

EQUILIBRIUM BETWEEN FeO - MnO SLAGS AND IRON-MANGANESE ALLOYS

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By

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SCOPE AND CONTENTS:

This dissertation describes the determination of the equilibrium constant for the reduction of ferrous oxide by manganese to yield manganese oxide and iron. The experimental work was carried out over the temperature range of 1650°C to 1870°C. The results from the present work were combined with reliable published data to give what is considered to be the best relationship between the equilibrium constant and the temperature. The difference between this study and previous work on this topic is the radically new experimental approach. While previous workers used crucible techniques to achieve equilibrium for their system and standard wet chemical analysis, the method used here involved levitation melting and analysis by the electron probe micro-analyser.

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CHAPTER I

Introduction

Manganese is an important alloying addition in Steel. This element influences such aspects of ferrous materials as tensile strength, the position of the nose of T.T.T. diagrams and the composition of the sulphides in steel. Over the years keen interest has been displayed in investigating the equilibrium between slag and metal in the Fe-Mn-O system. In this dissertation there will be a review of the important results obtained over the last thirty-five years.

The manganese reaction studied experimentally is the reduction of ferrous oxide by manganese giving manganese oxide and iron.



Most of the previous work has been done at temperatures close to 1600°C. The present investigation covers the temperature range of 1650°C to 1870°C.

The most significant factor concerning this dissertation is the new technique used to obtain the equilibrium data. Previously slag-metal systems were equilibrated in crucibles which caused a certain amount of contamination in the system. By using levitation melting, as done in the present work, contamination from crucible materials is completely avoided, and higher temperatures are easily attained.

CHAPTER II

Literature Review of the Slag Metal

Distribution of Elements in the Fe-Mn-O System

Recent work by Sanbongi⁽¹⁾ and Ohtani^(1,2) has shown that solutions of manganese in liquid iron show Raoultian behavior. Therefore, for the reaction

$$[\text{Mn}] = [\text{Mn}]_1^{(3)} \text{ wt\%}$$

$$\Delta G^\circ = - 9.11T .$$

Although carbon decreases the activity of manganese in iron-carbon-manganese alloys, other alloying elements have no significant effect on the activity of manganese^(2,4). These facts will not be challenged as the only other elements present will be at extremely low concentrations.

Iron-manganese solutions are in equilibrium with ferrous oxide and manganese oxide as shown by:



Some of the earliest work done on this reaction was by Korber and Oelsen⁽⁴⁾, and Krings et al⁽⁶⁾. The discrepancy between the results from

these early works and contemporary data is due to two major factors. Firstly, in not appreciating the speed of the manganese reaction, the investigators' method of sampling must bring censure from modern scientists. Instead of taking samples by inserting quartz or graphite tubes into the melt, they just allowed the bath to solidify⁽⁷⁾. The second, and to modern investigators the most important factor, was the error in optical pyrometer⁽⁸⁾ temperature measurements caused by fuming and by unreliability of these earlier instruments. Contemporary high temperature chemists have taken more precautions in using optical pyrometry.

The expression for the equilibrium constant is written:

$$K = \left(\frac{a_{\text{MnO}}}{a_{\text{FeO}}} \right) \times \frac{a_{\text{Fe}}}{[\text{wt}\% \text{ Mn}]}$$

where the activity of iron is assumed to be 1 in very dilute solutions

This value of K is the true value no matter what the slag composition as it involves the activities of MnO and FeO in the slag. If weight percentages are substituted instead of activities the value of the constant is somewhat different. Using weight percentages instead of activities, and a silicon saturated slag, Korber and Oelson⁽⁴⁾ obtained a relation for the constant:

$$\log K_{\text{Mn}} = \frac{7940}{T} - 3.172.$$

Values of the constant obtained from this equation are much higher than subsequent workers who worked with FeO-MnO slags that contained only small percents of other constituents.

In 1950 Chipman et al⁽⁷⁾ made the best attempt to sort out this problem. Their major problem was a great deal of scatter and therefore they could not accurately plot the slope of their relationship between $\log K$ and $\frac{1}{T}$. To overcome this, a theoretical calculation was made of the equilibrium constant from data on heats of formation, dissociation and solution. A line parallel to this line was then drawn through the experimental points. The resulting equation obtained was:

$$\log K_{Mn} = \frac{6440}{T} - 2.95$$

Chipman introduced a slight uncertainty into the calculations by applying the free energy of Fe_xO to an equilibrium constant involving $(FeO)_t$ where Fe_xO is the actual ferrous oxide formula and $(FeO)_t$ suggests that all of iron oxides exist in this form. A recalculation was done in the same work on an ionic basis and applied to the data. The resultant equation was found to be:

$$\log K_{Mn}^{++} = \frac{6760}{T} - 3.09$$

where K_{Mn}^{++} is the equilibrium expressed on an ionic basis.

Flood⁽⁹⁾ has derived an expression for presenting equilibrium data for complicated slags that contain a mixture of anions and cations. Values of their K' for various authors will be compared in the discussion using:

$$\log K' = \sum_i \frac{1}{N'_{\text{anion}}} \log K'_i$$

where K' is the equilibrium constant on an ionic basis

and N'_{anion} is the electrically equivalent fraction. For example

$$N'_{\text{PO}_4^{3-}} = \frac{3N_{\text{PO}_4^{3-}}}{N_{\text{Fe}} + 2N_{\text{O}^{2-}} + 3N_{\text{PO}_4^{3-}} + 4N_{\text{FeO}_4^{4-}} + \dots}$$

$$N'_{\text{O}^{2-}} = \frac{2N_{\text{O}^{2-}}}{N_{\text{Fe}} + 2N_{\text{O}^{2-}} + 3N_{\text{PO}_4^{3-}} + 4N_{\text{FeO}_4^{4-}} + \dots}$$

The slags that Chipman used contained up to 4 percent SiO_2 .

In his calculations both slag and metal are taken to be ideal. This assumption is valid as Bell⁽¹⁰⁾ et al, in 1952, showed that K'_{Mn} is not affected by the silica content until it exceeds 5 percent, where K'_{Mn} is the equilibrium constant expressed in percent rather than activities.

In 1953 Turkdogan⁽¹¹⁾ criticized Chipman's method of obtaining a mathematical relationship between $\log K'_{\text{Mn}}$ and $1/T$, by saying

"They [Chipman et al] calculated the free-energy change in reaction (1) $[\text{Fe} + \text{MnO} = \text{Mn} + \text{FeO}]$ from existing thermal data and a estimated heat of fusion for manganous oxide, and then drew a line through their experimental points but parallel to the calculated line. The possible errors in their estimate are so great as to make the slope of the calculated line no more reliable than that derived from their experimental points."

By statistical methods Turkdogan then derived the following from Chipman et al's data:

$$\log K_{Mn} = \frac{7406}{T} - 3.436$$

Of most importance is a close scrutiny of the FeO-MnO system to determine whether it is one or multi-phase when solid. In Bell's⁽⁸⁾ excellent review of this topic he says:

"Ferrous oxide and manganous oxide are completely miscible in the liquid state, but evidence of the solid structure of the mixed oxide is still conflicting. Hay, Howat and White⁽¹²⁾ and Benedicks and Lofquist⁽¹³⁾ have published diagrams showing a two phase region in the solid state while Andrew, Maddocks and Howat⁽¹⁴⁾ and Herty and Daniloff⁽¹⁵⁾ have indicated that FeO and MnO are completely miscible in the solid state. Jay and Andrews⁽¹⁶⁾ and Petterson⁽¹⁷⁾ carried out an X-ray study of the solid state and found only one phase present throughout the system. Carter, Murad and Hay⁽¹⁸⁾ have provisionally accepted the evidence of complete miscibility in their discussion of the FeO-MnO-SiO₂ system. Sloman and Evans⁽¹⁹⁾ and Whiteley⁽²⁰⁾ by examining FeO-MnO inclusions from steel found no evidence of immiscibility in the inclusions. The weight of evidence is in favour of complete miscibility in the solid state, the X-ray evidence being most convincing. The complete solid solubility in this system was also demonstrated by Foster and Welch by X-ray measurements⁽²¹⁾.

The question of the form of the oxide of manganese and iron in the slag has to be answered. It is widely accepted that the only oxide of manganese is MnO . The Handbook of Chemistry and Physics gives the dissociation temperature of MnO_2 to MnO as $535^\circ C$. None of the papers covered in this survey has mentioned manganese to be in the slag in any other form than MnO .

Chipman⁽⁷⁾ acknowledges that his system contained Fe_2O_3 in quantities generally less than 4%, although some values were as high as 5.69%. In the study of the $FeO-MnO-SiO_2$ system, Muan⁽²²⁾ thinks the Fe^{3+} content insignificant enough to neglect. In both of these cases the Fe_2O_3 content was lower at the higher temperatures.

Figure I shows a plot of % Fe_2O_3 / % $Fe_2O_3 + \% FeO$ against temperature for Chipman's⁽⁷⁾ data. As the temperature goes up the Fe_2O_3 content decreases. If this plot is extrapolated to $1900^\circ C$ the Fe_2O_3 content is about 1.5%.

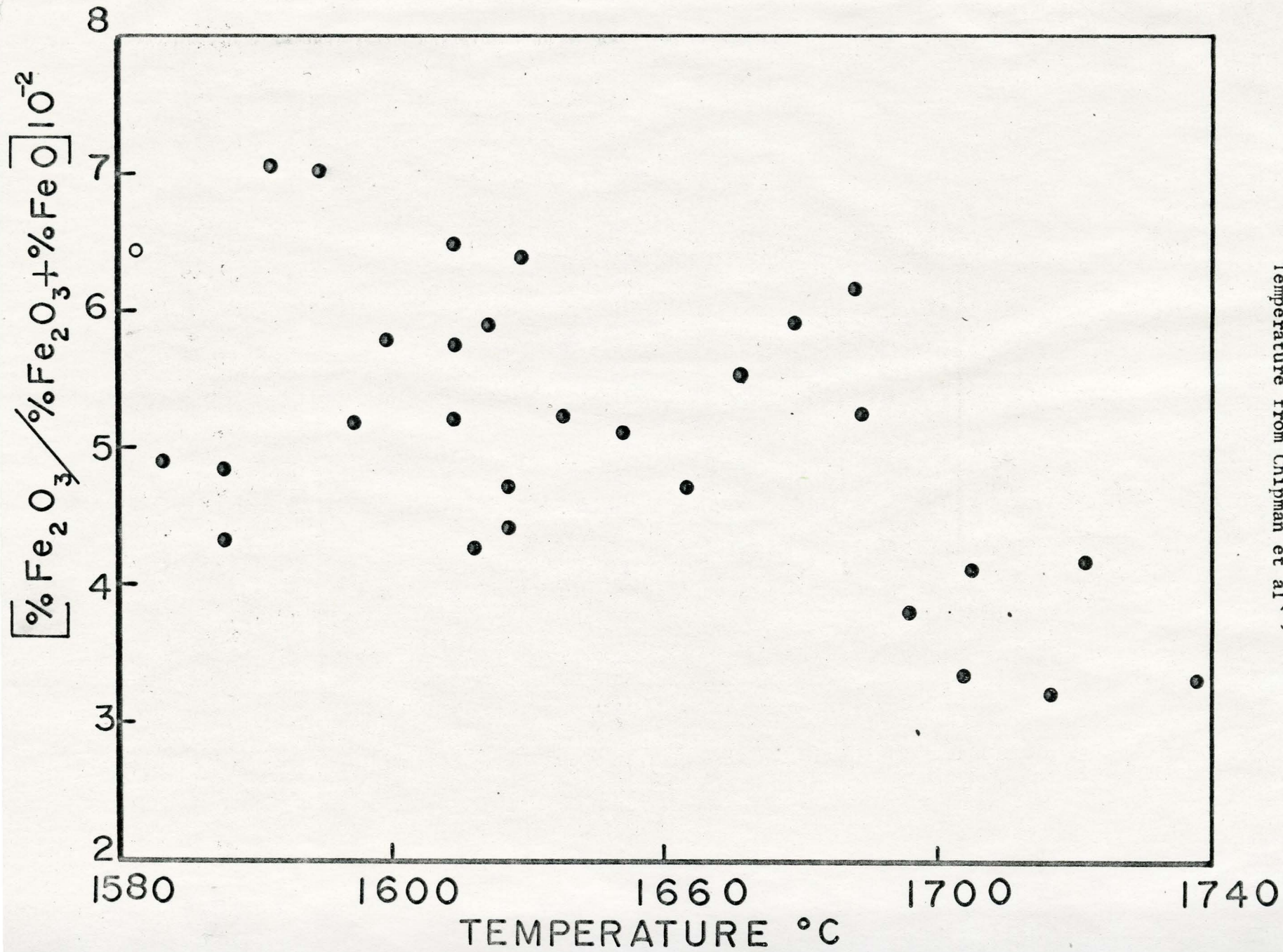


Fig. 1 Plot of $\frac{\%Fe_2O_3}{\%Fe_2O_3 + \%FeO}$ in Slag Against Temperature from Chipman et al (7)

CHAPTER III

Experimental Apparatus

Figure 2 shows the major components used - Levitation Coil, Casting Mechanism and Gas Supply - in obtaining specimens for analysis. The missing items are the Transformer, High Frequency Generator and Optical Pyrometer. Figure 3 shows a sectioned drawing of the apparatus.

A standard Jenkins⁽²³⁾ coil manufactured out of 1/8 inch, outside diameter, copper tube was used. The coil would slip around a 15 mm pyrex or vycor working tube. To facilitate handling while in operation the coil was wrapped in glass wool or asbestos.

The power for the levitation coil was supplied by a Tocotron 10 k.W, 200 amp high frequency generator that operated at 450 kc/sec. A 7.5:1 transformer was used to allow the lower temperatures to be reached more easily. (When not using the transformer, higher gas flow rates were required to reach the lower temperatures).

Temperature measurements were made with a Milletron two colour pyrometer with an operating range of 800°C to 1800°C. The instrument was calibrated over a range of 1300°C to 1650°C, with an error of $\pm 10^\circ\text{C}$ on a carbon saturated iron melt. The calibration was checked at frequent intervals against the melting point of the levitated specimen. The calibration was done with a 13% Rh-Pt thermocouple.

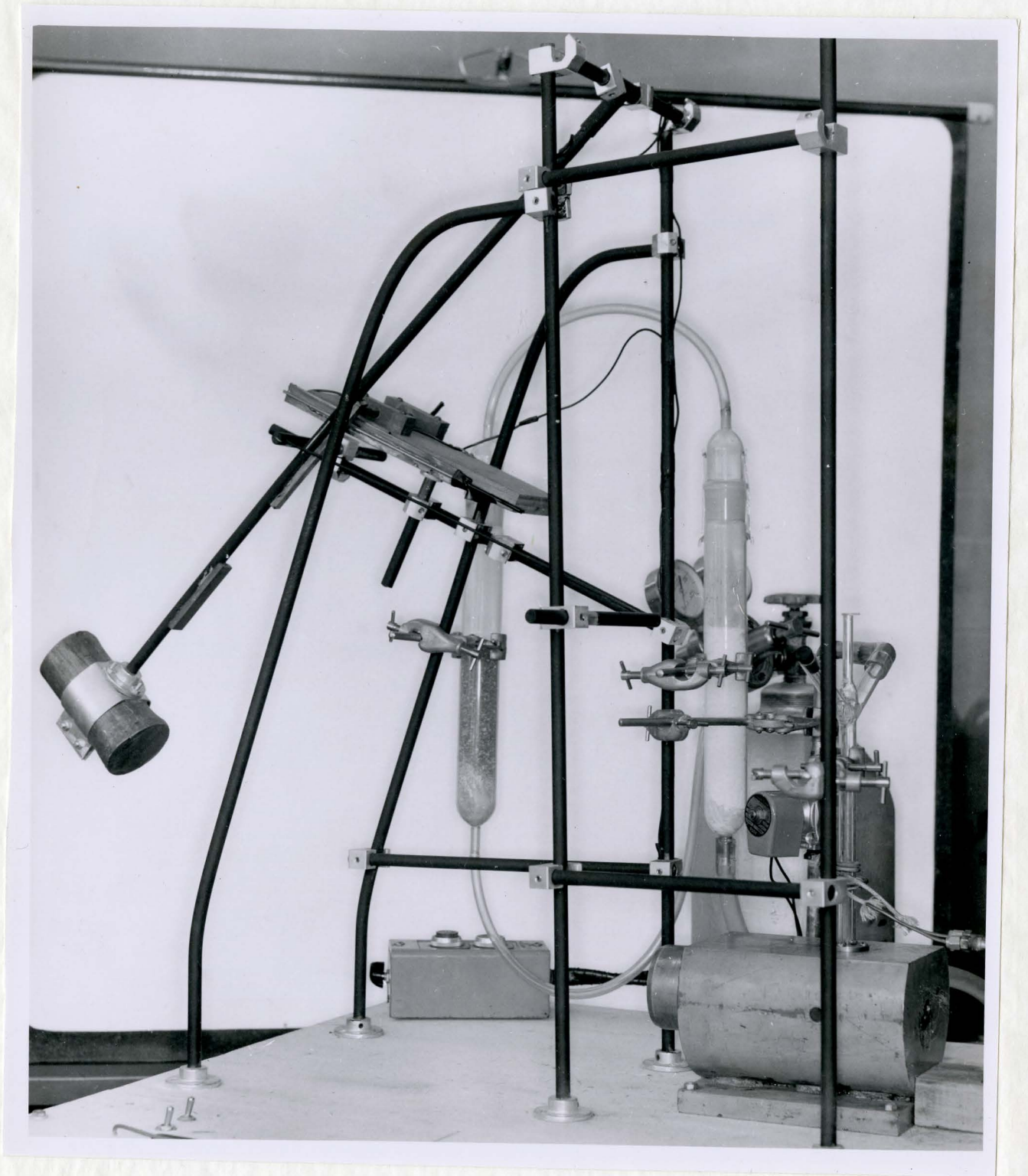


Figure 2 -- The Major Components of the Levitation Equipment --
Casting Mechanism, Gas Supply and Levitation Coil

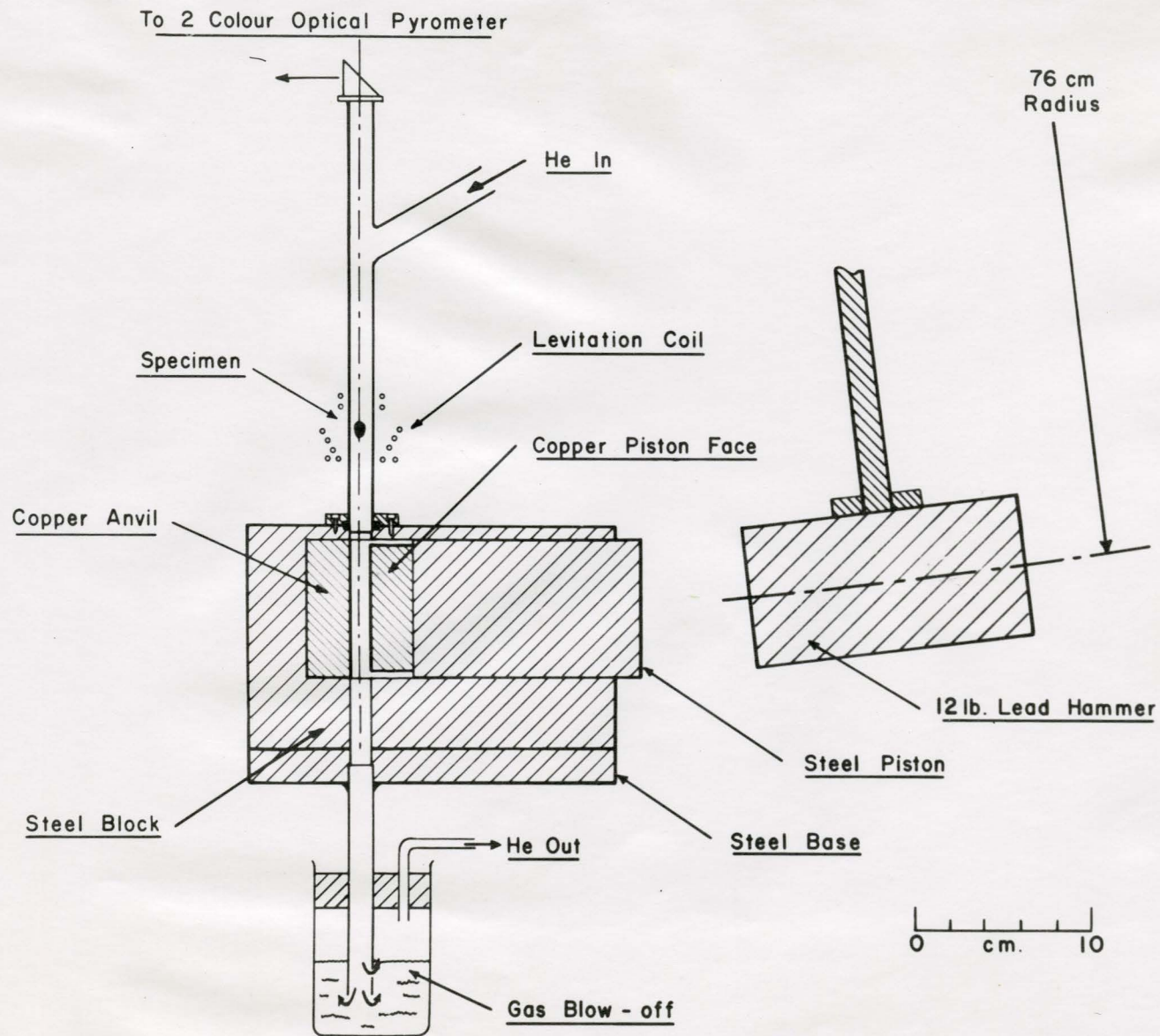


Fig. 3 Sectioned Drawing of Experimental Apparatus

The most critical part of the experimental technique was the quenching of specimens. It was imperative that the chemical equilibrium of the system be preserved. Therefore, the specimen had to be frozen very rapidly. A number of methods were considered. These will be discussed briefly.

It was necessary to try many unorthodox methods to try and obtain the equilibrated specimens in one intact piece, with the slag in one region on the surface of the specimens. The assumption used in all of the early quenching methods was that if solidification could be accomplished in under one second the equilibrium would not shift any significant amount.

The first technique tried was to pass helium over the specimen while still levitated. This method failed because, while the cooling gas removed heat, the induced current simultaneously heated the specimen. This reasoning led to the technique of allowing the specimen to fall down a sixteen foot pipe, filled with helium; elapsed time one sec. This method, nevertheless, did not work. If the drop had been long enough, the specimen would have eventually solidified, but only after a significant change in the equilibrium.

The technique tried next was to drop a copper mould down the apparatus trapping the specimen and subsequently cooling it by the time both had

plunged seven feet, with an elapsed time of 0.7 seconds. The major advantage of this technique was that the specimen was recovered as one intact piece with the slag located on a bottom surface in one area, making it very convenient for electron probe microanalysis. It makes little difference as to the shape of the hole in the mould. The only really important aspect of this technique was to make the walls of the leading edges of the mould thin enough so as not to strike the specimen until the specimen was completely enveloped by the mould. As it turned out the shift in equilibrium was too fast for this technique; however, for a reaction with slower kinetics this might work.

It was later discovered that if the levitated specimens were dropped on a brass plate, although the slag was broken up, large pieces were still left throughout the specimen and on the surface. The cooling rate appeared very fast as red heat was reached and passed in less than a second. Further evidence to substantiate this was the appearance of the quenched specimen as a plate rather than a lump. A copper plate was substituted for the brass which gave even a faster quench.

As the collected data in Chapter V will show all of the previously discussed methods failed to give good reproducibility. The best method of obtaining a rapid quench, once it was known that using one second as the criterion was totally inadequate, was to drop the liquid drop between two copper plates and hammer it into a thin plate. The quenched specimens, however, that were produced by this apparatus were much thinner than when dropped on a copper plate; ten thousandths of a centimeter compared with two millimeters. The problem with this technique is that the slag was badly broken

up. This makes it more difficult to find large areas on which to aim the electron beam. However, as the results will show, this method produced consistent results.

Figure 3 shows a section drawing of the hammer. It consisted of a hollowed steel cylinder and a steel piston weighing 5 kilograms. The face of the piston had a copper disk one inch thick fastened to it. The anvil part of the equipment was another copper disk bolted to the bottom of the cylinder.

The method of analysis was electron probe microanalysis. The probe used in this work was a converted electron microscope. The electron beam has a diameter of less than four microns with an acceleration voltage of 25 to 30 kV. The X-ray take-off angle was 55° . The instrument had twin spectrometers, one operated under vacuum, the other in a helium atmosphere.

CHAPTER IV

Experimental Procedure

A discussion will now follow on specimen preparation, levitation melting and equilibration, quenching, preparation of polished specimens and method of analysis.

Specimens were made from 1/4 inch diameter Armco Iron Rods. Pieces of about 0.7 gr. were cut and a hole drilled in them to facilitate holding the required amount of electrolytic manganese. The slag was added by oxidizing the specimens with a torch.

To equilibrate the specimens the following steps were followed:

- a) the system shown in Figure 3 was purged with helium for about one minute;
- b) the current was turned on to the maximum value of 200 amp. in the primary coil;
- c) the specimen was put into the levitation coil on the end of a glass rod. As soon as the temperature of the specimen passed the Curie point, after one or two seconds, it would levitate and the glass rod was removed and the apparatus sealed. Because the specimen was iron-manganese-oxygen, if any oxygen did diffuse against the flow of helium and cause more oxidation of the iron than originally given, no harm would have been done.

Once the specimen was levitated it had to be melted and brought to equilibrium. Three factors were responsible in reaching the final steady state temperature; the height of the specimen in the coil, the rate of flow of gas, and the density of the gas. The lower the specimen sits in the

coil (the lower the current) the stronger the effect of the magnetic field to produce an induced current to yield a higher temperature. The reverse is also true. The shape of the coil causes the co-planar turns at the bottom to be the major controlling factor. Any electro-magnetic properties are proportional to the square of the distance between conductors and specimen and the current. Therefore the distance is the overriding factor.

The faster the gas flows over the surface of the specimen the faster heat is removed. Therefore, the temperature of the specimen is lowered.

The density of the gas is an important factor in both getting the specimen to melt and to control the temperature. Helium, because of its low molecular specific heat will remove too much heat while trying to melt the specimen. The addition of a gas with higher specific heat, such as nitrogen, will enable the specimen to gain enough heat to melt.

The gas flow was not measured and neither was the helium to nitrogen ratio. The flow of both was regulated into a common mixing bottle by a needle valve on each gas cylinder.

Once the specimen had been brought to temperature it was left for about 30 seconds to equilibrate. The results, next chapter, give the actual times. To quench the specimen it was simply dropped three and one half inches and hammered against a copper anvil by a copper hammer. To initiate the quenching process the apparatus was set up in such a way that as the hammer was sent swinging, the current was cut off at a critical point, found

by trial and error. The specimen was dropped to be hammered to a thickness of 0.01 cm. Figure 5 shows a levitated drop, photographed from the bottom, with the slag attached to the droplet.

Electron probe micro-analysis has been used exclusively to determine the composition of both the metal and slag phases. The quenched foil was mounted in translucite with a sample of pure iron and pure manganese, and polished by standard metallographic methods using papers and diamond paste. It was then coated with a thin evaporated layer of carbon and examined by an electron probe micro-analyser built in our laboratories by Dr. G. R. Purdy and Mr. H. Walker. The concentration of the elements concerned in this study are given as follows:

$$\% X = \frac{I_X}{I_X^O} \quad \text{in the slag;}$$

$$\% \text{ Mn} = \frac{I_{\text{Mn}} - I_{\text{Mn}}^{\text{BG}}}{I_{\text{Mn}}^O} \quad \text{in the alloy,}$$

where I_X = intensity of either iron or manganese in the slag (time^{-1}),

I_X^O = intensity of pure iron or manganese (time^{-1}),

I_{Mn} = intensity of manganese in the alloy over a long enough period of time to get a significant statistical difference between it,

and $I_{\text{Mn}}^{\text{BG}}$ = the intensity of the background count on pure iron.

The above, are derived from Birks⁽²⁴⁾ whose equations simplify to those presented here because iron and manganese have little or no effect, caused by enhancement or absorption, on one another. Also, oxygen has no effect on these two elements.

A better method for analysis of this system would have been to produce a set of standards covering the range of compositions of interest. In the case of the alloy this was considered unnecessary, as the iron-manganese system is expected to exhibit ideal spectrochemical behaviour⁽²⁴⁾.

In the case of the slag, however, many attempts were made to produce standards. A mixture of Fe_2O_3 and MnO_2 was heated together in an iron crucible. A sample of this mixture was taken by placing a steel rod on the surface and withdrawing a drop. Although the crucible was in a nitrogen atmosphere so that the solution was not becoming richer in FeO the method failed. There was so much segregation in the material that it was useless. A set of standards was manufactured by melting the constituents in this instance FeO prepared by dissociating ferrous oxalate and MnO , prepared by dissociating either manganese dioxide or manganese oxalate, on the end of a tungsten filament. The material produced was so porous that it also was useless.

The method of obtaining data was straight forward. Alloy data was collected by counting on the alloy and pure iron for 30 minutes. The beam was allowed to traverse the surface so as to even out any segregation in the alloy. As for the slag, it was impossible to traverse the small slag surfaces so a series of spots were analysed. Total time counting on the slag was 10 minutes, 2 minutes on 5 points. As a guide to the order of magnitude of the probe readings the range for I_{Mn}^{O} was 100,000 to 120,000 counts/min. where as I_{Fe}^{O} ran between 20,000 and 60,000 counts/min. The I^{O} values remained constant for as long as the filament lasted.

CHAPTER V

Results

The following four tables show the weights of the various constituents put into the specimens, the results of the hammer quenched specimens, a comparison of the equilibrium constant as obtained using the hammer as against those obtained by dropping specimens onto copper and brass plates, and the results of Chipman⁽⁷⁾ that are included with the data of this work to give the final equilibrium equation.

TABLE I - Starting weights of specimens levitated and quenched by
the hammer and anvil and the time levitated at temperature

Sample Number	Weight Fe (gm)	Weight Mn (mg)	Weight O (mg)	Time (sec)
119	0.782	24	17	60
120	0.745	20	13	60
121	0.745	20	13	60
122	0.879	36	24	60
123	0.907	28	14	60
124	0.864	29	20	60
125	0.864	29	20	60
126	0.785	26	17	30
127	0.984	29	14	60
128	0.914	32	24	30
129	0.838	28	20	30
130	0.970	33	23	30
132	0.808	24	12	30
133	0.872	28	24	15
137	0.993	35	20	25
140	1.009	25	14	30

TABLE II - Results of Hammer Quenched Specimens

Sample Number	Metal Analysis		Slag Analysis		K [*]	Temperature	
	% Mn	% Mn	% Fe	% O*		Levitation	At Hammer
119	0.26	25.8	45.5	28.7	2.21	1665	1650
120	0.71	45.4	30.3	24.3	24.3	1750	1733
121	0.66	42.8	35.9	21.3	1.84	1750	1733
122	0.89	43.6	31.0	25.4	1.61	1750	1733
123	0.55	37.6	39.5	22.9	1.76	1795	1777
124	0.88	42.0	35.1	26.1	1.38	1860	1841
125	0.83	37.7	35.7	26.6	1.29	1860	1841
126	0.54	32.1	38.1	29.8	1.61	1850	1831
127	0.41	34.0	43.4	22.6	1.93	1760	1743
128	0.52	38.5	40.2	21.3	1.87	1770	1753
129	0.65	30.5	43.5	26.5	1.11	1890	1870
130	0.86	43.3	33.0	23.7	1.57	1825	1807
132	0.87	42.4	30.8	26.8	1.62	1760	1743
133	0.89	43.0	33.0	24.0	1.49	1890	1870
137	0.78	39.4	35.2	25.4	1.47	1845	1831
140	0.27	25.5	48.2	26.3	2.00	1725	1709

* by difference

TABLE IA

Data Collected From Electron Probe

Sample Number	Alloy			Slag			
	I _{Mn} ^o	I _{Mn}	I _{Mn} ^{Bg}	I _{Mn} ^o	I _{Fe} ^o	I _{Mn}	I _{Fe}
119	118,480	770	462	107,140	61,480	27,641	28,911
120	121,760	1362	457	111,314	55,705	50,522	16,877
121	115,421	1266	503	114,293	58,280	49,073	20,879
122	116,397	1545	512	120,463	60,471	52,561	18,732
123	117,462	1147	500	119,280	60,680	44,768	23,900
124	123,470	1165	477	123,840	57,180	51,995	20,125
125	119,976	1464	469	122,176	62,140	46,136	22,220
126	103,760	1018	478	102,655	58,175	32,920	22,131
127	103,760	923	500	102,655	58,175	34,808	25,204
128	103,760	1037	500	102,655	58,175	39,554	23,347
129	110,222	1158	440	117,633	62,051	35,903	28,228
130	115,142	1465	463	126,291	63,281	54,621	18,028
132	126,023	1628	543	122,735	56,707	52,004	17,506
133	119,595	1600	534	119,150	19,238	51,359	6,351
135	135,507	1730	670	122,735	56,707	48,423	20,041
140	76,670	655	445	80,973	20,200	20,648	9,747

TABLE III - Equilibrium Constant and Temperature Values of Chipman⁽⁷⁾

Temperature °C	K_{Mn}
1655	2.70
1640	2.73
1620	2.41
1680	2.01
1690	2.47
1610	2.47
1630	2.67
1672	2.24
1730	2.18
1738	1.62
1689	2.07
1583	3.24
1743	1.79
1750	1.58
1723	1.99
1637	2.62
1615	2.93
1587	3.31
1598	3.44
1597	3.62
1633	2.82
1638	2.70
1706	1.90
1718	1.85
1697	2.24
1646	2.45
1630	2.94
1568	3.91
1580	4.43

TABLE IV - Effect of Quenching Technique on the Apparent Value of K^1

Quench	Temperature ($^{\circ}\text{C}$)	No. of Specimens	K^1_{Observed}	K^1_{Chipman}
Brass Plate	1760	8	6.9 - 10.8	1.66*
Copper Plate	1645	11	2.6 - 8.5	2.52*
Hammer	1760	16	1.70*	1.66*

* calculated from statistical equations

CHAPTER VI

Discussion

The significance of this work is two fold. Firstly, there is the verification of the fact that Chipman's work was quite accurate within the experimental limits. Secondly, that the technique of levitation melting can be used for equilibrium problems at high temperature.

Data were collected in this work over the range of 1650°C to 1840°C with most of the data above 1730°C. Chipman's data covered the range of 1568 to 1750°C with the majority of points below 1700°C. A combination of both sets of data as shown in Figure 4 covers the entire range between 1650°C and 1840°C. By applying statistics to both sets of data an equation for the equilibrium constant was calculated to be:

$$\log K = \frac{5990}{T} - 2.706.$$

When this equation is compared with that of Chipman et al⁽⁷⁾ in Chapter II, $\log K = \frac{6440}{T} - 2.95$, one can see the striking similarity. It is of great significance that such a good correlation was obtained by both the usual crucible method and the new approach of levitation.

An interesting development is a comparison of the three equilibrium equations that can be statistically calculated from Chipman⁽⁷⁾ and the data gathered in this dissertation. The first equation is the one above

that is felt to be the true equation for the equilibrium constant:

$$\log K = \frac{5990}{T} - 2.706.$$

The second equation is calculated Chipman's data alone, the third is an equation calculated from the data collected in this dissertation.

They are, respectively:

$$\log K = \frac{7118}{T} - 3.293,$$

$$\log K = \frac{4572}{T} - 2.011,$$

and are shown in Figure 4.

These last two equations show the pitfalls that can occur if not enough points are taken or the range of temperatures is too narrow.

The following table shows a comparison of the equilibrium constant as obtained by different workers.

TABLE V - Comparison of Equilibrium Constants of Many Workers

	Bell ⁽⁸⁾	Korber and Oelsen ⁽⁵⁾	Chipman ⁽⁷⁾ et al	Krings ⁽⁶⁾ et al	Fisher ⁽²⁵⁾ Fleischer	Present Work
at 1550°C K'_{Mn}	3.5	2.4	3.8	3.1	3.4	3.7
at 1600°C $K'_{O=}$	2.4	2.3	3.2	--	--	3.1

The equilibrium constants of Chipman et al and the present work are equivalent to K'_{Mn} , whereas with the rest, K'_{Mn} represents the equilibrium constant of the reaction in a complicated slag. The $K'_{O=}$ values are equilibrium values with respect to melts that contain only oxides.

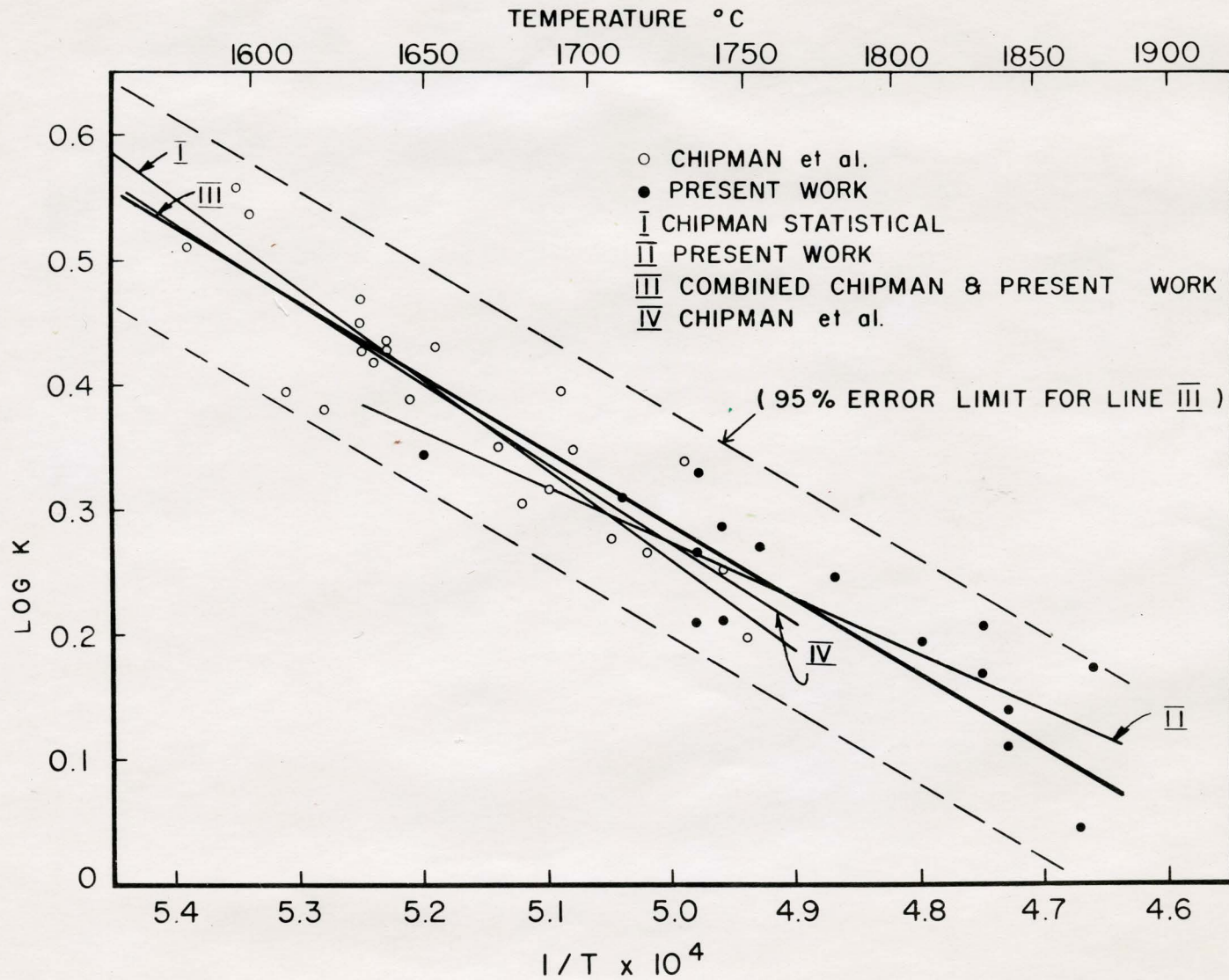


Fig. 4 Plots of log K vs 1/T

The sources of error in measuring K were temperature measurement, estimation of temperature decrease while specimen falls from coil to be quenched, and analytical errors involving the electron probe.

The two color pyrometer, as described in Chapter III, was accurate to $\pm 10^\circ\text{C}$ which gives an error of $\pm 0.5\%$ at 2000°K . Pure iron (melting point 1535°C) was used as a calibration standard.

When the specimens had been equilibrated they were dropped 3 1/2 inches before being quenched by the hammer. In the very short time, it takes for this drop (0.14 sec) the specimen loses heat. An estimation of the heat loss and the consequent temperature drop was calculated as a summation of the heat losses due to conduction - convection and radiation. The standard heat transfer formulae are:

$$q = h \Delta T A$$

where q is the total heat transferred by conduction-convection
 ΔT is the difference between the specimen and the flowing gas
 A is the surface area of the specimen
 h is the heat transfer coefficient

$$\frac{hD}{K_f} = 2 + 0.6 \left(\frac{D \rho_f V_a}{\mu_f} \right)^{1/2} \left(\frac{C_p \mu}{K} \right)^{1/3}$$

where

D is the diameter of the specimen
 K_f is the thermal conductivity of the fluid at the mean temperature of the specimen and the fluid, i.e. mean conduction layer temperature

ρ_f density of the fluid at mean temperature of fluid and specimen

V_α is velocity of fluid as specimen falls

C_p is specific heat of fluid at 0°C

μ_f is viscosity of fluid at mean temperature of specimen and fluid

μ is viscosity of fluid at 0°C

K is the thermal conductivity of fluid at 0°C

By substituting the latter equation into the former, and expressing V_α in terms of time, the integration gives the total heat loss due to conduction-convection.

For the radiation component the following equation was used:

$$\frac{q_r}{A} = 0.1714 \epsilon_w \left[\left(\frac{t_w + 460}{100} \right)^4 - \left(\frac{t + 460}{100} \right)^4 \right]$$

where:

q is the total heat loss

A is the area of the sphere

ϵ_w is the emissivity of the surface

t_w is the temperature of the surface of the specimen

t is the temperature of the surroundings

For a specimen of 0.6 gm it was estimated that the temperature loss was 16°C at 1730°C and 19°C at 2000°C giving a cooling rate of 120°C/sec and 140°C/sec respectively. The final temperature assigned to each specimen was levitated temperature minus the interpolated value between 16°C and 19°C.

Two sources of error are involved in this calculation: Firstly, the levitated specimens are not spherical but slightly tear shaped. However, it is suspected that they become, if not completely, more spherical once out of the influence of the electro-magnetic field. Secondly, the weights of the specimens were not the same. The calculation was done over the range of weights of 0.6 gm to 1.0gm and found to increase by only 0.5°C.

The major source of error was the analysis of the specimens. These errors were two fold; electronic drift in the instrument and a statistical error involved in counting. To obtain numbers that would have statistical significance for the manganese content it was necessary to count on the alloy for thirty minutes and similarly on the pure iron for the same period of time. To take into account any drift in the electronics the procedure was to do a background count on the iron for fifteen minutes then count on the alloy for thirty minutes followed by fifteen more minutes on the iron. To ensure a correction against a drift in the I_{Mn}^O values, a series of three one minute counts was made every time a shift from alloy to iron or iron to alloy was made. The counting time on the slag was much shorter, only ten minutes. In this case counts were made on the standard to obtain I_{Mn}^O and I_{Fe}^O before and after the data was collected from the slag. These precautions should keep the errors due to drift at a minimum. If the drift was perfectly linear between the start and end of an analysis there should be negligible error. However, because the probe could pick up interference from outside sources there is the possibility of a small error.

When counting, it is a statistical fact that the 95% confidence limits lie in the range $N \pm 2\sqrt{N}$. The order of magnitude of the slag data is such that only 1% error can be attributed to it; whereas, the alloy data yielded an error of 6%. These values were calculated on the mean values of I_{Fe}^0 , I_{Mn}^0 . This last figure can be diminished even further if lower and lower counts were taken. In figure 4 the 95% confidence limits for the equilibrium equation are plotted. Visually one can see that the statistical spread of the data is good in that all but one point fell within the 95% confidence limits. This is borne out by the correlation coefficient's value of 0.94, which is considered good for least squares plots.

Table II in the results shows a comparison of equilibrium values obtained using various quenching techniques. The only technique that gave good reproducibility was the hammer. First impressions were that a specimen dropped on a copper block would be quenched rapidly enough. To the eye, red heat was reached in well under a second. An estimation of the order of magnitude of the cooling rate for a hammer quenched specimen will be attempted using a standard equation due to Carslaw and Jaeger⁽²⁶⁾. The model is for linear flow of heat in a solid bounded by two parallel planes and boundary condition of zero boundary temperature.

The formula is:

$$V = V_0 \cos \frac{\pi x}{2l} e^{-K\pi^2 t/4l^2}$$

where:

- V is the final temperature ($^{\circ}\text{C}$)
 V_0 the initial temperature ($^{\circ}\text{C}$)
 l the distance between boundaries (cm)
 t the time (sec)
 x the position between the boundaries
 $K = k/\rho c$
 $= \frac{\text{conductivity}}{\text{density} \cdot \text{specific heat}}$

If the rate of cooling is considered at the centre of the slab, where $X=0$, the above simplifies to:

$$V = V_0 e^{-K\pi^2 t/4l^2}$$

The hammer quenched specimens were gauged and found to be 10 thou-cm. The cooling rate was calculated on a liquid slab 10 thou-cm over a cooling cycle of 1800°C to 1500°C . The calculated rate was 10^6 $^{\circ}\text{C}/\text{sec}$. The actual value was less than this. A calculation done on a slab with a thickness of 0.6 cm (the diameter of a levitated drop) gave a value of about 10^3 $^{\circ}\text{C}/\text{sec}$, however, a realistic value for the cooling rate is probably 10^5 $^{\circ}\text{C}/\text{sec}$.

A theoretical calculation for the time required for equilibrium may be estimated if it is assumed that the rate of attainment of equilibrium between slag and metal was controlled by diffusion in the slag phase. This is entirely reasonable as transport in the induction stirred metal droplet will be rapid, chemical reaction at the interface should also be rapid at the temperatures considered (1650°C to 1850°C), and diffusion in the unstirred

slag phase will be relatively slow. The time (t) required to achieve a close approach to equilibrium can be obtained by considering the relation⁽²⁷⁾

$$t = \text{constant} \frac{x^2}{D}$$

for diffusional process in a stagnant phase, where D is the diffusion coefficient, X is the thickness of the phase. The constant is unity for 93% achievement of equilibrium, and equal to 2 for 99% approach to equilibrium. Thus, to calculate the time for equilibration typical values of D and x are required. Accurate data for the coefficients of diffusion of ions in molten slags are very scarce. However, the coefficient of self diffusion of calcium in lime-alumina - silica slags is about 10^{-5} cm²/sec at 1550°C, and about 10^{-4} cm²/sec at 1750°C⁽²⁸⁾. The slags in this study are much more fluid than lime-alumina-silica slags. Also because of the rapid quench needed to obtain equilibrated specimens it is not unlikely that D could be 10^{-3} or 10^{-2} cm²/sec. Using this as a typical value for D along with $x = 10^{-2}$ cm one finds $t = 0.2$ sec. Therefore, the estimated quenching rate is more than sufficient to prevent a shift in equilibrium.

If the slag was pure FeO-MnO the oxide content should lie between 22.3% and 22.6%. The fact is that the majority of oxygen values found by difference, were above this value. It is possible that some of this oxygen is present as Fe₂O₃. However, there is oxygen available to take care of even the most pessimistic estimate of Fe³⁺ ion content. Figure 5 shows a photomicrograph of alloy and slag taken at 500 magnification. It is therefore suggested that because of the holes on the surface

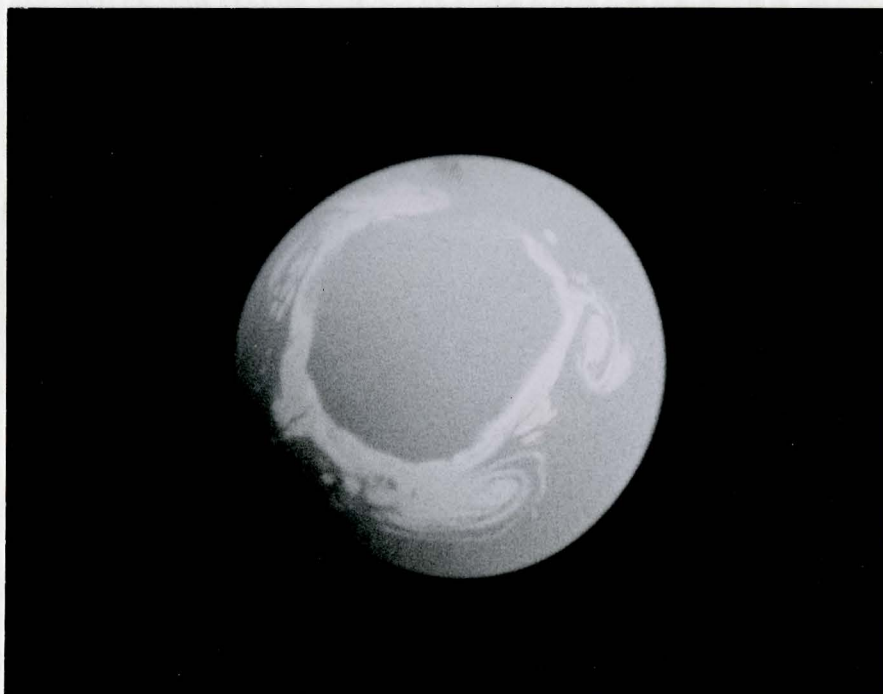
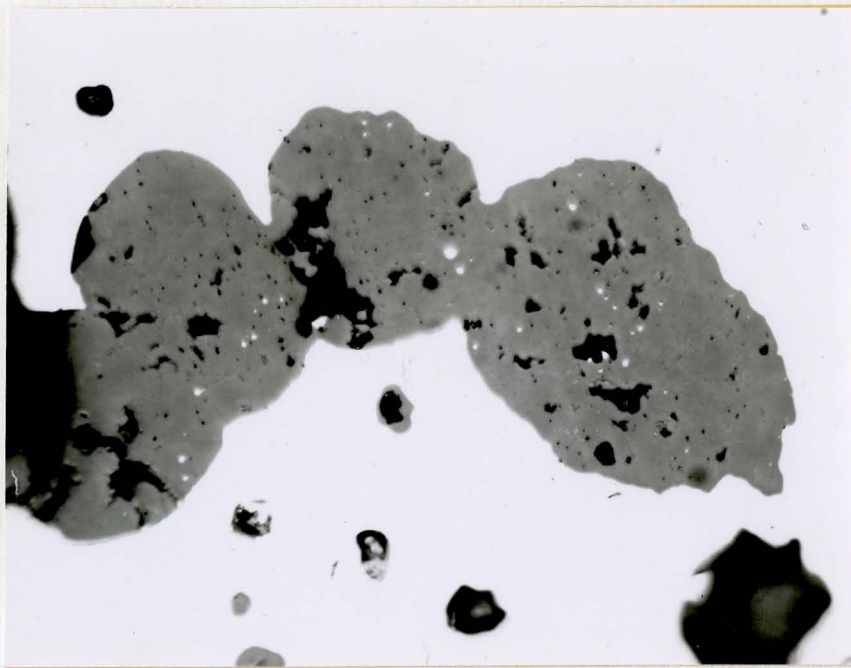


Figure 5 - a) Photomicrograph showing typical slag sample at 500X, unetched
b) Bottom of levitated drop showing slag attached to drop.

and internal porosity, the spectrometers collect X-rays as if less iron and manganese were present. However, because of the similarities between the properties of the two elements, this has no effect on the iron to manganese ratio. It should be emphasized that this ratio, and not the absolute values of the iron and manganese contents, determine K_{Mn} (see page 3).

In Chapter IV the formula for iron or manganese content in the slag was given as $I_{Fe(Mn)} / I_{Fe(Mn)}^{\circ}$. When compared with Birks⁽²⁴⁾ calculations there is a difference of 0.5%. However, the error, quoted by Birks, in his tables of data is "not better than 5%" and therefore, the difference mentioned above can be neglected.

CHAPTER VII

Conclusions

The conclusions to this work are as follows:

- 1) The data obtained in this work, when combined with Chipman's⁽⁷⁾ data for the reaction



give what is considered to be the best equation for the dependence of the equilibrium constant on temperature:

$$\log K_{\text{Mn}} = \frac{5990}{T} - 2.706$$

where

$$K_{\text{Mn}} = \frac{(a_{\text{FeO}})}{(a_{\text{MnO}})} \times \frac{[a_{\text{Mn}}]}{[a_{\text{Fe}}]}$$

this leads to a standard free energy for the reaction:

$$\Delta G^\circ = -27,404 + 12.4T \text{ cal mole}^{-1}$$

- 2) High temperature equilibrium problems can be studied using levitation melting, hammer quenching, and electron micro-probe analysis of the quenched specimens.
- 3) Suggested future work would be to investigate systems of more complex nature. For example, the FeO - MnO - SiO₂ ternary would be a good starting point. The results from such work in conjunction with data from the present study could be used to check the validity of Flood's ionic theory of slags.

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