

KINETICS OF MANGANESE OXIDE REDUCTION FROM BASIC SLAGS  
BY SILICON AND CARBON DISSOLVED IN LIQUID IRON

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## NOMENCLATURE

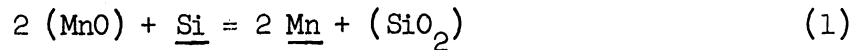
A	Interfacial area, $\text{cm}^2$
B	Constant
$C_i$	Concentration of component i, moles/ $\text{cm}^3$
D	Diffusion coefficient, $\text{cm}^2/\text{sec}$
E	Energy of activation
$\Delta F^\circ$	Standard free energy of reaction
$J_i$	Molar flux of component i, moles/ $\text{cm}^2/\text{sec}$
$K_i, K'_i, K''_i$	Equilibrium constants for equation i
M, M'	Metallic element
<u>M</u> , <u>M'</u>	Element in solution in iron
M	As subscript, metal phase
(MO)	Oxide in solution in slag
MW	Molecular weight
P	Pressure, atmospheres
Q	Slag-metal ratio defined by $\frac{W_M}{W_S} \frac{MW_{MnO}}{MW_{Mn}}$
R	Gas constant, 1.987 cal/mole/ $^\circ\text{K}$
S	As subscript, slag phase
T	Temperature, $^\circ\text{K}$
V	Volume, $\text{cm}^3$
W	Weight, grams
$a_i$	Thermodynamic activity of component i
$f_i$	Activity coefficient of component i $\equiv \frac{a_i}{(\%i)}$
g	As subscript, indicates component is a gas
$h_i$	Height of phase i, cm
$k_1, k_2, k'$	Reaction rate constants, mole/ $\text{cm}^2 \text{ min}$
ln	Natural logarithm

$n_i$	Moles of component i
t	Time in seconds unless stated otherwise
$x_i$	Mole fraction of component i
y	Rectangular coordinate
$\gamma_i$	Activity coefficient of component i $\equiv \frac{a_i}{x_i}$
$\delta$	Effective thickness of the concentration boundary layer, cm
$\nu$	Kinematic viscosity, $\text{cm}^2/\text{sec}$
$\rho$	Fluid density, $\text{gm}/\text{cm}^3$
o	As a superscript, concentration of reactant at zero time
%	Concentration in weight percent



## ABSTRACT

The reduction of manganese oxide from a basic slag by silicon and carbon dissolved in liquid iron at steelmaking temperatures was studied to determine the rate-controlling step for each process. The two reactions studied were:



The experiments were carried out under an argon atmosphere in a resistance-heated vertical-tube furnace. Crucibles made of zirconia or of graphite held the two liquid phases during the experiment. Sampling and analyzing the slag phase gave time-concentration curves for the system. This data was applied to theoretical models derived for possible diffusion and chemical reaction rate-limiting steps. Results obtained by varying parameters such as temperature, stirring rate, concentration, and melt geometry indicated which of these theoretical models described the limiting reaction mechanism for the system.

The reduction of manganese oxide by silicon is a fast reaction and reaches equilibrium within ninety minutes. The rate of stirring has a marked effect on the rate of this reaction, while on the other hand, the effect of temperature is very small. This identifies the rate-controlling step as diffusion rather than interfacial chemical reaction. The effect of other variables revealed that (a) diffusion of manganese in the iron phase is the slow step, (b) the value of  $\frac{D}{\delta}$  for manganese in iron at 1550°C is  $7 \times 10^{-4}$  cm/sec, (c) the energy of activation for the apparent rate constant is 7 Kcal per mole, and (d) increasing the amount of silicon in the iron decreases the diffusion coefficient of manganese.

The reduction of manganese oxide by carbon is slower by an order of magnitude than reduction by silicon. Since its rate is quite sensitive to temperature but unaffected by stirring, the rate-controlling step is an interfacial chemical reaction. Of several plausible interfacial reactions, only the reaction  $(O) = \underline{O}$  provides a model that is consistent with all the observed data. Therefore, it is postulated that this is the rate-limiting step for manganese oxide reduction by carbon.

## INTRODUCTION

In steelmaking, as in any money-making venture, it is essential to produce the desired product as cheaply as possible. From a technical standpoint, the economics of steelmaking depend to a great extent upon the thermodynamics and kinetics of the two-phase system producing the steel. The thermodynamics of the system determine whether or not the desirable components are largely in a reduced state and the undesirable components are in an oxidized state, as desired at the end of the process; kinetics determines how fast the desired conditions can be obtained.

In making stainless steel, an oxidizing slag is first used to remove undesirable components from the iron, such as carbon and phosphorus. At the same time, however, valuable components, such as manganese, will also be oxidized. The economics of the process can be greatly improved by a high recovery of these alloying elements by reducing them again to the metallic state. Of course, the rate of reduction, or time required for the process, is very important.

The equilibrium relations pertinent to the reduction of manganese oxide from the slag by silicon and carbon have been studied to some degree, but little is known about the mechanisms that control the rate of the processes. The purpose of this investigation is to study the rate of reduction by silicon and by carbon and to determine the rate-limiting steps for each process. The effects of stirring rate, temperature, composition, and melt geometry are investigated as a means of identifying the slow step.

The experimental technique used was to hold slags containing manganese oxide in contact with liquid iron containing silicon or carbon at steel-making temperatures. The rate of transfer of components in the system

was determined by sampling the slag phase at regular intervals and sampling the metal phase when necessary. The two-phase system was held in a graphite crucible, thus maintaining carbon saturated iron as the metal phase for the reduction of manganese oxide by carbon. A zirconia crucible was used for the reaction when silicon dissolved in liquid iron was the reducing agent.

Once the rate-limiting mechanism for these two reactions has been determined, steps could be taken to speed up the commercial process. For instance, if diffusion is found to be the controlling step in the process, then the rate of the reaction can be increased by increased stirring of the system. On the other hand, any temperature change made would be relatively ineffective in changing the rate of the reaction. If an interfacial chemical reaction is the rate-controlling step, just the opposite would be true.

It is hoped that the results of this basic study on slag-metal kinetics will contribute to process development in the area of steelmaking kinetics.

## REVIEW OF LITERATURE

A review of the literature was made in two general areas. Kinetic studies that have been carried out on slag-metal reactions in iron and steelmaking are summarized, and thermodynamic studies that give information pertinent to this investigation are also reviewed.

### A. Kinetic Studies of Slag-Metal Systems

Relatively little work has been done in the area of slag-metal kinetics on a laboratory scale. Two reasons for this are the complexities of the systems and the difficult materials problem confronted in trying to hold liquid metals and oxides in a laboratory crucible at steelmaking temperatures long enough for reactions to occur. Graphite crucibles are stable for these two-phase systems, however, and several investigations have been made on two fundamental reactions.

One of these is the study of desulphurization of iron. Chang and Goldman<sup>1</sup> made one of the earliest investigations and determined that the rate of this reaction is increased by increasing the basicity of the slag. Derge, Philbrook, and Goldman<sup>2</sup> investigated the rate of diffusion of sulphur in the slag and came to the conclusion that the concentration gradient of sulphur in the slag was removed by convection rather than by diffusion. Grant, Kalling, and Chipman<sup>3</sup>; Grant, Troili, and Chipman<sup>4</sup>; and also Derge, Philbrook, and Goldman<sup>5</sup> studied the effect of various alloying elements in iron on the rate of desulphurization. Some alloys, such as silicon and manganese, greatly improved the rate of reaction and it was felt that these metals act as carriers for sulphur across the slag-metal interface. The same elements found in excess in the slag hindered the desulphurization process. The theory that the rate is controlled by two opposing first-order chemical reactions was proposed by the latter

investigators. Ramachandran, King, and Grant<sup>6,7,8</sup> made studies and presented the possibility that the reaction is electrochemical in nature. Chipman and Fulton<sup>9</sup> made a further investigation that showed some effect of stirring on the reaction rate, thereby claiming that diffusion controlled the reaction under constant chemical conditions; however, they concluded that chemical factors had an overriding importance in determining the rate of transfer. Kirkbride and Derge<sup>10</sup> studied the sulphurization of iron and found this reaction much slower than desulphurization. They concluded that the rate-limiting step for this reaction is the transport of silicon or other reducible electro-positive ions to and from the interface so that electrical neutrality was preserved in the slag. Schulz<sup>11</sup> determined the rate-controlling step to be a first-order chemical reaction in both the forward and reverse direction.

The second slag-metal reaction that has been studied is the reduction of silica from slag by carbon in graphite-saturated iron. Chipman and Fulton<sup>12</sup> did the original work in this area. As for most of these studies, Chipman's and Fulton's work was done in an induction furnace under an atmosphere of carbon monoxide. The research showed that metal composition and stirring rate had very little effect on the rate of reaction. Due to the slow rate and the high energy of activation for the system, the authors concluded that the rate-controlling step was the breaking of the silicon-oxygen bond. Yoshii and Tanimura<sup>13</sup> concluded that the rate of reaction was controlled by a chemical reaction with the driving force for the reaction being the concentration of silica in the slag. Rawling and Elliott<sup>14</sup>, in their study of the same reaction, found that transport of oxygen in the metal boundary layer at

the slag-metal interface was rate-limiting. They also concluded that another step involving either silicate complexes in the slag or interfacial reactions at the slag-metal interface was only an order of magnitude faster than the slow step.

Turkdogan, Grieveson, and Beisler<sup>15</sup> used a somewhat different experimental approach. Instead of having approximately equal amounts of slag and metal in a graphite crucible, as did the above investigators, they used a slag to metal ratio of 33:1. The purpose of this was to minimize changes in slag composition during the experiment. The system was devised to allow the release of carbon monoxide bubbles at the slag-metal interface. This approach was successful in some runs, but apparently went awry in others. They concluded that when gas bubbles are present at the slag-metal interface, the interfacial chemical reaction is the rate-controlling process in the transfer of silicon from slag to metal. They also postulated that the slower reaction occurring when gas bubbles were not present at the interface was limited by the transport of oxygen from the slag-metal interface to the walls of the graphite metal container.

The reduction of chromium oxide by carbon in graphite-saturated iron was studied by McCoy and Philbrook.<sup>16</sup> A rotating crucible, which maintained the slag in a whirlpool of iron so it would not contact the walls of the graphite crucible, was used. These investigators concluded that the system was reaction-rate controlled and that the reaction was a first-order reaction with respect to chromium concentration in the slag. They found that the rate was independent of temperature and slag basicity. Their rate constant had values ranging over an order of magnitude with an average value of  $10^{-3}$  in units of  $\text{gm min}^{-1} \text{ cm}^{-2} (\% \text{Cr})^{-1}$ .

Sano, Shiomi, and Matsushita<sup>17</sup> made an investigation of the manganese transfer rate between molten iron and basic slags, using a resistance furnace. They produced crucibles made of calcium oxide and titanium oxide to hold the two-phase system during the experiment, but, because of the difficulty of making the crucibles, only a handful of runs were made. Four or five of these involved the reduction of iron oxide in the slag by manganese in the metal, and then two runs were made of the reduction of manganese oxide in the slag by silicon in the iron. Because of the small number of runs made, only qualitative statements could be made about the reaction. They concluded that the diffusion of silicon in iron was very important and could be the rate-limiting step for the process. Initial conditions for the two runs made using silicon as the reducing agent were silicon 0.2 and 0.5% and manganese oxide 9 and 12% respectively. With these low silicon concentrations their conclusion is logical.

Theoretical considerations for reaction kinetics in the two-phase slag-metal system are presented by Wagner<sup>18</sup> and Ward<sup>19</sup>.

#### B. Thermodynamic and Transport Data Sources

A great deal of material is available in the literature concerning the thermodynamics of the systems involved in this research. Data on viscosities, densities, activities and activity-coefficients, free energies of formation, equilibrium data, diffusion constants, and energies of activation have helped immensely in the experimental design and calculations involved in this project. The primary source for this information has been Volume II, Thermochemistry for Steelmaking by Elliott, Gleiser, and Ramakrishna<sup>20</sup>, which is a compilation of thermodynamic and transport properties. Additional sources of data are summarized below.



Viscosity and liquidus data for the quaternary slag system used in this investigation are found in Osborn, DeVries, Gee, and Kraner<sup>21</sup>; Turkdogan and Bills<sup>22</sup>; Kato and Minowa<sup>23</sup>; and Kekelidze, Mikiashvili, and Odilavadze<sup>24</sup>.

Standard free energy of formation revisions for the silicon-silicon oxide system are given by Taylor<sup>25</sup>. More free energy data is found in Sawamura and Sano<sup>27</sup>.

Activities of slag components are given for silica by Rein and Chipman<sup>26</sup>, for manganese oxide by Abraham, Davies, and Richardson<sup>27</sup>, and also by Turkdogan and Pearson<sup>28</sup>, and for oxygen ions by Toop and Samis<sup>29</sup>.

The activity of silicon in iron alloys is given by Chipman, Fulton, Gokcen, and Caskey<sup>30</sup> and also by Chipman and Baschwitz<sup>31</sup>.

Studies concerning equilibrium of manganese between slag and metal phases have been made by Rassbach and Saunders<sup>32</sup> and by Philbrook and Tarby<sup>33</sup>.

Schwerdtfeger<sup>34</sup> has recently determined the diffusion constant of oxygen in liquid iron to be  $1.2 \times 10^{-4}$  cm<sup>2</sup>/sec.

Riddiford<sup>35</sup> has developed a relationship between energy of activation found as a function of the diffusion coefficient and the energy of activation found as a function of the diffusion coefficient divided by the boundary-layer thickness. He found that the boundary-layer thickness varied exponentially with temperature. Based on his study, one would expect the energy of activation to be nearly the same, whether it is calculated from D or from  $\frac{D}{\delta}$ .

## EXPERIMENTAL PROGRAM

In order to determine the rate-limiting step for the two reactions under consideration, it was necessary to vary certain parameters in the system such as stirring rate, temperature, and melt geometry. Also, it was necessary to find a crucible material other than graphite for melting down the two-phase system in order to study the reduction of manganese oxide by silicon without simultaneous side effects of graphite reduction. The design of the experimental system chosen takes these factors into account.

In this section, theoretical models are derived for many of the possible rate-limiting steps. Then the experimental apparatus and procedures are described and discussed in detail.

### A. Theoretical Models

The derivation of the theoretical models is dependent upon the experimental conditions under which the reactions take place. Typical conditions are presented here as a basis for understanding the assumptions and approximations made in the derivations which follow.

The reduction of manganese oxide by silicon was a fast reaction. Samples were taken to follow the reaction for twenty-four minutes and to indicate equilibrium conditions at the end of two hours. A typical change in concentration of the various components from the first sample taken at three minutes to the final one at the end of twenty-four minutes is given below in weight percent.

Mn	0.5 - 1.5%
Si	1.2 - 0.95%
MnO	3.8 - 2.0%
SiO <sub>2</sub>	33.7 - 34.5%

Initially, there was no manganese in the metal phase.

The reduction of manganese oxide by carbon was a slow reaction and samples were taken for two hours to follow the reaction. Typical concentrations of the various components from the first sample taken fifteen minutes after the start of the reaction to the final one at the end of two hours are given below.

Mn      0.7 - 1.5%

MnO     3.4 - 2.0%

Initially, there was no manganese in the metal phase. The iron remained saturated with graphite throughout the run. The carbon monoxide produced by the reaction maintained one atmosphere CO pressure at the interface between the slag and the metal, although the system was swept out with a very low flow of argon gas at one atmosphere pressure.

If a two-phase slag-metal reaction occurs, such as



the kinetics of the reaction can be broken down into the following principal steps.

1. Transport of the reactants from the bulk phases to the slag-metal interface.

2. The phase boundary reaction, which may involve several steps.

3. Transport of the reaction products from the slag-metal interface into the bulk phases.

Under most conditions, significant concentration differences are found only in the vicinity of an interface. Therefore, according to Wagner<sup>18</sup>, considerations may be confined to the concentration distribution in the boundary layer, and concentration differences in the bulk liquid may be disregarded.

The possible rate-controlling step for the process can be broken down into one of two main categories, diffusion control or chemical reaction control. If the chemical reaction step is much faster than one or more of the diffusion steps, equilibrium is reached at the interface, and the rate of the process is determined by the diffusion of one or more of the reacting species to or from the interface. If, on the other hand, the chemical reaction step is the slow step in the process, then the concentration of any component is essentially the same at the slag-metal interface as it is in the bulk of the phase, and the rate of the process is determined by the rate of the phase-boundary reaction. This is chemical reaction control. A schematic illustration for these two limiting steps is shown in Figure 1.

When the rate of the process is being controlled by a slow diffusion step, the rate can be defined mathematically by applying Fick's First Law, which states that the flux of component i is proportional to the concentration gradient of component i in the direction of diffusion. Stating this mathematically gives\*

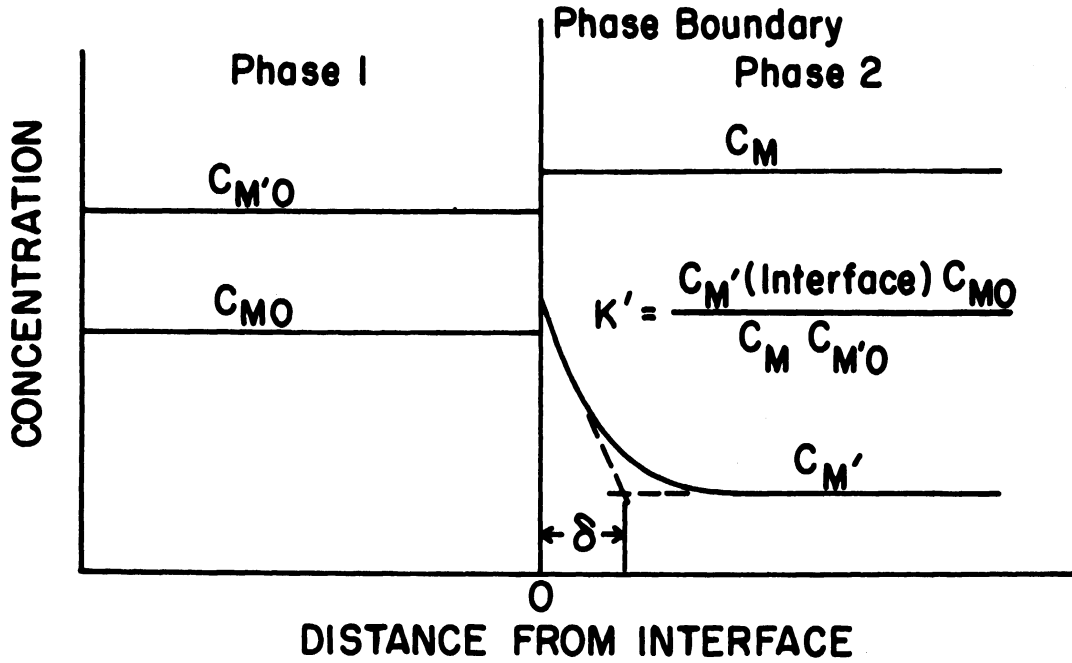
$$J_i = -D \frac{\partial C_i}{\partial y} \quad (4)$$

By describing the driving force in terms of concentration and distances as shown in Figure 1a and rewriting the flux in terms of moles, time, and interfacial area, then

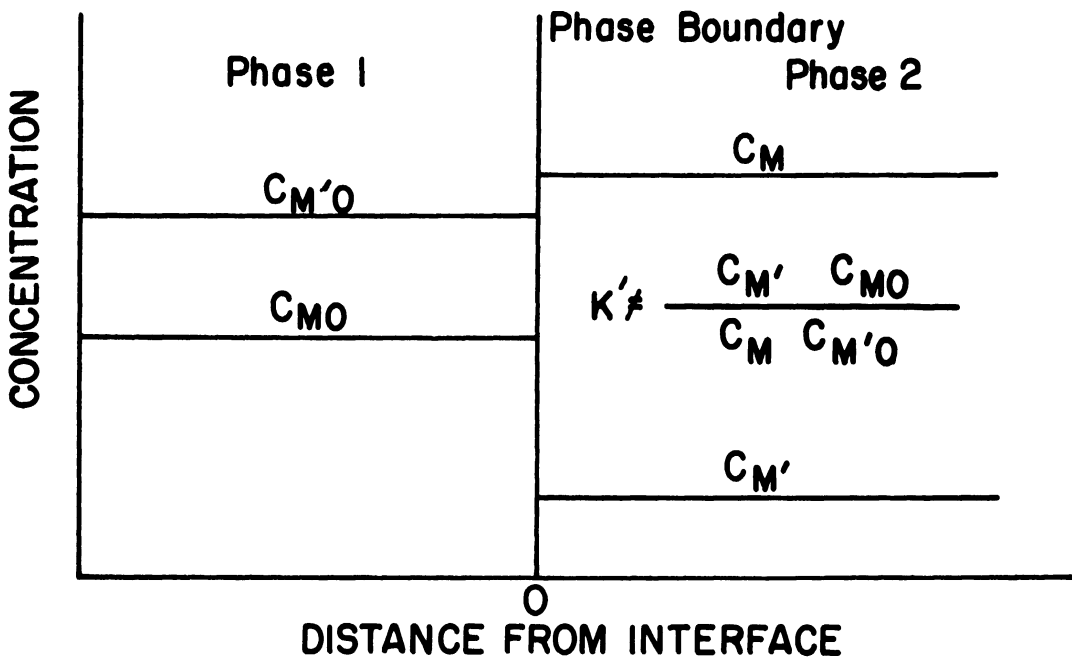
$$\frac{dn_i}{dt} = \frac{DA}{\delta} \left[ C_{i(\text{interface})} - C_{i(\text{bulk})} \right] \quad (5)$$

---

\*Mathematical terms are defined in the nomenclature at the beginning of the thesis.



(a) Diffusion of  $M'$  in Phase 2 Controls Reaction



(b) Chemical Reaction at Phase Boundary Controls Reaction

Figure 1. Illustration of Diffusion and Chemical Reaction Control for Reaction  $M'O + M = MO + M'$ .

The concentration of component  $i$  at the interface is that concentration which is in equilibrium with the other components at their instantaneous compositions in the bulk phase.

The law of mass action states that in any system, the rate at which a reaction proceeds is proportional to the activities of the reactants. This law can be applied here in the case of chemical reaction control of the process. In the case of Equation (3), then, the rate in the forward direction is

$$-\frac{dn_M}{dt} = k_1 a_M^p a_{M'O}^q \quad (6)$$

Also, the rate in the reverse direction is

$$\frac{dn_M}{dt} = k_2 a_{M'}^r a_{MO}^s \quad (7)$$

The powers  $p$ ,  $q$ ,  $r$ , and  $s$  are defined by the stoichiometry of the system. When the system reaches equilibrium, the forward rate will be equal to, but opposite in direction of, the reverse rate. Therefore, the ratio of the two rate constants,  $k_1$  and  $k_2$ , is equal to the equilibrium constant for Equation (3) as follows:

$$\frac{k_1}{k_2} = K_3 \quad (8)$$

At any time during the reaction, the net rate of reaction is the sum of the forward and reverse rate.

$$-\frac{dn_M}{dt} = k_1 a_M^p a_{M'O}^q - k_2 a_{M'}^r a_{MO}^s \quad (9)$$

Combining Equations (8) and (9) and eliminating  $k_2$  gives

$$-\frac{dn_M}{dt} = k_1 \left[ a_M^p a_O^q (M'O) - \frac{1}{K_3} a_M^r a_{(MO)}^s \right] \quad (10)$$

Using these concepts as a basis, theoretical models are derived on the following pages for cases where one particular step in the overall reaction is rate-limiting. This is done for all possible diffusion rate-limiting steps for both reactions studied and for several postulated chemical reaction rate-limiting steps. The question of whether the reaction can be defined as limited by only one step will be discussed later.

1. Reduction by Silicon - Diffusion Control

There are four possible diffusion models for the reaction presented in Equation (1). They are for the diffusion of manganese in the metal and in the slag phase and for diffusion of silicon in the metal and in the slag phase. All four models are derived below.

a. Diffusion of Manganese in the Metal

Adapting Equation (5) to the reaction shown in Equation (1), when the diffusion of manganese in the metal is the rate-limiting step:

$$\frac{dn_{Mn}}{dt} = \frac{DA}{\delta} \left[ C_{Mn}(\text{interface}) - C_{Mn}(\text{bulk}) \right] \quad (11)$$

Changing concentrations to weight percent,

$$\frac{d(\%Mn)}{dt} = \frac{D}{\delta h_M} \left[ \%Mn(\text{interface}) - \%Mn(\text{bulk}) \right] \quad (12)$$

At equilibrium, for Equation (1):

$$K_1 = \frac{(a_{Mn})^2 (a_{SiO_2})}{(a_{MnO})^2 (a_{Si})} \quad (13)$$

Over the small change in composition involved in an experiment, it can be assumed that the activity coefficients for the different components remain constant and that the change in concentration of silicon dioxide is negligible. Combining these constant values with  $K_1$  gives

$$K_1' = \frac{(\%Mn)^2}{(\%MnO)^2 (\%Si)} \quad (14)$$

This constant can be obtained by allowing the two-phase system to reach equilibrium and then analyzing for manganese, silicon and manganese oxide. Since the manganese in the metal phase at the interface is in equilibrium with the manganese oxide and silicon in the system, Equation (14) can be rewritten

$$\%Mn(\text{interface}) = \%MnO \sqrt{K_1' \%Si} \quad (15)$$

Substituting this in Equation (12), separating variables, and integrating:

$$\int_{\%Mn_{t=0}}^{\%Mn_{t=t}} \frac{d(\%Mn)}{[\%MnO \sqrt{K_1' \%Si} - \%Mn]} = \frac{Dt}{\delta h_M} \quad (16)$$

At any time during the run, the concentration of manganese oxide in the slag can be related to that of manganese in the metal by the relationship

$$\%MnO = \%MnO^0 - \left[ \frac{W_M}{W_S} \frac{MW_{MnO}}{MW_{Mn}} \right] \%Mn \quad (17)$$

Similarly, the concentration of silicon in the metal is

$$\%Si = \%Si^0 - \left[ \frac{MW_{Si}}{2MW_{Mn}} \right] \%Mn \quad (18)$$

Substituting these two terms into Equation (16):



$$\int_{\%Mn_{t=0}}^{\%Mn_{t=t}} \frac{d(\%Mn)}{\left[ (\%MnO^{\circ} - Q\%Mn) \sqrt{K_1' \%Si^{\circ} - 0.258 K_1' \%Mn} - \%Mn \right]} = \frac{Dt}{\delta h_M} \quad (19)$$

where  $Q = \frac{W_M}{W_S} \frac{MW_{MnO}}{MW_{Mn}}$

Now the only variable under the integral sign is the concentration of manganese in the metal and the integral can be evaluated. For convenience in data analysis, all theoretical models will be derived in terms of changing manganese concentration in the metal.

b. Diffusion of Manganese in the Slag

If the diffusion of manganese in the slag is the rate-limiting step, then the basic equation will be

$$\therefore \frac{dn(\text{MnO})}{dt} = \frac{DA}{\delta} \left[ C(\text{MnO bulk}) - C(\text{MnO interface}) \right] \quad (20)$$

Going through the same steps as for the diffusion of manganese in the metal, and using the same basic relationships, yields the final rate equation:

$$\int_{\%Mn_{t=0}}^{\%Mn_{t=t}} \frac{Q d(\%Mn)}{\left[ \%MnO^{\circ} - Q\%Mn - \frac{\%Mn}{\sqrt{K_1' \%Si^{\circ} - 0.258 K_1' \%Mn}} \right]} = \frac{Dt}{\delta h_S} \quad (21)$$

c. Diffusion of Silicon in the Metal

Following the same procedure as for the last two systems, there is, first of all, the basic equation

$$-\frac{dn_{Si}}{dt} = \frac{DA}{\delta} \left[ C_{Si}(\text{bulk}) - C_{Si}(\text{interface}) \right] \quad (22)$$

which yields the final rate equation

$$\int_{\%Mn_{t=0}}^{\%Mn_{t=t}} \frac{0.258 d(\%Mn)}{\left[ \%Si^{\circ} - 0.258 \%Mn - \frac{(\%Mn)^2}{K_1' \%MnO^{\circ} - K_1' Q \%Mn} \right]} = \frac{Dt}{\delta h_M} \quad (23)$$

d. Diffusion of Silicon in the Slag

The basic equation for this system is

$$\frac{dn(SiO_2)}{dt} = \frac{DA}{\delta} \left[ C_{(SiO_2 \text{ interface})} - C_{(SiO_2 \text{ bulk})} \right] \quad (24)$$

The final form in terms of manganese in the metal is

$$\int_{\%Mn_{t=0}}^{\%Mn_{t=t}} \frac{d(\%Mn)}{\left[ \frac{(K_1'' \%Si^{\circ} - 0.258 K_1'' \%Mn)(\%MnO^{\circ} - Q \%Mn)^2}{0.79 (\%Mn)^2} - \frac{\%SiO_2^{\circ}}{0.79} - \%Mn \right]} = \frac{Dt}{\delta h_S} \quad (25)$$

A new equilibrium constant is used to define the equilibrium condition for this reaction as follows:

$$K_1'' = \left[ \frac{(\%SiO_2)(\%Mn)^2}{(\%Si)(\%MnO)^2} \right]_{\text{equilibrium}} \quad (26)$$

2. Reduction by Silicon - Chemical Reaction Control

No work was done in this area since the energy of activation for the reaction was low and stirring had a marked effect on the reaction rate, both atypical of chemical reaction control. However, one possible model can be set forth as follows:

$$\frac{dn_{Mn}}{dt} = Ak_1 a^{a}_{MnO} a^b_{Si} - Ak_2 a^c_{Mn} a^d_{SiO_2} \quad (27)$$

Changing concentrations to percent, letting  $K_1 = \frac{k_2}{k_1}$  and integrating:

$$\int_{\%Mn_{t=0}}^{\%Mn_{t=t}} \frac{d(\%Mn)}{\left[ (0.0086 \gamma_{MnO} \%MnO)^a (\%Si)^b - K_1 (\%Mn)^c (.01 \gamma_{SiO_2} \%SiO_2)^d \right]} = * \quad (28)$$

$$* = \frac{100Mn k_1 t}{\rho_M h}$$

### 3. Reduction by Carbon - Diffusion Control

These models were derived in a manner identical to that used for the models for reduction by silicon. Simpler equations resulted for this system, however, and so it was possible to go one step further and analytically evaluate the integral to arrive at the final model.

#### a. Diffusion of Manganese in the Metal

Equations (11) and (12) apply to the diffusion of manganese in the metal for the reduction by carbon also. However, at equilibrium, for Equation (2):

$$K_2 = \frac{a_{Mn} P_{CO}}{a_{MnO} a_C} \quad (29)$$

The pressure of carbon monoxide at the interface remains constant at one atmosphere at the interface during the experiment. The liquid iron is maintained at carbon saturation; hence, the activity of carbon is constant. For the few experiments carried out in zirconia crucibles at less than graphite saturation, the concentration of the carbon changed very

little, such that an average value can be used. It can be assumed that the activity coefficients for the other components remain constant over the small change in composition involved in an experiment. Then a new equilibrium constant is defined as

$$K'_2 = \left[ \frac{\%Mn}{\%MnO} \right] \quad (30)$$

This constant is available from the literature for the carbon-saturated system<sup>33</sup> and can also be calculated from the relationship

$$K'_2 = \frac{K_2 a_C \gamma_{MnO}}{124 P_{CO} f_{Mn}} \quad (31)$$

where the factor for changing the concentration of MnO from mole fraction to weight percent is 124. Since the manganese in the metal phase at the interface is in equilibrium with the manganese oxide in the slag, Equation (3) can be combined with Equation (12) and Equation (17), and the variables separated to give

$$\frac{d(\%Mn)}{\left[ K'_2 \%MnO^0 - (QK'_2 + 1)\%Mn \right]} = \frac{D}{\delta h_M} dt \quad (32)$$

Integrating, the final rate equation is

$$\frac{-1}{K'_2 Q + 1} \ln \left[ K'_2 \%MnO^0 - (K'_2 Q + 1) \%Mn \right] = \frac{Dt}{\delta h_M} \quad (33)$$

b. Diffusion of Manganese in the Slag

If the diffusion of manganese in the slag is the rate-limiting step, then the basic rate equation is given by Equation (20). Going through the same steps as for the diffusion of manganese in the metal, and using the same basic relationships, the final rate equation is

$$\frac{-K_2'Q}{K_2'Q+1} \ln \left[ \frac{\%MnO^{\circ}}{Q} - \left( \frac{K_2'Q+1}{K_2'Q} \right) \%Mn \right] = \frac{Dt}{\delta h_S} \quad (34)$$

c. Diffusion of Carbon in the Metal

If diffusion of carbon in the metal phase is the rate-limiting step, then the basic rate equation is

$$\frac{-dn_C}{dt} = \frac{DA}{\delta} \left[ C_C(\text{bulk}) - C_C(\text{interface}) \right] \quad (35)$$

From the stoichiometry of Equation (2) it can be seen that  $-dn_C = dn_{Mn}$ . Substituting this relationship into Equation (35), changing concentrations to percent and rearranging,

$$\frac{MW_C d(\%Mn)}{MW_{Mn} \left[ \%C(\text{bulk}) - \%C(\text{interface}) \right]} = \frac{D}{\delta h} dt \quad (36)$$

At equilibrium, the equilibrium constant can be written as

$$K_2'' = \left[ \frac{\%Mn}{\%MnO \%C} \right] \quad (37)$$

This constant can readily be evaluated using the same methods used to calculate  $K_2'$  in Equation (31). Then rewriting Equation (37),

$$\%C(\text{interface}) = \left[ \frac{\%Mn}{\%MnO K_2''} \right] \quad (38)$$

Combining Equations (17), (36) and (38) and integrating gives the final rate equation for the diffusion of carbon in the metal phase as follows:

$$\frac{0.218K_2''Q\%Mn}{K_2''Q\%C+0.218} + \left[ \frac{0.218K_2''Q\%C\%MnO^{\circ}}{K_2''Q\%C+0.218} - \frac{0.218K_2''\%MnO^{\circ}}{K_2''Q\%C+0.218} \right] \times \ln \left[ \frac{K_2''\%C\%MnO^{\circ}}{0.218} - \left( \frac{K_2''Q\%C}{0.218} + 1 \right) \%Mn \right] = \frac{Dt}{\delta h_M} \quad (39)$$

d. Diffusion of Oxygen in the Metal

The basic equation for diffusion of oxygen in the metal is:

$$\frac{dn_{\underline{O}}}{dt} = \frac{DA}{\delta} \left[ C_{\underline{O}}(\text{interface}) - C_{\underline{O}}(\text{bulk}) \right] \quad (40)$$

The concentration of oxygen at the interface can be calculated from the standard free energy of reaction for the reaction



For this reaction, at equilibrium, the equilibrium constant is

$$K_{41} = \frac{a_{\underline{\text{Mn}}} a_{\underline{\text{O}}}}{a_{(\text{MnO})}} \quad (42)$$

The activity coefficients of these components are essentially constant for the small composition change occurring during an experiment. Therefore, an equilibrium constant can be defined in terms of percent composition at equilibrium as follows:

$$K'_{41} = \frac{\% \underline{\text{Mn}} \% \underline{\text{O}}}{\% \text{MnO}} \quad (43)$$

This constant can be readily evaluated using the same procedure as described previously.

From the known thermodynamic data for the graphite-saturated system under consideration, it is estimated that the value of  $C_{\underline{O}}(\text{interface})$  is greater than that of  $C_{\underline{O}}(\text{bulk})$  by about two orders of magnitude for the conditions present during an experimental reaction. Therefore,  $C_{\underline{O}}(\text{bulk})$  can be omitted from Equation (40). It can be seen from Equation (41) that the same number of moles of oxygen and manganese is transferred across the interface. Using these facts, changing concentrations in Equation (40)

to percent, combining Equations (17), (40) and (43), separating the variables, and integrating, the final rate equation for oxygen diffusion in the metal is as follows:

$$\frac{-0.29\%Mn}{K_{41}'Q} - \frac{0.29\%MnO^{\circ}}{K_{41}'Q^2} \ln \left[ K_{41}'\%MnO^{\circ} - K_{41}'Q\%Mn \right] = \frac{Dt}{\delta h_M} \quad (44)$$

#### 4. Reduction by Carbon - Chemical Reaction Control

Three reactions are presented here which could represent the rate-limiting step for the overall process. Rate equations are developed for each of the chemical reactions.

##### a. Reaction 1

The first considered is the overall reaction shown in Equation (2). Assuming that the rate of the reaction agrees with the stoichiometry of Equation (2), then the rate can be written as

$$\frac{dn_{Mn}}{dt} = Ak_1 a_{MnO} a_C - Ak_2 a_{Mn} P_{CO} \quad (45)$$

The pressure of carbon monoxide can be assumed to be one atmosphere at the interface. The activity of graphite in the iron will remain constant throughout the experiment since the iron is saturated with carbon. Then, letting  $K_2 = \frac{k_2}{k_1}$ , changing concentrations to percent, and integrating:

$$\frac{-1}{K_2 + 0.0086 a_C \gamma_{MnO} Q} \ln \left[ 0.0086 a_C \gamma_{MnO} \%MnO^{\circ} - (K_2 + 0.0086 a_C \gamma_{MnO} Q) \%Mn \right] = \frac{900k_1 t}{h_M} \quad (46)$$

##### b. Reaction 2

The chemical reaction given by Equation (41) is assumed to be the slow step in the overall reaction here. Again the basic equation can be written as

$$\frac{dn_{Mn}}{dt} = Ak_1 a_{MnO} - Ak_2 a_{Mn} a_O \quad (47)$$

The activity of oxygen in the metal,  $a_O$ , is very small and can be assumed constant. Therefore, setting  $k'_2 = k_2 a_O$  and  $K''_2 = \frac{k'_2}{k_1}$  and again changing concentrations to percent and integrating:

$$\frac{-1}{K''_2 + 0.0086 \gamma_{MnO}^Q} \ln \left[ 0.0086 \gamma_{MnO} \%MnO^O - (K''_2 + 0.0086 \gamma_{MnO}^Q) \%Mn \right] = \frac{900k_1 t}{h_M} \quad (48)$$

c. Reaction 3

Assuming that the slow step in the reaction is the chemical change of oxygen going from the slag to the metal phase, the reaction can be represented by

$$(O) = \underline{O} \quad (49)$$

The rate equation for this chemical step can be written as

$$\frac{dn_O}{dt} = Ak_1 a(O) - Ak_2 a_{\underline{O}} \quad (50)$$

For the overall reaction, the number of moles of oxygen and of manganese that cross the interface are equal, or  $n_{\underline{O}} = n_{\underline{Mn}}$ . Also, for a slag of given composition, it can be assumed that the activity of oxygen will remain constant. The activity of oxygen in the metal phase will also be constant and will be very small compared with that in the slag so that the second term of the equation can be ignored. These last two conditions hold only when the system is not close to equilibrium. For the reaction under study, the rate is studied for two hours and equilibrium is not attained in twenty hours, so these two conditions are valid. Then, letting  $k' = k_1 a(O)$ , changing concentration to percent, and integrating:



$$\underline{\%Mn} = \frac{900k't}{h_M} \quad (51)$$

## B. Experimental Procedures

### 1. Apparatus

The slag-metal reactions in this program were carried out in a vertical-tube resistance-heated furnace although most previous slag metal studies have been made in induction furnaces. The advantages of a resistance furnace over the induction furnace are better temperature control and better stirring rate control. The equipment was designed and built specifically for this research program. The apparatus consisted of the furnace, the atmosphere system, the temperature measuring and controlling circuits, and the crucibles and stirrers.

#### a. Furnace

The design of the furnace used for this experimental study is illustrated in Figure 2. It was a cubic furnace, 24 inches high by 24 inches wide by 24 inches deep. It was insulated with low density alumina and silica Harbison-Walker brick, with an 8-inch cube hot zone in the center of the furnace. Eight vertical silicon-carbide heating elements surrounded the furnace tube. Power was supplied to the heating elements through a 240 volt, 25 amp Variac. The power requirement for heating the furnace to the desired temperature was from three to four kilowatts. The heating elements had a nominal resistance when new of 1.5 ohm each, but the resistance increased as the elements aged. When the elements were new, the heat requirements were met by having the eight elements connected in series. However, a point was reached, as the resistance of the elements increased, at which the desired temperatures could no longer be reached with the elements in series. Then, by rewiring the

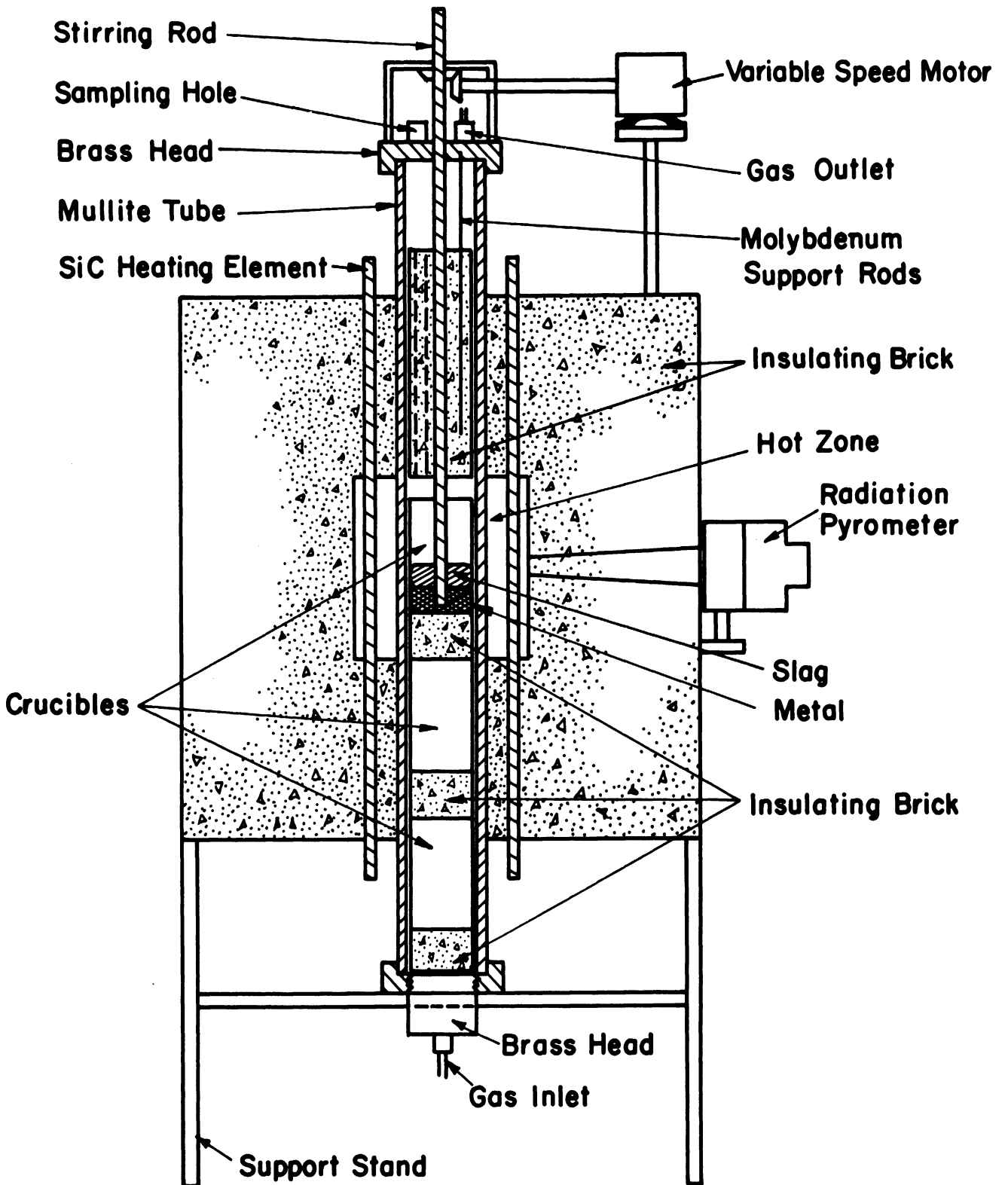


Figure 2. Illustration of Reaction Furnace.

elements in parallel, the power requirement of the system was achieved for the remainder of the life of the heating elements.

The vertical reaction chamber was a mullite tube 36 inches long and 3 inches in inside diameter, sealed at both ends by a combination brass head o-ring arrangement. The crucibles were held in the hot zone as illustrated in Figure 2. The crucible was covered with a graphite lid. The reaction tube was insulated above the crucible by an alumina brick cylinder that was attached to the top head and was therefore removed from the furnace when the head was taken off. A stirring rod was centered in the system and was driven by a variable speed motor capable of speeds from 10 to 100 revolutions per minute. There was a sample hole through the top head, insulation, and crucible lid alongside the stirrer. All access holes into the reaction tube were sealed by vacuum seal fittings.

b. Atmosphere System

The apparatus was designed to maintain an argon atmosphere in the reaction tube during an experimental run. A diagram of the gas system is shown in Figure 3.

High purity argon was passed through a drying-deoxidizing train before entering the reaction tube. The train consisted of a tube containing anhydrous calcium sulphate, a tube filled with copper gauze that was maintained at 500°C in a small auxiliary resistance furnace, and a second calcium sulphate drying tube. Indicating anhydrous sulphate was employed. Bubblers were used both before and after the reaction tube in order to maintain a slight positive pressure of argon in the system during an experimental run.

c. Temperature Measuring and Controlling Equipment

The temperature was controlled in the reaction chamber by a "high-low" circuit arrangement. Power was provided to the furnace through

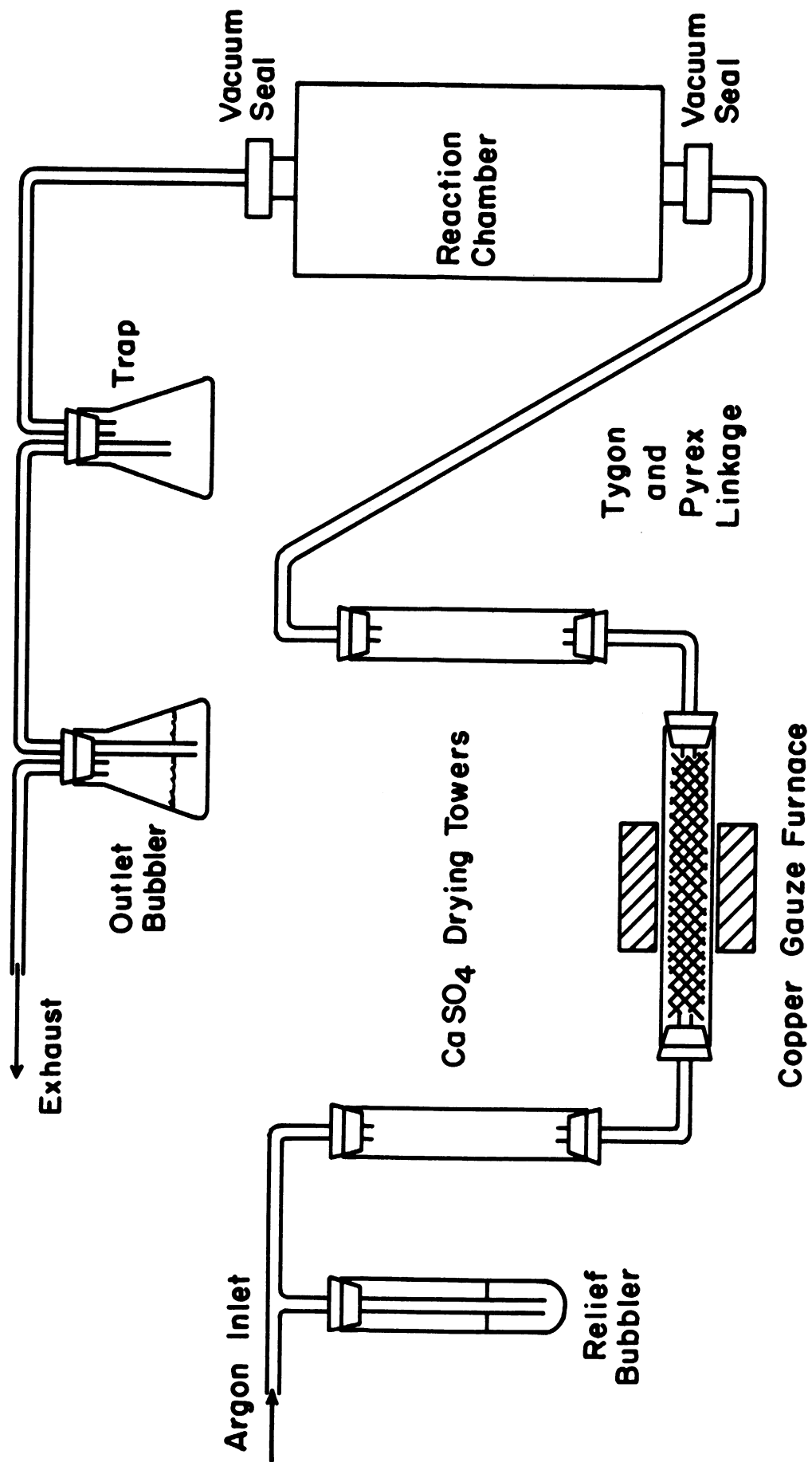


Figure 3. Illustration of Gas Train.

a 240 volt Variac auto-transformer wired so two unequal voltages could be tapped. Regardless of the voltage setting of the Variac, the tapped voltages were 40 volts apart. Either a high or a low voltage was fed to the furnace by a relay controlled by a Leeds and Northrup Speedomax H Circular Chart Indicating Recording Controller, Model R. A Leeds and Northrup Rayotube No. 8890 temperature detector, having a full-scale response time of 8 seconds, was used for temperature measurement. As shown in Figure 2, the detector was attached to the side of the furnace and was focused on the outside of the mullite reaction tube, in the middle of the hot zone.

The temperature measuring and controlling equipment was calibrated periodically by placing a platinum-6% rhodium vs platinum-30% rhodium thermocouple in an alumina protection tube in a liquid metal melt in the reaction zone. Simultaneous readings were taken on the Leeds and Northrup Recorder and the thermocouple setup over a wide temperature range and calibration curves made. Periodic checks of this calibration curve showed that an accuracy to within two degrees centigrade was maintained. The controller was also checked by this same thermocouple system, and it was found that the controller maintained the temperature in the slag-metal system to within one degree centigrade. The thermocouple was checked for calibration against the melting points of pure copper and nickel.

d. Crucibles and Stirrers

High-purity graphite rods, one foot long and  $3/8$  inch in diameter, were used to make stirring rods. One end of these rods was flattened to a thickness of  $1/8$  inch to provide a stirring surface. For one experimental run, to study the effect of higher stirring rate, a  $3/4$  inch graphite rod was flattened in the same manner for use as a stirrer. The stirrers were

connected to a  $1/4$  inch steel rod which extended up through the top head of the furnace tube.

Graphite crucibles were machined from  $2-3/4$  inch diameter commercial-grade graphite rod. The crucibles were made  $4-3/4$  inches high with a bore  $4-1/2$  inches deep and  $2-1/4$  inches in diameter.

For the reduction by silicon studies, slip-cast, fine-grain, low-porosity, lime-stabilized cubic zirconia crucibles were used. They were  $4-1/2$  inches high and  $2-1/8$  inches in outside diameter with a two inch diameter bore. These crucibles were only slightly attacked by the slag during the process of a run. The amount of zirconia dissolved in the slag during an experiment was less than three percent of the total slag mass and did not vary significantly from run to run. The crucibles were supplied by Zirconium Corporation of America.

Several other crucibles were tried but proved unsuccessful in holding the two-phase system. Among these were zirconia, magnesia, and alumina crucibles.

The zirconia crucibles had no strength at the high temperatures at which they were used and had to be held inside a graphite crucible, as described above, during the run. This worked very well and there was no apparent reaction between the two crucibles.

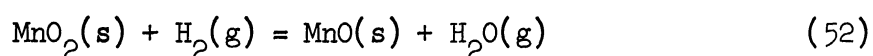
A sampler was made using Vycor tubing with a copper gauze chill inside the tubing to quench the sample and limit the size of the sample. A suction bulb was used on the other end of the tube to draw the desired sample into the Vycor tubing. Both metal and slag samples were taken in this manner. They were both easily removed from the Vycor tubing.

## 2. Materials

High-purity materials were used as components for the slag and metal phases. The source of these materials and the quoted purity of each are

summarized in Table I. These materials came in a form ready for immediate use with two exceptions: the silicon oxide had to be crushed and the manganese dioxide had to be reduced to manganese monoxide.

The manganese dioxide was reduced by placing it in a quartz combustion boat in a horizontal tube furnace at 1000°C and passing hydrogen gas over it. This deoxidation process is rapid, reaching completion in about fifteen minutes. Mass balances were made to determine the oxidation state of the product. The loss in weight showed that the reaction occurring was



and that the reaction reached completion. Also, Moore<sup>36</sup>, using the same system, analyzed the resulting manganese oxide using x-ray diffraction techniques and verified that it was manganese monoxide.

The slag components were periodically checked to make sure that they were not hydrated. Calcium oxide was found to hydrate rapidly, so it was purchased in one-pound containers and used before hydration could occur to any extent.

### 3. Procedures for Using Equipment and Making Experimental Runs

The description which follows is in terms of runs made to study the reduction of manganese oxide by graphite. Changes in the procedures for the reduction by silicon are noted.

First, it was necessary to prepare the crucible-support stand assembly shown in Figure 4. For the reduction by silicon study, a zirconia crucible was placed inside the graphite crucible to hold the two-phase system.

The desired components were then weighed out and placed in the crucible. First the iron and the reducing agent, either graphite or silicon, were placed in the crucible. Then the four slag components (aluminum oxide, magnesium oxide, silicon oxide, and calcium oxide) were weighed out. These

TABLE I  
EXPERIMENTAL MATERIALS

Material	Source	Grade	Quoted Purity - %	Form, as Received
Fe	Glidden	A-104	99.8	Fragments
Si	Var-Lac-Oid	Purified	99.999	50 Mesh
C	Ultra-Carbon	Ultra-Pure	99.999	200 Mesh
Mn	Union Carbide	Electrolytic	99.9	Pieces
CaO	Baker and Adamson	Reagent	98.0	Powder
MgO	Norton	Magnorite	98.2+	14/24 Mesh Grain
Al <sub>2</sub> O <sub>3</sub>	Morganite	High Purity	99.7	100 Mesh Grain
SiO <sub>2</sub>	General Electric	CFQ Scrap	99.9	Pieces
MnO <sub>2</sub>	Fisher Scientific	Reagent	99.9	Fine Grain



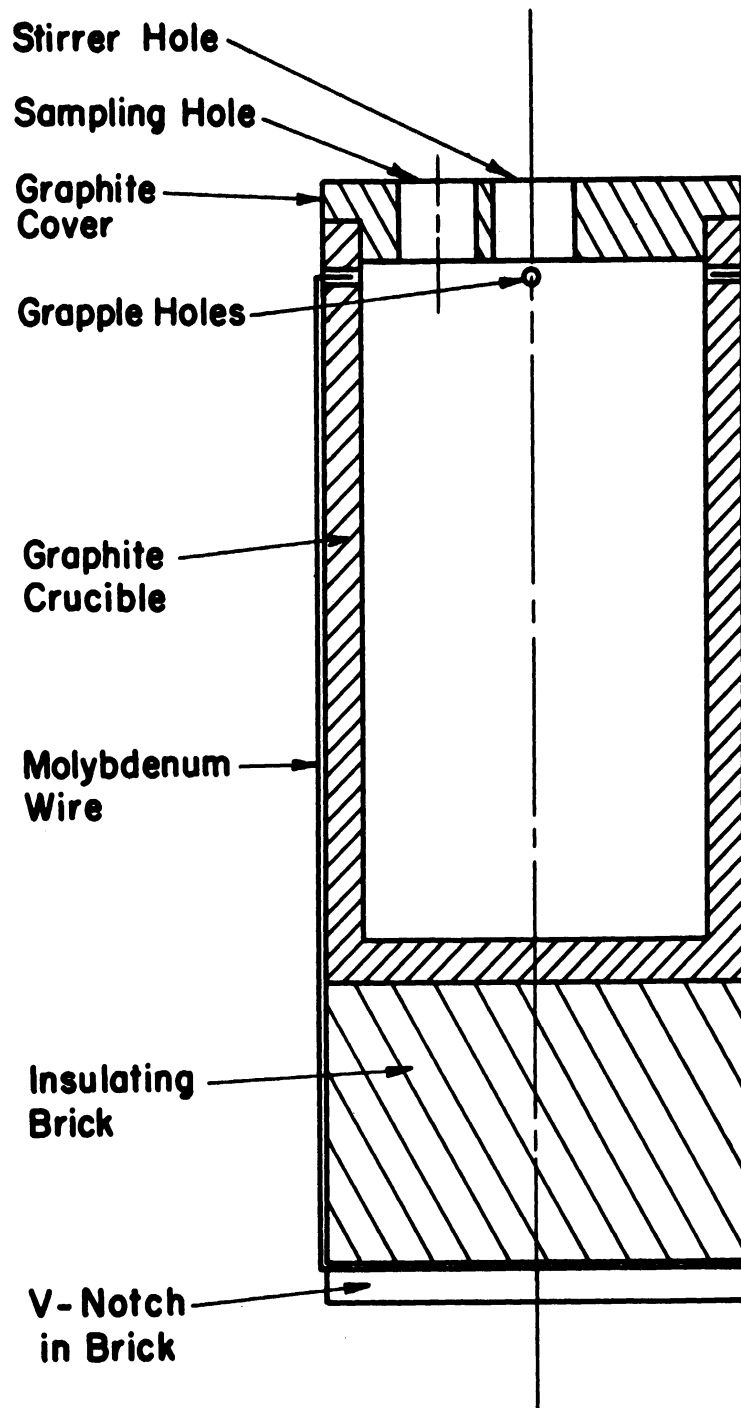


Figure 4. Crucible and Support.

components were thoroughly mixed before being placed inside the crucible on top of the metal.

For a standard run, 400 grams of iron and 10 grams of graphite were used. By adding some graphite, the dissolution of the crucible was minimized. The slag phase was composed of 90 grams of calcium oxide, 70 grams of silicon oxide, and 20 grams each of magnesium oxide and aluminum oxide for a total of 200 grams. For the reduction by silicon system, 300 grams of iron and 4 grams of silicon were used.

Most of these materials were weighed on a triple-beam balance that had a sensitivity of 0.01 gram and weight divisions down to 0.01 gram. Silicon and manganese oxide, which were used in smaller quantities, were weighed on an Ainsworth Type LC Analytical Balance using Class S weights. Therefore, the difference between the reported composition and the actual composition for components of the system should not be more than 0.1% of the reported composition.

When the crucible assemblies had been prepared and the ingredients weighed into them, three assemblies were placed in the furnace tube, as shown in Figure 2. The purpose for using this arrangement will be discussed later. The bottom and top heads were secured tightly in place preparatory to starting the run. The alignment of the stirring hole and sampling hole in the crucible lid with the corresponding holes in the top head was checked. The argon gas supply was turned on and an argon atmosphere was maintained in the furnace tube throughout the run.

The power was turned on and increased gradually so that the furnace tube would not be broken by thermal shock. After the reaction zone had attained approximately 1000°C, full power required to reach the desired temperature could be applied to the system. After this initial start-up,

the furnace was kept at approximately 1000°C, hence the procedure normally would start from this point. It took approximately 6 to 8 hours for the furnace to reach the desired operating temperature from this level.

By the time the system had reached temperature, usually 1550°C, the iron-graphite phase would have been above its melting point for about two hours. Therefore, it can be assumed that it had reached graphite saturation.<sup>38</sup>

The stirrer was lowered into position, just off the bottom of the crucible, and started at the desired rate. The revolutions of the stirrer were counted manually and the rate was checked periodically throughout the run. The rate of stirring as reported was accurate to within + 2 revolutions per minute. For the reduction by silicon system, the stirrer was lowered to the bottom of the crucible and then raised one inch so that the stirrer was only in the slag phase. Otherwise the iron would dissolve the graphite stirrer in contact with it, thus becoming contaminated with graphite.

The temperature was controlled by the Leeds and Northrup Controller, which was set at the desired temperature at the beginning of the heat-up.

The manganese oxide was now added to the system through a Vycor tube-funnel arrangement. The moment that the manganese oxide was added to the system was considered zero time for the actual reaction. In a normal run, 10 grams of manganese oxide was used. The Vycor tube-funnel arrangement was long enough to extend inside the crucible lid to insure that all of the manganese oxide was added to the system. Occasionally some of the manganese oxide fused to the wall of the Vycor tube as it flowed through; this did not happen often and when it did, the amount of manganese oxide lost was approximated. Samples were then taken of the

slag and metal phase as desired to monitor the progress of the run. In this investigation, samples of the slag were taken every 15 minutes for two hours for reduction by graphite, with a metal sample being taken at the end of the two hours to check the mass balance of the system. For reduction by silicon, slag samples were taken every three minutes for 24 minutes and then a slag and a metal sample were taken at the end of two hours when the system had reached equilibrium. Samples of the slag and metal were taken in some instances before the start of the run to check on any side reaction which might have occurred during heat-up.

Thirty-six inch lengths of 6 mm OD Vycor tubing were used to take the samples. Copper gauze was placed in one end of the Vycor tubing to chill the sample and limit the size of the sample taken; a suction bulb was used on the other end to draw the sample into the sample tube. For taking metal samples, the Vycor tubing was lowered to the bottom of the crucible and the metal sample drawn from there. It was quenched in water immediately. The sample tube was lowered into the system a predetermined distance so that slag would be drawn into it when a slag sample was desired. The Vycor tubing was reused until the lengths became too short to reach the slag-metal system. The slag samples taken during the run were usually 2 grams or less in size, while the metal samples were approximately 5 grams.

The amount of time required for the reduction by silicon reaction to reach equilibrium was determined by taking samples over a wide range of time intervals. The reduction by graphite reaction was allowed to run for 20 hours in one instance and still had not reached equilibrium. Therefore, it was decided to use equilibrium values from the literature instead of trying to reach equilibrium for each run made in the carbon study.

At the end of the experimental run, the graphite stirrer was pulled out of the reaction zone and the power input into the system was reduced to allow the temperature to fall back to 1000°C. When the temperature had reached this level, the top head of the furnace tube was removed and the crucible with its supporting brick was pulled out of the furnace. This was accomplished using two small steel rods with hooks on one end to grab the crucibles by the grapple holes shown in Figure 4. The graphite stirrer was then replaced if necessary and the top head arrangement was again secured on the furnace tube. Meanwhile, another crucible with supporting brick was prepared, and metal and slag ingredients weighed into it. Then it was preheated to about 200°C, using a heating mantle. It was now ready to be placed in the furnace. The adaptor in the bottom head of the furnace tube was screwed out and the new crucible was pushed up into the furnace through the bottom head, thus pushing the other crucibles farther up into the furnace. The adaptor was then replaced, sealing the system. The top crucible was now in position to begin another run. Again, the alignment of the stirring hole and sampling hole in the crucible cover was checked. The system was now ready to heat up to the desired temperature for another experimental run.

The assembly line approach, i.e., placing the crucibles into the furnace in series, was a necessary procedure. At first an attempt was made to use a permanent insulation-support stand in the furnace. Then the crucibles would be lowered into position from the top of the tube. Two problems arose in trying to use this method. First of all, excessive oxidation of the equipment occurred while trying to lower the crucible slowly into the hot zone. Secondly, the effect of placing a relatively cold crucible into the hot mullite furnace tube was to cause serious

thermal shock in the mullite tube; in fact, after two or three times, it would usually break the furnace tube. Therefore, the present method was devised. In this method the bottom head was removed for only a few moments while the crucible was being pushed into position. Because the other two crucibles had been in the system for some time, they were pre-heated to the extent that when they were pushed into a hotter zone of the furnace, the temperature differential was not great enough to cause failure in the furnace tube. The only difficulty with this method was that it was necessary to know three runs in advance what conditions would be desired for the run currently being prepared.

The crucibles could only be used one time in this experimentation. The stirring rod was not attacked by the slag phase and was only slightly attacked by the metal phase and could be used for two and often three runs before being replaced. The supporting brick was used repeatedly.

#### 4. Chemical Analysis of Samples

Wet chemistry methods were used for the analysis of both the slag and the metal samples. Analytical procedures were supplied by McLouth Steel Company of Detroit, Michigan, who also demonstrated the use of the procedures in their laboratories.

A volumetric quantitative analysis was used for the determination of manganese in the metal and in the slag. This method involved dissolving the sample, oxidizing the manganese into the form of a permanganate ion and then titrating with a standard sodium arsenite solution to determine the concentration of manganese.

A gravimetric quantitative analysis was used for the determination of silicon in the iron. The sample was first brought into solution and then the silicon was oxidized into the insoluble form,  $\text{SiO}_2$ . The solution was

then filtered and the filter paper containing the  $\text{SiO}_2$  was ignited and weighed to determine the  $\text{SiO}_2$  in the original sample.

The amount of iron in the slag was determined using a volumetric quantitative analysis method. In this procedure, the slag was dissolved and the ferric iron was reduced to the ferrous state by treatment with hydrochloric acid and stannous chloride. The excess stannous chloride was oxidized with mercuric chloride and the ferrous iron was titrated with a standard potassium dichromate solution.

All of these methods gave results that could be reproduced to within one percent. Samples from the National Bureau of Standards were analyzed to check the accuracy of the method. Their analysis was reproduced to within one percent also.

#### 5. Treatment of Data

The theoretical models for the reactions under study had been derived in terms of manganese concentrations in the metal. Therefore, manganese concentrations in the metal as a function of time were calculated from the slag manganese oxide concentrations which had been determined by chemical analysis. These calculations were made manually and were based on the material balance in the slag-metal system.

Further computations were made on an IBM 7090 computer using programs written in the MAD language for each theoretical model. The computer program determined the value for the left-hand side of these derived models as a function of time. It then made a least-squares fit of the calculated points. The slope of this line was equal to  $\frac{D}{h\delta}$  for the diffusion models and  $\frac{900k_1}{h}$  for the chemical reaction model. The desired rate constant,  $\frac{D}{\delta}$ , or  $k_1$ , could readily be evaluated from this slope.

For those integrals that were too complicated to be integrated mathematically, a Gauss-Legendre numerical analysis procedure was incorporated into the program to evaluate the left side of such equations.

Another program was written to evaluate the energy of activation for the two reactions under consideration. The data were submitted to the program as temperature vs reaction constant. The program then made a least-squares fit of the data in terms of natural logarithm of the reaction constant vs reciprocal absolute temperature. The slope of this line is  $-\frac{E}{R}$  from which the energy of activation can be readily calculated.



## EXPERIMENTAL RESULTS

The results will be presented in two parts. The first section will deal with manganese oxide reduction by silicon; the second section will present the results of manganese oxide reduction by carbon.

In order to determine the rate-limiting step for each reaction, the effect of several variables on the systems was studied. These variables were stirring rate, temperature, melt geometry, and concentrations.

What might be expected to happen as a result of varying these parameters can be explained in terms of the following equation:

$$\text{Rate} = B \times \text{Force} \quad (53)$$

This is the basic rate equation under consideration. It says that the rate at which the reaction will occur is proportional to the driving force which moves the reaction. For a diffusion controlled reaction, B is equal to the diffusion constant divided by the length of the diffusion path. If an interfacial chemical reaction controls the rate of the process, B is the reaction rate-constant designated by k. These two constants,  $\frac{D}{\delta}$  and k, have certain limitations on them.

The rate of stirring has no effect on D or k but has a marked effect on  $\delta$ . A change in temperature has a small effect on D and  $\delta$ , but a greater effect on k. Changes in melt geometry, specifically phase depth, should not affect any of the constants. The purpose of including this variable is to indicate which phase controls the overall reaction. The effect of concentration on these constants should again be negligible, except possibly for secondary influences on the diffusion coefficient. If the concentration change is large, the character of the medium through which diffusion occurs could be altered enough to cause a change in D. Generally, moderate changes in concentration alter the driving force for the reaction, thereby modifying the rate, whereas D remains constant.

In this section, the results obtained by applying the experimental results to the theoretical models derived earlier will be explored in terms of a model meeting the conditions listed above. The model that successfully meets these conditions will define the rate-limiting step for the process.

#### A. Manganese Oxide Reduction by Silicon

This was a rapid reaction reaching equilibrium in less than ninety minutes. The change in concentration of the various components as a function of time is shown in Figure 5 for a typical experimental run. Figure 6 is a plot of  $F(\text{Mn})$ , the left side of Equations (19), (21), (23), and (25) versus time,  $t$ , which shows the results obtained upon application of the theoretical diffusion models to the data shown in Figure 5. A good fit is obtained for each model. A compilation of all the experimental data taken during this study is found in Appendices A and B.

##### 1. The Effect of Stirring Rate

The rate of stirring had a marked effect on the rate of this reaction, as shown in Figure 7. Here shown are the results of runs using no stirring, stirring with a  $3/8$  inch stirring rod at 100 rpm, and stirring with a  $3/4$  inch stirring rod at 100 rpm. The slope is doubled and tripled respectively for the latter two cases, relative to the first case with no stirring. The results shown are those derived using the theoretical model for the diffusion of manganese in the metal, Equation (19). A tabulation of results obtained for each theoretical model using stirring rate as the variable is given in Table II.

Since the chemical reaction constant,  $k$ , would not be influenced by stirring rate, it can be immediately deduced that this reaction is not controlled by a chemical reaction, but rather is controlled by diffusion.

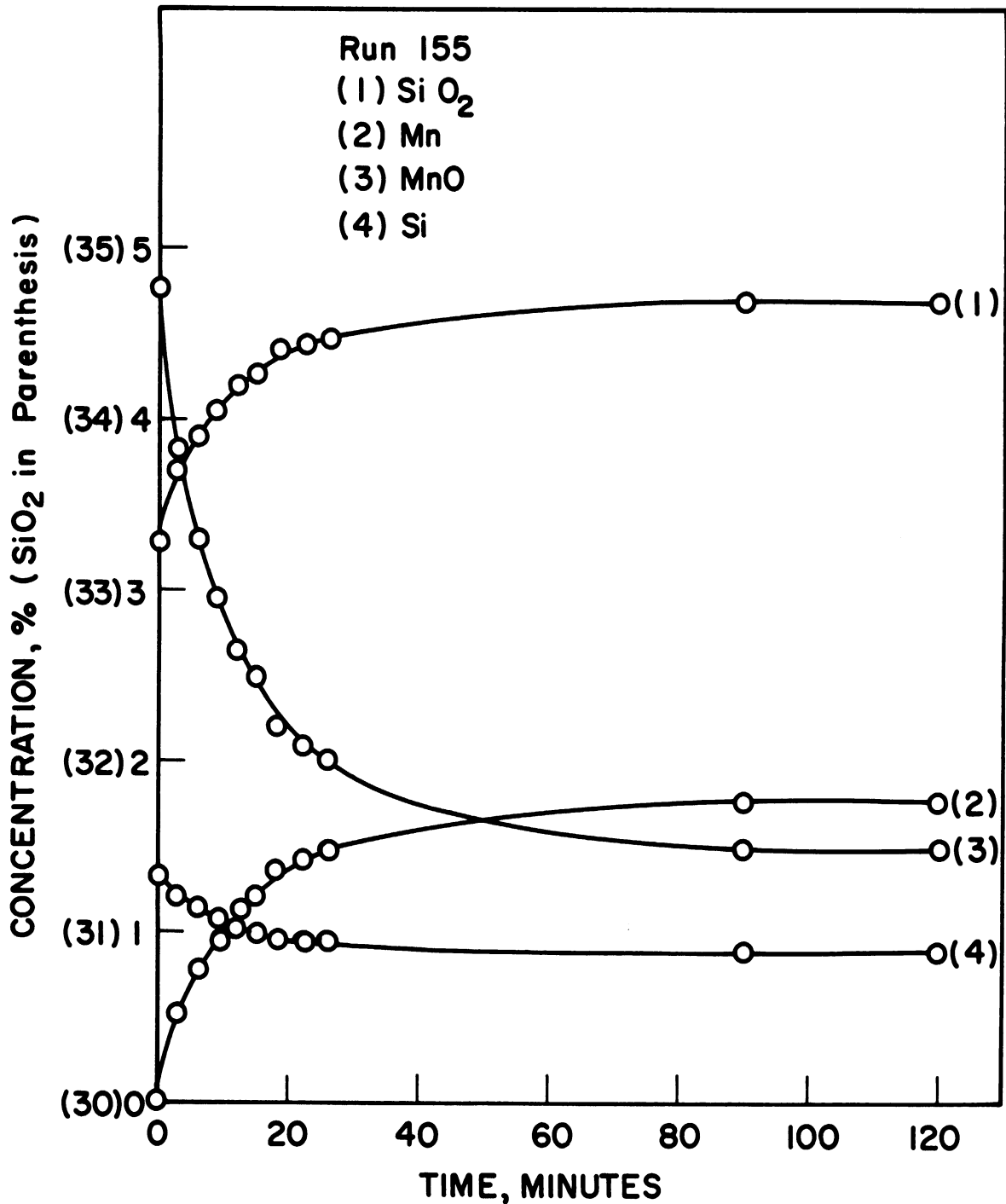


Figure 5. Concentration-Time Curves for the Reaction  $2 \text{ (MnO) + Si} = \text{(SiO}_2\text{)} + 2 \text{ Mn}$ .

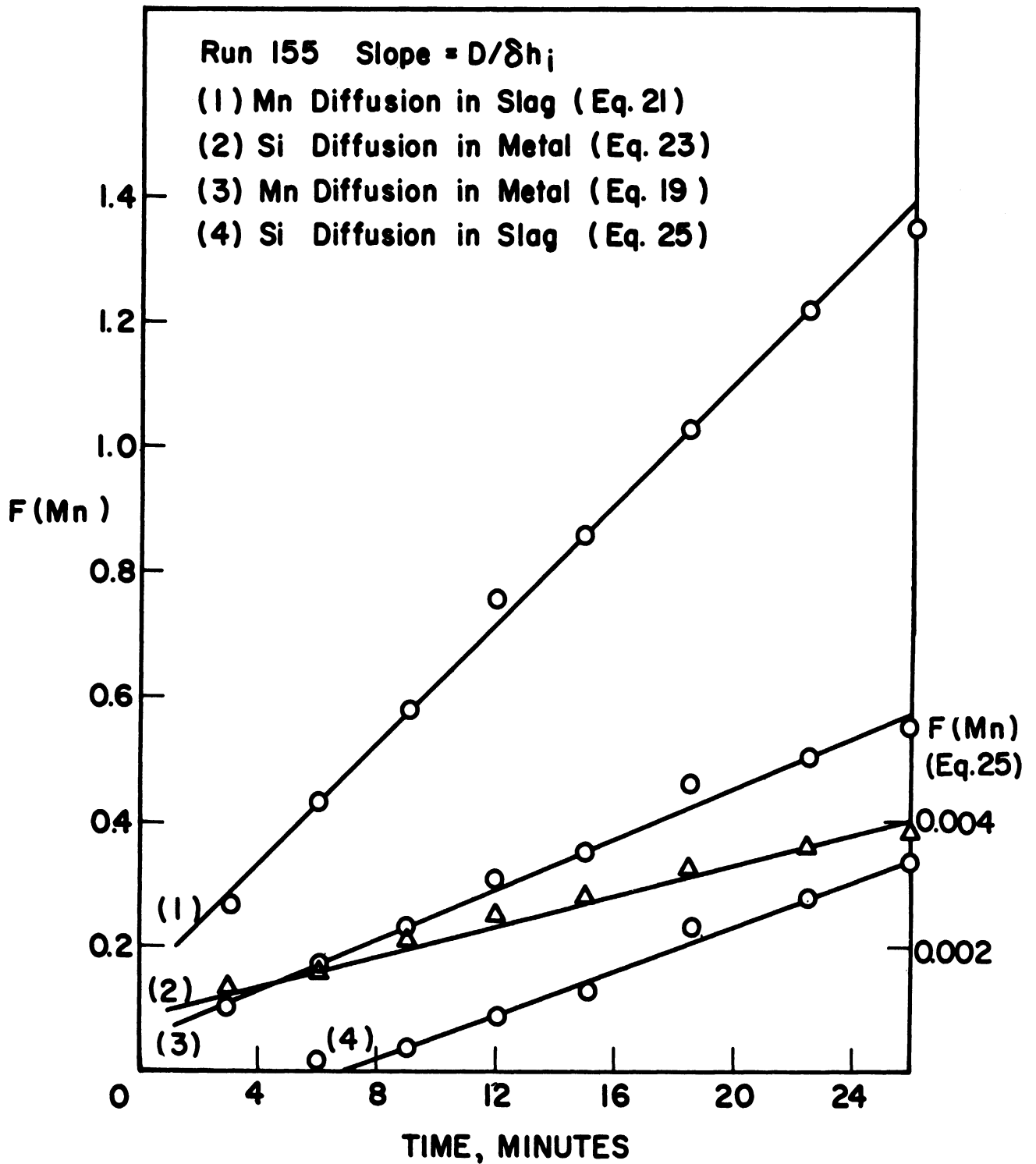


Figure 6. Determination of  $D/\delta$  for Various Theoretical Models for the Reaction  $2(\text{MnO}) + (\text{SiO}_2) + 2 \underline{\text{Mn}}$ .

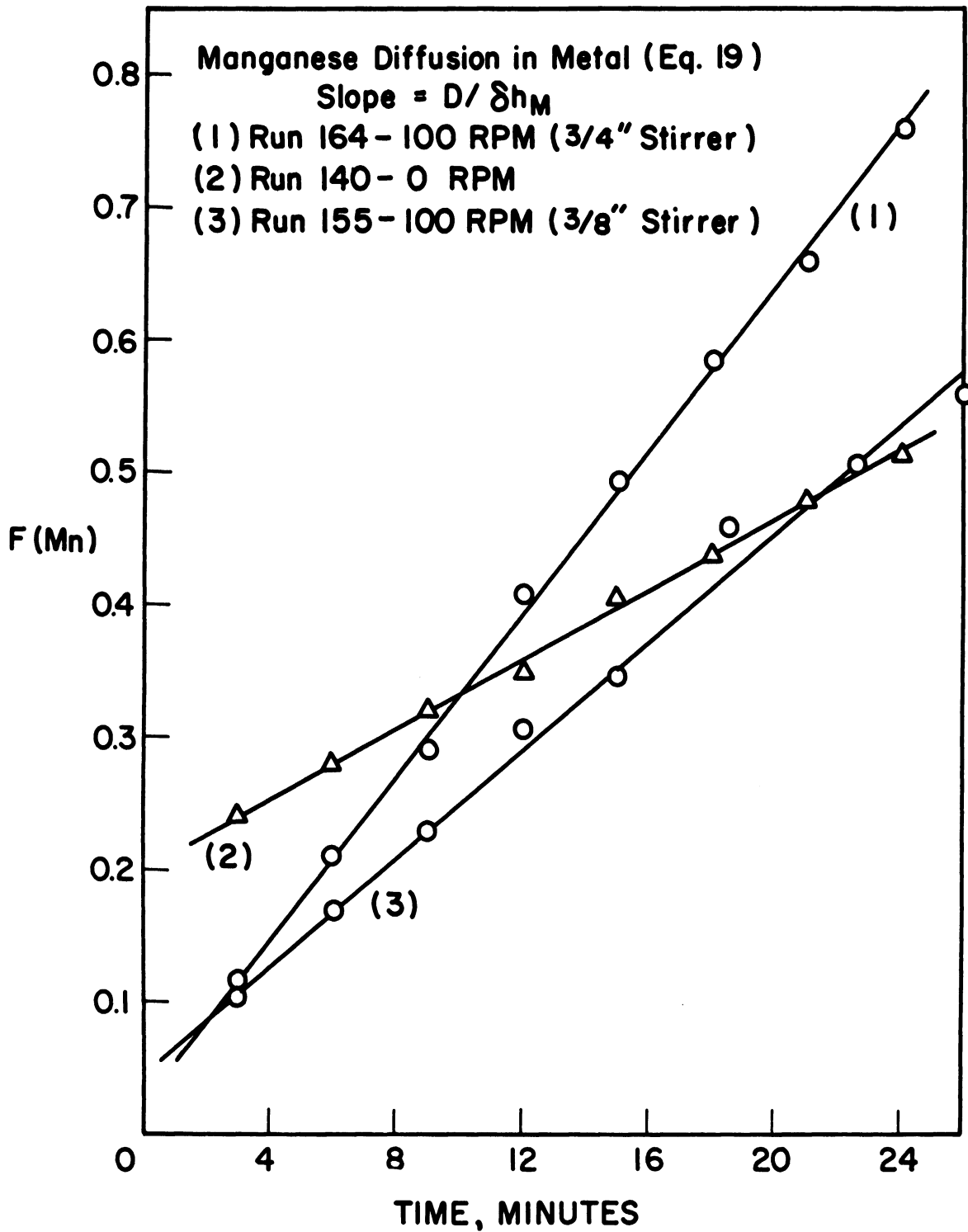


Figure 7. The Effect of Stirring Rate on the Reaction  
 $2(\text{MnO}) + \underline{\text{Si}} = (\text{SiO}_2) + 2 \underline{\text{Mn}}$ .

TABLE II  
 THE EFFECT OF STIRRING RATE ON THE REDUCTION OF  
 MANGANESE OXIDE BY SILICON

Run	Stir Rate, RPM	$(D/\delta) \times 10^4, \text{ cm/sec}$			
		Metal Phase		Slag Phase	
		Mn	Si	Mn	Si
140	0	3.23	1.65	12.9	0.069
133	0	3.26	1.59	9.8	0.046
131	0	2.49	1.30	8.0	0.031
129	0	2.75	1.21	8.1	0.011
166	40	7.06	3.87	27.5	0.112
155	100	7.39	4.28	23.9	0.078
154	100	7.30	3.45	22.5	0.105
163	100	7.35	3.89	22.2	0.080
146	100	7.43	4.51	23.7	0.061
143	100	6.94	3.07	21.2	0.109
164	100*	11.31	5.67	36.0	0.157

\* A paddle  $3/4$ " wide was used for this run. Ordinarily a  $3/8$ " wide paddle was used.

## 2. The Effect of Temperature

Temperature had very little effect on the rate of this reaction. The results obtained by varying temperature are presented in Table III. The effect of temperature can be examined quantitatively by calculating the energy of activation for the process. The diffusion constant,  $D$ , is influenced by the temperature exponentially. This relationship can be presented in an Arrhenius-type equation:

$$D = D_0 e^{-\frac{E}{RT}} \quad (54)$$

If  $\delta$  is either not affected by temperature or is affected exponentially by temperature, then

$$\frac{D}{\delta} = \left(\frac{D}{\delta}\right)_0 e^{-\frac{E}{RT}} \quad (55)$$

Taking the logarithm of both sides of this equation:

$$\ln \frac{D}{\delta} = \ln \left(\frac{D}{\delta}\right)_0 - \frac{E}{RT} \quad (56)$$

Then, by plotting  $\ln \frac{D}{\delta}$  vs  $\frac{1}{T}$ , the resulting slope will have the value  $-\frac{E}{R}$ , giving the energy of activation for the reaction under consideration. This is done in Figure 8. A regression analysis of this data gives a value of 7 Kcal/mole Mn for the energy of activation,  $E$ . This result, along with the energy of activation reported in the literature for the relevant diffusion steps, is presented in Table IV. No value is available in the literature for the diffusion of manganese in slag. However, values for other components in slag are comparable to those for the diffusion of silicon in slag<sup>20</sup>. Therefore it is assumed that the value for the energy of activation for manganese in slag will also be a relatively high number with the same order of magnitude as that for silicon in slag. The energy of activation obtained is much lower than would be expected for diffusion of a component in the slag.

TABLE III  
 THE EFFECT OF TEMPERATURE ON THE REDUCTION OF  
 MANGANESE OXIDE BY SILICON

Run	T, °C	$(D/\delta) \times 10^4, \text{ cm/sec}$			
		Metal Phase		Slag Phase	
		Mn	Si	Mn	Si
160	1540	7.21	3.71	22.6	0.103
155	1550	7.39	4.28	23.9	0.078
154	1550	7.30	3.45	22.5	0.105
163	1550	7.35	3.89	22.2	0.080
146	1550	7.45	4.51	23.7	0.061
143	1550	6.94	3.07	21.2	0.109
159	1560	7.43	4.49	23.5	0.069
148	1570	7.51	4.68	24.5	0.069
199	1580	7.61	3.08	25.6	0.112
149	1590	7.61	4.07	24.1	0.092



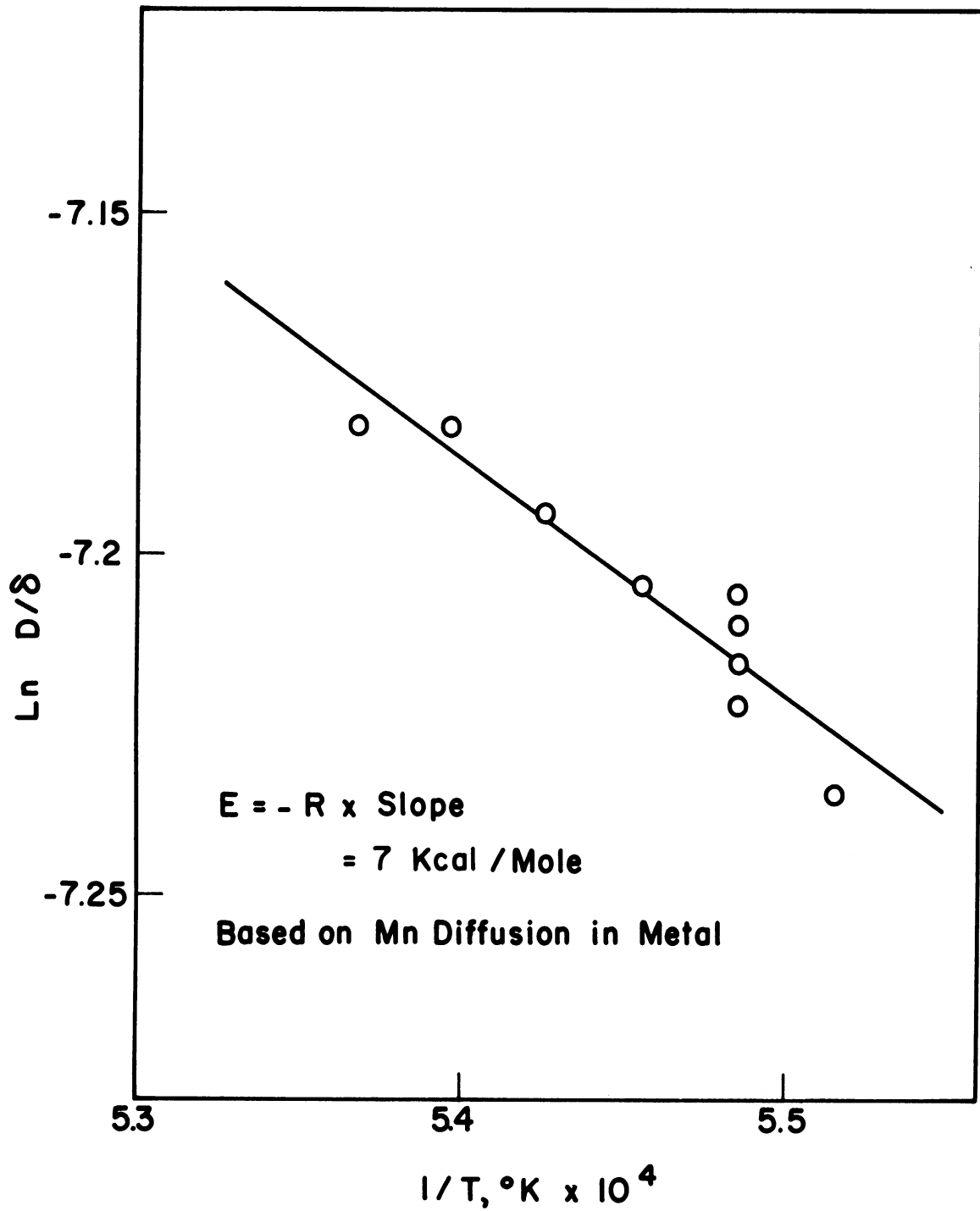


Figure 8. The Effect of Temperature on the Reaction  $2(\text{MnO}) + \underline{\text{Si}} = (\text{SiO}_2) + 2\underline{\text{Mn}}$ .

TABLE IV

COMPARISON OF EXPERIMENTAL ENERGIES OF ACTIVATION WITH  
THOSE REPORTED IN THE LITERATURE FOR THE REDUCTION OF  
MANGANESE OXIDE BY SILICON

Diffusion Step	E, Experimental	E, Literature (Ref. 40, 42)
Manganese in Iron	7 Kcal/mole Mn	5.8 Kcal/mole Mn
Silicon in Iron	14 Kcal/mole Si	8.6 Kcal/mole Si
Manganese in Slag	7 Kcal/mole Mn	---
Silicon in Slag	14 Kcal/mole Si	70 Kcal/mole Si

The results of the study on the effect of temperature shows that the controlling mechanism for this reaction is the diffusion of manganese or silicon in the metal phase.

### 3. The Effect of Melt Geometry

Runs varying the slag-to-metal ratio were made to determine in which phase the controlling step occurred. In calculating the diffusion constant, a function of the manganese concentration (applicable to the diffusion step under consideration) is plotted versus time. The resulting slope has a value  $\frac{D}{\delta h}$ , where h is the height of the phase in which the diffusion is taking place for the derived model. When the slag-to-metal volume ratio is varied, then the relative value of h between a model derived for the slag phase and one derived for the metal phase is also varied. For example, let us assume that one phase depth is increased and the other is decreased. If, because of this change in melt geometry, the slope of the curve for the theoretical model increases, then for  $\frac{D}{\delta}$  to remain constant, h would have to decrease. In one phase, this would occur. In the other phase, just the opposite would occur and the resulting calculated values for  $\frac{D}{\delta}$  would not remain consistent. This, indeed, happened as can be seen in Table V.

Experiment 223 had a slag depth half that of the standard run and a metal depth twice the standard. The slope of the curves for the theoretical models was only half that of a typical run. Since  $\frac{D}{\delta} = \text{Slope} \times h_i$ ,  $\frac{D}{\delta}$  for the diffusion of manganese and silicon in the metal phase remained constant, but was only one-fourth the normal value for diffusion in the slag phase.

Run 172 had a slag depth greater than normal and a metal depth only one-third of normal. Under these conditions the slope of the curves for

TABLE V  
 THE EFFECT OF MELT GEOMETRY ON THE REDUCTION OF  
 MANGANESE OXIDE BY SILICON

Run	Slag Depth, cm	Metal Depth, cm	$(D/\delta) \times 10^4, \text{ cm/sec}$			
			Metal Phase		Slag Phase	
			Mn	Si	Mn	Si
223	1.5	4.4	7.26	1.74	5.3	0.029
122	3.0	2.92	6.98	7.12	15.2	0.058
155	3.0	2.2	7.39	4.28	23.9	0.078
154	3.0	2.2	7.30	3.45	22.5	0.105
163	3.0	2.2	7.35	3.89	22.2	0.080
146	3.0	2.2	7.43	4.51	23.7	0.061
143	3.0	2.2	6.94	3.07	21.2	0.109
121	3.0	1.47	7.57	3.85	30.3	0.157
172	4.5	0.75	7.75	2.09	75.6	2.666

the theoretical model was much greater than normal. Again this was corrected for by the depth of the metal phase, giving consistent results of  $\frac{D}{\delta}$  for the components in the metal phase, and again  $\frac{D}{\delta}$  for the components in the slag phase were inconsistent, being much greater than usual.

The result of the melt geometry study is that the process is controlled by the rate of diffusion of manganese or silicon in the metal phase. This agrees with the results of the temperature study above.

#### 4. The Effect of Concentration

By this process of elimination, the controlling step had now been limited to diffusion, and also it had been limited to diffusion of one of the components in the metal phase. It was now necessary to devise a method of determining which diffusion step in the metal phase was the slow one. To do this, runs were made increasing the initial silicon concentration in the metal. A summary of the results obtained is given in Table VI. As can be seen, as the initial silicon concentration is increased, the value for  $\frac{D}{\delta}$  decreases for both manganese in the metal and silicon in the metal. However, the decrease in  $\frac{D}{\delta}$  for silicon diffusion is much greater, as is shown in Figures 9 and 10.

The small decrease in values of  $\frac{D}{\delta}$  for manganese in the metal as the silicon concentration is increased, is not unrealistic. In the collection of diffusion data by Elliott, et al.<sup>20</sup>, the same phenomenon is noted. The diffusion coefficient of carbon in iron is reduced by increasing the concentration of carbon in the iron. Likewise, the diffusion coefficient of silicon in iron is reduced by increasing the concentration of silicon in the iron. However, the changes of the diffusion coefficients are small as is the implied change of the diffusion coefficient for manganese in iron evaluated in this study as the silicon concentration is increased.

TABLE VI

THE EFFECT OF THE CONCENTRATION OF SILICON ON THE REDUCTION  
OF MANGANESE OXIDE BY SILICON

Run	Initial Si Concentration, %	$(D/\delta) \times 10^4$ , cm/sec			
		Metal Phase		Slag Phase	
		Mn	Si	Mn	Si
155	1.32	7.39	4.28	23.9	0.078
154	1.32	7.30	3.45	22.5	0.105
163	1.32	7.35	3.89	22.2	0.080
146	1.32	7.43	4.51	23.7	0.061
143	1.32	6.94	3.07	21.2	0.109
162	1.96	6.14	2.61	25.2	0.070
167	3.85	4.27	0.66	22.7	0.074

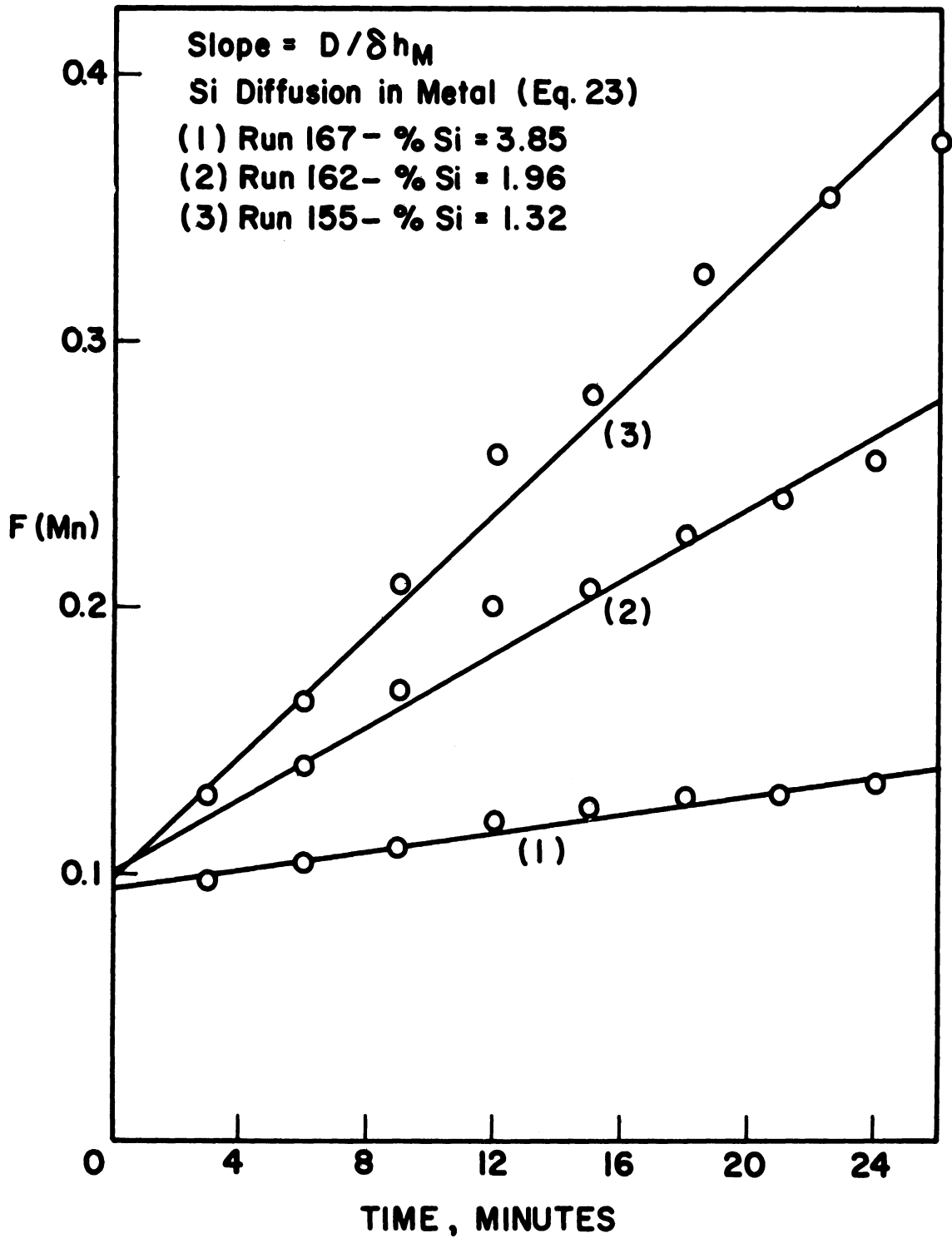


Figure 9. The Effect of Silicon Concentration on the Reaction  $2(\text{MnO}) + \underline{\text{Si}} = (\text{SiO}_2) + \underline{2\text{Mn}}$ .

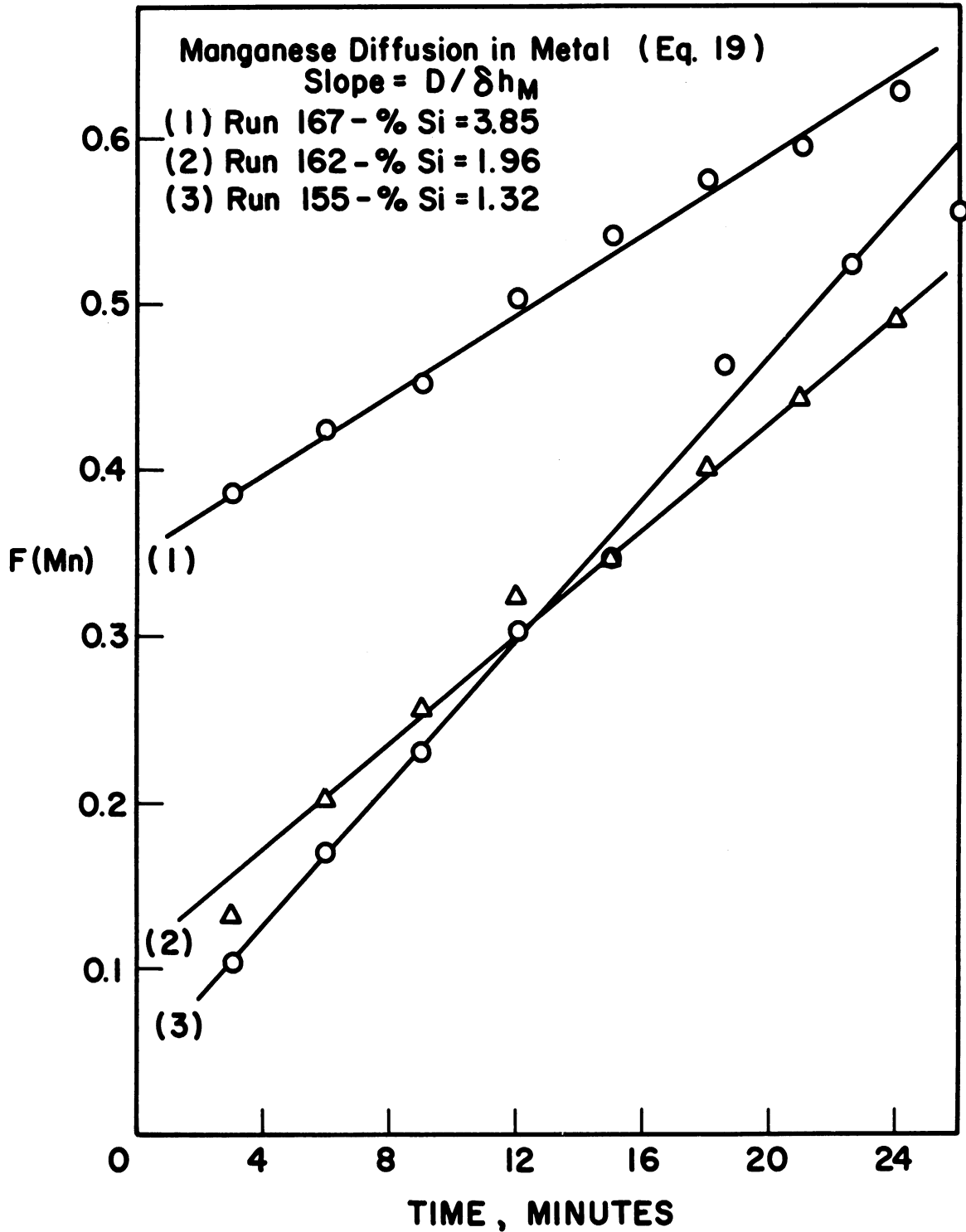


Figure 10. The Effect of Silicon Concentration on the Reaction  $2(\underline{\text{MnO}}) + \underline{\text{Si}} = (\underline{\text{SiO}_2}) + 2 \underline{\text{Mn}}$ .



The change of  $\frac{D}{\delta}$  for silicon in the iron evaluated in this experimental study as the concentration of silicon in the iron is increased, is not small. It varies by almost an order of magnitude as the silicon concentration is increased. Considering Equation (44), the inconsistency becomes more apparent. The driving force is increased by approximately a factor of three with increased silicon concentration. The rate of the reaction should also increase by a factor of three. This did not happen. In fact, the rate of the reaction was even slower than before.

These results show that the theoretical model describing the rate-controlling step as the diffusion of silicon in the metal is not valid for this chemical reaction, so only the model for diffusion of manganese in the metal has consistently described the experimental results.

#### 5. Other Considerations

One more piece of information available for consideration is the value of  $\frac{D}{\delta}$  calculated for each of these diffusion models. By comparing the experimental values with the values of  $D$  for these same diffusion steps as reported in the literature, the possible diffusion steps are defined. These comparisons, along with the values of  $\delta$  calculated from the comparisons, are presented in Table VII. The  $\delta$ 's obtained are all reasonable for a diffusion process. Therefore, in view of the values obtained for  $\frac{D}{\delta}$ , any of these diffusion models could define the rate-limiting step for the reaction.

#### 6. Summary

The results obtained above are summarized in Table VIII, which reviews the results obtained from a study of each of the variables. From this summary it can be seen that only the model for the diffusion of manganese in the metal phase gives consistent results throughout. The diffusion of manganese in the metal is therefore postulated to be the rate-limiting step for the reduction of manganese oxide by silicon.

TABLE VII  
COMPARISON OF EXPERIMENTAL DIFFUSION CONSTANTS WITH THOSE REPORTED  
IN THE LITERATURE FOR THE REDUCTION OF MANGANESE OXIDE  
BY SILICON AT 1550°C

Diffusion Step	D/δ, cm/sec, Experimental	D, cm <sup>2</sup> /sec, Literature*	δ, cm, Calculated
Manganese in Iron	$7 \times 10^{-4}$	$4 \times 10^{-5}$	0.06
Silicon in Iron	$4 \times 10^{-4}$	$4 \times 10^{-5}$	0.1
Manganese in Slag	$2 \times 10^{-3}$	--	--
Silicon in Slag	$1 \times 10^{-5}$	$10^{-6}$	0.1

\* Ref. 39, 40, 41, 42

TABLE VIII  
 APPLICABILITY OF POSSIBLE MODELS FOR THE REDUCTION  
 OF MANGANESE OXIDE BY SILICON

Variable	Results	Is Model Applicable?				
		Diffusion				Chemical Reaction
		Metal Phase		Slag Phase		
		Mn	Si	Mn	Si	
Stirring rate	Pronounced effect on the reaction rate	Yes	Yes	Yes	Yes	No
Tempera- ture	Energy of Activation very low; $E = 7 \text{ Kcal/mole Mn}$	Yes	Yes	No	No	No
Melt Geo- metry	Only models for diffusion in the metal phase main- tained a consistent reaction constant	Yes	?	No	No	--
Concentra- tion (Si in Metal)	The silicon diffusion in metal model did not give consistent results for varied silicon concentra- tions	Yes	No	Yes	Yes	--
	Diffusivities	Yes	Yes	Yes	Yes	--

## B. Manganese Oxide Reduction by Carbon

This reaction was much slower than the reduction by silicon. A comparison of the two is presented in Figure 11. If this reaction is controlled by a diffusion step, results similar to those obtained for the reduction by silicon would be expected; the slow rate of reaction, however, indicates the reaction is controlled by a slower chemical reaction step. The data obtained on this system is compiled in Appendices A and B. This data has been analyzed in terms of the theoretical models derived for this particular reaction. Figure 12 shows the results obtained for a typical run when the diffusion models, Equations (33), (34), (39), and (44), are applied to it. Figure 13 shows the results obtained when the chemical reaction models, Equations (46), (48), and (51), are applied to this same data. As can be seen, a good data fit is obtained for all of these models, so any of them could define the rate-limiting step. The effect of stirring rate, temperature, melt geometry and concentrations, as well as the magnitude of the rate constant, is considered in determining the rate-limiting step for the reduction of manganese oxide by carbon.

### 1. The Effect of Stirring Rate

The model for diffusion of manganese in the metal is used in Figure 14 to demonstrate the effect of stirring rate on this reaction. No apparent effect of stirring is visible. A compilation of all the results obtained when varying the stirring rate is given in Table IX. Since the rate of stirring has no effect on the reaction, it has to be classified as one controlled by a chemical reaction rather than by diffusion. This result is exactly the opposite of the result obtained for reduction by silicon.

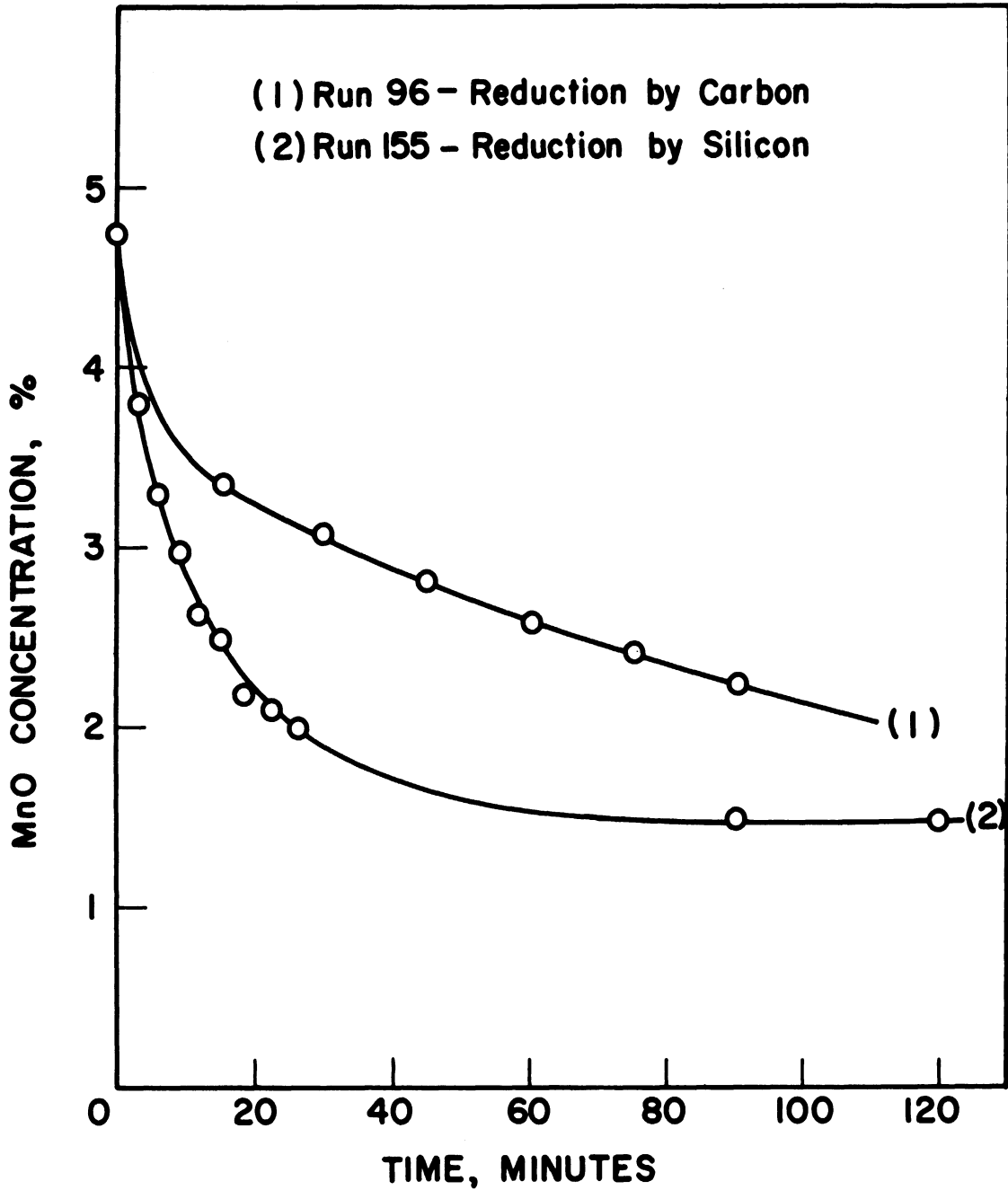


Figure 11. Comparison of Concentration-Time Curves for Reduction by Silicon and Reduction by Carbon.

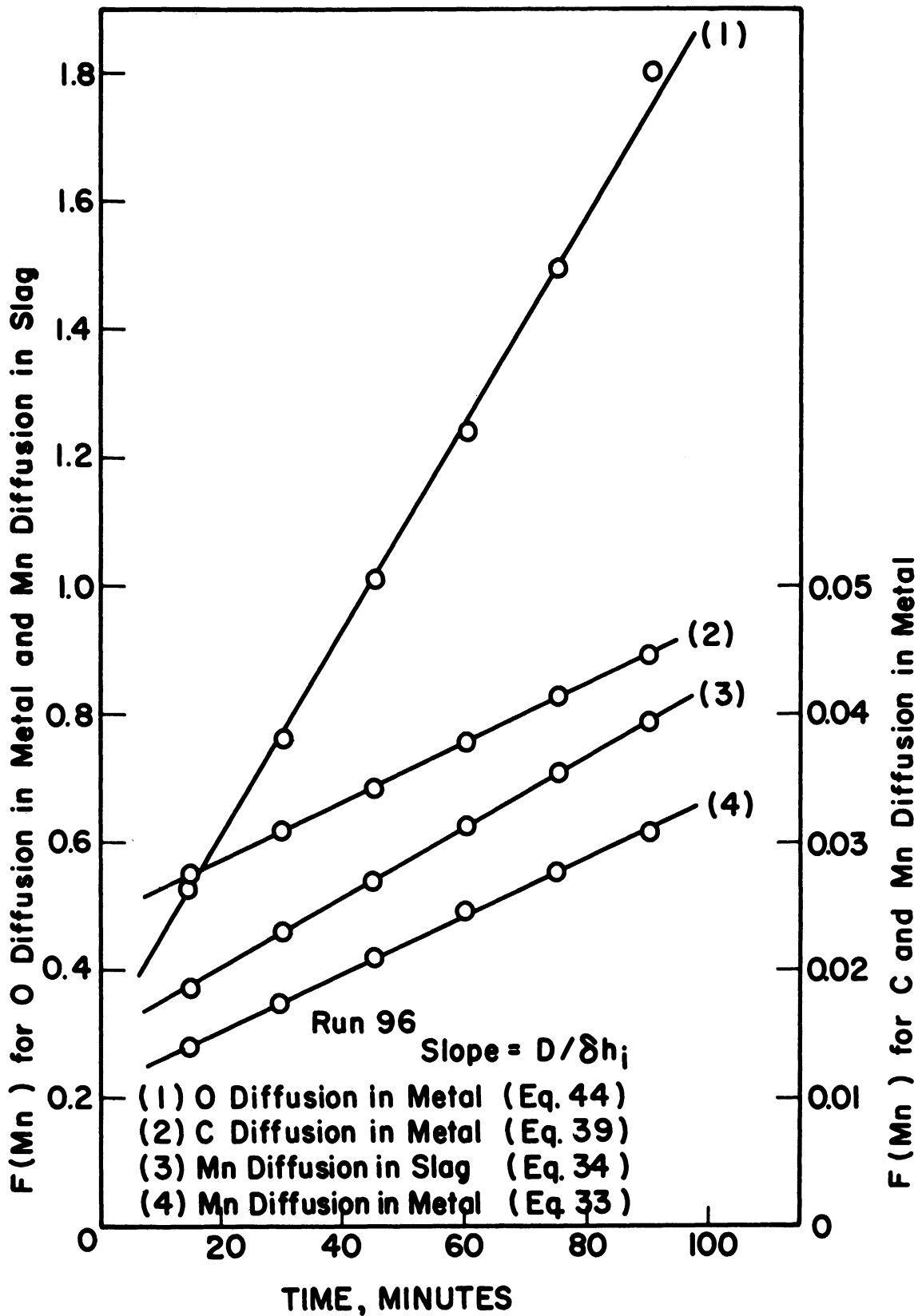


Figure 12. Determination of  $D/\delta$  for Various Theoretical Models for the Reaction  $(\text{MnO}) + \underline{\text{C}} = \underline{\text{Mn}} + \text{CO}_{(g)}$ .

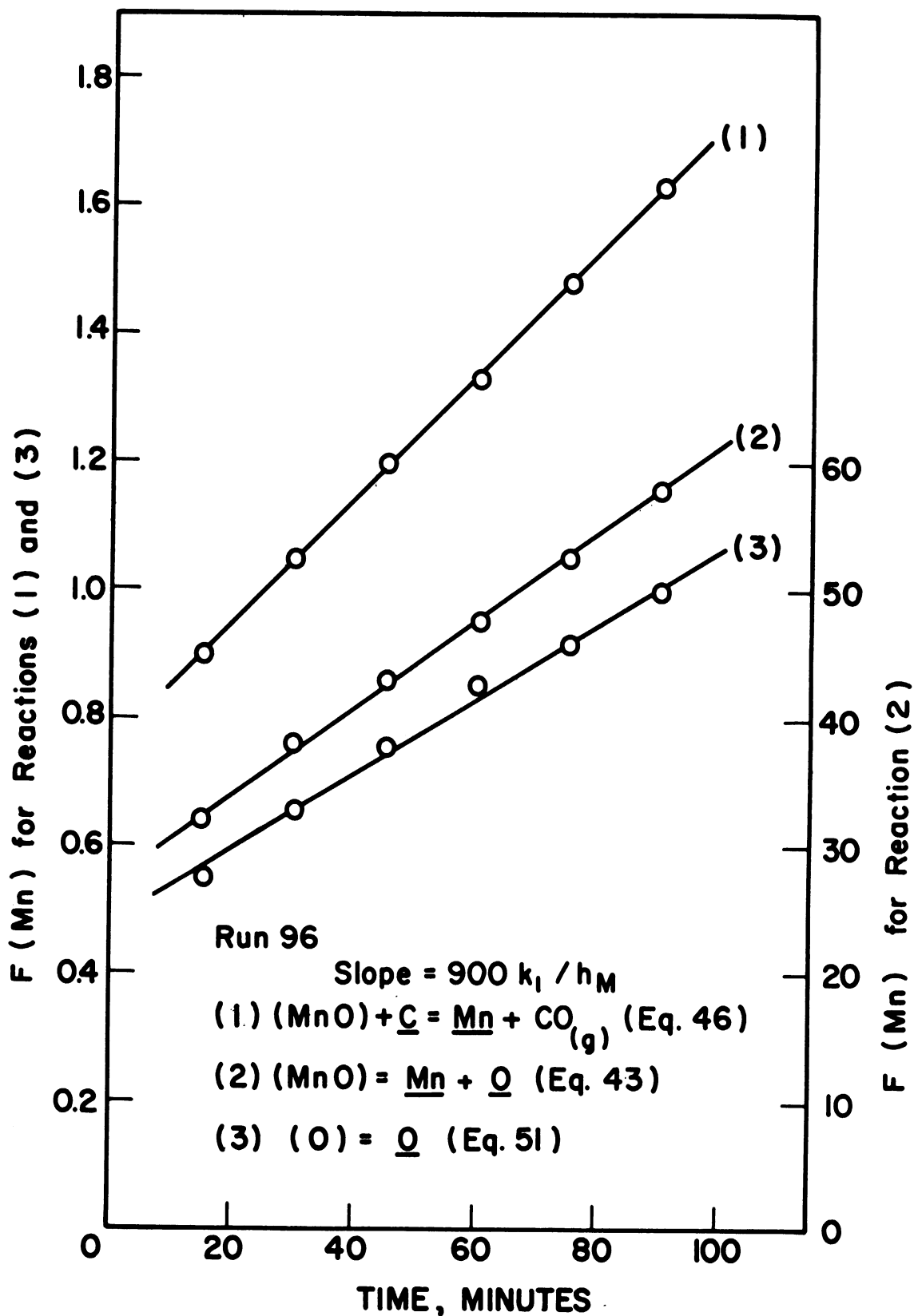


Figure 13. Determination of  $k_1$  for Various Theoretical Models for the Reaction  $(\text{MnO}) + \underline{\text{C}} = \underline{\text{Mn}} + \text{CO}_{(g)}$ .

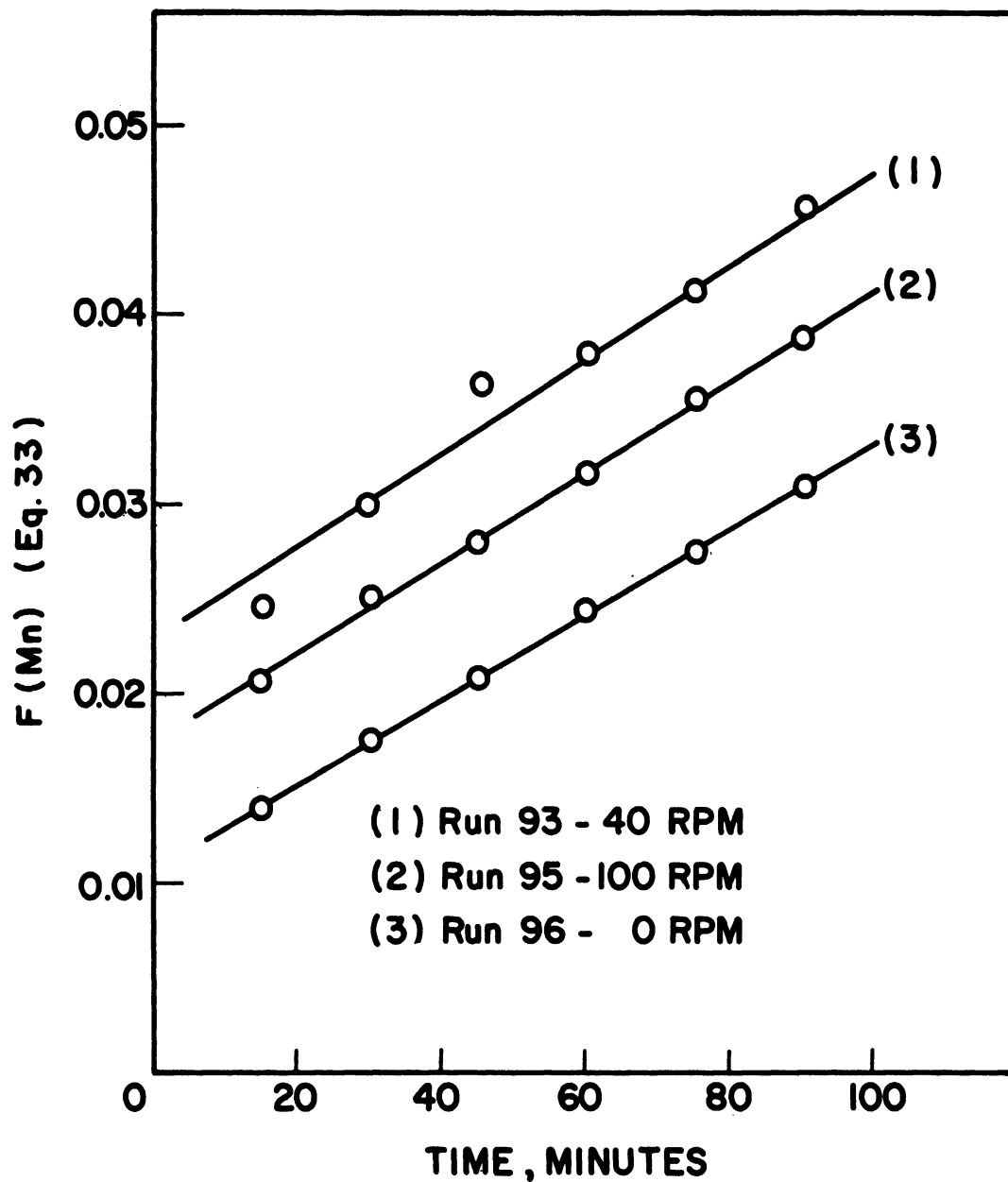
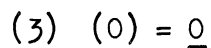
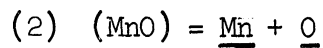
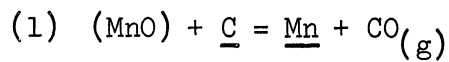


Figure 14. The Effect of Stirring Rate on the Reaction  $(\text{MnO}) + \underline{\text{C}} = \underline{\text{Mn}} + \text{CO}_{(g)}$ .



TABLE IX  
THE EFFECT OF STIRRING RATE ON THE REDUCTION OF  
MANGANESE OXIDE BY CARBON

Run	Stir Rate, RPM	$(D/\delta) \times 10^4, \text{ cm/sec}$				$k_1 \times 10^4, \text{ mole/cm}^2 \text{ min}$		
		Metal Phase			Slag Phase	(1)*	(2)*	(3)*
		Mn	C	O	Mn			
96	0	0.075	0.090	6.1	1.90	0.238	8.5	0.125
124	0	0.074	0.078	7.2	1.89	0.238	8.5	0.104
126	0	0.139	0.126	16.2	3.55	0.456	16.3	0.141
58	20	0.063	0.077	5.1	1.60	0.206	7.3	0.109
93	40	0.113	0.113	12.1	2.89	0.372	13.3	0.113
21	40	0.096	0.112	7.7	2.45	0.315	11.3	0.127
45	40	0.089	0.099	8.5	2.27	0.297	10.6	0.133
108	40	0.130	0.135	13.4	3.32	0.431	15.4	0.139
20	100	0.067	0.086	5.0	1.70	0.218	7.8	0.086
22	100	0.071	0.083	6.4	1.81	0.235	8.4	0.113
95	100	0.100	0.107	9.6	2.54	0.321	11.4	0.142



## 2. The Effect of Temperature

A change in temperature had a greater effect on this reaction than it did on the first reaction studied. This is shown in Figure 15, where the natural logarithm of the rate constant is plotted against reciprocal absolute temperature to give the energy of activation for the system. The energy of activation determined by a regression analysis of the data, 25 Kcal/mole Mn, is difficult to rationalize in terms of the possible rate-limiting mechanisms for the reaction. It is too high for the diffusion of the components in the metal; but, on the other hand, it is lower than one would expect for the diffusion of manganese in the slag or for the chemical reactions under consideration. However, there has been no work done in this area, so the energy of activation is undefined for these processes. The value determined in this study could be valid for the diffusion of manganese in the slag or for the chemical reactions postulated here as the possible slow steps in the overall reaction. The results obtained when varying the temperature are given in Table X.

In summary, then, the energy of activation for this system indicates that the rate-limiting step for the reaction is either the diffusion of manganese in the slag or a chemical reaction.

## 3. The Effect of Melt Geometry

The slag-to-metal ratio was varied from 1:4 to 4:1 in this study to see what effect this would have on the calculated rate constants. The results are presented in Table XI. Melt geometry should have no effect on either  $\frac{D}{\delta}$  or on  $k_1$ ; therefore, consistent results should be obtained regardless of the slag-to-metal ratio. As can be seen, there is a great deal of scatter in the results for every model. However, the models for diffusion of carbon in the metal phase, Equation (39), and for the chemical

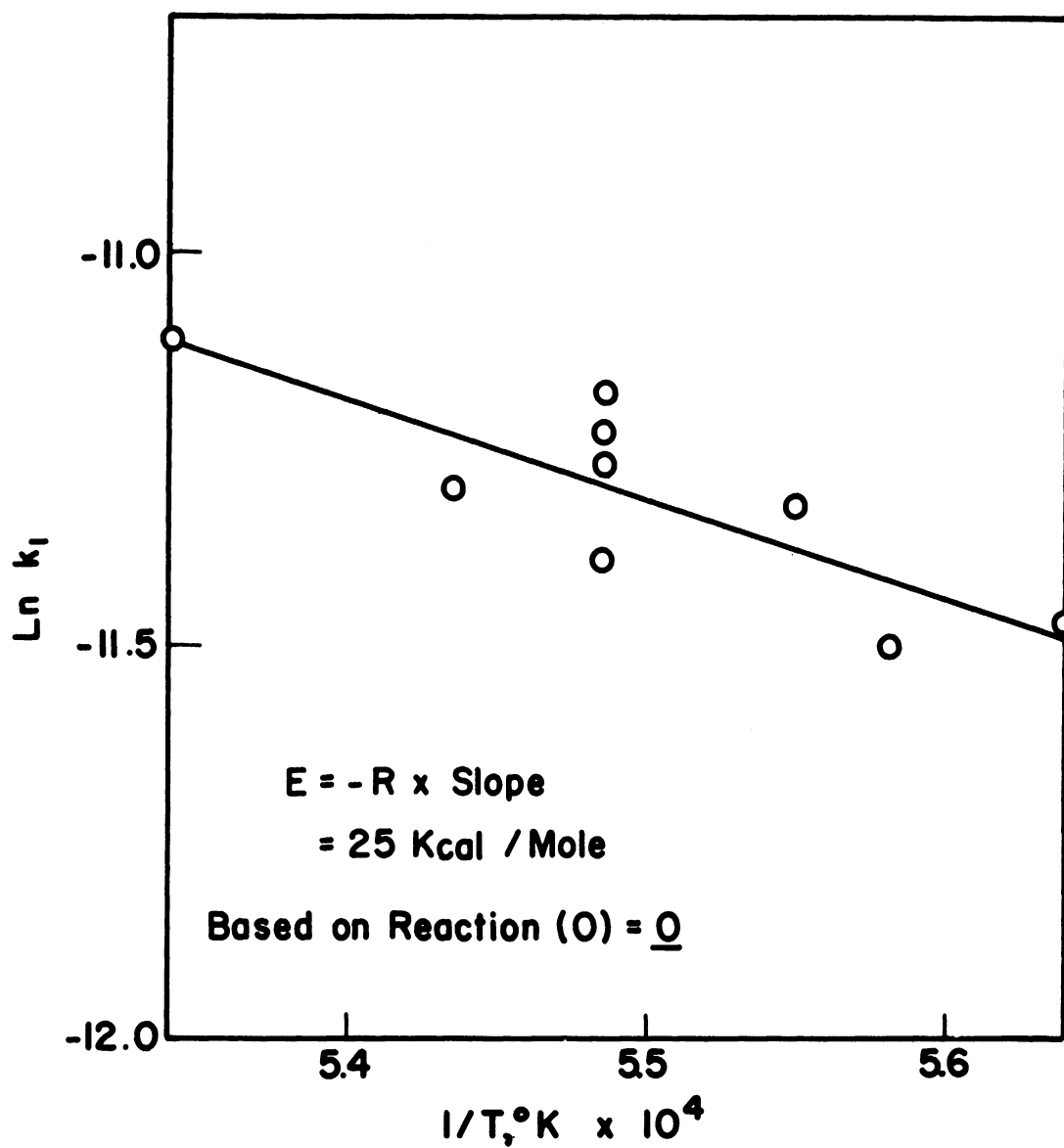


Figure 15. The Effect of Temperature on the Reaction  $\text{MnO} + \underline{\text{C}} = \underline{\text{Mn}} + \text{CO}(\text{g})$ .

TABLE X  
THE EFFECT OF TEMPERATURE ON THE REDUCTION OF  
MANGANESE OXIDE BY CARBON

Run	T, °C	$(D/\delta) \times 10^4, \text{ cm/sec}$				$k_1 \times 10^4, \text{ mole/cm}^2 \text{ min}$		
		Metal Phase			Slag Phase	(1)*	(2)*	(3)*
		Mn	C	O	Mn			
44	1500	0.117	0.092	8.2	1.88	0.251	8.6	0.104
92	1519	0.102	0.092	8.2	1.98	0.253	8.8	0.101
90	1544	0.089	0.089	7.7	2.06	0.260	9.2	0.123
93	1550	0.113	0.113	12.1	2.89	0.372	13.3	0.113
21	1550	0.096	0.112	7.7	2.45	0.318	11.3	0.127
45	1550	0.089	0.099	8.5	2.27	0.297	10.6	0.133
108	1550	1.30	0.135	13.4	3.32	0.431	15.4	0.139
91	1567	0.079	0.098	8.1	2.33	0.290	10.5	0.122
47	1600	0.081	0.174	10.6	3.19	0.418	15.5	0.148

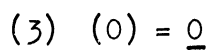
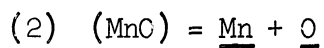
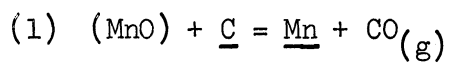
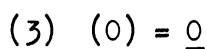
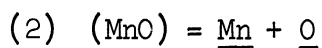
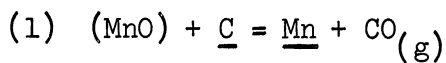


TABLE XI  
THE EFFECT OF MELT GEOMETRY ON THE REDUCTION OF  
MANGANESE OXIDE BY CARBON

Run	Slag Depth, cm	Metal Depth, cm	$(D/\delta) \times 10^4, \text{ cm/sec}$				$k_1 \times 10^4, \text{ mole/cm}^2 \text{ min}$		
			Metal Phase			Slag Phase	(1)*	(2)*	(3)*
			Mn	C	O	Mn			
224	1.25	5.0	0.306	0.162	9.9	7.65	1.045	37.2	0.188
48	1.88	2.5	0.076	0.097	8.4	1.90	0.259	9.2	0.129
98	1.88	2.5	0.059	0.087	5.2	1.48	0.189	6.7	0.124
93	2.5	2.5	0.113	0.113	12.1	2.89	0.372	13.3	0.113
21	2.5	2.5	0.096	0.112	7.7	2.45	0.318	11.3	0.127
45	2.5	2.5	0.089	0.099	8.5	2.27	0.297	10.6	0.133
108	2.5	2.5	0.130	0.135	13.4	3.32	0.431	15.4	0.139
49	3.12	2.5	0.141	0.126	14.3	3.62	0.472	16.8	0.112
99	3.12	2.5	0.101	0.105	7.8	2.59	0.325	11.6	0.144
100	3.12	2.2	0.077	0.122	19.8	1.90	0.240	8.6	0.099
101	3.12	1.88	0.129	0.128	19.6	3.30	0.413	14.8	0.082
59	3.12	1.56	0.085	0.099	9.4	2.21	0.276	9.9	0.128
225	5.0	1.25	0.072	0.095	22.4	1.83	0.199	7.2	0.083



reaction of oxygen in the slag going to oxygen in the metal, Equation (51), give much better results than the other models. The scatter for these two models is small and random, and is reasonable in view of the overall accuracy of the data. For the other models, the scatter is three or four times greater than for these two models.

#### 4. The Effect of Concentration

Two variables were studied with respect to the effect of concentration on the reaction rate. First of all, the amount of manganese oxide added to start the runs was varied. Secondly, the concentration of graphite in the iron was varied. Zirconia crucibles were used which allowed the use of carbon contents below graphite saturation.

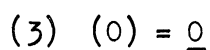
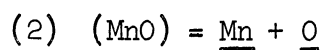
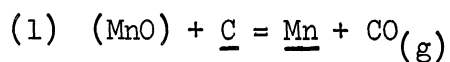
The rate constant should not vary as a result of changes in concentration; only the rate itself should be affected. In other words, a higher driving force should give a higher reaction rate, the rate constant remaining the same. The one exception to this is for the reaction of oxygen in the slag being reduced to oxygen in the metal. In the derivation of this model, Equation (51), the activity of the oxygen in the slag was assumed constant and is included in the rate constant. From the work by Toop and Samis<sup>29</sup>, it can be assumed that the activity of oxygen in the slag increases very slightly as the concentration of manganese oxide in the slag increases. Therefore, we would expect the rate constant as evaluated with this model also to increase slightly when a higher percentage of manganese oxide is used for the run. This, in fact, turned out to be the case.

The effect of manganese oxide concentration on the rate of reduction of manganese oxide by carbon is presented in Table XII. As can be seen, the only models which give consistent results as the concentration of

TABLE XII

THE EFFECT OF MANGANESE OXIDE CONCENTRATION ON THE  
REDUCTION OF MANGANESE OXIDE BY CARBON

Run	%MnO <sup>o</sup>	$(D/\delta) \times 10^4, \text{ cm/sec}$				$k_1 \times 10^4, \text{ mole/cm}^2\text{min}$		
		Metal Phase			Slag Phase	(1)*	(2)*	(3)*
		Mn	C	O	Mn			
138	0.49	0.207	0.022	2.2	5.52	0.667	23.8	0.041
153	0.99	0.300	0.080	6.9	5.58	0.967	34.5	0.093
156	0.99	0.297	0.074	5.0	7.89	0.965	34.4	0.111
135	1.48	0.254	0.077	10.0	6.72	0.985	35.2	0.136
109	2.44	0.190	0.084	12.1	4.98	0.651	23.3	0.099
93	4.75	0.113	0.113	12.1	2.89	0.372	13.3	0.113
21	4.75	0.096	0.112	7.7	2.45	0.318	11.3	0.127
45	4.75	0.089	0.099	8.5	2.27	0.297	10.6	0.133
108	4.75	0.130	0.135	13.4	3.32	0.431	15.4	0.139



manganese oxide at the start of the run was varied were for the chemical reaction  $(O) = \underline{O}$  and for the diffusion of carbon in the metal.

The effect of carbon concentration on the reduction of manganese oxide by carbon is shown in Table XIII. Again the majority of the models do not give consistent results as the graphite concentration is varied. Only chemical reaction models (2) and (3) give consistent results here.

In summary, only the model for the activation of oxygen going from the slag to the metal phase gives consistent results as concentrations in the slag-metal system are varied.

#### 5. The Effect of Slag Variation

Changes in composition of the slag phase were made to see what effect this would have on the reaction. The results are tabulated in Table XIV. With each change in slag composition it is necessary to estimate a new activity coefficient for manganese oxide in the slag. This involves extrapolations and approximations, and yields results of limited accuracy. This is evident from the general scatter of the results. No influence can be detected on the rate constants as a result of varying the slag composition.

#### 6. The Effect of Silicon Additions to the Melt

A run was made adding silicon to the graphite-saturated melt to see what effect this would have on the overall reaction. In effect, this situation involves a simultaneous occurrence of both of the reactions under study in this research program. Figure 16 gives a comparison of the raw data obtained on this run as compared with that for reduction by silicon alone and by graphite alone. The diffusion coefficient of manganese in the metal for this run is  $\frac{D}{\delta} = 3 \times 10^{-4}$  cm/sec. This value is lower than the value for the diffusion coefficient of manganese in metal



TABLE XIII  
THE EFFECT OF CARBON CONCENTRATION ON THE REDUCTION OF  
MANGANESE OXIDE BY CARBON

Run	%C <sup>o</sup>	(D/δ) x 10 <sup>4</sup> , cm/sec				k <sub>1</sub> x 10 <sup>4</sup> , mole/cm <sup>2</sup> min		
		Metal Phase			Slag Phase	(1)*	(2)*	(3)*
		Mn	C	O	Mn			
196	1.32	3.07	0.789	7.7	4.42	9.40	12.9	0.201
218	2.60	2.04	0.404	25.4	8.70	6.46	20.7	0.141
228	4.75	0.231	0.254	15.4	4.41	0.742	19.8	0.157
93	5.28	0.113	0.113	12.1	2.89	0.372	13.3	0.113
21	5.28	0.096	0.112	7.7	2.45	0.318	11.3	0.127
45	5.28	0.089	0.099	8.5	2.27	0.297	10.6	0.133
108	5.28	0.130	0.135	13.4	3.32	0.431	15.4	0.139

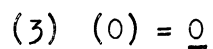
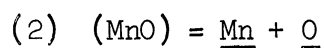
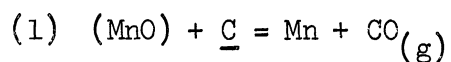
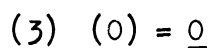
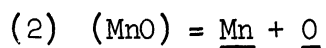
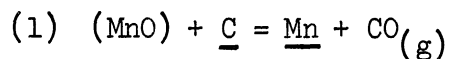


TABLE XIV  
THE EFFECT OF SLAG COMPOSITION ON THE REDUCTION OF  
MANGANESE OXIDE BY CARBON

Run	Slag Composition % CaO-MgO-SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	(D/δ) x 10 <sup>4</sup> , cm/sec				k <sub>1</sub> x 10 <sup>4</sup> , mole/cm <sup>2</sup> min		
		Metal Phase			Slag Phase	(1)*	(2)*	(3)*
		Mn	C	O	Mn			
17	49-6-0-45	0.225	0.113	14.9	3.52	0.859	31.0	0.110
18	40-15-35-10	0.075	0.088	6.8	1.92	0.253	9.1	0.097
50	45-10-45-0	0.116	0.065	7.0	1.81	0.379	13.6	0.062
51	45-10-25-20	0.056	0.132	8.7	2.48	0.189	6.7	0.127
52	55-0-45-0	0.125	0.091	5.9	1.95	0.409	14.6	0.106
53	35-20-45-0	0.116	0.080	5.8	1.82	0.375	13.4	0.096
54	55-5-10-30	0.045	0.323	20.3	4.42	0.157	5.6	0.185
55	45-5-20-30	0.049	0.153	9.7	2.64	0.160	5.7	0.136
56	50-5-15-30	0.047	0.507	13.6	3.60	0.161	5.8	0.180
57	40-5-25-30	0.062	0.109	6.8	2.13	0.203	7.2	0.120



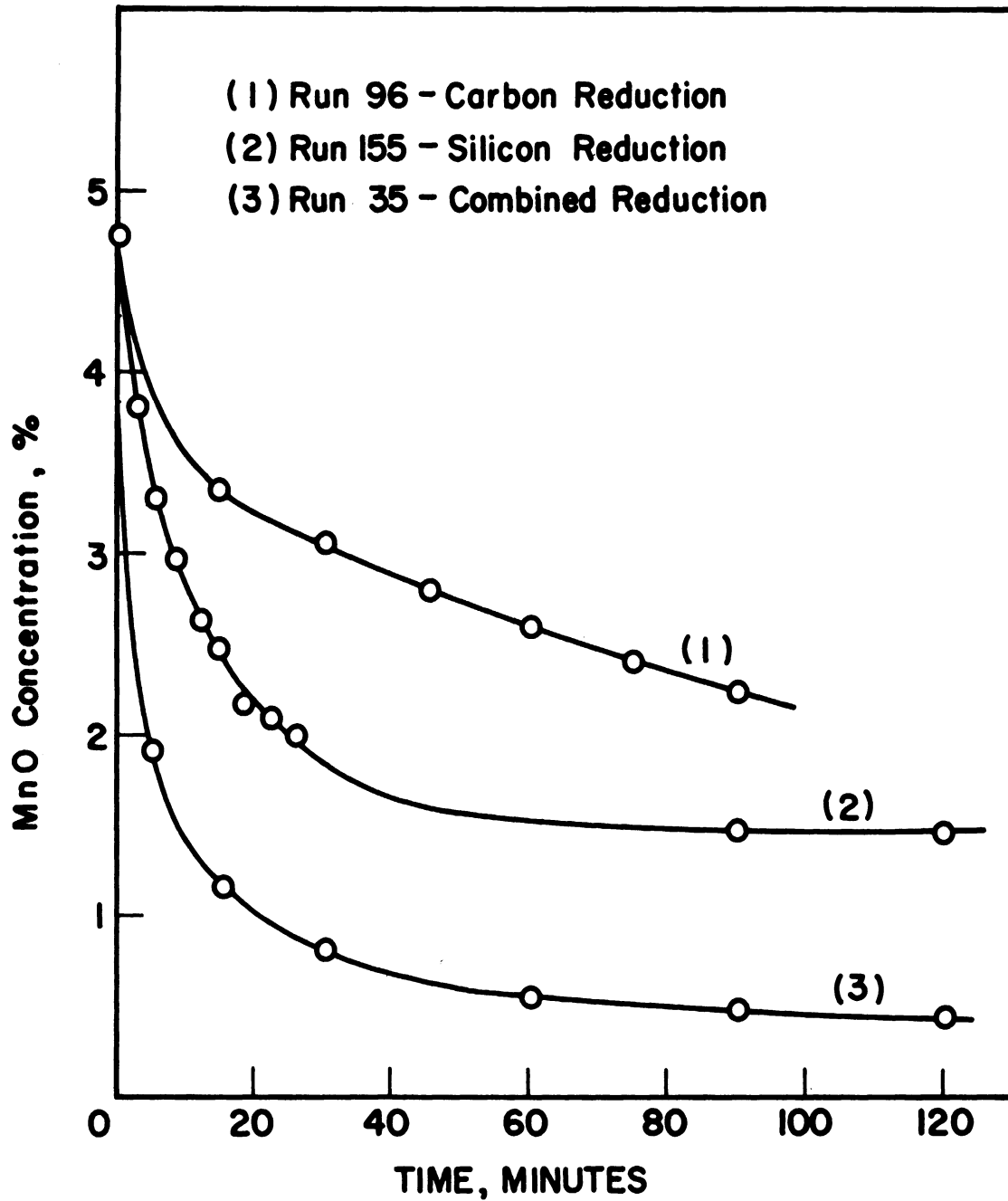


Figure 16. The Effect of Simultaneous Reduction by Silicon and Carbon.

evaluated for the first reaction studied, indicating that graphite in iron slows down the diffusion of manganese. However, this value is much higher than the corresponding coefficient for the reduction by carbon. This shows that diffusion of manganese in slag or metal cannot be the rate-limiting step for the reduction of manganese oxide by carbon.

#### 7. Other Considerations

The values of  $\frac{D}{\delta}$  obtained in this study can be compared with those given in the literature. This is done in Table XV. As can be seen, the rate of this reaction is much too slow for the controlling step to be diffusion of manganese or carbon in the metal. Also, since the first reaction studied is much faster than this one, and both reactions involve the diffusion of manganese in the slag, that step can be eliminated as a possible rate-limiting step for this reaction. Of the diffusion steps studied, only the diffusion of oxygen in the metal can qualify as a possible rate-limiting step for this reaction.

A further study was made to check on the possibility that diffusion of oxygen in the metal was the slow step of the reaction. Argon was bubbled through the slag-metal interface, offering sites for carbon monoxide nucleation. This would decrease the diffusion path for oxygen and speed up the rate of the reaction if diffusion of oxygen was the rate-limiting step. However, the rate of the reaction was not affected by this experimental procedure, indicating that diffusion of oxygen in the metal is not the rate-limiting step for the reduction of manganese oxide by carbon.

#### 8. Summary

A summary of the applicability of possible models to the reduction of manganese oxide by carbon as influenced by the variables under consideration is presented in Table XVI. The effect of stirring rate, temperature,

TABLE XV

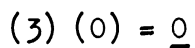
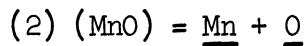
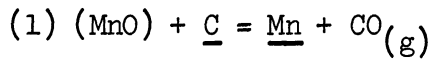
COMPARISON OF EXPERIMENTAL DIFFUSION CONSTANTS WITH THOSE  
 REPORTED IN THE LITERATURE FOR THE REDUCTION OF  
 MANGANESE OXIDE BY CARBON AT 1550°C

Diffusion Step	$D/\delta$ , cm/sec, Experimental	$D$ , cm <sup>2</sup> /sec, Literature*	$\delta$ , cm, Calculated
Manganese in Iron	$1 \times 10^{-5}$	$4 \times 10^{-5}$	4
Manganese in Slag	$3 \times 10^{-4}$	--	-
Carbon in Iron	$1 \times 10^{-5}$	$7 \times 10^{-5}$	7
Oxygen in Iron	$1 \times 10^{-3}$	$1.2 \times 10^{-4}$	0.1

\* Ref. 34, 39, 40, 41, 45

TABLE XVI  
 APPLICABILITY OF POSSIBLE MODELS FOR THE REDUCTION OF  
 MANGANESE OXIDE BY CARBON

Variable	Results	Is Model Applicable?						
		Diffusion				Chemical Reaction		
		Metal Phase		Slag Phase		(1)*	(2)*	(3)*
		Mn	C	O	Mn			
Stirring rate	Negligible effect	No	No	No	No	Yes	Yes	Yes
Temperature	Energy of activation; E = 25 Kcal/mole	No	No	No	Yes	Yes	Yes	Yes
Melt Geometry	Most models gave quite scattered data	No	Yes	No	No	No	No	Yes
MnO Concentration	Only models not directly involving MnO gave good results	No	Yes	Yes	No	No	No	Yes
C Concentration	Only models not involving C gave good results	No	No	No	No	No	Yes	Yes
	Diffusivities	No	No	Yes	No	--	--	--



and the values of the diffusivities effectively eliminate the possibility of diffusion as being the rate-limiting step. Of the chemical reaction models, only the model for the activation of oxygen going from the slag phase to the metal phase gives consistent results throughout this study. Therefore, it is postulated that the rate-limiting step for the reduction of manganese oxide by carbon is the chemical reaction involved in the process of oxygen going from the slag into the metal.

## DISCUSSION

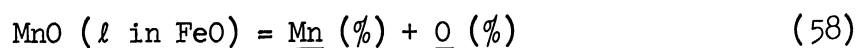
There are certain areas of this study which demand further explanation, and it is the purpose of this section of the thesis to explore these areas. First, the equilibrium constants,  $K'$ , which were used in calibrations, will be discussed. Next, the effect of  $\delta$  on the calculation of the energy of activation,  $E$ , will be considered. The derivation of theoretical models and the application of these models to the experimental data involved the premise that one particular step controlled the rate of the overall reaction. The matter of possible mixed control for the reactions will be discussed here also. Then the accuracy of the results obtained by this study will be reviewed.

### A. Evaluation of the Equilibrium Constant, $K'$

For the reduction of manganese oxide by silicon, each run was allowed to proceed to equilibrium and the equilibrium conditions existing at the end of the run were used to determine  $K'$  in the rate equation. As a check, equilibrium conditions were calculated from data available in the literature. The sources of this data were reviewed in the literature survey and will not be repeated here. The equilibrium constant was calculated from values of free energy of reaction from the literature according to

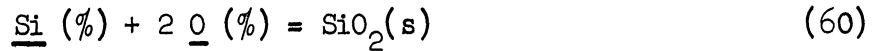
$$\Delta F^\circ = -RT \ln K \quad (57)$$

For the reduction of manganese oxide by silicon, the values of the free energy of reaction from the literature for the reactions involved are as follows:



$$\Delta F^\circ = -58,400 - 25.98 T \text{ (Ref. 20, 43)} \quad (59)$$

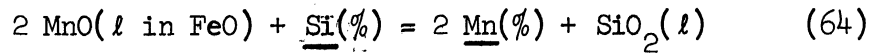




$$\Delta F^\circ = -142,000 + 55.0 T \text{ (Ref. 20)} \quad (61)$$



$$\Delta F^\circ = 3,100 + 1.56 T \text{ (Ref. 44)} \quad (63)$$



$$\Delta F^\circ = -22,100 + 4.6 T \quad (65)$$

Equations (58) through (63) are taken from the literature. Equations (64) and (65) are the summation of the preceding equations.

Using the equilibrium constant evaluated from these data, the calculated quotient for manganese in the two phases at 1550°C is

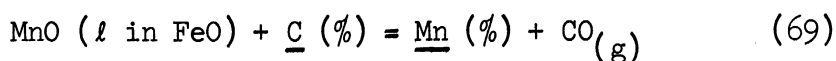
$$\left[ \frac{\% \text{Mn}}{\% \text{MnO}} \right]_{\text{Equilibrium}} = 0.54 \quad (66)$$

The value for the same equilibrium as determined experimentally in this study ranged from 1.1 to 1.2, a factor of two higher than the calculated value. There are factors which could contribute to this. The activity coefficient for manganese oxide in the slag is an approximation taken from the work of Abraham, et al.<sup>27</sup> Their data had to be extrapolated in respect to both temperature and composition of the slag to obtain an activity coefficient for the experimental conditions. In view of this, the difference between the calculated and experimental equilibrium value is reasonable. A secondary effect could be attributed to experimental error.

For the reduction of manganese oxide by carbon, Equations (58) and (59) and the following equations apply:



$$\Delta F^\circ = -5,350 - 9.48 T \text{ (Ref. 20)} \quad (68)$$



$$\Delta F^\circ = 53,050 - 35.46 T \quad (70)$$

Equations (69) and (70) are the summation of Equations (58), (59), (67), and (68). For this reaction, the ratio of manganese in the metal to manganese oxide in the slag at equilibrium at 1550°C was calculated to be 4.95. Since this reaction was so slow, equilibrium conditions were not determined in this experimental program. However, Philbrook and Tarby<sup>33</sup> did make an investigation of this system and found that the ratio of manganese in the metal to manganese oxide in the slag at equilibrium at 1550°C would be approximately ten. Again the discrepancy between the calculated and experimental equilibriums is approximately a factor of two. The same explanation that was made in the preceding paragraph applies to this reaction. The calculation of the equilibrium constant using the approximation of the activity coefficient of manganese oxide in the slag is common to both reactions. For the reduction by carbon study, a value of ten for the equilibrium ratio between percent manganese in the metal and percent manganese oxide in the slag was used in all the calculations.

B. Effect of  $\delta$  on the Calculation of the Energy of Activation,  $E$

In this section a comparison of Equations (54) and (55) will be made. They are repeated below for convenience.

$$D = D_o e^{-\frac{E}{RT}} \quad (54)$$

$$\frac{D}{\delta} = \left(\frac{D}{\delta}\right)_o e^{-\frac{E}{RT}} \quad (55)$$

Equation (54) is generally accepted as showing the relationship between the

diffusion coefficient and temperature. In this experimental study, the relationship shown in Equation (55), which involves the added term  $\delta$ , is being used. This relationship requires that  $\delta$  must also vary exponentially with temperature as does  $D$  or otherwise be temperature invariant. In the past, the latter has sometimes been assumed to be the case. Riddiford<sup>35</sup> shows that, in fact,  $\delta$  varies exponentially with temperature. He derived the following equations showing the relationship between the energy of activation defined in Equation (55) with that in Equation (54).

$$E_{\left(\frac{D}{\delta}\right)} = \frac{(4 E_D + E_v)}{6} \quad (\text{for laminar flow}) \quad (71)$$

$$E_{\left(\frac{D}{\delta}\right)} = 2/3 (E_D + E_v) \quad (\text{for turbulent flow}) \quad (72)$$

In these equations,  $E_v$  is the energy of activation associated with the shear stress of flow. This term is usually of the same order of magnitude as  $E_D$ . Therefore, the energy of activation as determined from  $\frac{D}{\delta}$  will be very close to the energy of activation found as a function of  $D$ . They should be at least within twenty percent of one another.

For this study on the reduction of manganese oxide by silicon, a qualitative comparison is sufficient. The reason for finding the energy of activation in this study was primarily to determine which of many steps could be the rate-controlling step for the process. If the two energies are within twenty percent of one another, then  $E_D$  would have a value from 5.5 to 8.5 Kcal per mole. This would indicate that the rate-controlling step for the process is the diffusion of manganese or silicon in the metal. This is the same result that was obtained before.

C. Problems of Mixed Control

As illustrated in Figure 1, all the calculations made in this study were based on the assumption that one step in the reaction was slower than the rest and controlled the overall rate of the reaction. The results obtained seem to justify this basic assumption. However, it is possible that another step in the reaction, although faster than the rate-controlling step, could be slow enough to cause secondary effects; this possibility is illustrated in Figure 17. The following equations demonstrate the effect of this second slow step on the apparent diffusion constant.

$$\frac{dn}{dt} = \frac{DA}{\delta} \left[ C_{M'}(\text{interface}) - C_{M'}(\text{bulk}) \right] \quad (73)$$

$$C_{M'}(\text{interface}) = \frac{K' C_M C_{M'O}(\text{bulk})}{C_{MO}(\text{bulk})} \quad (74)$$

Equation (73) is the basic rate equation showing that the rate is a function of the concentration difference across the phase boundary. Equation (74), a rearranged equilibrium relationship, defines the concentration of the diffusing component at the interface. The value of the concentration of  $C_M$  is different when taken as the bulk concentration than when taken as the interfacial concentration. When assuming that one step controls the overall reaction, the bulk concentration of  $C_M$  is used. If, in fact, there is mixed control, as is shown by Figure 17, the interfacial value of  $C_M$  should be used. This is a smaller number, and when placed in Equation (74) gives a smaller number for  $C_{M'}(\text{interface})$ . This error carries on into Equation (73). The calculated value for the driving force is greater than the actual value. Then for Equation (73) to balance, the calculated value of  $\frac{D}{\delta}$  has to be proportionally smaller than the actual value. The same effect would result if  $C_{MO}$  or  $C_{M'O}$  were involved due to slow diffusion of MO or M'O.

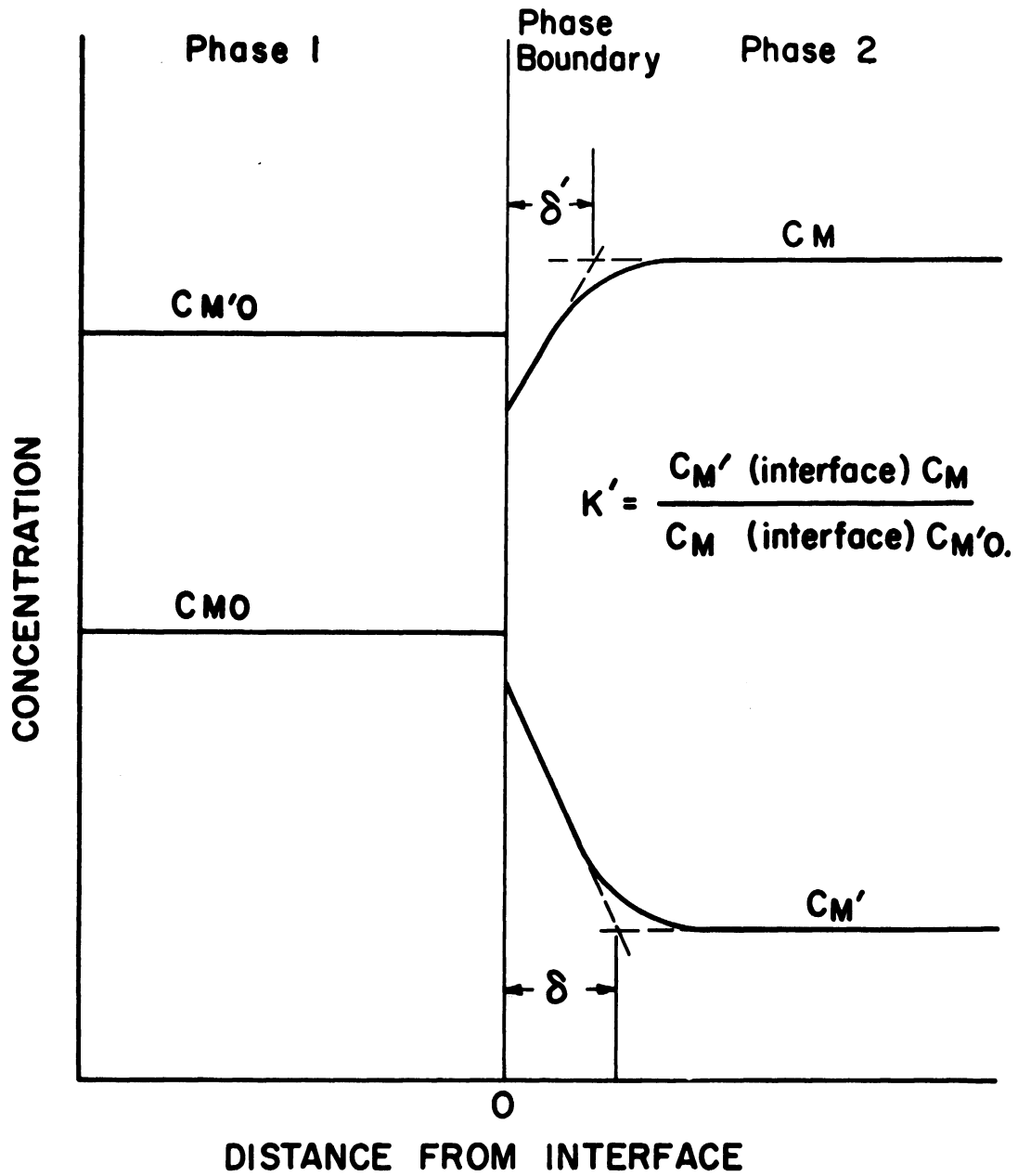


Figure 17. Illustration of Mixed Control for Reaction  $M'O + M = MO + M'$ .

This consideration can be applied to the reduction of manganese oxide by silicon. A value of  $\frac{D}{\delta}$  was obtained for the rate-limiting step, the diffusion of manganese in the metal. This value was calculated on the assumption that all other diffusion steps were fast enough to maintain their interfacial concentrations equal to their bulk concentrations. If, in fact, one of the other diffusion steps was slow enough so that this condition was not maintained, then the value of  $\frac{D}{\delta}$  obtained for the diffusion of manganese in the metal is actually too small. Because of the complexity of this two-phase system, it is impossible to determine if a second diffusion step is contributing to the rate of the overall reaction. All that can be said is that it is a possibility.

#### D. Possible Side Reactions

A possible source of error in the calculations of this study is that another reaction is occurring simultaneously with the one under consideration. For the study of the reduction of manganese oxide by silicon, a possible side reaction would be the reduction of manganese oxide by iron. Analyses of the slag were made before the run was started and at the completion of the run to check for this possibility. In all cases investigated, the amount of iron oxide in the slag was always very low and never exceeded 0.3 percent. Therefore, if this side reaction did occur, it was slow enough that it should not affect the accuracy of the calculations for the main reaction under consideration.

A possible side reaction that could occur during the reduction of manganese oxide by graphite would be the reduction of silicon oxide by graphite. The study documented in the literature survey on this reaction indicates that it proceeds very slowly. The metal phase was sampled before the start and at the conclusion of several runs and analyzed for silicon.

These tests indicated that the silicon level in the metal at the beginning of the run was never more than about 0.1 percent and no trace of silicon was present in the metal at the end of these runs.

At the end of each run the metal phase was sampled to give a mass balance check on the system. Agreement was obtained for the manganese in the system: the manganese reduced from the slag phase was found to be in the metal phase. Also, for reduction by silicon, a proportionate amount of silicon had been oxidized from the metal phase. This balance verifies that the reaction postulated is the one actually occurring.

Therefore, it is submitted that the effect of any side reaction on the two reactions under study is minimal.

#### E. Accuracy of Results

An analysis of replicate runs was made to determine the accuracy of the results obtained in this study. For the reduction of manganese oxide by silicon, Runs 143, 146, 154, 155, and 163 were made under identical conditions. The mean value for  $\frac{D}{\delta}$  obtained for the diffusion of manganese in the metal was  $7.28 \times 10^{-4}$  cm/sec with a standard deviation of  $0.197 \times 10^{-4}$  cm/sec. Runs 21, 45, 93, and 108 were replicate runs for the reduction of manganese oxide by carbon. The mean value of k obtained for the chemical reaction involved in the transfer of oxygen from the slag to the metal phase was  $1.28 \times 10^{-5}$  moles/cm<sup>2</sup> min with a standard deviation of  $0.115 \times 10^{-5}$  moles/cm<sup>2</sup> min. These replicate runs were made at 1550°C.

The energy of activation for the two reactions being studied was calculated by making a regression analysis of the data presented in Figures 8 and 15. For the reduction of manganese oxide by silicon the energy of activation was calculated to be  $E = 6.9$  Kcal/mole with a standard error of 1.0 Kcal/mole. For the reduction of manganese oxide by carbon the result was  $E = 24.9$  Kcal/mole with a standard error of 6.5 Kcal/mole.

## SUGGESTED FURTHER RESEARCH

Immediately after the manganese oxide is added to the experimental system to start a run, a very rapid reaction is evident. This undoubtedly is partially due to the fact that the manganese oxide does not become completely fused in the slag for a few moments and is present at the interface at greater than average slag concentration. The effect of this can be seen in Figures 7, 12, and 13. The curves do not go through the origin. It is possible that during the initial moments while the reaction is far from equilibrium, that some other step than the one determined as the rate-limiting step for the bulk of the run is controlling the reaction. This possibility is illustrated further by Figure 18. For this particular run, a slag-to-metal ratio of 1:6 was used in comparison with the normal slag-to-metal ratio of 2:3. For several minutes, the run proceeded at a greater rate than was normally observed for runs studying the reduction of manganese oxide by silicon. Since a large amount of metal was used for this run, the concentration of manganese in the metal was at a very low level. Wagner<sup>18</sup> predicted that the diffusion of a component into a phase in which it is at low concentration will not be the rate-limiting step because there is an infinite driving force into that phase. This principle would apply here.

Research in this area could be very profitable. By determining the rate-limiting step under these conditions, it would be possible to determine if this step was slow enough during the remainder of the run to be affecting the calculated values of  $\frac{D}{\delta}$  for the diffusion of manganese in the metal.

This same initial condition is noted for the reduction of manganese oxide by carbon. Studies of this system during the early moments of reaction would be informative.



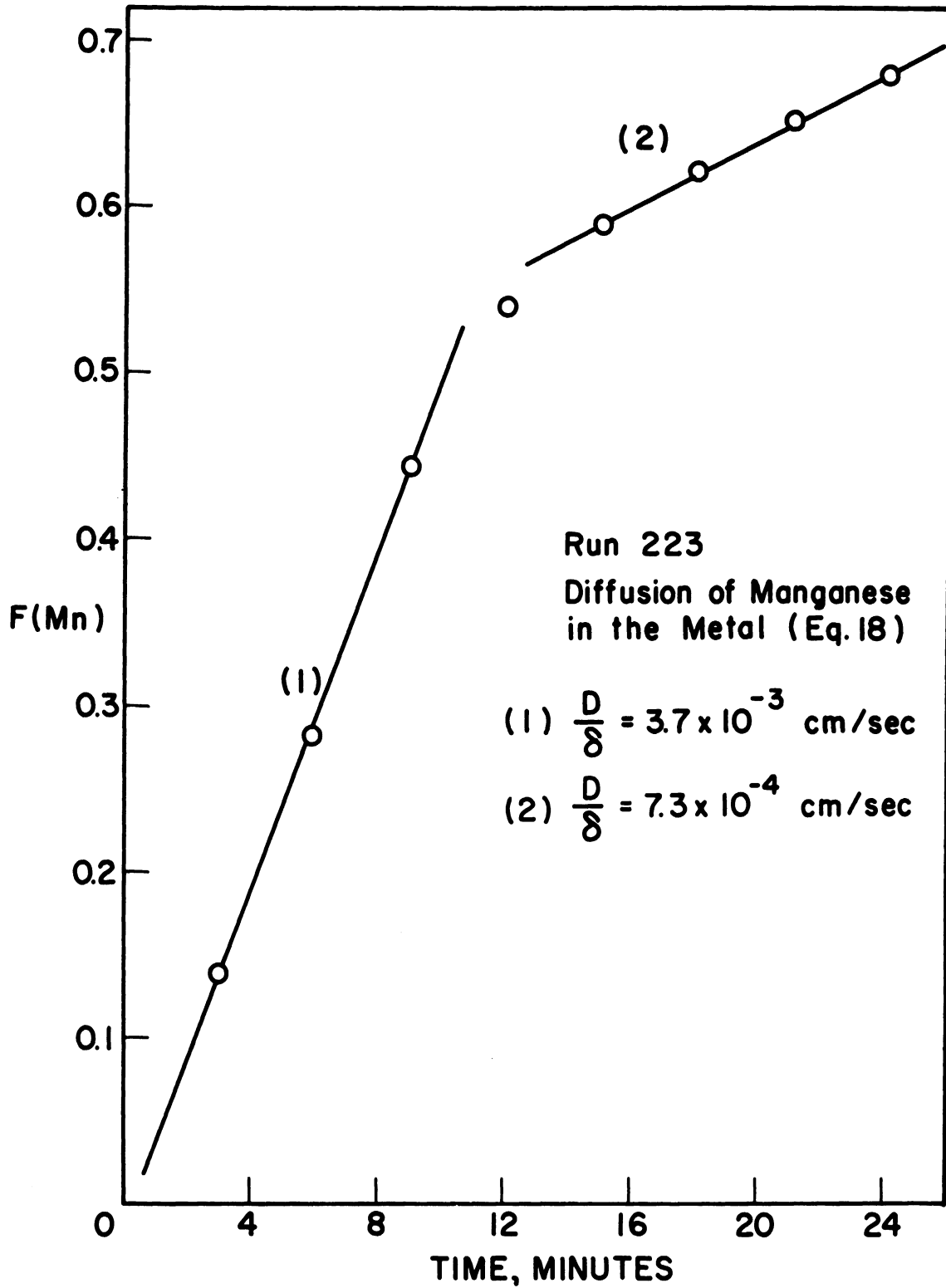


Figure 18. Illustration of Mixed Control for Reaction  $2(\text{MnO}) + \underline{\text{Si}} = (\text{SiO}_2) + 2 \underline{\text{Mn}}$ .

## SUMMARY AND CONCLUSION

The reduction of manganese oxide by silicon is a fast reaction reaching equilibrium in less than ninety minutes. The rate of stirring in the system has a marked effect on the rate of this reaction. The effect of temperature is very small, with a calculated energy of activation for the system of 7 Kcal per mole. The effect of changing the slag-to-metal ratio over a wide range of values was to indicate that the rate-controlling step was in the metal phase and not in the slag phase. By varying the silicon concentration in the metal at the beginning of the run, it was possible to show that the diffusion of silicon in metal was not the rate-controlling step.

The reduction of manganese oxide by carbon, on the other hand, was a very slow reaction. It failed to reach equilibrium in twenty hours. There was no apparent effect on the rate of this reaction as the stirring rate was varied. The effect of temperature changes was moderate, giving a calculated energy of activation for the reaction of 25 Kcal per mole. Only the model for the reaction  $(O) = \underline{O}$  at the interface gave consistent results as the melt geometry and concentration of manganese oxide and graphite were varied.

It is interesting to find such different results for these two reactions when the only difference in the two is the reducing agent. However, upon examination of the reaction, one important difference is noticed. When silicon is the reducing agent, only metal species cross the slag-metal phase boundary. When graphite is the reducing agent, it is necessary to remove oxygen from the slag phase into the metal phase. The chemical reaction necessary to do this was found to be the slow step for the reaction.

In conclusion, the reduction of manganese oxide by silicon is a diffusion-controlled process. The slow step that controls the rate of the reaction is the diffusion of manganese in the metal phase. The value for the diffusion of manganese in the metal was found to be  $\frac{D}{\delta} = 7 \times 10^{-4}$  cm/sec. If mixed control is a factor in the reaction, this value could be somewhat higher.

The reduction of manganese oxide by carbon was a very slow reaction and was controlled by a chemical reaction at the interface. This chemical reaction involves the activation of oxygen going from the slag to the metal phase and is represented by the equation  $(O) = \underline{O}$ . The reaction constant was found to be  $k' = 1.3 \times 10^{-5}$  mole/cm<sup>2</sup> min.

APPENDIX A  
EXPERIMENTAL PARAMETERS

Run	T, °C	Stir Rate, RPM	Type Crucible	Weight, Grams							
				Fe	Si	C	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO
17	1550	40	C	400	0	10	98	12	0	90	10
18	1550	40	C	400	0	10	80	30	70	20	10
20	1550	100	C	400	0	10	90	20	70	20	10
21	1550	40	C	400	0	10	90	20	70	20	10
22	1550	100	C	400	0	10	90	20	70	20	10
35	1550	40	C	400	4	10	90	20	70	20	10
44	1500	40	C	400	0	10	90	20	70	20	10
45	1550	40	C	400	0	10	90	20	70	20	10
47	1600	40	C	400	0	10	90	20	70	20	10
48	1550	40	C	400	0	10	67.5	15	52.5	15	10
49	1550	40	C	400	0	10	112.5	25	87.5	25	10
50	1550	40	C	400	0	10	90	20	90	0	10
51	1550	40	C	400	0	10	90	20	50	40	10
52	1550	40	C	400	0	10	110	0	90	0	10
53	1550	40	C	400	0	10	70	40	90	0	10
54	1550	40	C	400	0	10	110	10	20	60	10
55	1550	40	C	400	0	10	90	10	40	60	10
56	1550	40	C	400	0	10	100	10	30	60	10
57	1550	40	C	400	0	10	80	10	50	60	10
58	1550	20	C	400	0	10	90	20	70	20	10
59	1550	40	C	250	0	5	112.5	25	87.5	25	10
90	1544	40	C	400	0	10	90	20	70	20	10

## APPENDIX A - Continued

Run	T, °C	Stir Rate, RPM	Type Crucible	Weight, Grams							
				Fe	Si	C	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO
91	1567	40	C	400	0	100	90	20	70	20	10
92	1519	40	C	400	0	100	90	20	70	20	10
93	1550	40	C	400	0	100	90	20	70	20	10
95	1550	100	C	400	0	100	90	20	70	20	10
96	1550	0	C	400	0	100	90	20	70	20	10
98	1550	40	C	400	0	100	67.5	15	52.5	15	10
99	1550	40	C	400	0	100	112.5	25	87.5	25	10
100	1550	40	C	350	0	100	112.5	25	87.5	25	20
101	1550	40	C	300	0	100	112.5	25	87.5	25	10
108	1550	40	C	400	0	100	90	20	70	20	10
109	1550	40	C	400	0	100	90	20	70	20	5
121	1550	100	ZrO <sub>2</sub>	200	4	0	90	20	70	20	10
122	1550	10	ZrO <sub>2</sub>	400	4	0	90	20	70	20	15
124	1550	0	C	400	0	10	90	20	70	20	10
126	1550	0	C	400	0	10	90	20	70	20	10
129	1550	0	ZrO <sub>2</sub>	400	4	0	90	20	70	20	7
131	1550	0	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
133	1550	0	ZrO <sub>2</sub>	300	4	0	67.5	15	52.5	15	10
135	1550	40	C	400	0	10	90	20	70	20	3
138	1550	40	C	400	0	10	90	20	70	20	1
140	1550	0	ZrO <sub>2</sub>	200	4	0	90	20	70	20	10
143	1550	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
146	1550	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10

## APPENDIX A - Continued

Run	T, °C	Stir Rate RPM	Type Crucible	Weight, Grams							
				Fe	Si	C	CaO	MgO	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	MnO
148	1570	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
149	1590	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
153	1550	40	C	400	0	10	90	20	70	20	2
154	1550	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
155	1550	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
156	1550	40	C	400	0	10	90	20	70	20	2
159	1560	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
160	1540	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
162	1550	100	ZrO <sub>2</sub>	300	6	0	90	20	70	20	10
163	1550	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
164	1550	100*	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
166	1550	40	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
167	1550	100	ZrO <sub>2</sub>	300	12	0	90	20	70	20	10
172	1550	100	ZrO <sub>2</sub>	100	4	0	135	30	105	30	10
196	1550	100	ZrO <sub>2</sub>	300	0	4	90	20	70	20	10
199	1580	100	ZrO <sub>2</sub>	300	4	0	90	20	70	20	10
218	1550	100	ZrO <sub>2</sub>	300	0	8	90	20	70	20	10
223	1550	100	ZrO <sub>2</sub>	600	6	0	45	10	35	10	10
224	1550	100	C	800	0	30	45	10	35	10	5
225	1550	100	C	200	0	5	180	40	140	40	20
228	1550	100	ZrO <sub>2</sub>	300	0	15.3	90	20	70	20	10

\* A paddle 3/4" wide was used for this run. Ordinarily a 3/8" wide paddle was used.

APPENDIX B

EXPERIMENTAL TIME-CONCENTRATION DATA

Run 17		Run 22		Run 47		Run 51	
t*	%**	t	%	t	%	t	%
5	4.02	5	3.24	10	2.23	15	3.53
15	3.04	15	3.06	20	1.84	30	2.94
30	2.53	30	2.61	31	1.68	60	2.41
60	1.91	90	2.24	60	1.26	90	2.03
120	1.24	122	1.90	95	1.08	120	1.88
180	0.83			120	1.06		

Run 18		Run 35		Run 48		Run 52	
t*	%	t	%	t	%	t	%
5	3.93	5	1.91	5	3.84	5	3.75
15	3.20	15	1.15	15	3.30	15	3.17
30	2.99	30	0.80	31	3.12	30	2.99
61	2.58	60	0.54	60	2.93	60	2.49
120	2.12	90	0.50	90	2.23	90	2.34
180	1.68	120	0.43	120	1.83	120	2.15

Run 20		Run 44		Run 49		Run 53	
t	%	t	%	t	%	t	%
5	3.66	5	3.77	5	2.59	5	3.43
15	3.05	15	3.51	15	2.28	15	3.07
30	2.85	30	3.17	30	1.95	30	2.68
61	2.44	60	2.76	60	1.59	60	2.44
90	2.24	90	2.50	90	1.38	90	2.16
120	2.18	120	2.30	120	1.17	120	2.10

Run 21		Run 45		Run 50		Run 54	
t	%	t	%	t	%	t	%
5	3.65	5	3.20	6	2.85	5	3.73
15	3.06	15	3.02	15	2.36	15	2.92
30	2.70	30	2.52	30	2.05	30	2.35
60	2.36	35	2.58	60	1.78	60	1.72
90	2.12	60	2.19	90	1.75	90	1.32
120	1.74	90	2.01	120	1.68	120	1.06
		120	1.71				

\* Time, t, in minutes

\*\* Concentration of manganese oxide in slag, weight percent

APPENDIX B - Continued

Run 55		Run 90		Run 96		Run 108	
t	%	t	%	t	%	t	%
12	3.47	25	3.15	15	3.35	15	2.86
20	3.19	40	2.81	30	3.07	30	2.42
30	2.88	55	2.58	45	2.81	45	2.09
60	2.41	70	2.48	60	2.58	60	1.86
93	2.00	85	2.30	75	2.42	90	1.62
120	1.73	100	2.11	90	2.24	600	0.57
						660	0.48
						720	0.46
						780	0.46
						840	0.43
						1020	0.39
						1140	0.37
Run 56		Run 91		Run 98		Run 109	
t	%	t	%	t	%	t	%
5	4.16	15	2.79	15	4.23	15	1.11
15	3.26	30	2.45	30	3.80	30	0.82
30	2.75	45	2.04	45	3.53	45	0.65
60	2.14	60	1.94	60	3.20	60	0.59
90	1.82	75	1.88	75	3.10	75	0.52
120	1.42	90	1.63	90	2.89	90	0.45
Run 57		Run 92		Run 99		Run 121	
t	%	t	%	t	%	t	%
5	3.74	15	3.59	15	2.71	2	3.13
15	3.20	30	3.16	30	2.45	4	2.90
30	2.95	45	2.94	45	2.32	6	2.65
60	2.41	60	2.81	60	2.07	8	2.53
90	2.21	75	2.66	75	2.06	60	1.86
120	2.04	90	2.53	90	1.86	90	1.73
						120	1.69
Run 58		Run 93		Run 100		Run 122	
t	%	t	%	t	%	t	%
15	3.32	15	2.58	20	2.45	4	4.71
30	2.98	30	2.19	35	2.35	6	4.46
60	2.85	45	1.86	50	2.21	10	4.13
90	2.45	60	1.81	66	2.11	15	3.81
120	2.21	75	1.68	80	2.01	120	2.56
		90	1.50	95	1.92	150	2.55
Run 59		Run 95		Run 101			
t	%	t	%	t	%		
5	3.01	15	2.84	15	1.42		
15	2.90	30	2.53	30	1.32		
30	2.64	45	2.37	45	1.20		
60	2.41	60	2.17	60	1.10		
90	2.15	75	1.96	75	1.05		
120	1.90	90	1.82	90	0.97		



APPENDIX B - Continued

Run 124		Run 133		Run 143		Run 149	
t	%	t	%	t	%	t	%
15	2.72	5	3.05	3	2.82	3	3.46
30	2.65	10	2.95	6	2.60	6	2.99
45	2.30	15	2.71	9	2.30	9	2.69
60	2.25	21	2.36	12	2.19	12	2.41
78	2.09	28	2.46	15	2.11	15	2.28
90	1.96	35	2.14	18	2.02	18	2.15
105	1.78	45	2.05	21	1.87	21	2.02
120	1.70	150	1.63	25	1.89	24	1.96
				60	1.74	90	1.56
				90	1.55	120	1.50
				120	1.53		
Run 126		Run 135		Run 146		Run 153	
t	%	t	%	t	%	t	%
15	2.52	10	0.86			5	0.68
30	2.18	20	0.63			10	0.59
45	1.91	30	0.49			15	0.54
60	1.72	40	0.33	3	4.13	20	0.49
75	1.59	50	0.35	6	3.29	25	0.45
90	1.44	61	0.35	9	2.84	30	0.41
105	1.22	70	0.33	12	2.69	35	0.38
120	1.06			15	2.49	40	0.35
				18	2.26		
				21	2.17		
				24	2.07		
				90	1.46		
				120	1.48		
Run 129		Run 138		Run 148		Run 154	
t	%	t	%	t	%	t	%
2	2.20	5	0.30			3	3.03
4	2.15	10	0.27			6	2.71
6	2.07	15	0.25			9	2.43
8	1.97	20	0.23			12	2.26
15	1.69	25	0.21			15	2.15
30	1.49	30	0.20			18	2.06
45	1.46	35	0.19	3	3.74	21	1.96
150	1.10	45	0.17	6	3.25	24	1.89
		60	0.15	9	2.92	120	1.51
				12	2.64	150	1.49
				15	2.39		
				18	2.26		
				21	2.11		
				75	1.52		
				90	1.47		
Run 131		Run 140		Run 155			
t	%	t	%	t	%		
5	2.77	3	3.30	3	3.80		
10	2.73	6	3.14	6	3.31		
15	2.49	9	2.94	9	2.97		
20	2.38	12	2.86	12	2.64		
25	2.19	15	2.66	15	2.49		
30	2.19	18	2.56	18.5	2.17		
35	2.15	21	2.47	22.5	2.09		
40	2.09	24	2.39	26	2.00		
140	1.49	240	1.69	90	1.47		
				120	1.48		

APPENDIX B - Continued

Run 156		Run 163		Run 167		Run 218	
t	%	t	%	t	%	t	%
5	0.66	3	3.46	3	2.04	5	2.74
10	0.64	6	3.27	6	1.86	10	2.58
15	0.58	9	2.88	9	1.75	15	2.54
20	0.51	12	2.58	12	1.58	20	2.50
25	0.47	15	2.62	15	1.48	25	2.14
30	0.43	18	2.30	18	1.40	30	2.01
35	0.42	21	2.19	21	1.37	45	1.73
40	0.42	24	2.06	24	1.31	60	1.61
		120	1.55	120	0.95	75	1.53
				130	0.93	90	1.37
				140	0.93		
Run 159		Run 164		Run 172		Run 223	
t	%	t	%	t	%	t	%
3	3.98	3	3.74	3	1.69	3	7.03
6	3.35	6	3.10	6	1.49	6	5.64
9	2.95	9	2.73	9	1.40	9	4.66
12	2.71	12	2.34	12	1.34	15	4.08
15	2.49	15	2.13	15	1.32	18	3.97
18	2.38	18	1.96	18	1.32	21	3.88
21	2.19	21	1.87	15	1.32	24	3.81
24	2.09	24	1.77	135	1.24	128	2.95
120	1.51	110	1.48			148	2.96
		120	1.45				
		130	1.47				
Run 160		Run 166		Run 196		Run 224	
t	%	t	%	t	%	t	%
3	3.10	3	2.88	9	3.91	5	3.25
6	2.82	6	2.43	12	3.76	10	2.37
9	2.49	9	2.23	15	3.64	15	1.89
12	2.26	12	2.06	20	3.52	20	1.58
15	2.15	15	1.89	25	3.40	25	1.28
18	2.08	18	1.76	30	3.30	30	1.16
21	1.95	21	1.70	45	3.18	35	0.99
24	1.85	24	1.61			40	0.87
120	1.46	124	1.61				
		120	1.28				
		132	1.30				
		140	1.27				
Run 162		Run 199		Run 199			
t	%	t	%	t	%	t	%
3	3.46	3	3.20	3	3.20		
6	2.90	6	2.81	6	2.81		
9	2.58	12	2.34	12	2.34		
12	2.62	15	2.19	15	2.19		
15	2.19	19	2.11	19	2.11		
18	2.00	22	2.04	22	2.04		
21	1.89	25	1.98	25	1.98		
24	1.78	30	1.96	30	1.96		
120	1.22	140	1.27	90	1.64		

Run 225	
<u>t</u>	<u>%</u>
5	3.99
10	3.77
15	3.77
20	3.51
25	3.46
30	3.46
35	3.27
40	3.12
60	3.06
120	2.76
180	2.49
240	2.22
300	2.01
360	1.82
420	1.67
480	1.55
540	1.43
600	1.31

Run 228	
<u>t</u>	<u>%</u>
3	4.57
6	4.01
9	3.81
12	3.64
15	3.42
25	3.20
35	2.63
45	2.58
60	2.38
75	2.21
90	1.94

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