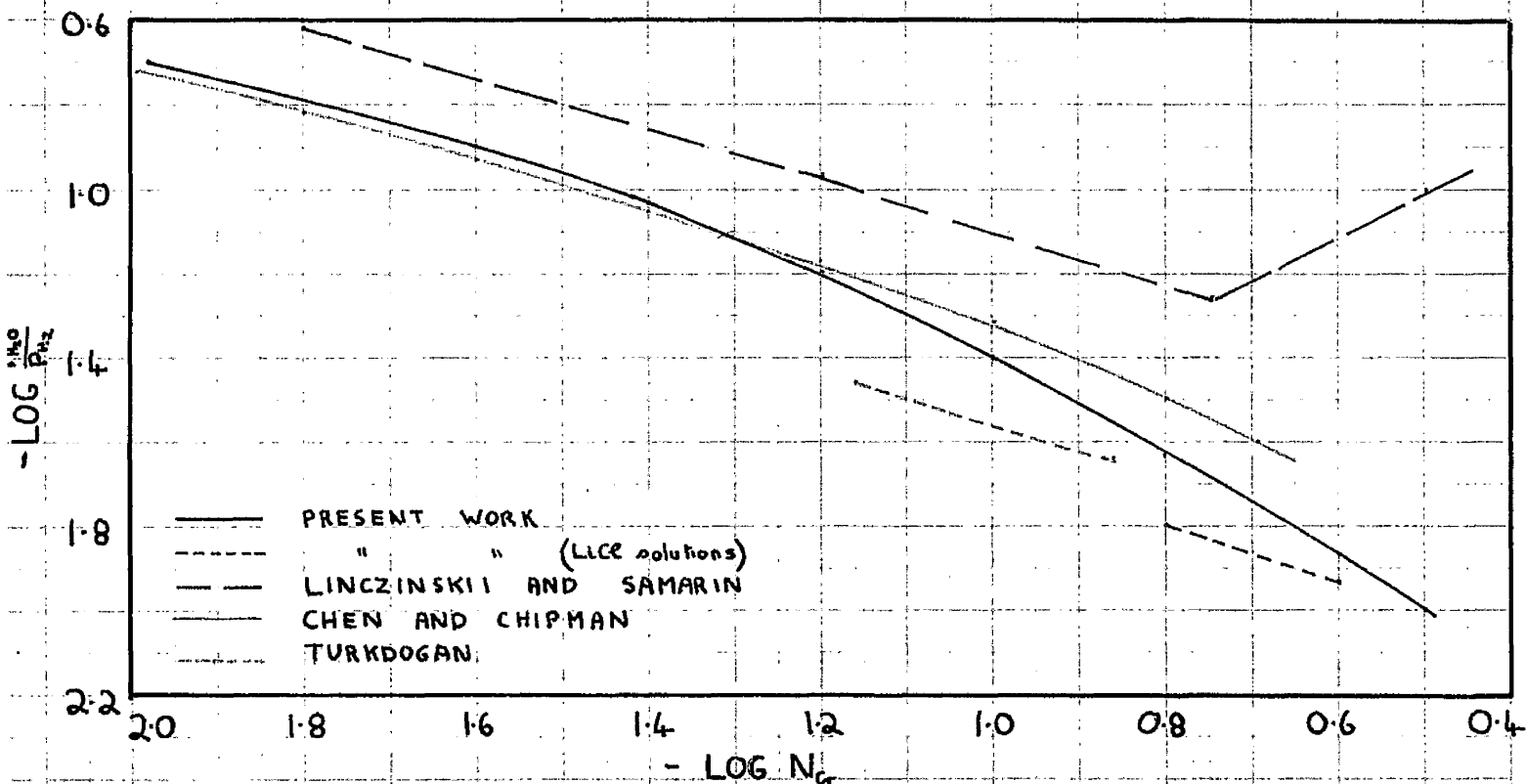


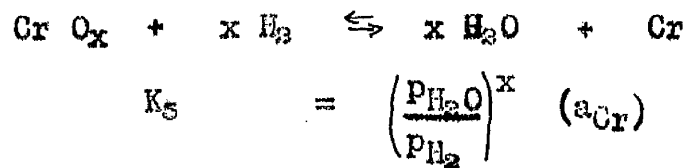
FIG. 15.  $\text{LOG} \frac{P_{H_2O}}{P_{H_2}} - \text{LOG} N_G$  EQUILIBRIA (AVAILABLE DATA)

experiments had been over longer periods, the chromium contents would probably have decreased to such an extent that no change in sign of the slope (Fig. 15) would have been observed. Therefore, in concluding gas-metal studies these results have been ignored.

Turkdogan's <sup>30</sup> data covers a very restricted composition range. Experiments were carried out in alumina crucibles and so it is only possible to achieve gas-metal-oxide equilibrium by oxidising chromium out of the melt, i.e. always start with more chromium than is present at equilibrium. Sometimes an attempt was made to approach equilibrium in the opposite direction by admitting air to form a slag, then reducing this with the gas mixture. This would seem rather pointless. Sometimes all the slag was reduced and so the melt would probably be lower in chromium since no more was available. Some of the results, where slag remained after two hours reduction by the gas, may be reliable. Even when there was some slag it would probably contain some alumina, thus reducing the activity of chromic oxide which was assumed unity. Due to the shortage of experimental data and the restricted composition range studied, Turkdogan's results are not discussed in very great detail.

#### Interpretation of Data

Equilibrium between chromium in iron and its oxides can be conveniently expressed as follows:-



$$\log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \propto -\frac{1}{x} \log (a_{\text{Cr}})$$

Such a plot would only be one or more straight lines if the oxides of chromium are stoichiometric and iron-chromium solutions are ideal. Both these assumptions were thought to be valid at the time of the previous investigations and so results have always been interpreted as a series of straight lines. Hilty Forgens and Folkman<sup>28</sup> have examined inclusions in chrome steels and have found that the composition of the oxides can change gradually. This would result in a continuous change in gradient of the  $\log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$  v  $\log (a_{\text{Cr}})$  plot.

Previous work has always assumed that  $\log \% \text{Cr}$  was equivalent to  $\log a_{\text{Cr}}$ . (The error involved in using percentages rather than mole fractions is quite small as chromium and iron have similar atomic weights). The recent work by Wada Kawai and Saito<sup>28</sup> has shown that, in the range 5 to 40 wt per cent chromium, the activity coefficient varies by a factor of about four. This would hardly confirm the theories that iron and chromium form ideal solutions.

Thus the variation of chromium concentration with the  $\frac{\text{H}_2\text{O}}{\text{H}_2}$  ratio, shown in Figs. 14 and 15, can arise from two causes:-

- (a) gradual variation of Cr/O ratio in the oxide phase;  
 (b) deviations from ideality in Fe-Cr liquid solutions.

The two possibilities are discussed separately as follows:-

- (a) Variations in Cr/O ratio in the oxide phase,  $\gamma_{Cr}$  assumed unity.

In the low chromium range, 0  $\rightarrow$  3% chromium, the slope of Fig. 14 is approximately  $-\frac{1}{2}$ , indicating the following equilibrium:-



$$K_3 = \frac{\left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}\right)^4 (N_{\text{Cr}})^2}{1}$$

$$\log K_3 = 4 \log \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}\right) + 2 \log N_{\text{Cr}}$$

$$\therefore \log \left(\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}\right) \propto -\frac{1}{2} \log N_{\text{Cr}}$$

In the chromium range, crucible crusts all gave brown streaks, additional evidence that equilibrium with chromite is achieved.

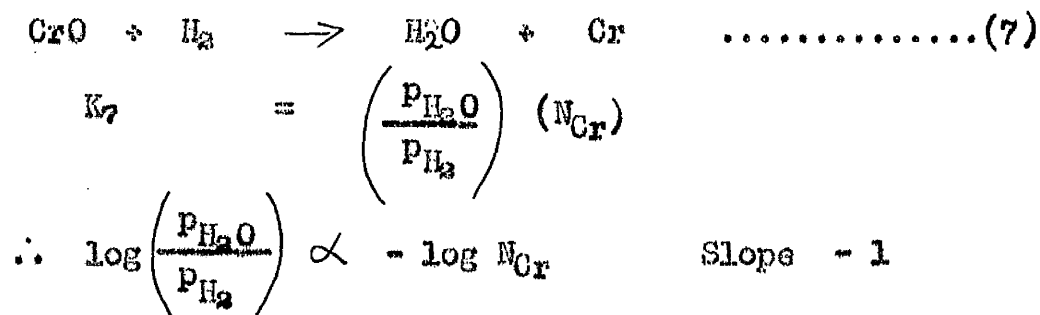
The data are in fairly good agreement with those of Chen and Chipman<sup>24</sup>.

These authors considered that equilibrium with chromite extended as far as 5.5% chromium. After a publication by Hilty et alia<sup>33</sup>,

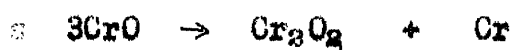
Chipman<sup>35</sup> reviewed the results and decided that equilibrium with chromite only occurred in the range 0  $\rightarrow$  3% chromium. The plot,  $\log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$  v  $\log \% \text{Cr}$ , showed a continuous change in gradient in the range 3  $\rightarrow$  9% Cr indicating replacement of iron in chromite by chromium.

The present results show a fairly rapid change in gradient in the range 3 - 7% chromium which could be explained as a continuous change in composition of the oxide phase in

equilibrium with Fe-Cr-O melts. Above 7% chromium, and over the remainder of the range investigated, the gradient is approximately unity. This could be interpreted as equilibrium with chromous oxide.



Equilibrium with chromous oxide may be possible. Chromous oxide does not exist at low temperatures but there is indirect evidence<sup>36,37,39</sup> that it exists at high temperatures. If so, it must disproportionate on cooling to form chromic oxide and chromium metal.



The streak test is therefore of no use in distinguishing chromic and chromous oxide equilibrium. Both would give the green streak.

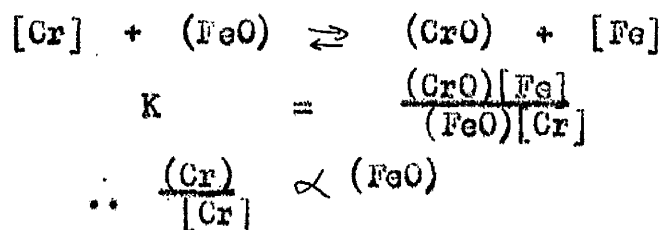
If the data involving lithium chloride solutions are reliable the gradient is less than -1 at high chromium concentrations (16 - 25% Cr). The existence of an oxide having a formula  $\text{Cr}_{1.2}\text{O}$  seems unlikely and one again queries the reliability of these data.

In the range 9 - 21% Cr, Chen and Chipman's results are best served by a line having an approximate slope of 0.9. In the original paper the slope was drawn as  $-\frac{2}{3}$  corresponding to equilibrium with chromic oxide but the line did not cover the experimental data very well. When the paper was reviewed later,

it was considered that the slope was steeper than that corresponding to  $\text{Cr}_3\text{O}_4$  but hardly steep enough for  $\text{CrO}$ .

Turkdogan's <sup>30</sup> results indicate equilibrium with chromic oxide in the range 6 - 12% chromium. For a given  $\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$  ratio, the results are lower in chromium than the other data. This may well be due to equilibrium with a solid solution of chromic oxide and alumina <sup>53</sup>. If the activity of chromic oxide was less than one there would be a corresponding decrease in chromium content for a given oxygen potential in the gaseous phase.

The existence of sub-oxides, particularly silicon monoxide, has been a subject of much discussion in the past <sup>54,55</sup>. There is no direct evidence that a separate compound  $\text{CrO}$  exists. Zapffe <sup>30</sup> has observed blue-black slags over high chromium melts and considers this to be due to the presence of  $\text{CrO}$ . Tesche <sup>30</sup> has studied chromium distribution between metal and slag at different oxidation levels. The slag metal reaction considered relevant was



For this relationship to hold

- (a) Chromium must behave ideally in liquid iron
- (b) Chromous oxide and ferrous oxide must behave ideally in a slag containing appreciable amounts of lime and silica.

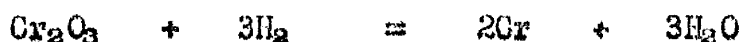


The results of the works data are shown in Fig. 16 where the chromium distribution ratio is plotted against the FeO content of the slag. An approximate straight line is obtained for FeO contents up to 35%. After that a departure from linearity is observed but the results were presented as evidence for the existence of chromous oxide in slags. Other workers (Fig. 16) have not found this linear relationship and so the evidence is inconclusive. Kramers and Smith<sup>34</sup> have examined several metal-oxygen systems including the Cr - O system, and found no evidence for a CrO phase. Indeed the greatest departure from stoichiometry corresponded to a formula  $\text{Cr}_2\text{O}_{2.8}$ .

From Hilty's<sup>37</sup> data on the decarburisation of chrome steels, chromous oxide ought to become more stable as the temperature is lowered. Neither Boericke<sup>56</sup> who studied the equilibrium

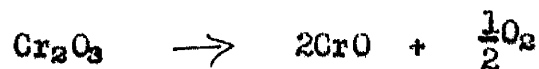


up to 1400°C, nor Okada, Kokubo, and Matsuo<sup>57</sup> who investigated the equilibrium



up to 1310°C, could find any evidence of chromous oxide.

There is only indirect evidence of existence of chromous oxide, no one claiming to have isolated the substance and examined its properties. If chromous oxide is a high temperature oxide phase, one might expect chromic oxide crucibles to have lost oxygen during an experiment



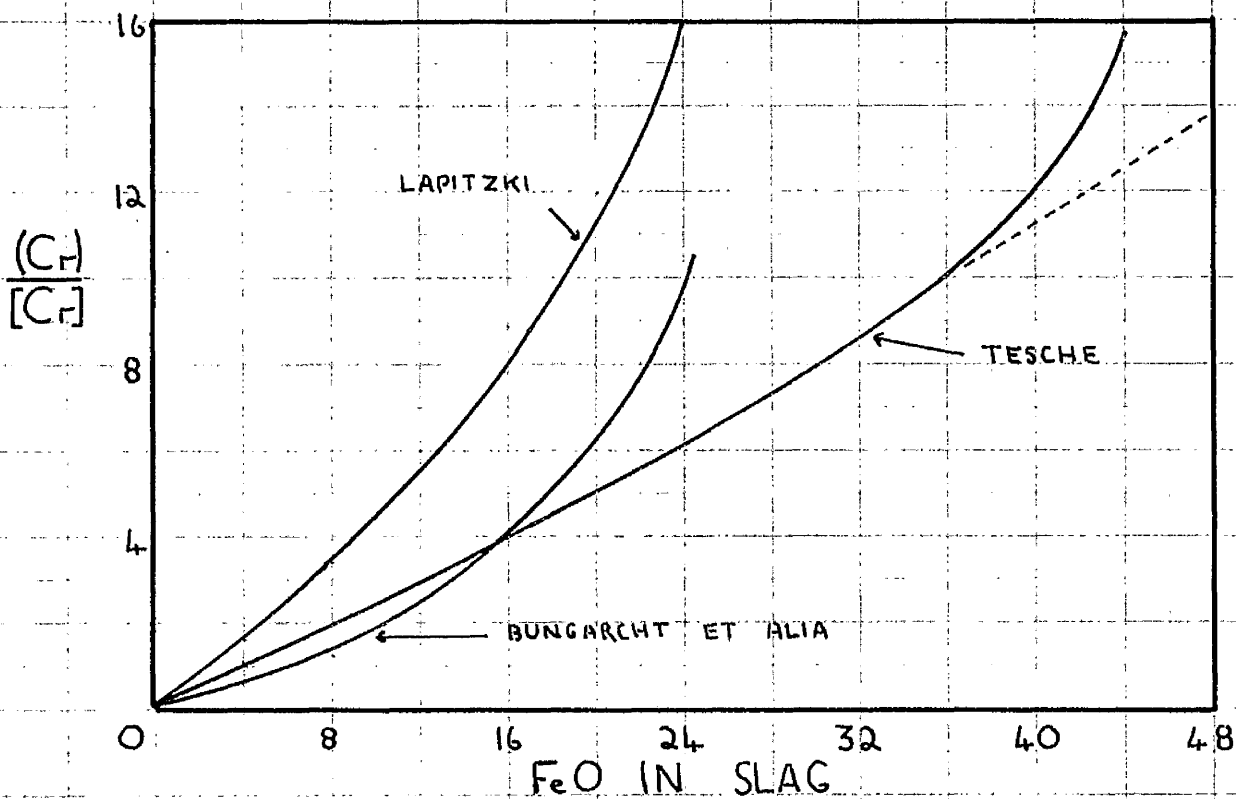


FIG. 16. EFFECT OF FeO IN SLAG ON THE CHROMIUM DISTRIBUTION RATIO

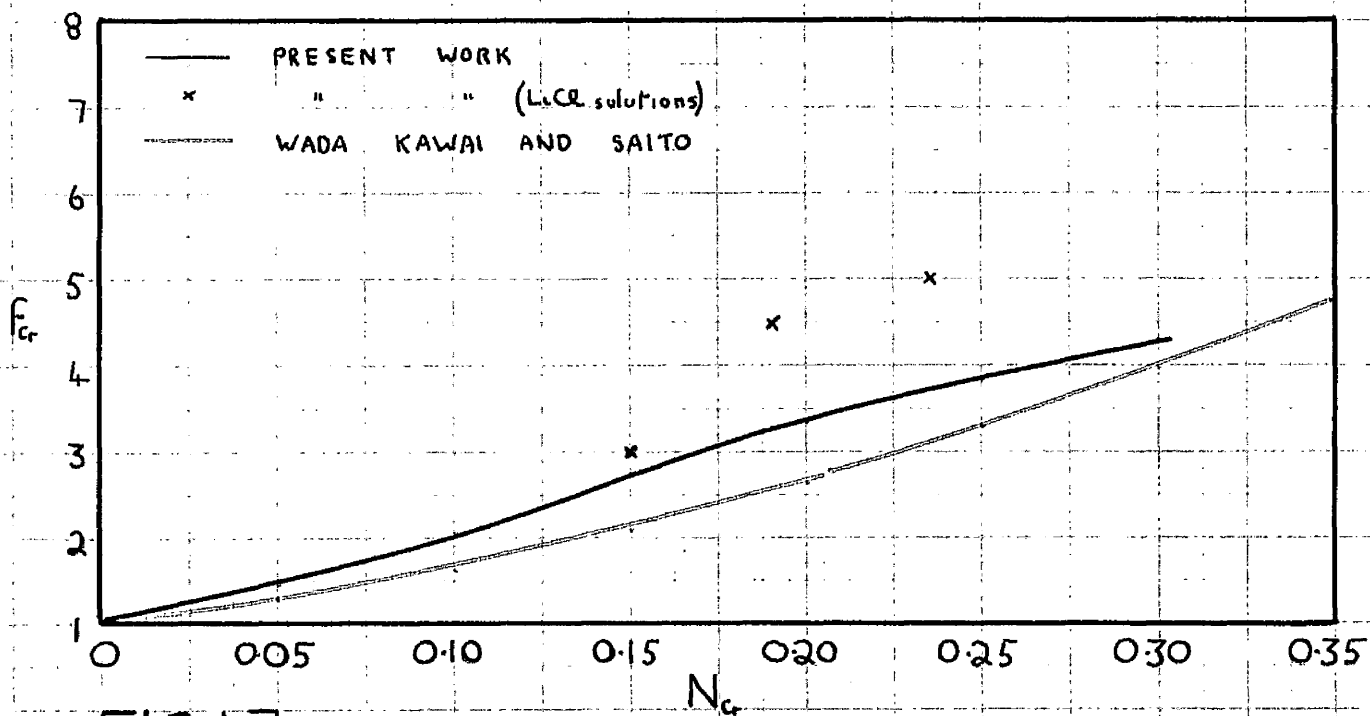


FIG. 17. ACTIVITY COEFFICIENTS OF CHROMIUM IN IRON (INF. DIL'N. SCALE)

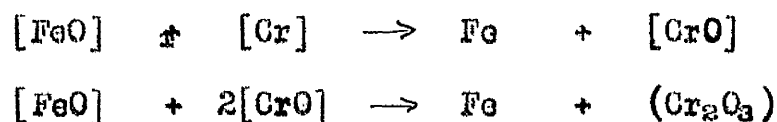
On cooling



The chromic oxide crucibles used in the present work have been examined metallographically after experiments and no evidence for the presence of chromium metal obtained. A pellet was made up containing chromium powder and chromic oxide in the proportions corresponding to  $3\text{CrO}$ . The powders were mixed, compressed, and held for 4 hours in argon on a molybdenum plate at  $1650^\circ\text{C}$ . On cooling the pellet was sectioned and examined. It contained islands of chromium metal and some finely dispersed chromium in chromic oxide. The non-uniformity of structure casts doubt on the existence of one homogeneous phase at high temperatures. The existence of a volatile  $\text{CrO}$  phase also appears untenable. Hydrogen was passed over heated chromic oxide for 3 hours, then through a condenser. No condensate whatever was obtained.

However, the thermodynamic data obtained by Chen and Chipman<sup>24</sup> and the author are such that the evidence for  $\text{Cr}-\text{O}-\text{CrO}$  equilibrium cannot be completely dismissed even though there is no definite evidence for the existence of a separate chromous oxide phase. From the present results chromous oxide could be the oxide phase in the range 9-22% Cr. From Chen and Chipman's data the phase is  $\text{Cr}_6\text{O}$  in this range.

Supporting evidence for the existence of CrO is that above 7% Cr the oxygen content increases with the chromium content. (Fig. 22) This must be due to the association of oxygen with chromium in solution in iron. Some investigators have postulated that CrO may be a soluble oxide and this could be used to explain the increased solubility of oxygen as the chromium content is increased as shown:-



If the activity of  $\text{Cr}_2\text{O}_3$  is unity

$$[\text{CrO}] = \frac{K'}{(\text{FeO})^{\frac{1}{2}}}$$

Thus as steel is deoxidised with respect to FeO its oxygen content is increased with respect to CrO. The corollary of this statement is that as the chromium content increases so must also the [CrO] content.

To sum up, the data presented in Fig. 14 could be explained by assuming that equilibrium in melts containing more than 7% chromium is between  $\text{CrO} - \text{Cr} - \frac{\text{H}_2\text{O}}{\text{H}_2}$  rather than  $\text{Cr}_2\text{O}_3 - \text{Cr} - \text{H}_2\text{O}/\text{H}_2$ . Increasing oxygen concentration as the chromium concentration rises might be explained on the basis of a soluble oxide CrO. This does not in any way prove the existence of such a compound.

Table 5 lists the free energy of formation of the different oxides of chromium as found in the present work. The results of previous investigations are shown for comparison.

The values are all given at 1600°C, the pure substance being taken as standard state.

TABLE 5

<u>Oxide</u>	<u>Author</u>	<u><math>-\Delta G_{1600}^f</math> cal</u>
FeO.Cr <sub>2</sub> O <sub>3</sub>	Chen and Chipman <sup>24</sup>	196,000
	Present Work	194,500
	Turkdogan <sup>30</sup>	208,700
	Linczinski and Samarin <sup>29</sup>	188,400
	Boerliche and Bangert <sup>31</sup>	199,000
Cr <sub>2</sub> O <sub>3</sub>	Chen and Chipman <sup>24</sup>	152,250
	Present Work	-
	Turkdogan <sup>30</sup>	158,500
	Linczinski and Samarin <sup>29</sup>	146,250
	Thermal data <sup>32</sup>	155,700
Cr <sub>3</sub> O <sub>4</sub>	Hilty <sup>33</sup>	205,500
CrO	Chipman <sup>35</sup>	51,500
CrO	Present Work	52,400

(b) The effects of possible variations in chromium activity

Despite inferences by several investigators concerning the existence of an oxide CrO it would be much more satisfactory if there were concrete evidence for the existence of the compound. Chromic oxide crucibles were used for most of the present experiments. Crusts were always formed between metal and crucible. At low chromium concentrations i.e. below 3% Cr, these crusts gave brown streaks and, as mentioned earlier, were shown to contain chromite. The slope of the curve (Fig. 14) and experimental observations both indicate clearly that chromite equilibrium is established even

though chromic oxide crucibles were used. The few experiments involving chromite crucibles merely confirmed this to be the case.

In the range 3 to 6% the streak test was inconclusive. Above that, in all cases the crusts gave green streaks indicating the presence of chromic oxide. As chromic oxide crucibles were used and the crusts were shown to contain  $\text{Cr}_2\text{O}_3$ , equilibrium between  $\text{Cr-O-Cr}_2\text{O}_3$  should be attained. If this is in fact the case the activity of chromium can be calculated from the free energy data available.

From the experimental curve (Fig. 13) the activity of chromium was calculated as follows:-

Data used:

(i) Chromite (Boerliche and Bangert<sup>31</sup>)



$$\Delta G_{1173-1700}^{\circ} = -131,600 + 24.2T \text{ cal (} \pm 3 \text{ k cal)}$$

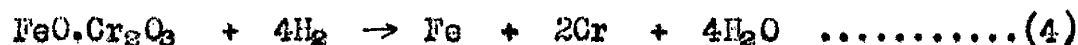
(ii) Chromic oxide (Elliot and Gleiser<sup>32</sup>)

<u>T°K</u>	<u><math>\Delta G_f^{\circ}</math> (cal)</u>
1800	-160250 ( $\pm$ 500)
1900	-154100 ( $\pm$ 500)

(iii) Water vapour<sup>32</sup>

<u>T°K</u>	<u><math>\Delta G_f^{\circ}</math> (cal)</u>
1800	-35110
1900	-33710

From these data, at 1600°C,  $\Delta G$  for the equilibrium between  $\text{FeO} \cdot \text{Cr}_2\text{O}_3$ , Cr,  $\text{H}_2$  and  $\text{H}_2\text{O}$  was calculated



$$\Delta G^\circ = 62535 \text{ cal}$$

$$\log K_3 = \frac{-\Delta G}{R T}$$

$$= -7.298$$

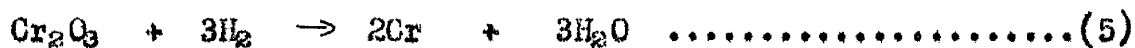
$$K_3 = \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^4 (\text{Fe}) (a_{\text{Cr}})^2 = 5.035 \times 10^{-8}$$

The figures relate to the pure substances. From the equilibrium constant the activity of chromium can be calculated and the results are shown in Table 6.

TABLE 6

<u>Wt % Cr</u>	<u><math>N_{\text{Cr}}</math></u>	$\frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$	<u><math>a_{\text{Cr}}</math></u>	<u><math>\gamma_{\text{Cr}}</math></u>
1.00	0.0106	0.206	0.00564	0.532
2.94	0.0310	0.110	0.0185	0.606

In the range 5 - 30% Cr the activity was calculated on the basis of equilibrium with chromic oxide.



at 1600°C  $\Delta G = 53,460 \text{ cal } (\pm 500)$

From this  $\log K_4 = -6.238$

$$\therefore K_4 = \left( \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} \right)^3 (a_{\text{Cr}})^2 = 5.78 \times 10^{-7}$$

The figures given in Table 7 refer to pure solid chromic oxide and chromium as the standard state.

TABLE 7

<u>Wt. % Cr</u>	<u>N<sub>Cr</sub></u>	$\frac{P_{H_2O}}{P_{H_2}}$	<u><math>\Delta_{Cr}</math></u>	<u><math>\gamma_{Cr}</math></u>
5	0.0533	0.0735	0.03814( $\pm$ 0.002)	0.716 ( $\pm$ 0.035)
6	0.0642	0.062	0.0492	0.765
7	0.0747	0.053	0.0623	0.834
8	0.0853	0.046	0.0770	0.906
10	0.1062	0.037	0.106	1.00
14	0.1486	0.025	0.192	1.29
17.7	0.1875	0.019	0.291	1.55
30.5	0.320	0.011	0.660	2.04
+ (14.0	0.1486	0.023	0.218	1.47
{ 17.7	0.1875	0.015	0.414	2.20
{ 22.6	0.2364	0.012	0.578	2.44

+ LiCl results

The possible errors due to the quoted uncertainties in free energy data are also shown. The error in the free energy of formation of chromic oxide may be considerably greater than the uncertainty given in Elliott and Gleiser. The free energy of formation of silica has been revised recently by 6000 calories. In view of this, perhaps  $\pm$  500 cal is an optimistic estimate of the accuracy of data for chromic oxide. If, indeed, the error were



more like  $\pm 5000$  cal, this would have a considerable effect on the level of the activity as seen below.

$$\text{At } N_{\text{Cr}} = .0533 \quad \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = .0735$$



(a) Taking  $\Delta G = 5$  k cal

$$K'_4 = 2.82 \times 10^{-6} = (.0735)^3 (a_{\text{Cr}})^2$$

$$a_{\text{Cr}} = .0843$$

$$\gamma_{\text{Cr}} = 1.58$$

(b) Taking  $\Delta G + 5$  k cal

$$K'_4 = 1.514 \times 10^{-7}$$

$$a_{\text{Cr}} = .0195$$

$$\gamma_{\text{Cr}} = .366$$

$$\Delta G = 5 \text{ k cal} \quad \gamma_{\text{Cr}} = 1.58$$

$$\Delta G_{\text{quoted}} \quad \gamma_{\text{Cr}} = .716$$

$$\Delta G + 5 \text{ k cal} \quad \gamma_{\text{Cr}} = .366$$

It can be seen that an error of  $\pm 5$  k cal can have a very pronounced effect on the level of the activity coefficients.

The activities all refer to pure solid chromium as the standard state. These were converted to activities relative to pure liquid chromium.

$$\text{For chromium } \Delta H_f = 5000 \text{ cal} \quad (\text{Kelley})^{5B}$$

$$T_m = 2176^\circ\text{K}$$

$$\log a_L = \frac{-\Delta H_f (T_m - T)}{4.575 T_m} + \log a_s$$

where  $a_L$  is activity of chromium relative to pure liquid

$a_s$  is activity of chromium relative to pure solid

$$\text{At } N_{Cr} = 0.0533$$

$$\log a_L = \frac{-5000 \times 303}{4.575 \times 1873 \times 2176} + \log 0.03814$$

$$\log a_L = -1.5006$$

$$a_L = 0.0316$$

Other results were calculated as above and are given in Table 8.

<u>Wt. % Cr</u>	<u><math>N_{Cr}</math></u>	<u>TABLE 8</u>		
		<u><math>a_{Cr}</math></u>	<u><math>\gamma_{Cr}(L)</math></u>	<u><math>f_{Cr}</math> (inf. diln)</u>
1.00	0.0106	0.00468	0.446	1.10
2.94	0.0310	0.0153	0.493	1.22
5.00	0.0533	0.0316	0.590	1.50
6.00	0.0642	0.0408	0.635	1.60
7.00	0.0747	0.0517	0.690	1.73
8.00	0.0853	0.0639	0.750	1.88
10.00	0.1062	0.0879	0.828	2.08
14.00	0.1486	0.159	1.065	2.66
17.70	0.1875	0.241	1.29	3.21
30.55	0.3200	0.547	1.71	4.27
+ (14.00	0.1486	0.181	1.21	3.01
(17.70	0.1875	0.343	1.83	4.67
(22.60	0.2364	0.490	2.03	5.07

+LiCl results

Because they are similar chemically, iron and chromium have been considered to form ideal solutions. Considering the phase diagram (Fig. 5) the liquid and solid systems cannot both be ideal. The above table indicates quite a large variation in the activity coefficient of chromium, so great, in fact, that one might suspect the reliability. If this were done, curvature of the line shown in Fig. 14 would be due to variable oxide composition, not variations in chromium activity. It is striking to note, however, that the order of variation in  $\gamma_{Cr}$  shown in Table 8 is approximately the same as that obtained by Wada Kawai and Saito<sup>23</sup> whose results were presented on the infinite dilution scale. To enable a direct comparison to be made, the present activity coefficients have been converted to this scale and are given in Table 8. The conversion factor, to obtain Henry's Law activity coefficients, was obtained from Fig. 20. The two sets of data are in excellent agreement showing much the same order of variation in activity coefficient. (Fig. 17).

It would have been more useful if the results of Wada et alia had been presented relative to pure chromium as the standard state. Their data will now be re-examined in an attempt to ascertain the level of the activity coefficients based on Raoult's Law standard state.

Wada Kawai and Saito<sup>23</sup> defined the activity of

chromium as

$$a_{\text{Cr}} = N_{\text{Cr}} \gamma_{\text{Cr}} = \frac{C_t}{C_t^0}$$

where  $C_t$  was relative wt. of chromium condensed from alloy at 1630°C.

$C_t^0$  " " " " " " " " chromium " "

$$\log \gamma_{\text{Cr}} = \log \frac{C_t}{N} - \log C_t^0 = \frac{W}{4.575} (1 - N_{\text{Cr}})^2$$

$\log \frac{C_t}{N}$  was found to vary linearly with  $(1 - N_{\text{Cr}})^2$ .

To obtain  $\gamma_{\text{Cr}}$  the results must be extrapolated back to  $N_{\text{Cr}} = 1$

to obtain a value of  $C_t^0$  which corresponds to the vapour pressure

of pure chromium. The experimental data only covers the range

$N_{\text{Cr}} = 0$  to  $N_{\text{Cr}} = 0.4$ . The extrapolation is shown in Fig. 18,

where  $\log C_t^0 = 2.5$ . The activity coefficients can be calculated

from the previous equation and are listed in Table 9.

TABLE 9

<u><math>N_{\text{Cr}}</math></u>	<u><math>\log \frac{C_t}{N}</math></u>	<u><math>\log \frac{C_t}{N} - \log C_t^0</math></u>	<u><math>\gamma_{\text{Cr}}</math></u>
• 05	1.44	- 1.06	• 09
• 10	1.57	- 0.93	• 12
• 15	1.66	- 0.84	• 145
• 20	1.76	- 0.74	• 18
• 25	1.85	- 0.65	• 20
• 30	1.92	- 0.58	• 26
• 40	2.08	- 0.42	• 38

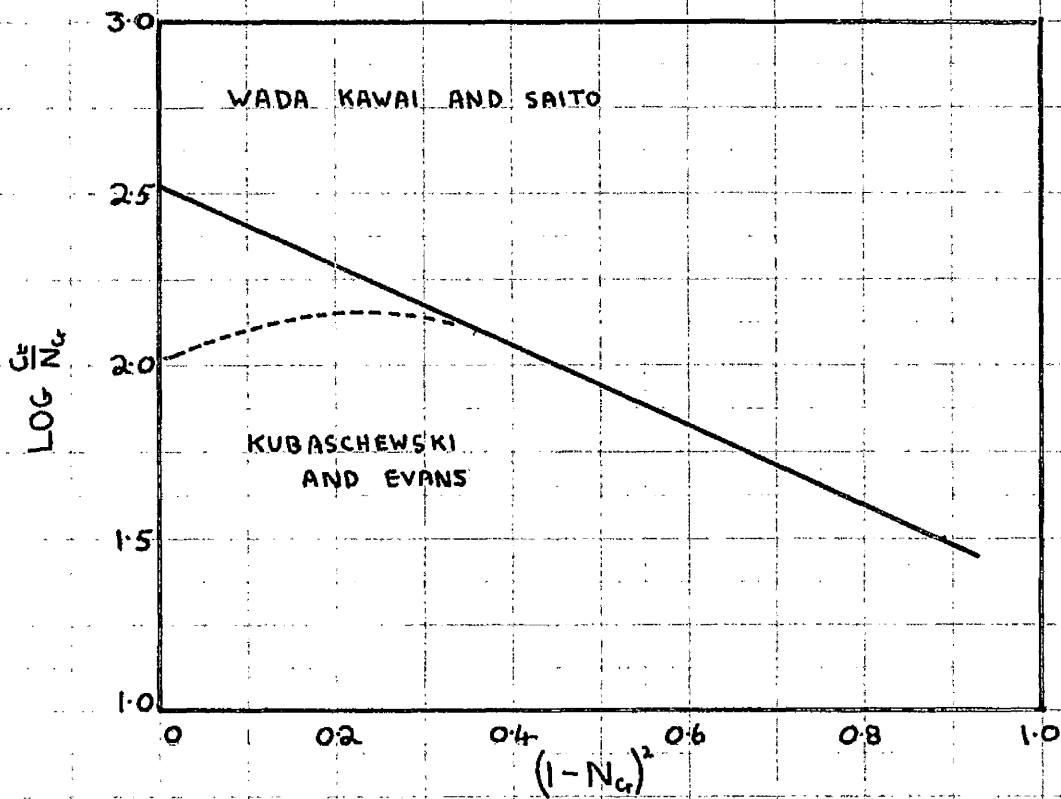


FIG. 18. EXTRAPOLATION TO FIND LOG  $\frac{C_{Cr}^0}{N_{Cr}}$

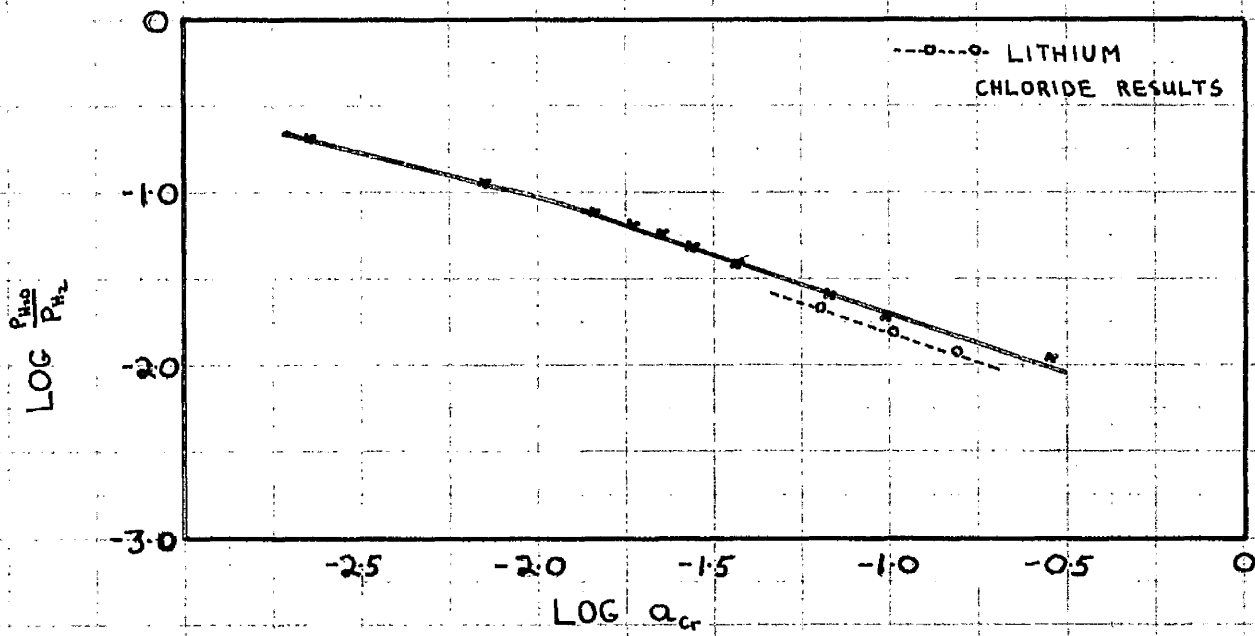


FIG. 19. RELATION BETWEEN LOG  $\frac{P_{H_2O}}{P_{H_2}}$  AND LOG  $a_{Cr}$

This also is a considerable variation in  $\gamma_{Cr}$ . The results of the experimental data seem consistent and so the variation should be reliable although one might query the level of the results calculated above. The extrapolated value of  $\log C_t^0$  may not be justified and should be considered further.

The equation used can be written as

$$\log \frac{C_t}{N} = k \log \gamma_{Cr} = \frac{W}{4.575} (1 - N_{Cr})^2$$

Now  $\frac{\log \gamma_i}{(1 - N_i)^2}$  is known as the  $\alpha$  function and its variation with composition has been studied in several different metallic systems.

Darken and Gurry<sup>59</sup> have shown that in the thallium-tin system the  $\alpha$  function is essentially constant over the entire range  $N_{Te} = 0$  to  $N_{Te} = 1$ . Many other systems are then quoted showing that the  $\alpha$  function cannot be regarded as a constant. Lumsden<sup>60</sup> theoretically infers that one would not really expect it to be constant. The extrapolation for  $\log C_t^0$  from  $N_{Cr} = .4$  to  $N_{Cr} = .1$  would only be a straight line if the  $\alpha$  function were constant and this is probably not the case.

The value of  $C_t^0$  can be converted into a vapour pressure and compared with a value quoted in Kybaschewski and Evans<sup>61</sup>. The equation for the rate of weight loss from a heated surface is given by

$$m = \alpha' p \sqrt{\frac{M}{2\pi R T}}$$

$$\therefore p = m \sqrt{\frac{2\pi R T}{M}}$$

where  $m$  is rate of evaporation ( $\text{g/cm}^2/\text{sec}$ )

$p$  is vapour pressure ( $\text{g/cm}^2$ )

$R$  is gas constant ( $\text{erg}/^\circ\text{C}$ )

$M$  is mol. wt. of vapour

$\alpha'$  is accommodation coefficient.

$\alpha' = 1$  when all vapourising atoms striking the surface are retained. It has been widely tested for metal surfaces and found to hold for copper, iron, chromium, etc. [Kingery<sup>62</sup>].

$$\log C_t^\circ = 2.5$$

$$C_t^\circ = 316 \text{ mg}$$

Each experiment lasted 16 minutes.

$$\therefore \text{wt loss per sec} = \frac{316}{1000} \times \frac{1}{960} \text{ g}$$

$$p = \frac{316}{1000} \times \frac{1}{960} \sqrt{\left( \frac{2 \times 3.142 \times 6.314 \times 10^7 \times 1903}{981 \times 52} \right)}$$

$$= 1.451 \text{ g/cm}^2$$

$$= 1.07 \text{ mm mercury}$$

The equation for the vapour pressure of chromium, as quoted in

Kubaschewski and Evans<sup>61</sup> is

$$\log p = AT^{-1} + B \log T + CT + D \quad \text{mpt} \Rightarrow \text{C.pt.}$$

$$A = -20400 \quad B = -1.82 \quad D = 16.23$$

No value is given for C.

this

From the vapour pressure of chromium at  $1630^\circ\text{C}$  is found to be

0.355 mm Hg.

The reliability of the two results must now be assessed.

The results of Wada Kawai and Saito<sup>23</sup> may be in error due to  $\alpha \neq 1$ .

The equation used in calculating vapour pressures from weights condensed may not hold either. It was derived for free evaporation from solids and may not hold for liquids.

The vapour pressure from the data of Kubaschewski and Evans<sup>61</sup> may be in error as the equation has been applied to the supercooled liquid and may not hold. If the results are correct, the value of  $\log C_t^0$  should have been 2.020. (Fig. 18). This would cause a considerable increase in the value of the activity coefficient of chromium as shown in Table 10.

Table 10

$N_{Cr}$	$\log \frac{C_t}{N}$	$\log \frac{C_t}{N} - \log \theta_t^0$	$\gamma_{Cr}$
0.05	1.44	0.58	0.26
0.10	1.57	0.45	0.355
0.15	1.66	0.36	0.436
0.20	1.76	0.264	0.55
0.25	1.85	0.17	0.676
0.30	1.92	0.10	0.79
0.40	2.08	0.06	1.15

These results should be nearer the true  $\gamma$  values but may not be accurate in view of assumptions<sup>made</sup> and accuracy of the data used in the calculations.

Fig. 14 has been re-plotted as Fig 19 using  $\log a_{Cr}$  instead of  $\log N_{Cr}$ , the above activity coefficients being used. Points are taken from the curve established in Fig. 14 and are shown in Table 11.



TABLE 11

$N_{Cr}$	$\gamma_{Cr}$	$a_{Cr}$	$\frac{P_{H_2O}}{P_{H_2}}$
0.0106	0.21	0.00223	0.200
0.031	0.233	0.00723	0.110
0.0533	0.264	0.0141	0.0735
0.0642	0.283	0.0182	0.062
0.0747	0.298	0.0223	0.053
0.0853	0.312	0.0266	0.046
0.1062	0.348	0.0368	0.037
0.1486	0.435	0.0648	0.023
0.1875	0.520	0.0975	0.019
0.2364	0.638	0.151	0.014
0.32	0.87	0.279	0.01
+ 0.1486	0.435	0.0648	0.023
+ 0.1875	0.520	0.0975	0.015
+ 0.2364	0.638	0.151	0.012

+ LiCl results.

In the low chromium range under 3% the slope of the curve is  $-\frac{1}{2}$ , chromite being the solid phase in equilibrium with chromium oxygen solutions in iron. In the range 3 - 11% Cr a linear relation holds, the slope of the line being  $-\frac{2}{3}$ , indicating that chromic oxide is the solid phase. The slope then steepens to  $-\frac{3}{4}$  corresponding to equilibrium with  $Cr_3O_4$ . However one questions the validity of the latter conclusion as two of the points

rely on the dubious lithium chloride data. A relatively slight shift in the value of  $\log \frac{P_{H_2O}}{P_{H_2}}$  would put these results on the line indicating equilibrium with chromic oxide. It may also be significant that the two results involving lithium chloride solutions also give a slope of  $-\frac{2}{3}$  but this line would be displaced from that in the 3 - 11% chromium range. This again suggests a systematic error in the results involving lithium chloride solutions.

The present results can be interpreted as involving only the two equilibria,  $Cr - O - Cr_2O_3$  and  $Cr - O - FeO \cdot Cr_2O_3$  using the variation in chromium activity determined by Wada, Kawai and Saito.

#### (c) Relative merits of the two explanations

At low chromium contents, chromite is the solid phase in equilibrium with Fe-Cr-O solutions on either explanation. A sudden change from equilibrium with chromite to chromous oxide would be unexpected since  $\Delta G_f^\circ$  of chromic oxide lies between the two. Chromium-oxygen equilibria with either CrO or  $Cr_3O_4$  in a chromic oxide crucible seems unlikely. Crusts inside the crucibles all contained  $Cr_2O_3$  and other tests to confirm the existence of CrO at high temperatures were inconclusive if not entirely negative.

The relative variation in chromium activity as calculated from the present data agrees too well with that of Wada, Kawai and Saito<sup>23</sup> to be considered entirely fortuitous. An explanation for the difference in actual levels is yet called for. There are so many uncertainties in calculating Raoult's Law activities from

the data of Wada et alia that this may account for the discrepancies. Activity coefficients calculated from the present results should differ from those of Wada et alia due to the presence of oxygen in the melt. The chromium content is so much higher than the oxygen content that one would not expect  $f_{Cr}^O$  to depart far from unity.

The research work of Hilty Forger and Folkman<sup>33</sup> should be considered since they presented data which would explain gradual changes from one oxide phase to another on the assumption that iron and chromium form ideal solutions. Oxygen was supplied to the melt by the addition of ferric oxide. A summary of their conclusions is given below, together with the theoretical slope of a  $\log \frac{H_2O}{H_2} - \log Cr$  plot, necessary for agreement with the equilibria given.

<u>Chromium Content</u>	<u>Solid Phase</u>	<u>Theoretical Slope</u>
0 → 3%	$FeO.Cr_2O_3$	$-\frac{1}{2}$
3 → 9%	Substitution of Fe by Cr in $FeO.Cr_2O_3$	
9 → 100%	$Cr_3O_4$	$-\frac{3}{4}$

Examination of the present and earlier data gives no indication that the gradient at higher chromium contents should be  $-\frac{3}{4}$ . From experimental results in the present work and that of Chen and Chipman<sup>34</sup>, equilibrium with  $CrO$  seems more likely than  $Cr_3O_4$ . The other data are so incomplete or unreliable that no theories can be drawn as regards oxide phases at high chromium concentrations. Experiments with Cr -  $Cr_2O_3$  mixtures to make lower

oxides of chromium were completely unsuccessful. Nor was any evidence obtained to suggest the existence of a volatile oxide of chromium. Unless more conclusive data are obtained, it seems safer to reject theories which involve equilibria with possible high-temperature oxides of chromium.

The increasing oxygen solubility with chromium content has yet to be explained on the basis of chromite<sup>and</sup> chromic oxide equilibria. The concept of soluble suboxides appears unsound. To justify this concept, Cr-O interactions must be much greater than Fe-Cr or Fe-O interactions. Since  $\Delta G_f^\circ$  of FeO and CrO should be similar, Fe-O interaction cannot be ignored. A more satisfactory explanation, involving no hypothetical soluble oxides, can be found by considering the effect of chromium on the activity of oxygen and this will be discussed in detail later.

(d) Comparison of the solid and liquid data for the iron-chromium system.

Data on the solid iron-chromium system are far from consistent. Since Kubaschewski and Heymer<sup>36</sup> measured actual vapour pressures of chromium by a radioactive tracer technique, their results are probably the most reliable. To convert these activities to the liquid an accurate thermal equilibrium diagram is required. This is not available at the present time. The one used for the present calculation was published by Hellowell<sup>63</sup> (Fig. 5). All the available data were considered in drawing the most probable thermal equilibrium diagram. It is perhaps worth

mentioning that there is an uncertainty of about 100°C in the melting point of chromium alone.

Kubaschewski and Heymer's activities at 1230°C refer to pure solid chromium as the standard state. These can be converted to activities at the solidus temperature, assuming that the system forms a regular solution.

$$i. e. T_1 \log \gamma_1 = T_2 \log \gamma_2$$

The liquid, in equilibrium with a particular solid can be determined from the phase diagram. This liquid activity can be converted to an activity at 1600°C assuming the liquid system forms a regular solution. The activity obtained refers to pure solid chromium as the standard state and can be converted relative to pure liquid chromium using the following equation:

$$\log a_{LSS} = \frac{-\Delta H_f \Delta T}{R T T_m} + \log a_{SSS}$$

The results of Kubaschewski and Heymer have been converted to activities at 1600°C in the above manner and are listed in the following table.

TABLE 12

<u>N<sub>Solid</sub></u>	<u>a<sub>Solid</sub> C<sub>r</sub></u>	<u>a<sub>Liquid</sub> C<sub>r</sub><sup>1600°C</sup></u>
0.0458	0.110	0.083
0.0820	0.152	0.114
0.296	0.394	0.308
0.501	0.540	0.452
0.699	0.727	0.601
0.900	0.910	0.756

The results are shown graphically in Fig. 20 together with other available data. McCabe's<sup>25</sup> results are not shown but they indicate slight positive deviations from ideality. Vintakin's<sup>27</sup> data are also shown. Due to the paucity of experimental results, this work may not be reliable.

Activity measurements in the solid and liquid iron-chromium system are seen to be far from concordant (Fig. 20). Both the solid and liquid systems show positive deviations from ideality according to Kubaschewski and Heymer. From consideration of the thermal equilibrium diagram this would appear rather surprising. If the solid were approximately ideal, the liquid should show a negative deviation below the minimum (20% Cr) then a positive deviation from ideality. The present results do show this trend although the change from negative to positive deviation is at 14 rather than 20% chromium. As has already been shown, relatively small errors in the free energy data would account for this. The results of Wada, Kawai and Saito cannot be used for direct comparison with the present work since accurate absolute activities cannot be calculated. The order of variation is in good agreement with the present work. If absolute activities could be calculated, it would be possible to present a more complete picture of the thermodynamics of the iron-chromium system.

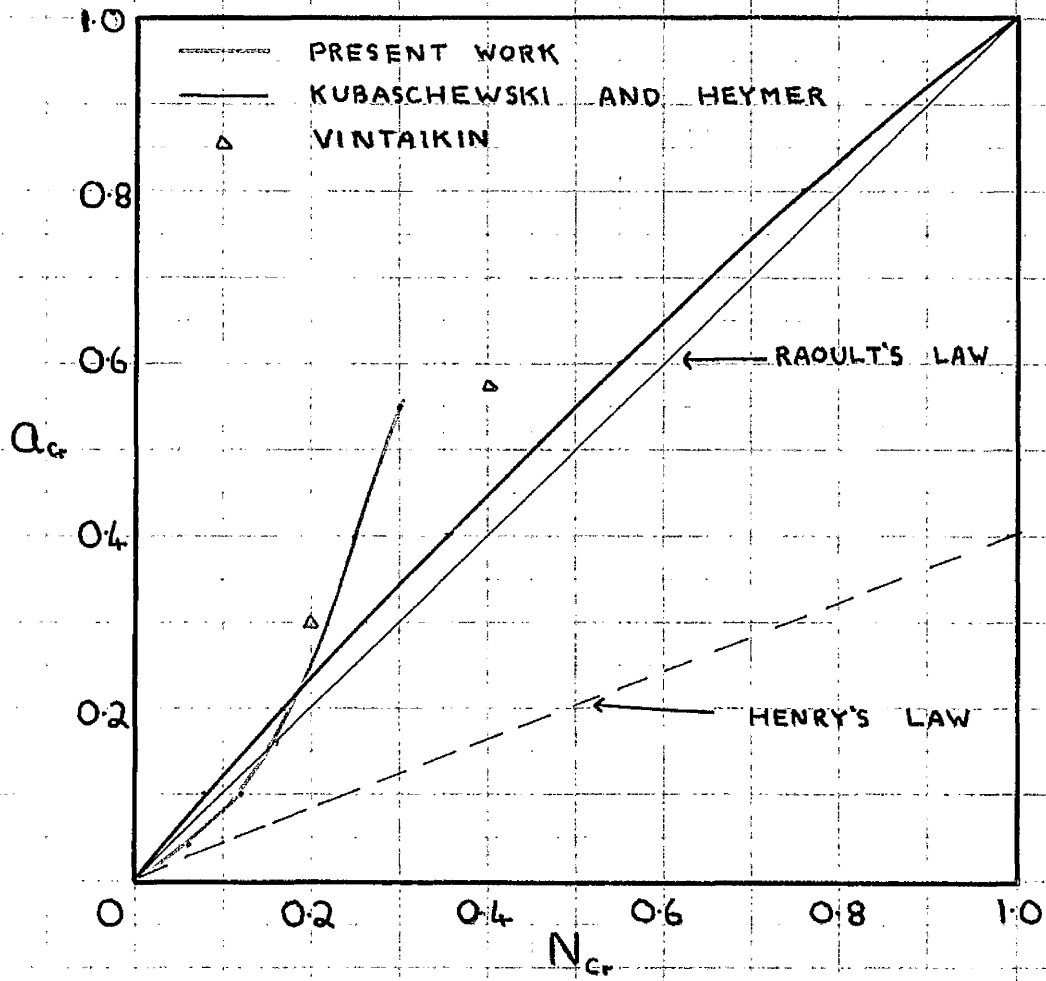


FIG. 20. THE ACTIVITY OF CHROMIUM IN IRON (1600°C)

(2) Chromium-oxygen Equilibrium

The oxygen concentrations of various melts at 1600°C are listed in Table 13. The analyses were duplicated and, if reproducibility poor, further determinations were made provided sufficient clean sample remained. Not all runs were analysed for oxygen since some samples were not good enough. It takes a considerable time to assemble and de-gas the vacuum fusion apparatus and for this reason some of the preliminary experiments, obviously far from equilibrium, were not analysed for oxygen.

TABLE 13

<u>Run No.</u>	<u>Atomic % Cr</u>	<u>% O<sub>2</sub></u>	<u>Run No.</u>	<u>Atomic % Cr</u>	<u>% O<sub>2</sub></u>
18	8.08	○.043	38	4.86	○.037
19	7.92	○.045	40	8.16	○.039
21	5.12	○.047	43	6.14	○.031
23	6.49	○.040	47	9.93	○.056
24	8.15	○.036	48	2.01	○.048
30	8.51	○.041	52	18.97	○.052
31	7.90	○.030	54	14.28	○.038
33	12.92	○.037	74	19.13	○.047
37	5.17	○.035	75	15.10	○.035
78	25.07	○.057	84	21.48	○.0495
79	35.05	○.096	85	23.00	○.060
82 <sup>+</sup>	23.46	○.055	86	18.23	○.055
83	24.18	○.068	87	18.02	○.0515

+ Argon atmosphere



These results are shown graphically in Fig. 21 where the range of scatter is immediately obvious. However, the results in themselves are more consistent than those of Hilty et alia<sup>33</sup> or Chen and Chipman<sup>34</sup>. Certain relevant factors have been taken into account which helped to fix the position of the line. Firstly, the direction of movement towards equilibrium is considered important. Special emphasis is placed on experimental results which lie on or very near the established equilibrium line in Fig. 12, i.e. points where gas-metal equilibrium has been established. As a final guide to drawing the line, low oxygen results are thought to be more reliable than high ones. A vacuum fusion apparatus can yield low results due to adsorption of the evolved gas on cooler parts of the furnace tube. This is normally a very small error, only significant when the oxygen content of the sample is quite low (e.g. 0.007%), On the other hand results can be very high if there are even small inclusions in the metal. The results show beyond all doubt, that above 8 atomic % chromium, the oxygen concentration increases quite markedly with increasing chromium content.

The available data are all shown in Fig. 22. Wt. % have been used for direct comparison with other data. Chen and Chipman's<sup>34</sup> results from melts made in chromic oxide crucibles showed an increase in oxygen concentration with increase in chromium, at chromium levels above 6%. This they considered unlikely and an extrapolated curve was drawn as shown. It was suggested that oxygen results were high and erratic due to porosity or inclusions

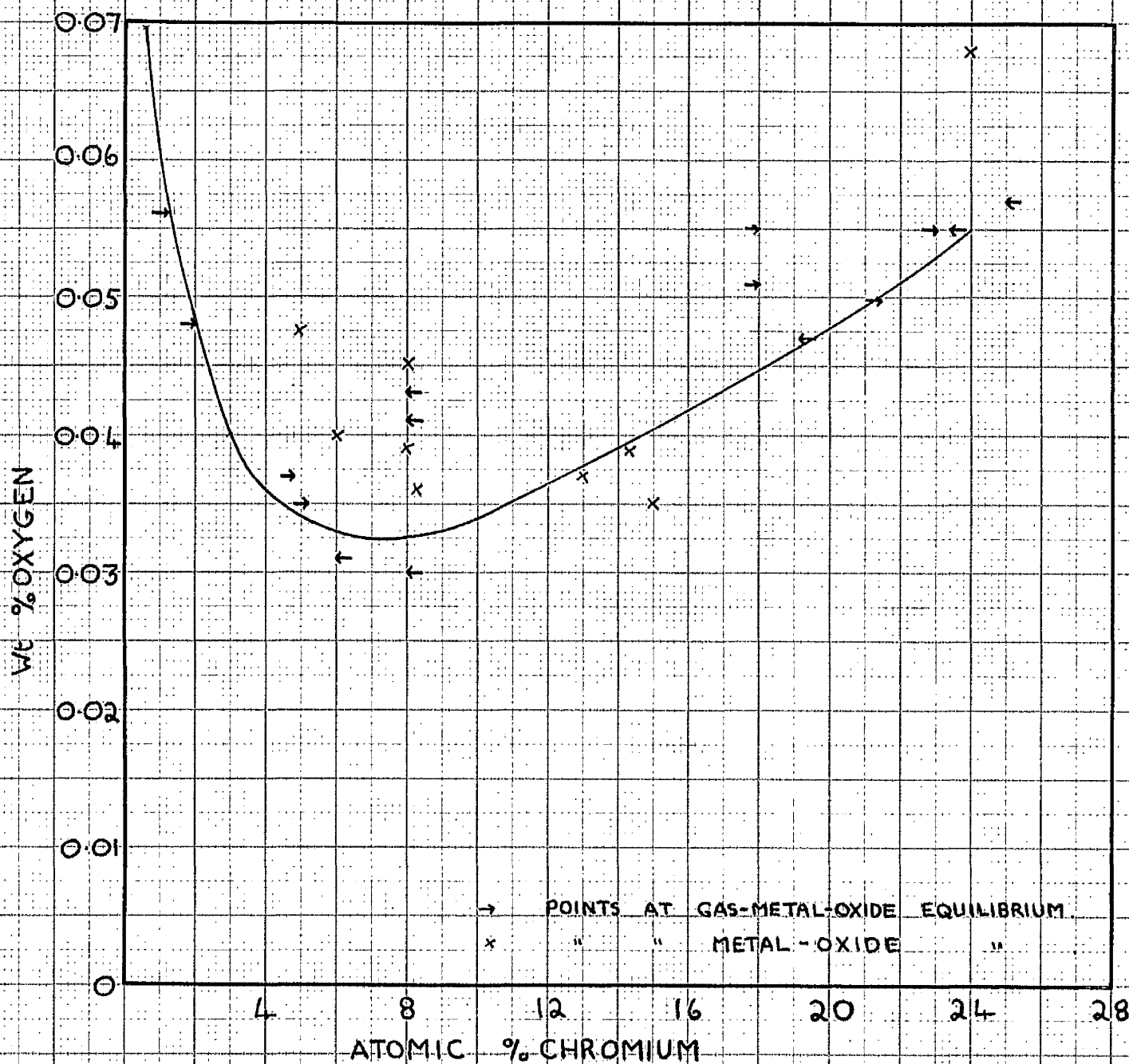
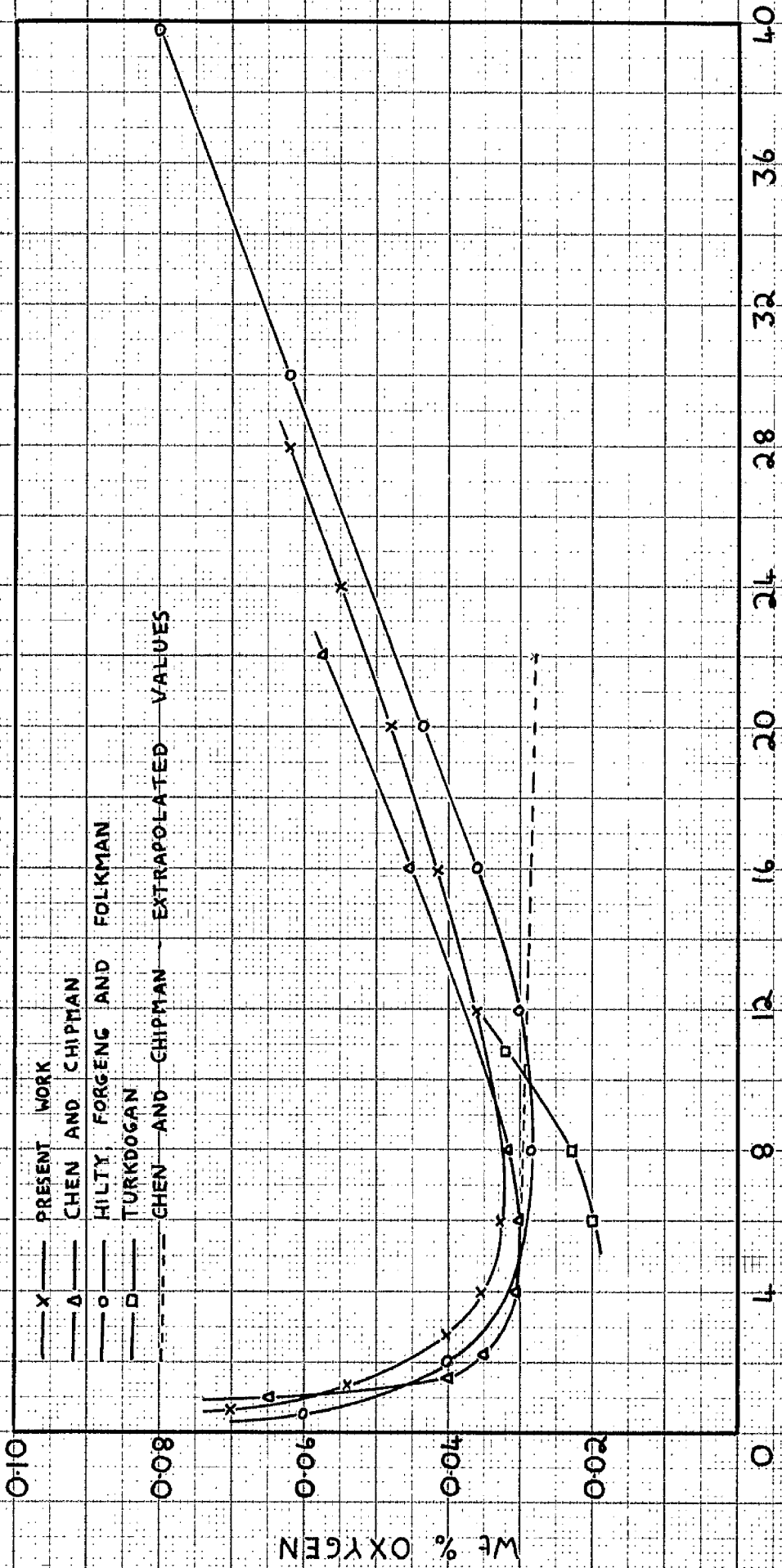


FIG. 21. CHROMIUM-OXYGEN EQUILIBRIUM (1600°C)



WE % CHROMIUM

FIG. 22. CHROMIUM - OXYGEN DATA (1600°C)

in the specimens. In Fig. 22 the line has been drawn through actual experimental results, the lower values being the main guide in fixing the curve.

The results of Hilty et alia<sup>33</sup> are also shown. In the original work the line was drawn slightly below the lowest experimental points, suggesting that even these were considered to be high. For the present interpretation the line has been raised to go through the lowest points so that all the available data can be judged on the same basis. The inflections shown in Hilty's<sup>33</sup> original work have not been repeated, the oxygen analysis not being sufficiently accurate to justify them. They were marked in to show that X-ray evidence<sup>33</sup> had indicated a change in oxide phase at the particular point.

Finally, Turkdogan's<sup>30</sup> experimental data at 1600°C are shown. When no slag was formed the oxygen concentrations were very low and these have been ignored.

The trends shown in the various data are all the same with the possible exception of Turkdogan's<sup>30</sup> whose results, one would suspect are not equilibrium values. Above a certain chromium concentration, the activity coefficient of oxygen is reduced to such an extent that the oxygen concentration increases. The present work indicates that the turning point is at 7 - 7.5% chromium. Chen and Chipman's<sup>34</sup> results place the minimum at about 6% chromium. From the results of Hilty, Fergeng and Folkman<sup>33</sup> it would appear that minimum oxygen concentrations extend over the range 5 to 10%

chromium. Turkdogan's <sup>30</sup> data show no minimum in the range covered (5 - 12% Cr).

It is perhaps significant that chromium has some de-oxidising as well as alloying effects at low concentrations. In more highly alloyed steels chromium has virtually no de-oxidising properties. Research, in recent years has shown that a number of elements lose their de-oxidising effects as the concentration is raised above a certain level. Recent theoretical treatment <sup>41</sup> has shown that a minimum might be expected. At the time of Chen and Chipman's research this had not been recognised. It had not been forecast from theoretical considerations, hence Chipman doubted the reliability of the data and made little attempt to explain increased oxygen contents at higher chromium concentrations. Zuffe <sup>68</sup> has explained the results on the basis of a soluble oxide, the most likely one being CrO. This may be possible but there is no direct evidence concerning the existence of such a compound. The theory relies on Cr-O interactions being so far in excess of other interactions in solution that the latter can be neglected. Iron and oxygen form ferrous oxide which probably has a similar free energy of formation as chromous oxide and consequently similar interactions. Postulating the existence of a soluble chromous oxide phase would therefore seem to be too specific. By comparing Fe-O and Fe-Cr-O data, an interaction coefficient  $E_0^{\text{Cr}}$ , can be determined which involves no assumptions whatever as regards oxide phases.

To calculate the magnitude of the interaction coefficient, reliable data on the iron-oxygen system are required. The recent results of Floridis and Chipman<sup>6</sup> are considered most reliable and have been used to calculate the activity of oxygen in pure iron at different  $\frac{H_2O}{H_2}$  ratios. Knowing the  $\frac{H_2O}{H_2}$  ratio, the oxygen and chromium concentrations, the interaction coefficients can be calculated as shown. The data are given in Table 14.

e. g. Fe - Cr - O system

$$\text{Atomic \% chromium} = 6.14$$

$$\frac{P_{H_2O}}{P_{H_2}} = 0.0534$$

$$\%O_2 = 0.031$$

From Floridis and Chipman's data at 1600°C

$$\frac{P_{H_2O}}{P_{H_2}} = 0.0534 \quad a_O = 0.0145$$

$$\therefore f_O^{CR} = \frac{a_O(Fe)}{\% O_2 \text{ (alloy)}}$$

$$= \frac{0.0145}{0.031}$$

$$= 0.468$$

TABLE 14

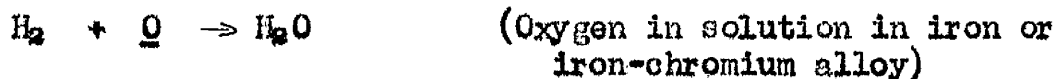
<u>Run No.</u>	<u>Atomic % Cr</u>	<u>Cr</u> <u>f<sub>o</sub></u>	<u>Cr</u> <u>f<sub>o</sub></u> (adjusted)
18	8.08	0.302	
19	7.92	0.222	
21	5.12	0.288	
23	6.49	0.338	
24	8.15	0.264	
30	8.50	0.280	
31	7.90	0.394	
37	5.17	0.415	
38	4.86	0.595	
40	8.16	0.238	
43	6.14	0.468	
47	0.93	0.980	
48	2.01	0.633	
52	18.97	0.083	
54	14.28	0.120	
74	19.13	0.081	0.10
75	15.10	0.109	0.134
78	25.07	0.058	0.070
79	35.05	0.0344	0.042
83	24.18	0.049	0.059
84	21.48	0.067	0.081
85	23.00	0.060	0.073
86	18.23	0.073	0.086
87	18.02	0.077	0.091

The final column applies to results using lithium chloride solutions only. The water/hydrogen ratio has been raised by an amount corresponding to the difference of the two curves in Fig. 12. Since the ratio is only raised to the first degree, the correction factor is almost negligible.

The results are shown graphically in Fig. 23 together with those of Chen and Chipman<sup>24</sup>. The method of calculation assumes that gas-metal equilibrium has been established. Thus, experimental points on or very near the equilibrium line in the original  $\frac{P_{H_2O}}{P_{H_2}}$  v Cr curve are considered most important. These are suitably distinguished from other data in the diagram.

Chen and Chipman's original line was slightly higher than the one shown, at chromium concentrations above 10%. Low oxygen concentrations were used, obtained by extrapolation from low chromium heats. In Fig. 23 actual experimental results have been used to enable a direct comparison to be made with the present work. The two sets of results are in good agreement and show that Chipman's original extrapolation is unnecessary and unjustified.

Agreement in interaction coefficients is better than one could expect, in view of the discrepancies between the  $\frac{P_{H_2O}}{P_{H_2}}$  v. Cr data. By examining the equilibrium constant for the reaction



the reason becomes more apparent

$$K_1 = \frac{P_{H_2O}}{P_{H_2} \times \%O}$$



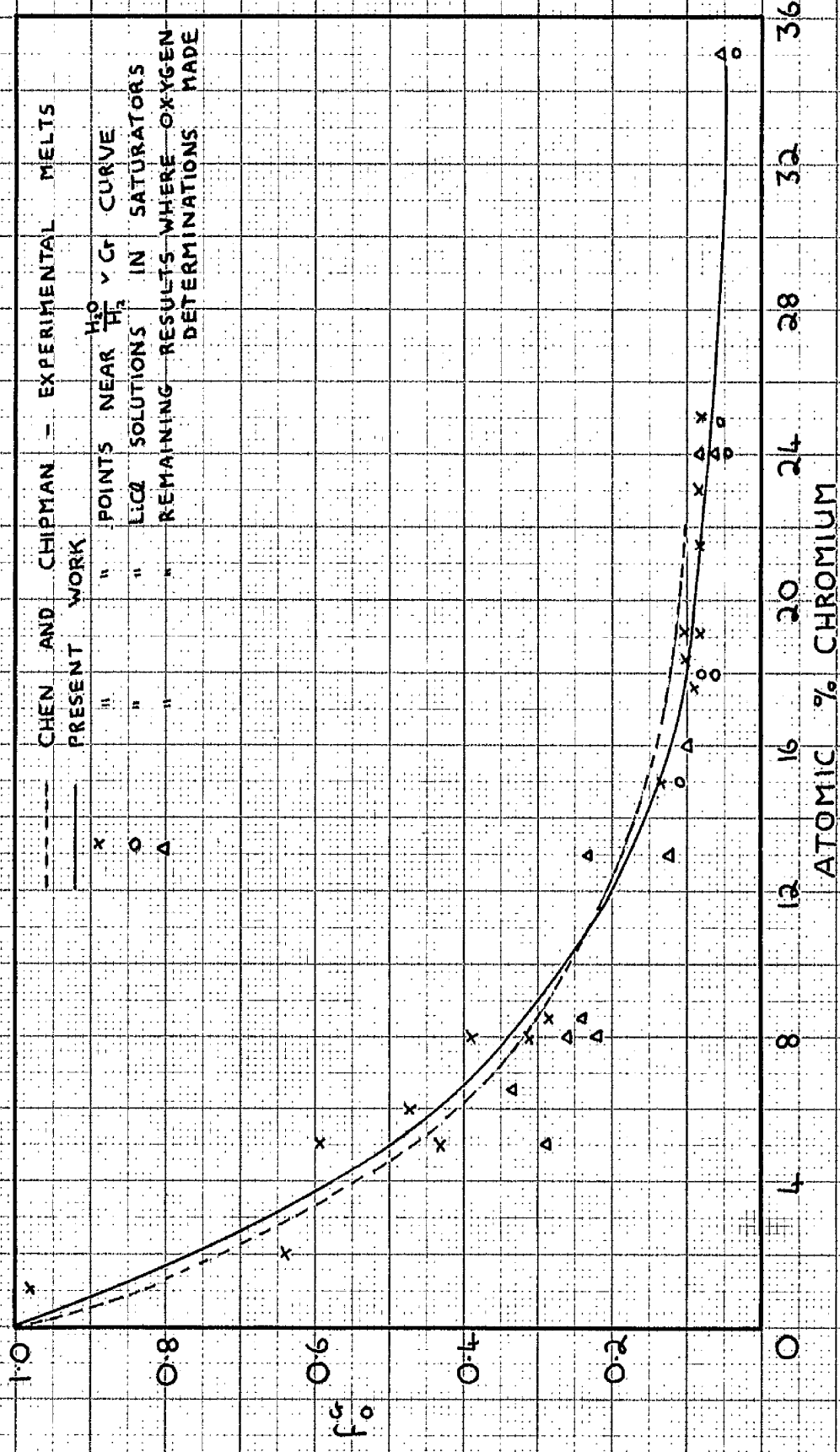


FIG. 23. THE EFFECT OF CHROMIUM ON THE ACTIVITY COEFFICIENT OF OXYGEN IN IRON (1600°C)

Due to interaction effects,  $K_1'$  will vary with chromium concentration. An extrapolation back to zero per cent chromium should give a value of  $K_1'$  relating to oxygen in pure iron. Extrapolated results can therefore be compared with accepted values and the reliability of the work assessed.

The present results and those of Chen and Chipman<sup>24</sup> have been carefully examined and points selected where gas-metal equilibrium is thought to have been established. Since gas-metal equilibrium and reliable oxygen results are required, the number of points is rather small. However, the trends can be seen from Fig. 24 where  $\log K_1'$  is plotted against weight per cent chromium. Floridis and Chipman<sup>6</sup> have recently shown that  $\log K_1'$  at 1600°C is about 0.57. Extrapolation of the present results to 0% Cr gives a value of  $\log K_1' = 0.59$ . Chen and Chipman's<sup>24</sup> results give a much greater value of  $\log K_1'$  (0.73) and this is probably due to errors arising out of thermal diffusion. Since interaction coefficients can be calculated from the equilibrium constants, agreement should be appreciably worse than is seen in Fig. 23. However, at the time of Chen and Chipman's investigations the most reliable data for oxygen in iron was that of Fontana and Chipman<sup>3</sup> who found  $\log K_1' = .62$  at 1600°C. This has since been found to be in error due to thermal diffusion. Partial cancellation of errors therefore accounts for the reasonable agreement of their interaction coefficients compared with the present ones. These

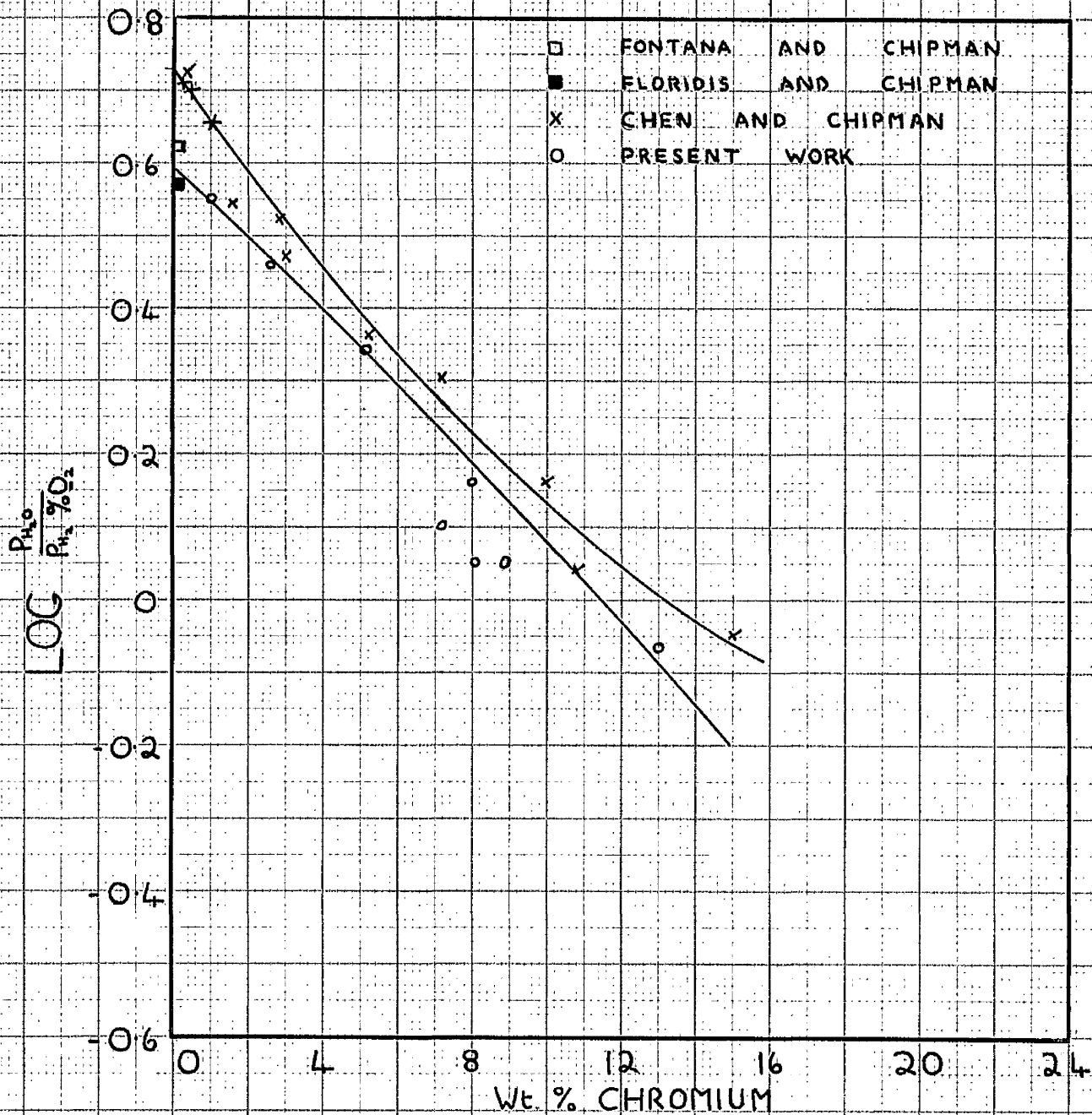
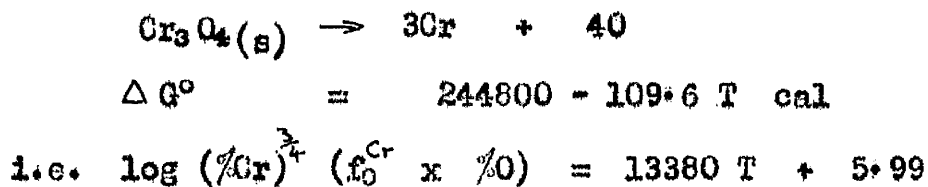


FIG. 24.      EXTRAPOLATION OF LOG  $\frac{P_{H_2O}}{P_{H_2.\%O_2}}$  BACK TO  
ZERO PER CENT CHROMIUM TO COMPARE  
WITH VALUES FOR PURE IRON

latter considerations tend to show that the present data are more reliable than the earlier work of Chen and Chipman.

The results of Hilty et alia<sup>33</sup> cannot be directly compared with the present work. In their case oxygen was supplied to the melt by additions of iron oxide and so the activity of oxygen cannot be determined from the oxygen potential of the gas. Chipman<sup>35</sup> has, however, calculated interaction coefficients from Hilty's data assuming their oxide phase theory to be correct. For example, in the range 9 - 25% chromium the stable oxide phase was said to be  $\text{Cr}_3\text{O}_4$ . The free energy of formation of this compound is not known but has been estimated by Chipman. He assumed that the enthalpy was  $\frac{4}{3}$  that of chromic oxide and the entropy term the same as  $\text{Mn}_3\text{O}_4$ . From this the free energy for the following reaction was calculated.



From this the interaction coefficient was calculated assuming the activity coefficient of chromium to be unity. In view of the assumptions made the value of the interaction coefficients cannot possibly be anything better than a very rough estimate.

Whenever possible, it is basically sounder to calculate interaction coefficients from  $\frac{\text{H}_2\text{O}}{\text{H}_2}$  data using the results of Floridis and Chipman<sup>6</sup> in pure iron as a basis. Experimental errors should

relatively small and no assumptions have to be made as regards activity of chromium in iron and free energy of formation of possible oxide phases. This is the treatment used for the present results and also those of Chen and Chipman.

To obtain a value of the interaction parameter a graph showing the relationship between  $\log f_o^{Cr}$  and weight % chromium was drawn. All the available data are included in Fig. 25. An approximately linear relationship exists in the range 0-14% chromium for all data and the interaction parameters are quoted for this range only.

$$e_o^{Cr} = \frac{\partial \log f_o^{Cr}}{\partial \% Cr}$$

Values of  $e_o^{Cr}$

Present work -0.058

Hilty et alia<sup>23</sup> -0.041

Chen and Chipman<sup>24</sup> -0.041  
(extrapolated values)

Chen and Chipman<sup>24</sup> -0.055  
(experimental data)

Turkdogan<sup>30</sup> -0.064

Chipman's calculations from Hilty's<sup>23</sup> data, and Chen and Chipman's extrapolation yield the same interaction parameter but this is probably fortuitous. From Turkdogan's<sup>30</sup> results the best straight line, passing through the data and the origin, is drawn.

A careful examination of all the data for possible errors indicates that the present value of 0.058 is probably the

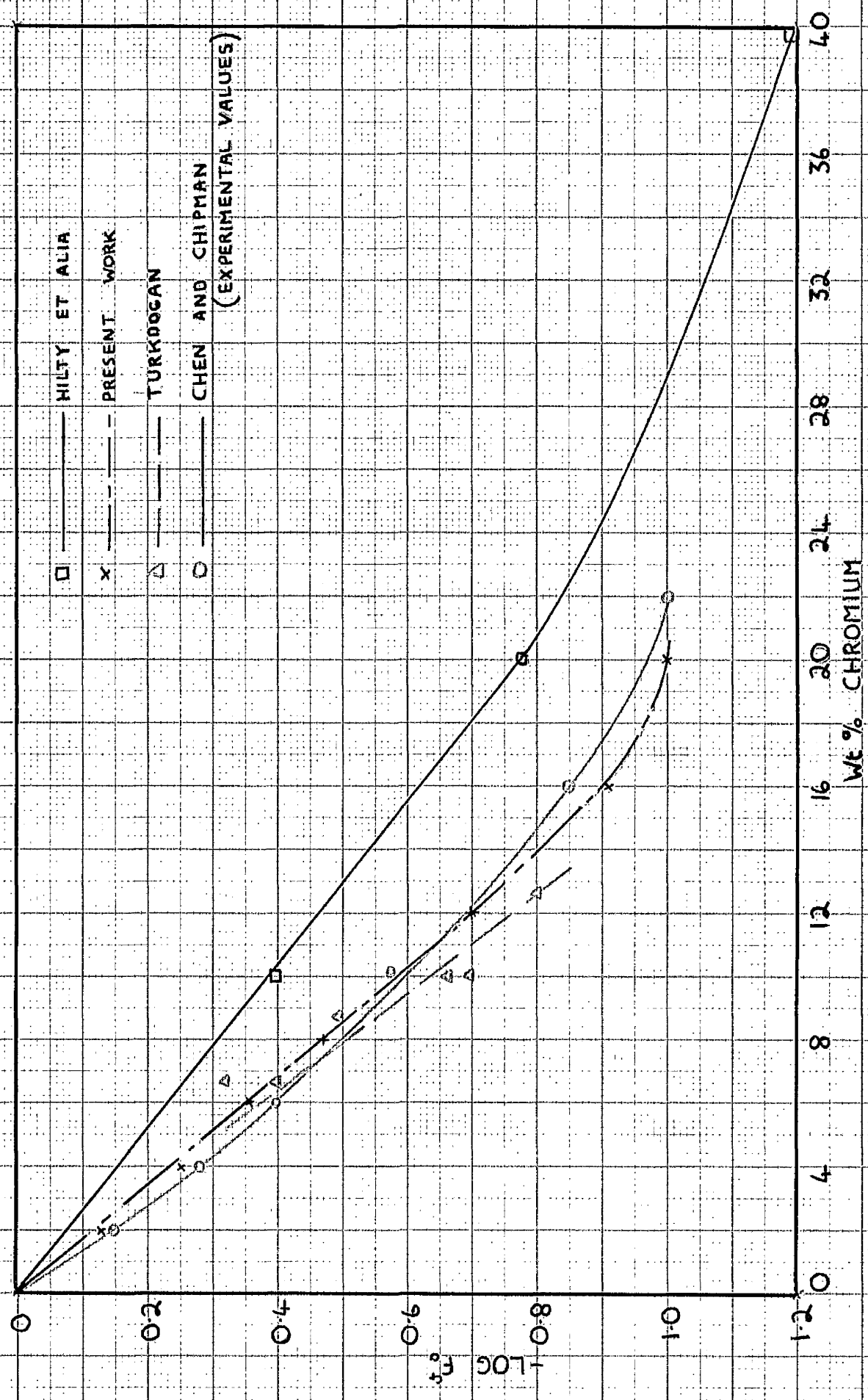


FIG. 25. EFFECT OF CHROMIUM ON THE ACTIVITY COEFFICIENT OF OXYGEN IN IRON (1600°C)

most accurate. Chen and Chipman's would have obtained almost the same value if thermal diffusion had been avoided and better data for the activity of oxygen in iron been available.

Wagner<sup>40</sup> has derived the following simple relationship between interaction parameters, namely,

$$e_j^i = e_i^j$$

The derivation is for dilute solutions only and may not apply in the present case. It is nevertheless of interest to calculate  $f_{Cr}^o$  to see if the assumption made earlier is likely to have caused significant errors.

$$\begin{aligned} e_o^w &= -0.058 = e_w^o \\ \therefore \log f_{Cr}^o &= -0.058 \times \frac{52}{16} \\ &= -0.188 [\% O_2] \end{aligned}$$

If the oxygen concentration is 0.05%

$$\begin{aligned} \log f_{Cr}^o &= -0.0094 \\ f_{Cr}^o &= 0.98 \end{aligned}$$

Therefore at an oxygen concentration of 0.05%, the interaction coefficient  $f_{Cr}^o$  is so near unity that it can be neglected. This would be expected considering the relative concentrations of the elements concerned.

#### Interaction parameters for other elements in iron

Interaction parameters are sometimes quoted on the basis of atom fraction

$$\text{e. g. } \epsilon_o^w = \frac{\delta \log f_o^w}{\gamma_{Cr}^w} = -5.8$$

The most recent values for other interaction parameters ( $\epsilon_o^j$ ) are given below"

<sup>64</sup> C	<sup>47</sup> Al	<sup>66</sup> Si	<sup>5</sup> V	Cr	<sup>35</sup> Mn	<sup>63</sup> Ni
-21(?)	-515	-12(?)	-57	-5.8	0.0	+1.2

For carbon and silicon there is considerable doubt as to the reliability of the data.

The full significance of these values is imperfectly understood. Negative values of the parameter can be explained on the basis of a very simple, but perhaps, incomplete model, as illustrated by Fe-Cr-O solutions. In Fe-O solutions each O atom is surrounded by an average of n Fe atoms which share the Fe-O bonding energy. Cr-O bonding is stronger and leads to two effects,

(1) The Cr/Fe ratio is greater amongst the nearest neighbours of oxygen than in the bulk of the solution.

(2) O atoms become more firmly bonded as the Chromium concentration increases.

For nickel the interaction parameter is positive indicating that Ni-O bonding is weaker than Fe-O bonding.

The large negative value of  $\epsilon_o^M$  is indicative of a very large Al-O bonding energy.

The model indicated above, takes no account of intermetallic bonding. Fe-Cr, Fe-Ni interactions one would suspect, will be quite small but this is probably not the case for Fe-Al interactions.



(3) The effect of temperature on Cr - O equilibria(a) Cr v.  $\frac{P_{H_2O}}{P_{H_2}}$  considerations

A number of melts were made at 1700°C but not all of these were successful. Insufficient data were obtained to establish the  $\log \frac{P_{H_2O}}{P_{H_2}}$  v  $\log Cr$  curve with any great accuracy. The curve was therefore calculated using free energy data and the activity variations found at 1600°C which are in good agreement with the data of Wada, Kawai and Saito<sup>23</sup>. The calculated curve could then be compared with the few experimental results obtained at 1700°C.

For the reaction



$$K_4 = \left( \frac{P_{H_2O}}{P_{H_2}} \right)^3 (a_{Cr})^2$$

$$= 5.78 + 10^{-7} \quad \text{at } 1600^\circ\text{C}$$

$$\text{At } 1700^\circ\text{C } \Delta G = 51490 \text{ cal}$$

$$\log K_4 = \frac{-\Delta G}{RT}$$

$$\therefore K_4 = 2.04 + 10^{-6}$$

$$\frac{K_{1700}}{K_{1600}} = \frac{2.04 + 10^{-6}}{5.78 + 10^{-7}} = \frac{a_{Cr}^2(1700^\circ\text{C})}{a_{Cr}^2(1600^\circ\text{C})} \quad \text{at the same } \frac{P_{H_2O}}{P_{H_2}} \text{ ratio.}$$

$$\text{From this } \frac{a_{Cr}^{1700^\circ\text{C}}}{a_{Cr}^{1600^\circ\text{C}}} = 1.88$$

$$\text{or } \log a_{Cr}^{1700^\circ\text{C}} = \log a_{Cr}^{1600^\circ\text{C}} + .274$$

In view of the practical significance it is of interest to calculate alteration in chromium content brought about by further increases in temperature.

At 1800°C

$$\Delta G \text{ for reaction (5)} = 49030 \text{ cal}$$

$$\therefore K_q = 6.61 \times 10^{-6}$$

$$\frac{K_{1800^\circ\text{C}}}{K_{1600^\circ\text{C}}} = \frac{6.61 \times 10^{-6}}{5.78 \times 10^{-7}} = \frac{a_{1800^\circ\text{C}}^2}{a_{1600^\circ\text{C}}^2}$$

$$= 11.44$$

$$\therefore \frac{a_{1800^\circ\text{C}}}{a_{1600^\circ\text{C}}} = 3.39$$

$$\log a_{\text{Cr}}^{1800^\circ\text{C}} = \log a_{\text{Cr}}^{1600^\circ\text{C}} + .53$$

Using the  $\log a_{\text{Cr}}$  v  $\log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}}$  values at 1600°C as a basis, the above equations were used to draw the curves at 1700°C and 1800°C as shown in Fig. 26. At low chromium contents the free energy data for chromite equilibria should have been used. Using Boerliche and Bangert's <sup>31</sup> data the following temperature effect can be calculated

$$\log a_{\text{Cr}}^{1700^\circ\text{C}} = \log a_{\text{Cr}}^{1600^\circ\text{C}} + .284$$

This is so close to the chromic oxide data that the difference was considered insignificant for the present purposes.

From Fig. 16 the effect of temperature on chromium concentration for a given oxygen potential can be obtained. Certain values of chromium activity were chosen and the equilibrium hydrogen/water ratios were read off for the two higher temperatures. The

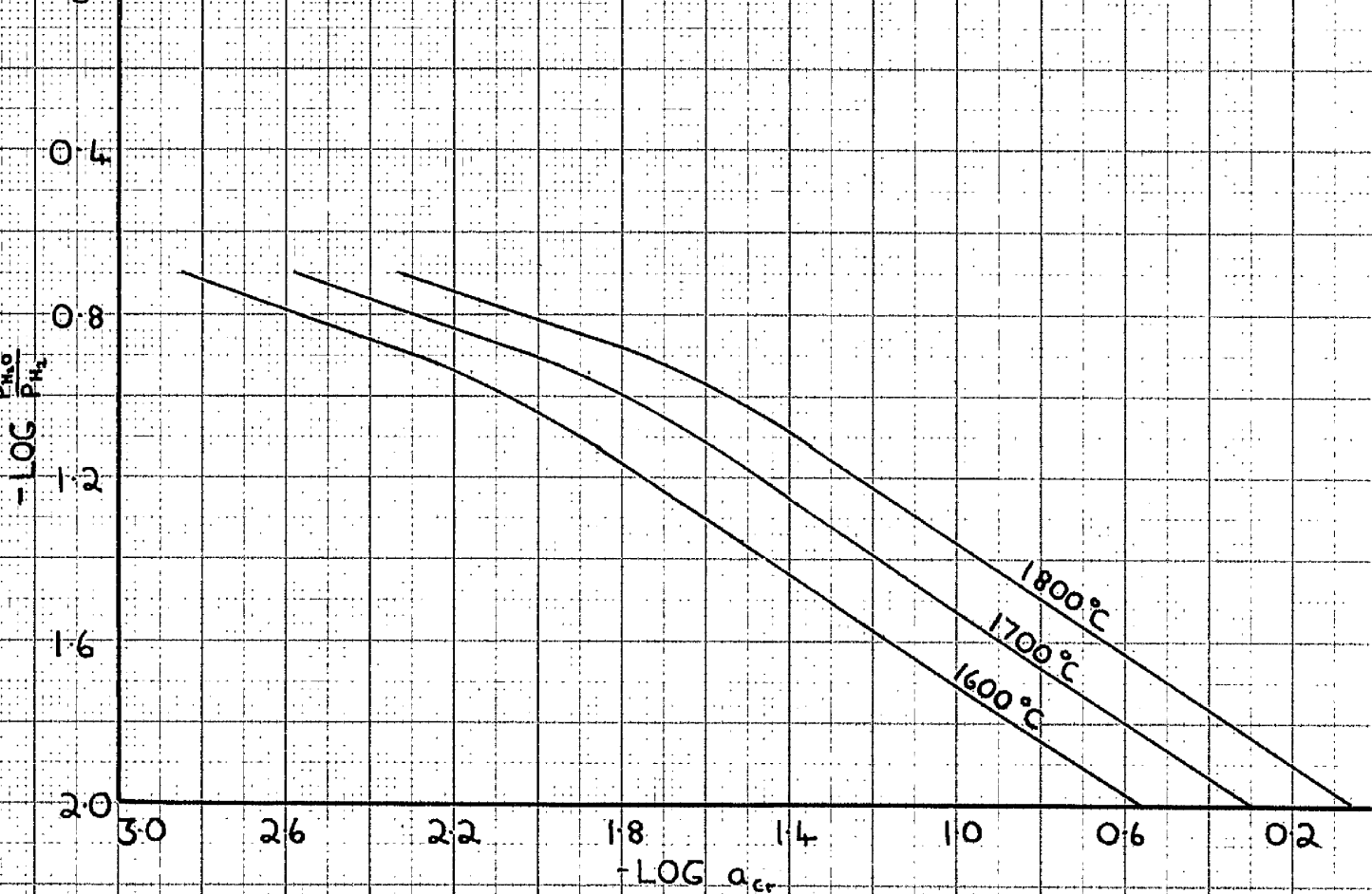


FIG. 26. THE VARIATION OF  $\text{LOG } a_{cr}$  WITH  $\text{LOG } \frac{P_{H_2O}}{P_{H_2}}$  AT 1600, 1700 AND 1800°C

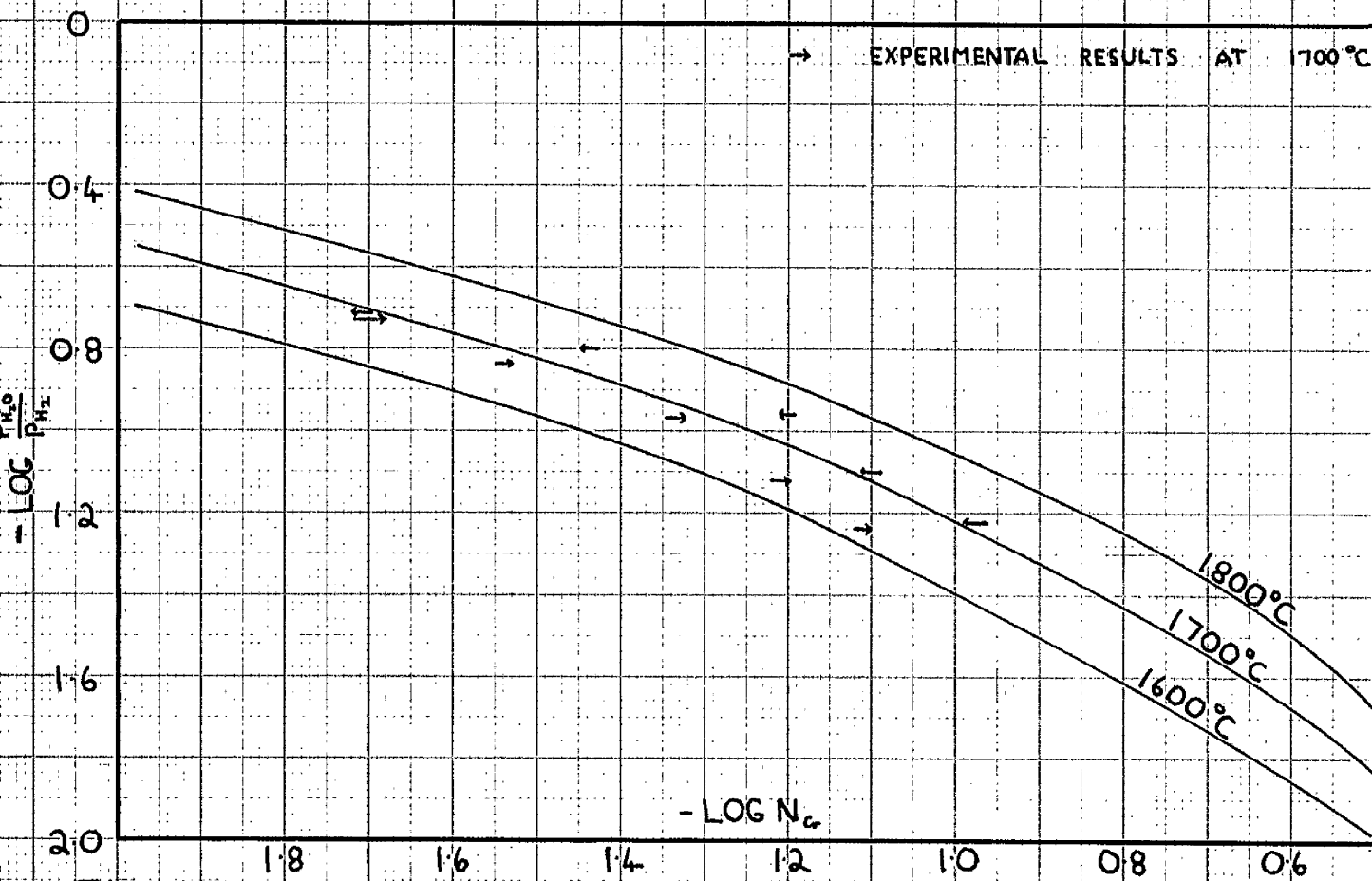


FIG. 27. THE EFFECT OF TEMPERATURE ON CHROMIUM CONTENT

activities chosen were taken from Table 11 so that the chromium concentration could be obtained directly.

TABLE 15

<u><math>a_{Cr}</math></u>	<u><math>N_{Cr}</math></u>	<u><math>\log a_{Cr}</math></u>	<u><math>\log \frac{P_{H_2O}}{P_{H_2}}</math></u>	
0.00222	0.0106	-2.65	-0.55	} 1700°C
0.00723	0.031	-2.14	-0.82	
0.0223	0.0747	-1.65	-1.10	
0.0648	0.1486	-1.19	-1.40	
0.279	0.32	-0.55	-1.83	
0.00222	0.0106	-2.65	-0.42	} 1800°C
0.00723	0.031	-2.14	-0.68	
0.0223	0.0747	-1.65	-0.94	
0.0648	0.1486	-1.19	-1.22	
0.279	0.32	-0.55	-1.67	

Changes in  $\gamma_{Cr}$  with increasing temperature have been neglected. The effect can be calculated if iron-chromium solutions are assumed to be regular.

$$\begin{aligned}
 \text{e.g. at } \gamma_{Cr}^{1600} &= 0.21 \\
 1873 \log 0.21 &= 1973 \log \gamma_{1700} \\
 \log \gamma_{1700} &= -0.644 \\
 \gamma_{1700} &= 0.205
 \end{aligned}$$

The other data used for the calculation are insufficiently accurate to justify applying this correction.

The derived lines for  $\log \frac{P_{H_2O}}{P_{H_2}} \nu \log N_{Cr}$  at 1700°C and 1800°C are shown in Fig. 27. The results of melts made at 1700°C, listed below, are also on the plot.

TABLE 16

<u>Run No.</u>	<u>Initial <math>N_{Cr}</math></u>	<u>Final <math>N_{Cr}</math></u>	$\frac{P_{H_2O}}{P_{H_2}}$	<u>%O<sub>e</sub></u>
55	0	0.0210	0.191	0.085
56	0	0.0293	0.145	-
57	0.0311	0.019	0.194	-
58	0.0427	0.0357	0.156	0.105
59	0.0214	0.0464	0.105	0.0775
60	0.0642	0.0621	0.105	0.078
61	0.0533	0.0613	0.0756	0.051
62	0.0859	0.0767	0.0773	0.079
63	0.0642	0.0775	0.0567	-
64	0.1062	0.102	0.0580	0.070
65	0.0853	0.1019	0.051	0.066

The experimental data are in reasonable agreement with the derived line at low chromium concentrations. However, further experimental data are required at higher chromium concentrations.

The lines in Fig. 27 tend to approach one another as the chromium content is increased. Increasing activity coefficients of chromium with chromium content account for this. Further results at 1700°C would be useful to confirm the calculated line and serve as added confirmation concerning the non-ideality of chromium in liquid-iron-chromium alloys.

(b) Chromium-oxygen relationships at 1700°C.

Insufficient oxygen data were obtained to establish a chromium-oxygen line at 1700°C. A line was calculated and compared with the experimental results obtained.

From the calculated line in Fig. 27, the hydrogen-water ratio at any particular chromium concentration can be found. Using Floridis and Chipman's data for 1700°C the activity of oxygen in iron can be calculated. If the interaction coefficient at 1700°C is substantially the same as at 1600°C, the oxygen concentration can be calculated.

$$\begin{aligned} \text{e.g. From Fig. 27} \quad \text{at } \log N_{\text{Cr}}^{\text{atomic}} &= -1.6 & \log \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} &= -0.77 \\ & (2.50\% \text{Cr}) & & \\ & & \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} &= 0.17 \end{aligned}$$

$$\begin{aligned} \text{From Floridis and Chipman's data, at} & \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = 0.17 \\ & a_{\text{O}} = 0.072 \end{aligned}$$

$$\begin{aligned} \text{At } 2.50 \text{ at. } \% \text{ Cr} \quad f_{\text{O}}^{\text{Cr}} &= 0.70 \\ \therefore \quad .70 \times \% \underline{\text{O}} &= 0.072 \\ \therefore \quad \% \underline{\text{O}} &= 0.103 \end{aligned}$$

The results were then plotted in Fig. 28. Experimental points are also shown. Hilty, Forging and Folkman<sup>33</sup> have obtained data at 1550°C, 1600°C and 1650°C and from it one would estimate that the minimum oxygen concentration should be in the range 0.05 - 0.06% at 5 → 10% chromium. Present results indicate the minimum to be somewhat higher, probably about 0.065% oxygen.

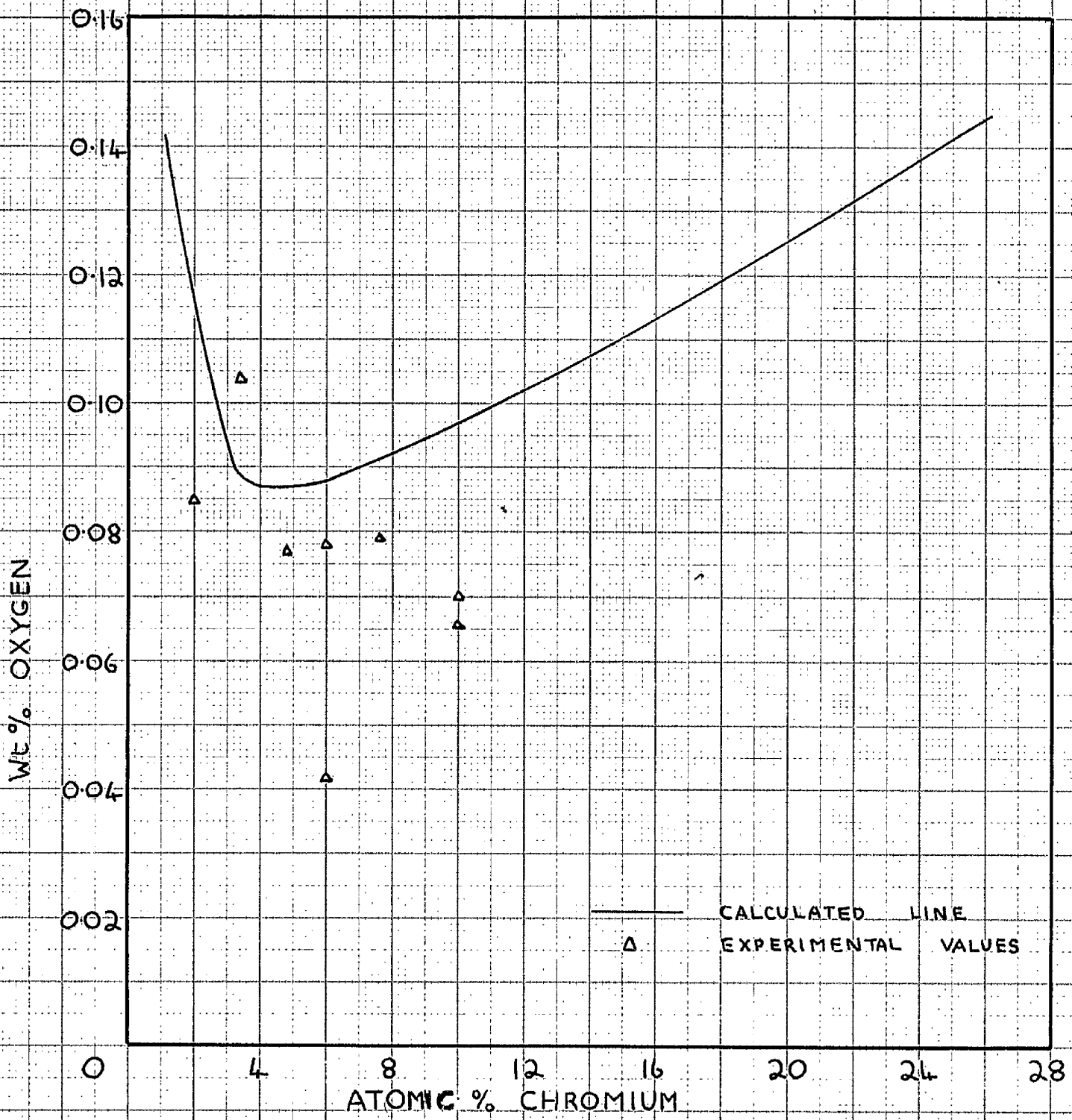


FIG. 28.

CHROMIUM - OXYGEN EQUILIBRIUM (1700°C)

It would seem certain that the minimum oxygen concentration should be in the range  $0.05 \rightarrow 0.07\% O_2$ , therefore the calculated results are too high. Possible errors which would account for the high oxygen contents are listed below.

- (1) Chromium activities incorrect.
- (2) Errors in Floridis and Chipman's <sup>6</sup> data.
- (3)  $f_0^{Cr}$  v % Cr at  $1600^\circ C$  not accurate
- (4) Effect of temperature on  $f_0^{Cr}$  not negligible.

If chromium and iron are assumed to form ideal solutions the fit between the calculated and observed results is worsened. The shape of the chromium-oxygen line would be wrong as well as the actual level. In view of this the activities have been accepted as correct.

Iron-oxygen data at  $1600^\circ C$  have been established with fair accuracy. However as the temperature is raised the various available data are divergent. An error up to 25% may be involved in using Floridis and Chipman's  $1700^\circ C$  figures.

Raising the  $f_0^{Cr}$  v %Cr line by a small amount decreases the calculated oxygen concentrations considerably. If the line is raised so that minimum oxygen concentrations are regarded as most reliable, at 5% chromium the equilibrium oxygen concentration will be 0.073%. This would account for most of the error in the calculated results.

Solutions usually tend to approach ideality as the temperature



is increased. Interaction coefficients would therefore be expected to approach unity. They are so imperfectly understood that it is impossible to calculate quantitatively the effect of an increase in temperature. Interaction coefficients at 1700°C should be greater than those at 1600°C and this could account for the high calculated oxygen contents.

Oxygen contents calculated from free energy data show the same order of variation at the same level as do results calculated from Floridis and Chipman's data. This suggests that the interaction coefficients used are too low. In view of the concordant data at 1600°C it is suggested that the interaction coefficients ( $f_o^{Cr}$ ) are increased on raising the temperature to 1700°C. Further experimental work at 1700°C is required to confirm this.

(L) Application of the Results to the Decarburisation of Chrome Steels.

It is of practical interest to calculate the equilibrium carbon content at any particular chromium concentration.

Richardson and Dennis have determined the activity of carbon in chrome steels at 1560, 1660 and 1760°C and used these to find the relation between carbon and chromium concentrations. It was assumed that chromium behaved ideally in iron and was in equilibrium with chromic oxide at unit activity in the slag. The results were calculated for temperatures ranging from 1550 to 1850°C and compared with the experimental data obtained, mainly at 1750°C, by Hilty. The line calculated by Richardson and Dennis lay below the observed values at 1750°C and so it is of interest to use the chromium activity coefficients obtained in the present work, to see if the discrepancy is lessened.

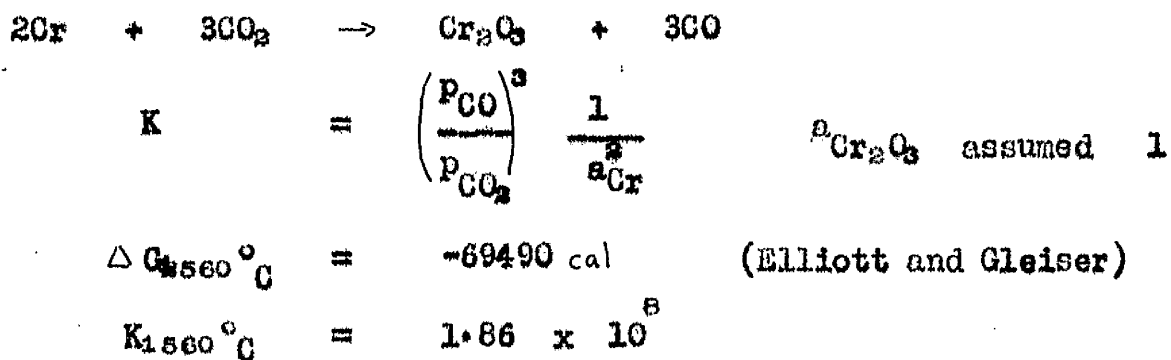
Richardson and Dennis studied this reaction:-



$$K = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2} a_{\text{C}}}$$

Results were plotted showing the % carbon against % chromium at different  $\frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}}$  ratios.

To use these values the following reaction was selected:-



Taking  $a_{\text{Cr}} = 0.1$

i.e. 11.0% chromium

$$\frac{P_{\text{CO}}}{P_{\text{CO}_2}} = 123$$

Since  $P_{\text{CO}} \approx 1$

$$\frac{(P_{\text{CO}})^3}{P_{\text{CO}_2}} = 123$$

Using the data obtained by Richardson and Dennis at this  $\frac{\text{CO}}{\text{CO}_2}$  ratio and chromium content, the equilibrium carbon content will be 0.38% at 1560°C. Calculations have been made for selected chromium activities at three different temperatures. These are listed in Table 17. The chromium activities obtained at 1600°C were used for all temperatures. The error incurred for the results at 1560 and 1660°C should be quite small but may be more significant at 1760°C. Values were calculated at relatively high chromium concentrations only, since chromic oxide was assumed to be the stable oxide phase.

TABLE 17

<u>Temperature</u> <u>°C.</u>	<u>a<sub>Cr</sub></u>	<u>Cr</u> <u>wt. %</u>	<u>(pCO)<sup>2</sup></u> <u>pCO<sub>2</sub></u>	<u>C</u> <u>wt. %</u>
1560	0.1	11.0	123	0.40
"	0.2	16.5	197	0.65
"	0.3	20.0	256	0.95
"	0.4	24.0	310	1.30
1660	0.1	11.0	88	0.20
"	0.2	16.5	141	0.36
"	0.3	20.0	184	0.49
"	0.4	24.0	223	0.70
1760	0.1	11.0	66	0.07
"	0.2	16.5	104	0.17
"	0.3	20.0	137	0.25
"	0.4	24.0	165	0.35

The results are shown graphically in Fig. 29 together with other available data. The use of chromium activities instead of concentrations raises the calculated lines by a relatively small amount. In the range 11 - 20% chromium the agreement with Hilty's observed values is quite satisfactory. At higher concentrations the discrepancy is greater and one would suspect that the activity coefficients used may be too

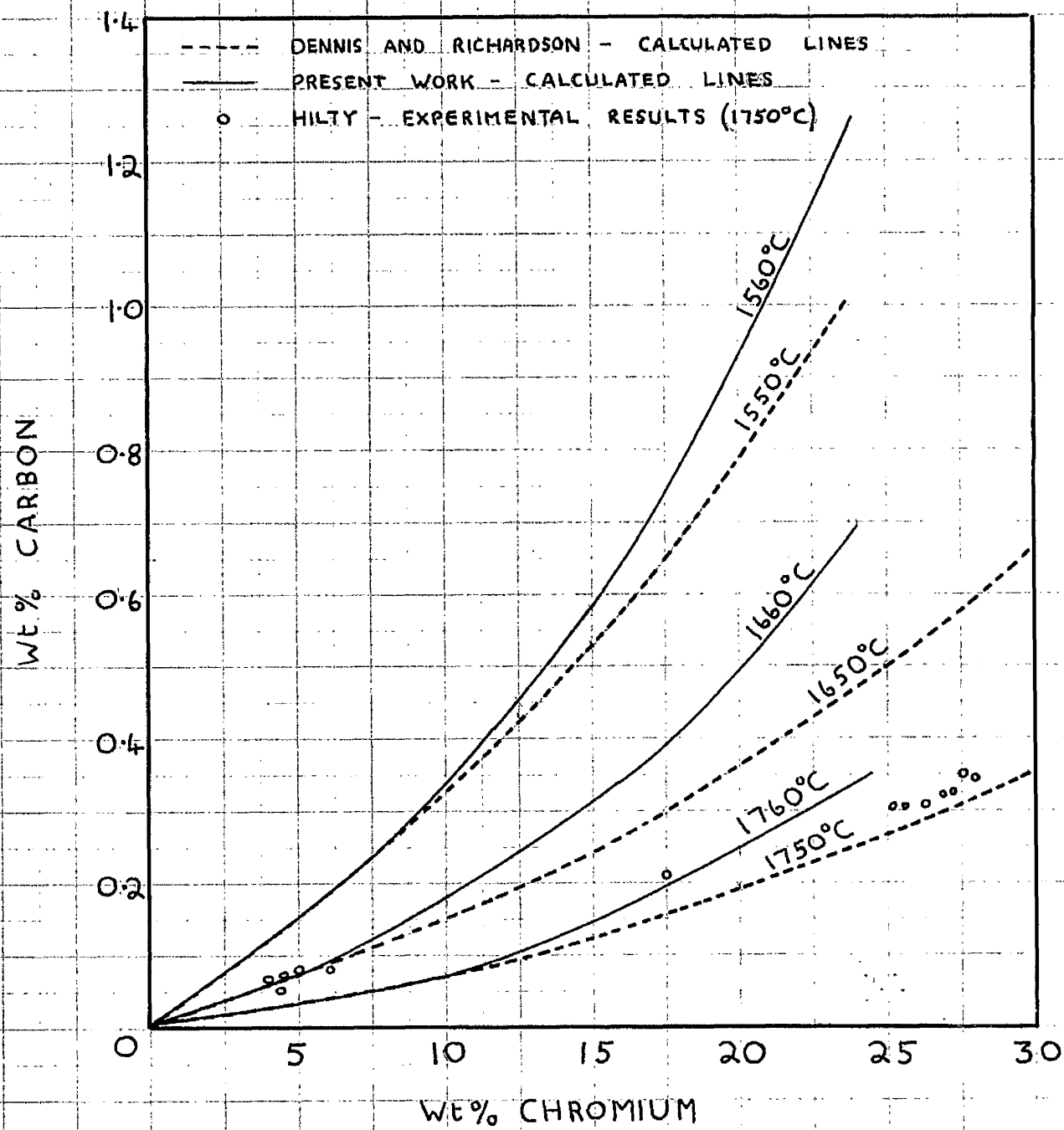


FIG. 29. EQUILIBRIUM BETWEEN CARBON AND CHROMIUM  
 IN LIQUID IRON

high. This is quite possible as solutions tend to approach ideality with increasing temperature.

Useful work on this subject could be obtained by equilibrating iron-chromium-carbon alloys with a gas of known  $P_{O_2}$  in chromic oxide crucibles. The effect of chromium content on the equilibrium carbon concentration could be obtained directly thus avoiding assumptions necessary for the present calculations.

A C K N O W L E D G E M E N T S  
= = = = =

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## R E F E R E N C E S

1. L.S. Darken and R.W. Gurry - Physical Chemistry of Metals  
McGraw-Hill Book Co. 1953 Ed. p 351.
2. J. Chipman Jnl. Am. Chem. Soc. 1933 Vol 55 p 3131
3. M.G. Fontana and J. Chipman Trans. A.S.M. 1936 Vol. 24 p 313.
4. J. Chipman and A.M. Samarin Trans. A.I.M.E. 1937 Vol.125 p.331.
5. M.N. Dastur and J. Chipman Trans.A.I.M.E. 1949 Vol.185 p.441.
6. T.P. Floridis and J. Chipman Trans. Met. Soc. A.I.M.E. 1958 Vol.212.p.541
7. N.A. Gokcen Trans.A.I.M.E. 1956 Vol.206 p.1558.
8. S. Matoba Anniversary Vol. Tohoku Imp. Univ.  
Sendai Japan 1936 p.548
9. W.W. Averin, A.Palyakov and A.M. Samarin Iy vest Akad Nauk S.S.S.R. Otdel  
Tekn Nauk No. 3 1955 p.90.
10. F.S. Tritton and D. Hanson J.I.S.I. 1924 Vol. 110 p. 90.
11. G.H. Herty and M. Gaines Mining and Met. investigation Bulletin  
1927 No. 34.
12. F. Korber and W. Oelsen Mitt K.W.I. 1932 Vol. 14 p. 181
13. J. Chipman and K.L. Fetters Trans. A.S.M. 1941 Vol. 29 p.955
14. C.R. Taylor and J. Chipman Trans. A.I.M.E. 1943 Vol. 154 p.228.
15. H.A. Sloman 3rd Report Oxygen Subcomm. Iron and Steel  
Inst. 1941 p. 311
16. W.A. Fischer and H von Ende Arch. Eisenhüttenw 1952. Vol 23 p. 21.
17. N.A. Gokcen and J. Chipman Trans.A.I.M. E. 1952 Vol,195. p. 171.
18. L.S. Darken and W.G. Gurry. Jnl.Am.Chem.Soc.1946.Vol68. p. 798.
19. F. Adcock J.I.S.I. 1931 Vol. 124. p. 99.
20. F.D. Richardson J.I.S.I. 1950 Vol.166 p.137
21. Basic Open Hearth Steelmaking - Seeley W. Mudd Series 1951 Edition  
p. 635.



22. A.P. Lyubimov and A.A. Gromovskaya *Primenenie Radioaktiv Izotopov v Met Moskov Inst. Stali im I.U. Stalina, Sbornik 1955. No. 34 p. 95.*  
(Chem. Abst. 1959 Vol 53 p. 1060)
23. H. Wada, Y. Kawai and T. Saito - *Science Reports of Research Inst. Tohoku Univ. Series A. Vol. 13 No. 2 (April, 1961) p. 96.*
24. H.M. Chen and J. Chipman *Trans. A.S.M. 1947, Vol. 38. p. 70.*
25. G.L. McCabe, R.G. Hudson and H.W. Paxton - *Trans A.I.M.E. 1958 Vol 212 p. 102.*
26. O. Kubaschewski and G. Heymer *Acta Met. 1960 Vol. 8 p. 416*
27. E.Z. Vintaşkin *Dokl Akad Nauk S.S.S.R. 1958 Vol 118 p.977*
28. M.P. Matveyeva and L.I. Ivanov *Issled po zharoprachn. Splacan T.Z. Moscow. Akad Nauk SSSR. 52 - 56 1957(15610) (Abst.J. Metallurgy 1958.7p.9)*
29. B.V. Linczinskiĭ and A.H. Samarin -*Izvestiya Akademii Nauk S.S.S.R. Otel Techn Nauk (1953) No.5 p.691.*
30. E. T. Turkdogan *J.I.S.I. 1954 Vol. 178 p.278.*
31. F.S. Boerliche and W.M. Bangert *U.S. Bureau of Mines 1945 Report 3813*
32. *Thermochemistry for Steelmaking Pergamon Press Vol 1*
33. D.C. Hilty, W.D. Forging and R.L. Folkman -*Trans A.I.M.E. 1955. Vol 203 p. 253.*
34. W.J. Kramers and J.R. Smith *British Ceramic Soc. Vol. LVI 1957. p.590.*
35. J. Chipman *J.I.S.I. 1955 Vol. 180 p. 97.*
36. C.A. Zaĭffe *J.I.S.I. 1946. Vol 154 No. 2 p.155.*
37. D.C. Hilty *Trans A.I.M.E. (1949) Vol. 185 p.91.*
38. W.E. Dennis and F.D. Richardson *2 papers J.I. S.I. (1953) Vol. 175 p.257 and p. 264*
39. K. Tesche *Archiv fur das Eisenhüttenw. Vol 32 (1961) p. 437.*

- 40.C. Wagner Thermodynamics of alloys. 1952 ed. p.53.  
Cambridge Mass. Addison-Wesley Press.
41. A.M. Samarin, W.A. Mtschedlischvili and W.W. Averin - Neue Hutte. Vol 7.  
(1962) p.206.
42. L. Enskog Physik 2 1911 12 . 56 p.533
43. S. Chapman and F. Dootson Phil. Mag. 1917 Vol. 33 p. 248.
44. P.H. Emmot and J.F. Schultz J. Am. Chem. Soc. 1933. Vol. 55. p. 1376.
45. M.N. Dastur and J. Chipman The Faraday Soc. Symposium on the phys.  
chem. of process metallurgy.
46. L.J. Gillespie J. Chem. Phys. 1939 Vol. 7. p. 530.
47. A. McLean Ph.D. thesis. Glasgow Univ. 1963.
48. N.A. Gokcen J. Am. Chem. Soc. 1951. No.3 Vol.73.  
p.3789.
49. H.F. Ramstad and F.D. Richardson Trans. Met. Soc. A.I.M.E. 1961  
Vol. 221. p.1021
50. Standard Methods of analysis of iron, steel and ferro-alloys  
The United Steel Cos. 1951
51. A.A. Murad Ph.D. thesis Glasgow Univ. 1950.
52. H.A. Sloman U.I.S.I. 1941 Vol. 143 p.298
53. E.N. Bunting Jnl. of Research National Bureau of  
Standards (1931)Vol 4 No.6 p.948.
54. C.A. Zapffe and C.E. Sims "Silicon Monoxide" Iron Age 1942 Vol.149  
No.4 p.29-31 No.5 p.34-39.
55. C.A. Zapffe Jnl. Am. Cer. Soc. 1944. Vol 27.  
p.293-298.
56. F.S. Boericko U.S. Bur. of Mines.Report Invest. No. 3747  
(1944)
57. S. Okada. S. Kokubo, and K. Matsuo - Jnl of Soc. of Chem.Ind. of  
Japan 1943 Vol.46 p.324.
58. K.K.Kelley U.S. Bureau of Mines Bull. No. 476. 1949.
59. L.S. Darken and R.W. Gurry Physical Chemistry of Metals  
McGraw-Hill Book Co. 1953 Ed. p. 266.

60. J. Lumsden Thermodynamics of alloys. 1952. Inst of Metals. London p. 328.
61. O. Kubaschewski and E.L. Evans - Metallurgical Thermochemistry  
3rd Ed. Pergamon London 1958
62. W.D. Kingery Property Measurements at high temperatures  
Chapman and Hall, London p.316 - 318.
63. A. Hallowell Annotated equilibrium diagrams No. 25. The  
Inst. of Metals.
64. S. Marshall and J. Chipman Trans. Am. Soc. Met. 1942 Vol. 30. p.695
65. H.A. Wriedt Dissertation 1954 Mass Inst. Tech.
66. J. Chipman and N.A. Gokcen Trans.A.I.M.E. 1953 Vol. 197 p. 1017
67. N.A. Gokcen and J. Chipman Trans. A.I.M.E. 1953 Vol.197 p.1017
68. C.A. Zapffe Trans. A.S.M. 1947 Vol. 38 p.70.