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SLAG-METAL REACTION KINETICS
A THEORETICAL STUDY OF SLAG-METAL REACTION KINETICS USING A NUMERICAL TECHNIQUE

By

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ABSTRACT

Currently available theoretical formulations for the kinetics of slag-metal systems have been extended to clarify certain aspects of the system. Coupling factors for electrochemical reactions and for ionic diffusion have been defined to clarify the significance of coupling phenomena in the kinetics of multi-component systems. Theoretical equations for the interfacial reactions and the diffusion processes in both phases, in seven hypothetical pseudo-ternary slag-metal systems have been numerically solved by a finite difference method. Typical features of coupling phenomena, i.e., acceleration and deceleration of reaction or diffusion, and uphill reaction or diffusion have been clearly demonstrated. Through numerical analysis, a modified form of "Sherwood Number", \( \text{Sh}^* \equiv \frac{k_i L}{\nu D_i} \) for a particular reaction \( i \), is defined and found to be proper to explain the rate controlling steps for the over-all reaction. In the present analysis, the relationships between the modified Sherwood Number and rate controlling steps were found to be as follows:

\[
\begin{align*}
\text{Sh}_i^* &> 360: \text{ diffusion control,} \\
0.05 \leq \text{Sh}_i^* \leq 360: \text{ mixed control,} \\
\text{Sh}_i^* &< 0.05: \text{ interfacial reaction control.}
\end{align*}
\]
Thus non-trivial numerical solutions for slag-metal systems have been developed for the first time.
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1. Introduction

Pyrometallurgical processes have been the most economical ways in the winning and refining of common metals from the ores. In smelting and refining processes, the presence of liquid metal and slag are common in most of the cases. High temperatures, in general, are required to shorten the processing time.

Smelting and refining reactions with slag and metal phases are heterogeneous in nature. It means that reactions take place only at the interface. Slag which is a molten mixture of oxides plays a role of a source of reactants or a sink of products, so does the metal. Two goals in pyrometallurgical operations, namely, metallization and separation can hardly be accomplished without the presence of slag phase.

If industry could afford to use raw materials of high purity, the metallurgical refining processes would be relatively simple. In reality, however, any raw materials contains various gangues with the valuable minerals. Therefore, the reactions between slag and metal in the practical process ought to be of multicomponent and simultaneous. Metallurgists always have to compromise in the consideration
of optimizing the recovery of valuable metals and the removal of impurities in metals.

Metallurgical industry has a relatively long history in comparison with other manufacturing sectors in our modern economy. The evolution of metallurgical technology throughout its history has been essentially empirical in nature. The hostile working conditions at high temperatures make it difficult to accumulate reliable information on the process and to advance the metallurgy as a branch of science.

In metallurgical processes, from raw materials to final products, there are many sequential steps involved. On most occasions each step has been manipulated with the aim of controlling one or two chemical elements at a time. The development of thermodynamics and kinetics of reactions in pyrometallurgy has followed the same pattern. It is to say that in multiple component systems involving several simultaneous reactions, the contributions of those which appear to be minor have been ignored in theoretical analyses.

The desire for energy and labor savings and the progress in the development of instrumentation and control devices stimulate the metallurgical industry to develop new reactors for faster and multi-purpose processing.
When the metal is being discharged from the reactor, simultaneous reactions are usually still active, but the composition of liquid metal is required to be just right to the specification. One would expect that it may not be an economically wise approach to accomplish the metallization and the separation in a traditional or an empirical way unless no other approach is available.

Failures of these attempts in last 15 years certainly would indicate that the lack of fundamental understanding of pyrometallurgical systems has led some courageous metallurgists to regrettable paths in their search for better processes or reactors. Some theoretical guidance for experimentation is needed in the present stage of development of metallurgical technology.

The constituents of slags are supposed to be ionized. It is generally accepted that the overall electrical neutrality of slag must be maintained. Even if there is any deviation from neutrality, it should be far too small to be detected chemically. The constraint of the electro-neutrality and the electrochemical nature of slag-metal reactions provide the necessary relationships for the interdependence of simultaneous reactions. The kinetic expressions for multi-component slag-metal systems consist of mass transport processes in both phases and of
simultaneous interfacial reactions, have been formulated at McMaster University.

The present work represents the first solution of those equations, other than some limiting cases, by numerical techniques. The contribution of this work lies in the better appreciation of (1) the evolution in a reacting slag-metal system, (2) the parametric dependency on the characteristics of the system.

Even though many simplifying assumptions have to be made, the present work, at least in our opinion, is a big step in the right direction.
CHAPTER 2
LITERATURE REVIEW

Here a selective rather than complete review of earlier works on slag-metal reaction kinetics will be presented in order to illustrate the problem. Firstly, a part of the convective mass transfer theory is reviewed because it is the most common theory for slag-metal kinetics. Following that some experimental studies are reviewed in two groups; (1) graphite crucible type experiments and (2) MgO crucible type experiments. Then more fundamental mechanisms such as diffusion processes in metal and in slag and the coupled interfacial reactions are reviewed.

2.1 Mass Transfer in Heterogeneous Reactions

Darken(1) postulated that local equilibrium will prevail within the liquid metal at steelmaking temperatures and the chemical reactions will proceed rapidly at slag-metal interfaces, so the over-all reaction rate will be primarily controlled by transport step.

The interphase mass transfer analysis is commonly done by introducing a boundary layer thickness \( \delta_c \). It is known that mass transfer boundary layer thickness \( \delta_c \) not only differs from the one of momentum transfer but also depends on the solute species being transferred.
In any case, whether the flow is laminar or turbulent, for most experiments the mass transfer boundary layer thickness, is not quantitatively predictable by boundary layer theory.

Since the turbulent flows and geometrical shapes of real systems are usually too complex for theoretical prediction, it is necessary to resort to the empirical mass transfer coefficient, \( k_m^{(2)} \). In this concept mass transport is supposed to be the sum of a diffusional contribution and a bulk flow contribution. It should be noted that scaling up from the laboratory experiment or even pilot plant to industrial operations in which experimentally obtained \( k_m \) values are to be utilized will remain hazardous until the nature of the rate controlling steps is better understood.

It is certain that whatever the flow condition, kinetic analysis of any real system should involve both reaction and diffusion. However, no quantitative analysis of the combined reaction and diffusion kinetics has been carried out except by Okongwu and Lu\(^{(3)}\) in which pseudo-binary systems are analyzed to show that their theoretical framework is suitable to explain the general mixed control reaction kinetics.
2.2 Experimental Studies of Slag Metal Reactions

Most of the experimental work on the kinetics of slag metal reactions has been done in graphite crucibles to analyze the ironmaking systems.

Since high quality (high density, low impurity) MgO crucible became available, some work has been done in MgO crucibles to analyze the steelmaking systems.

2.2.1 Graphite Crucible Experiments

Early studies\(^ {4-9}\) on the rate of the slag metal reactions were phenomenological and were described and interpreted primarily from a chemical viewpoint. Ramachandran, King, and Grant\(^ {6}\) demonstrated that the evolution of carbon monoxide was quantitatively involved in the conversion of mass and changes in sulfur transfer reaction.

Sulfur transfer and other slag metal reactions exhibiting apparent coupling effects in which Fe, Si or other elements show the "uphill" reaction which have inspired many critical experiments and efforts at interpretation.

In Ramachandran, King and Grant's experiment, they obtained the rate of sulfur transfer, in terms of other elements, from metal to slag as
\[ 2n_s = 2n_{Fe} + 2n_{Mn} + 3n_{Al} + 4n_{Si} + 2n_{C} \quad (2.1) \]

where the rate of transfer of each species \( n_i \) is given in mol/sec. The sign of \( n \) is positive for transfer from metal to slag, and negative from slag to metal. Equation (2.1) indicates that the slag-metal reactions are coupled, but due to the complexity of the system such as reaction site uncertainties and interfacial areas, the coupling between simultaneous reaction could not be formulated by any simple explicit expression.

In the case of the blast furnace type system, slag-metal reaction rate controlling steps, the slowness of silica reduction from slag and its apparent high activation energy pointed towards a thermally activated chemical reaction step as rate controlling\(^{(7)}\), although Schumann\(^{(10)}\) suggested that slow diffusion of oxygen because of its very low concentration in the boundary layer in the metal might limit the rate of reaction.

Numerous experiments\(^{(11-16)}\) have been devised to test whether electro-chemical reactions at slag metal or slag graphite interfaces might be implicated in limiting the rate of silicon reduction (and/or sulfur transfer). Most of the investigators deduced evidence for the existence of electrochemical steps to which they assigned
a significant role in determining the overall process, without necessarily proving exclusive responsibility.

2.2.2 Magnesia Crucible Experiments

In the above mentioned graphite crucible experiments, difficulties arise due to (1) CO generation, which prohibits the estimation of reaction interface and (2) the fact that there are two dominant reaction sites involved, one of which is the slag-metal interface, and the other is the slag-graphite interface and CO (gas) evolved in both sites. Thus the system is too complicated to analyze quantitatively. However, for the steelmaking slag-metal systems these difficulties can be avoided, provided carbon free alloys with a basic slag in Magnesia crucible are employed.

There are some reports on the steelmaking slag-metal systems (17-20). They all used a CaO-FeO-SiO$_2$ slag in fused magnesia crucibles which were found to be sufficiently resistant to slag erosion even to slags having a high FeO content. Sanbongi and Aratani\(^{(17)}\) studies phosphorus transfer, so did Kawai, Doi, Kaneko and Mori\(^{(18,19)}\), and G.J.W. Korf\(^{(20)}\) studies sulfur, phosphorus and oxygen transfer.

Aratani, and Sanbongi estimated that phosphorus transfer is rate controlled by interfacial reaction of first
order without mentioning any specific reaction. They analyzed their results by the following rate equation,

$$\frac{d[P]}{dt} = \frac{A}{V} k_s ([P]_{in} - [P])$$  \hspace{1cm} (2.2)

where $A$ = slag-metal interface area, $V$ = metal volume, $k_s$ = apparent rate constant [min$^{-1}$]. They found that the rate constant had a good correspondence with the activity coefficient of phosphorous oxide in slag. They suggested that this indicated that the overall reaction rate is controlled by the interfacial reaction. As another reason to assume the interfacial reaction rate control, they referred to the difference in the rate constants between dephosphorization and rephosphorization. On the other hand, Kawai, Doi, Kaneko and Mori\textsuperscript{(18,19)} investigated Fe - P - O/CaO - FeO - SiO$_2$ - P$_2$O$_5$ systems in two different conditions, one of them being dephosphorization and the other rephosphorization. They did not use the rate expression developed by Aratani et. al. Instead, they simply assumed the interfacial equilibrium or the mass transfer rate controlling mechanism and explained their results to their satisfaction.

All this tells us is that the rate controlling step depends on the model applied, which usually have some adjustable parameters to fit the data.
Even though the analytical model depends on the author, it should be noted that their observations must be objective. So their experimental results need to be reviewed.

Aratani and Sambongi observed the asymptotical behaviour of phosphorus and oxygen in the metal as shown in Fig. 2.1.

Kawai, Doi, Kaneko and Mori observed the reversal of oxygen in the metal as shown in Fig. 2.2 and Fig. 2.3.

Fig. 2.2 shows that oxygen in the metal has a maximum during the run in heats H34 and H42. They attributed this phenomenon to the results of faster oxygen transfer rate than phosphorus and of the MgO dissolution into the slag which lowers FeO activity in the slag, however such explanations are not fully convincing. Fig. 2.3 shows that oxygen in the metal has a minimum during the run in heat El7. They did not make any particular attempt to explain this phenomenon in their paper.

All these experimental results have shown that in this slag-metal system, three fluxes of Fe, P and O appeared to be coupled with each other, whatever the rate controlling steps would be.
Fig. 2.1 Change of oxygen and phosphorus contents in liquid iron with CaO - SiO₂ - FeO slag. (REFERENCE 17)
Fig. 2.2 Change of phosphorus and oxygen contents in liquid iron. (REFERENCE 18)
Solid lines show phosphorus contents and dashed lines show oxygen contents.
Fig. 2.3 Change of phosphorus and oxygen contents in liquid iron at 1595°C. (REFERENCE: 19)
Kor also observed such oxygen reversal in his experiments independently from Kawai, Doi, Kanako and Mori as shown in Fig. 2.4, even though he did not make an effort to point out the reversals of the reactions in his paper. Fig. 2.4 is the replotted results from his data.

If one accepts the fact that the reversal of a reaction is sufficient evidence to conclude that the simultaneous reactions are coupled, the transfer of phosphorus must be coupled with the transfer of oxygen, iron, sulfur and so on. It should be pointed out that the coupling in these data is too strong to be neglected and to accept the unrealistic but popular assumption that simultaneous slag-metal reactions can be adequately treated independently. Even for the species which does not show any reversal of reaction, it might have been speeded up or slowed down in its rate by virtue of the coupling.

In summary of this section, from the experimental studies of slag-metal reactions there is little agreement about the reaction mechanism and there is little generalization. Such diversified opinions suggest that in general, mixed control reactions scheme is most likely prevailing which is supposed to be really undistinguishable unless experiments are much more carefully designed and a theoretically more sound model is developed.
Fig. 2.4 Change in solute concentration in the metal and sulfur content of the slag, containing indicated amounts of flux. (REFERENCE 26)
However, one thing is clear, at least to the writer, that both in ironmaking and steelmaking systems the coupling among the species is prevailing no matter what the nature of the coupling is (that is, either the coupling is in the interfacial area), and no matter how the coupling strength is.

2.3 **Diffusion in Liquid Metal**

General diffusion equations, Fick's first and second laws can be seen in any metallurgical text, so those are to be passed over here. Only diffusivities are reviewed here.

Self diffusivities and some binary chemical diffusivities have been measured in liquid metal, primarily alloys of iron systems. However, there has been little theoretical analysis of chemical diffusivity data for liquid metals, other than Boltzmann-Matano treatment, because experimental methods of observing marker movement in liquid metals have not been developed. When more self-diffusivities become known, it will be possible to determine many chemical diffusivities for liquid iron and steel alloys with the aid of known activity data by means of generalized Darken's equation relating the chemical interdiffusivities and the self diffusivities.
Generalized Darken equation (21) is,

\[ D_{ij}^s = \sum_{k=1}^{s-1} \left\{ \delta_{ik} D_k^* - N_i (D_{ik}^* - D_k^*) \right\} \left( \frac{N_k}{N_j} \right) \left( \frac{n_i}{n_j} \right) \]  \hspace{1cm} (2.3)

where \( s \) is the number of components in the metal, and 
\( i, j, k \) represent any component: \( \delta_{ik} = \begin{cases} 1; & i = k \\ 0; & i \neq k \end{cases} \), \( D_k^* \) is a selfdiffusivity or a tracer diffusivity, \( D \) is a chemical interdiffusivity, \( N \) is molar fraction, and \( a \) is activity.

For binary systems, one could obtain the Darken equation,

\[ D_{12} = N_2 D_1^* + N_1 D_2^* \]

\[ = (N_2 D_1^* + N_1 D_2^*) (1 + \frac{d \ln \gamma}{d \ln N_2}) \]  \hspace{1cm} (2.4)

where \( D \) is intrinsic diffusivity, \( D^* \) is self or tracer diffusivity and \( \gamma \) is activity coefficient.

For systems of interest to the present work, the writer is not aware of any reports on the studies of interdiffusion in multicomponent liquid alloys. However, for elements in dilute concentration is multicomponent alloys, the pseudo-binary diffusivities may be an acceptable approximation in systems without strong interaction.
2.4 Diffusion in Liquid Slag

2.4.1 Diffusion Data of Iron and Steelmaking Slag

Diffusion data for ironmaking slag are reported in quite appreciable numbers, however for steelmaking slag at present it has not been reported. It is only because of the unavailability of the refractory crucible for the diffusion experiments of steelmaking slag.

Most of the contemporary data are summarized in the report of ISIJ\(^{(21)}\). Investigated systems are limited in CaO - SiO\(_2\) - Al\(_2\)O\(_3\) systems and the reported data is supposed to have approximately 20 or 30% of error.

In general, within the temperature range 1300 to 1600°C the diffusivities are fairly constant, for the species of network formers, they range from \(10^{-7}\) to \(10^{-6}\) cm\(^2\)/sec and for the species of network modifiers they range from \(10^{-6}\) to \(10^{-5}\) cm\(^2\)/sec.

2.4.2 Theoretical Model for Ionic Diffusion

There are some theoretical approaches\(^{(22-25)}\) to relate the tracer diffusivities, interdiffusivities, transport coefficients and so on.
Every theory starts from the generalized Fick's first law:

\[ j_i = \sum_{k=1}^{m} L_{ik} \overline{u}_k \]  \hspace{1cm} (2.5)

where \( \overline{u}_k \) is the electro-chemical potential of species \( k \) and \( L_{ik} \) is a transport coefficient which is assumed to be a function of composition, temperature, and pressure but not a function of electrochemical potential gradients.

On the other hand, the flux \( j_i \) may be represented by means of interdiffusivities and concentration gradients such that:

\[ j_i = -\sum_{k}^{j} \frac{D_{ik}}{D_{ik}} \overline{C}_k \]  \hspace{1cm} (2.6)

assuming that the local velocity of reference frame is negligible.

Nagata and Goto developed a theory relating the interdiffusivities \( D_{ik} \) and transport coefficient \( L_{ik} \).

Cooper \(^{(24)}\) has developed a model for multicomponent diffusion in which he assumed an ideal ionic solution and that coupling only occurs due to relaxation phenomena relative to the volume fixed reference frame. For a ternary case, he developed expressions for the independent forces and fluxes and the four chemical diffusivities in terms
of tracer diffusivities, concentrations and valences of ionic species.

Okongwu, Kirkaldy and Lu\(^{(25)}\) developed another model for multicomponent diffusion in which they started from the Nernst-Plank equation:

\[
J_i = -D_i \left( \frac{\partial C_i}{\partial x} + C_i \frac{\partial \ln \gamma_i}{\partial x} + \frac{Z_i C_i F}{k_T} \frac{\partial \varphi}{\partial x} \right) \quad (2.7)
\]

Since \(\gamma_i\), activity coefficients, are often slowly varying function of \(C_i\) or \(x\), \(\frac{\partial \ln \gamma_i}{\partial x}\) term could be dropped. With the aid of electro-neutrality condition they formulated \(D_i\) as functions of \(D_i\), \(C_i\) and \(Z_i\) eliminating \(\frac{\partial \varphi}{\partial x}\) from Eq. (2.7).

2.5 Coupled Reactions Model

2.5.1 Coupled Rate Expression by Means of Empirical Mass Transfer Coefficient

Mori, Nomura and Sakakibara\(^{(26)}\) developed a theory to express the overall rate for the coupled slag-metal reaction rate. They assumed that the reaction is controlled by mass transport for any pyrometallurgical system because of its high temperature involved, so at the interface chemical equilibrium may be considered to be maintained during the course of reaction.
As an example they formulated the rate expressions for the Mn and Fe exchange reaction:

\[
\text{Mn} + \text{FeO (slag)} \rightarrow \text{Fe(\ell)} + \text{MnO slag} \quad (2.8)
\]

this reaction is always accompanied by the following reaction.

\[
\text{FeO (slag)} \rightarrow \text{Fe(\ell)} + \text{O} \quad (2.9)
\]

They set up the following elementary mass transfer equations:

\[
\begin{align*}
\dot{n}_{\text{Mn}} &= k_{\text{Mn}} A (C_{\text{Mn}} - C_{\text{Mn}}^*) \\
\dot{n}_{\text{Mn}^{2+}} &= k_{\text{Mn}^{2+}} A (C_{\text{Mn}^{2+}} - C_{\text{Mn}^{2+}}^*) \\
\dot{n}_{\text{Fe}^{2+}} &= k_{\text{Fe}^{2+}} A (C_{\text{Fe}^{2+}} - C_{\text{Fe}^{2+}}^*) \\
\dot{n}_{\text{O}} &= k_{\text{O}} A (C_{\text{O}}^* - C_{\text{O}})
\end{align*}
\]

Interfacial equilibrium condition is

\[
\begin{align*}
K_1 &= \frac{C_{\text{Mn}^{2+}}}{C_{\text{Mn}} C_{\text{Fe}^{2+}} \text{ interface}} \\
K_2 &= \frac{C_{\text{O}}}{C_{\text{Fe}^{2+}} \text{ interface}}
\end{align*}
\]

Quasi-steady state condition is

\[
\begin{align*}
\dot{n}_{\text{Mn}} &= n_{\text{Mn}^{2+}} \equiv n_{\text{Mn}} \\
\dot{n}_{\text{Fe}^{2+}} &= n_{\text{Mn}} + n_{\text{O}}
\end{align*}
\]
One could eliminate all the interfacial values in Eqs. (2.9) to (2.13) by means of Eqs. (2.14) to (2.17) to yield the practical rate expressions.

In this theory there are two difficulties involved; one is the local equilibrium assumption, and second is the introduction of capacity constant $k_i$ which is subjective to system dimensional parameters and its physical meaning is to be clarified.

2.4.2 Electro-Chemical Rate Expression

In one of the first thorough analyses of the kinetics of slag-metal systems, Wagner\(^{(27)}\) has considered the slag metal interfacial reactions to consist of simultaneous anodic and cathodic reactions in a manner similar to the corrosion of a homogenous surface.

Wagner expressed the reaction rate in a Butler-Valmer type expression for current density giving the current carried out by a species in terms of the potential difference across the slag-metal interface:

$$J_i = k_i C_i^* \exp [(1 - \alpha_i) I_i \Delta \phi F/RT]$$

$$- k_i' C_i^* \exp [-\alpha_i I_i \Delta \phi F/RT] \quad (2.18)$$

where $\Delta \phi$ is the electro-static potential difference across
the interface (with some reference electrode, which is implicitly assumed to be the metallic phase). \( k_1 \) and \( k_1' \) are the rate constants for anodic and cathodic processes respectively. \( C_i^* \) is the interfacial concentrations. \( \alpha_i \) is the symmetry parameter whose value lies between zero and unity.

Difficulty in such an expression is the non-linearity and undeterminability of \( \Delta \phi \) and \( \alpha \) experimentally by independent experiments. However this expression gives a qualitative nature of coupling among the various anodic and cathodic reactions in that the combined effect of individual reactions is expressed by \( \Delta \phi \) and through which individual anodic or cathodic reaction current density \( J_i \) is interrelated to each other.

Frohberg, Kapoor and Nilas(27) developed the rate expression for Fe, S, C, Si, etc. transfer in Fe-C-S-Si/etc./CuO-Al\(_2\)O\(_3\)-SiO\(_2\) systems similar to the C. Wagner's expression, Eq. (2.18), to explain their electro-chemical experiment using only chemical potentials in their format. In the analysis they assumed that electro-static potential difference can be represented by the chemical potential difference of sulfur between the metal and the slag. This assumption is consistent with another assumption;
\[ |\mu^M_s - \mu^S_s|/RT << 1.0 \] (2.19)

In general electro-chemical potential of sulfur in metal and in slag are:

\[ \mu^M_s = \mu^M_s + Z_s F \phi^M \]
\[ \mu^S_s = \mu^S_s + Z_s F \phi^S \]

Thus,

\[ \Delta \phi \equiv \phi^M - \phi^S = \frac{1}{Z_s F} \left[-(\mu^M_s - \mu^S_s) + (\mu^M_s - \mu^S_s)\right] \]

and when the system is close to the equilibrium,

\[ \frac{\mu^M_s - \mu^S_s}{Z_s F} \approx 0 \]

therefore in that case,

\[ \Delta \phi \approx \frac{\mu^M_s - \mu^S_s}{Z_s F} \] (2.20)

From the two kinds of experimental results, they concluded that the sulfur transfer rate is controlled by the interfacial reaction rate. One of the facts is that the rate of sulfur transfer differs among the heat with different initial carbon content. The other fact is that they observed the reversal of reaction in sulfur, iron and manganese transfer like Ramachandran et. al.'s experiment, which is difficult to explain on the basis of transport controlled rates.
Then they assumed that the interfacial reaction is in the local equilibrium except the CO gas formation reaction, i.e.,

\[ C + O^{2-} \rightarrow \{CO\} + 2e^- \]  \hspace{1cm} (2.21)

However, those assumptions are not necessarily reasonable because if the rate is controlled by the interfacial reaction then the interfacial concentration should deviate from equilibrium values otherwise, complete equilibrium would prevail throughout the system. In addition to such difficulties in their assumptions, first experimental results may be interpreted differently from theirs in that sulfur transfer differs among the heat because the initial carbon content differs among them which could yield differences in CO evolution and hence the difference in reaction areas and turbulence near the interface. In short, the increase of sulfur transfer rate could be related to the increase of interfacial area and turbulence. Besides, the second results, i.e., reaction reversals, may occur under the mixed rate controlling scheme.

Thus there is no reason to assume that the rate controlling step is the interfacial reaction. It may be noteworthy that for such a complicated electro-chemical reaction without considering the mass transfer processes
as well as the interfacial reaction, overall reaction kinetics cannot be properly understood.

Lu\(^{(28)}\) has applied the irreversible thermodynamics to the slag-metal reactions to examine the coupling among simultaneous reactions. He showed that the resulting kinetic equation in which the reaction rate of each species is expressed in terms of the electro-chemical affinity is equivalent to the Butler-Volmer type expression used by C. Wagner. The theoretical implications of Lu's analysis appear consistent with the experimental results of Ramachandran et al. and Kawai. However, the differential equations have not been solved due to the complicated nature of the computation involved.

In his theory, the most fundamental kinetic parameter is introduced, which is an anodic reaction rate constant or an exchange reaction rate (product of an anodic reaction rate constant and the interfacial equilibrium activity), however this parameter has never been measured experimentally, except the attempt made by Derge and Birchenall\(^{(29)}\).

Derge and Birchenall studies the equilibrium exchange rate of radioactive tracer iron Fe\(^{55}\), between iron and iron-
silicate slag, and they got a figure, 0.006 (1/sec), for the equilibrium rate constant even though the data were not properly treated.
CHAPTER 3

THEORY

3.1 Phenomenological Rate Equations for Coupled Reactions at Slag-Metal Interface

3.1.1 The Scheme and Fundamental Assumptions

For the purpose of studying slag-metal reactions, it is reasonable to consider that the metallic phase consists of electrically neutral atoms when phenomenological thermodynamics or kinetics are to be described, even though it is necessary to consider that the metallic phase consists of ionic core and free electrons when the atomistic properties of metal are concerned. On the other hand, the ionic phase or slag phase, as it literally means, consists of several ionic species, single ions and/or complexed ions.

Therefore, the interfacial reactions are to be electrodic reactions. The most simple reaction may have the form:

\[ M_i \rightarrow M_i^{z_i} + z_i e^- \]  \hspace{1cm} (3.1)

For simplicity, the complexed ion formations are not taken into account in this work.

Equation (3.1) represents both of anodic and cathodic reactions, in which the metallic component \( i \) dissociates
into ion and electrons.

Basic assumptions are listed as follows:

(1) The slag phase is truly ionic with no free electrons and the metallic phase is truly metallic which means no electrical polarization in metal.

(2) The reactions take place only at the slag-metal interface.

(3) The interfacial reactions consist of anodic and cathodic reactions which always cancel out the net current production at the interface with respect to each reactant.

(4) All the reactions are of the first order.

(5) The very initial transient reactions can be neglected during which the electrified zone is established.

3.1.2 Formulations of the Reaction Rate Expressions

In the first part of this section the general formulations are introduced and then the linearization is discussed.

3.1.2.1 General Expression

It is assumed that Eq. (3.1) represents the fundamental slag-metal reactions by its combinations. Since it represents the elementary reaction, the mass action law should
be applicable. If the interfacial reaction rate of the reaction (i) is denoted as $\omega_i$,

$$\omega_i = k_i \bar{a}_i - k_i' \bar{a}_i'$$  \hspace{1cm} (3.2)

It is reasonable to assume that the electron concentration is essentially constant in metal which should be designated to be unity as a standard state.

Then,

$$\omega_i = k_i \bar{a}_i - k_i' \bar{a}_i'$$  \hspace{1cm} (3.3)

where $\bar{a}_i$ and $\bar{a}_i'$ are the electro-chemical activities of component $i$ in the reaction zone at the slag-metal interface. $k_i$ and $k_i'$ are the individual forward and backward reaction rate constants respectively.

The electro-chemical activity has been introduced by means of electro-chemical potentials $\mu_i$ as such:

$$\bar{\mu}_i = \mu_i + Z_i F \phi$$

$$= \mu_i^o + RT \ln a_i + Z_i F \phi$$

$$= \mu_i^o + RT \ln \bar{a}_i$$  \hspace{1cm} (3.4)

or

$$\bar{a}_i = a_i \exp\left(\frac{Z_i F \phi}{RT}\right)$$  \hspace{1cm} (3.5)

where $\mu_i^o$ is the standard chemical potential of component (i), $a_i$ is the activity and $\phi$ is the electro static potential which is in nature to be involved in $a_i$ because the chemical
potential itself is the superposition of electro-static potentials.

The reason why the \( \omega_i \) is introduced in the expression additively is that under the conditions in which additive electric field does exist in the region of interest by the external field or so-called polarization effect, the species must behave differently from bulk phase. Eq. (3.3) should be reformulated as follows:

\[
\omega_i = k_i \bar{a}_i \left( 1 - \frac{k_i}{a_i} \right)
\]

when equilibrium constants \( K_i \) and activity ratio \( Q_i \) are defined as follows:

\[
K_i = \frac{k_i}{k_i}, \quad Q_i = \frac{\bar{a}_i}{a_i}
\]  \( \text{(3.6)} \)

then,

\[
\omega_i = k_i \bar{a}_i \left( 1 - \frac{Q_i}{K_i} \right)
\]  \( \text{(3.7)} \)

The equilibrium constants have relationships with standard chemical potential difference \( \Delta \mu^o \) as follows:

\[
K_i = \frac{k_i}{k_i} = \exp \left( +\frac{\Delta \mu^o}{RT} \right)
\]  \( \text{(3.8)} \)

where \( \Delta \mu^o = \mu^o_{\text{reactant}} - \mu^o_{\text{product}} \) \( \text{(3.9)} \) and the activity ratio \( Q_i \) can be written:
\[ \frac{\overline{a}_i}{a_i} = \frac{a'_i}{a_i} \exp \left( \frac{Z_i F \phi_i}{RT} \right) = \frac{a'_i}{a_i} \exp \left( -Z_i F \phi_i / RT \right), \quad (3.10) \]

where

\[ \phi_i = - \frac{Z_i F \phi_i}{RT} \quad (3.11) \]

Since the electro-static potential is not necessarily absolute and \( \phi_M \) may be chosen as a reference potential as a zero voltage. Under this reference state,

\[ \overline{a}_i = a_i \]

\[ \overline{a}'_i = a'_i \exp \left( -Z_i F \phi_i / RT \right) \]

Thus,

\[ \omega_i = k_i a_i \left( 1 - \frac{\overline{a}'_i}{\overline{a}_i} \right) \quad (3.12) \]

In the following, Eq. (3.12) is to be related with the electro-chemical affinity. The affinity \( \Delta \) of a reaction is defined as the difference of chemical potential between the reactant and the product, so is the electro-chemical affinity \( \overline{\Delta} \):

\[ \overline{\Delta} = \overline{\mu}_{\text{products}} - \overline{\mu}_{\text{reactants}} \quad (3.13) \]

For \( i \)-th reaction represented by Eq. (3.1),

\[ \overline{\Delta}_i = \overline{\mu}_i - \overline{\mu}'_i \]

\[ = (\mu_i^0 + RT \ln \overline{a}_i) - (\mu_i^0 + RT \ln \overline{a}'_i) \]

\[ = \Delta \mu_i^0 - RT \ln (\overline{a}'_i / \overline{a}_i) \]

\[ = \Delta \mu_i^0 - RT \ln (a'_i / a_i) + Z_i F \Delta \phi \]
\[
\dot{\alpha}_i = \frac{A_i + Z_i F}{\mu_i} = RT\left[\frac{\dot{\mu}_i^0}{kT} - \ln\left(\frac{\alpha_i}{\bar{a}_i}\right)\right]
\]

or

\[
-\frac{\dot{\alpha}_i}{RT} = \ln\left(\frac{\bar{a}_i}{\alpha_i}\right) \exp\left(-\frac{\dot{\mu}_i^0}{RT}\right)
\]

\[
= \ln\left(\frac{\overline{Q}_i}{K_i}\right)
\]

Thus,

\[
\exp\left(-\frac{\dot{\alpha}_i}{RT}\right) = \frac{\overline{Q}_i}{K_i} \tag{3.15}
\]

Put this Eq. (3.15) into Eq. (3.7):

\[
\omega_i = k_i a_i \left[1 - \exp\left(-\frac{\dot{\alpha}_i}{RT}\right)\right] \tag{3.16}
\]

The Eqs. (3.7) or Eqs. (3.16) is the general expression for the interfacial electro-chemical reaction rate.

3.1.2.2 The Linear Flux-Force Expression

Lu(29) has shown Eq. (3.16) is equivalent to the Butler-Volmer expression for the interfacial reaction rate. Both equations, however, are not the best in elucidation of coupling among the reactions for the multicomponent slag-metal system because of non-linearity involved in the expression.
The linearized form of Eq. (3.16) can be obtained by expanding the exponential term in a series and truncating orders of $(A_i/RT)$ higher than the first order:

$$\exp\left(-\frac{\bar{A}_i}{RT}\right) \approx 1 - \frac{\bar{A}_i}{RT}$$  \hspace{1cm} (3.17)

under the condition that $\left|\frac{\bar{A}_i}{RT}\right| < 1.0$

The Eq. (3.16) becomes as follows:

$$\omega_i = k_i a_i \left(\frac{\bar{A}_i}{RT}\right)$$  \hspace{1cm} (3.18)

In the following, using Eqs. (3.14) and (3.18), the electro-chemical affinities and the electric potential difference are eliminated from the rate expression by demanding the no net current condition at the interface.

The condition is

$$\sum_i z_i \omega_i = 0$$  \hspace{1cm} (3.19)

Starting from Eq. (3.18),

$$\omega_i = k_i a_i \left(\frac{\bar{A}_i}{RT}\right) = k_i a_i \left(\frac{1}{RT}\right) (A_i + z_i F \Delta \phi)$$  \hspace{1cm} (3.20)

Eq. (3.19) gives

$$\sum_i z_i \omega_i = \sum_i \left(\frac{z_i k_i a_i A_i}{RT}\right) + \Delta \phi \sum_i \left(\frac{2 z_i F k_i a_i}{RT}\right) = 0$$

or

$$\Delta \phi = -\frac{1}{F} \frac{\sum_i z_i k_i a_i A_i}{\sum_i z_i^2 k_i a_i}$$  \hspace{1cm} (3.21)
Put Eq. (3.21) into Eq. (3.20),

\[
\varphi_i = \frac{k_{i}a_{i}}{RT} \left\{ A_i - \frac{Z_iF}{\overline{Z_i}} \frac{\sum_{j} Z_j k_{i}a_{i} A_j}{\sum_{j} Z_j^2 k_{j}a_{j} A_j} \right\} = \left\{ \frac{Z_i^2 k_{i}a_{i}}{RT} \sum_{j} Z_j k_{j}a_{j} (Z_j A_j - Z_i A_l) \right\} \]

\[
= \frac{k_{i}a_{i}}{RT} \left\{ \frac{Z_i^2 k_{i}a_{i}}{RT} \sum_{j} Z_j k_{j}a_{j} (Z_j A_1 - Z_i A_j) \right\} \]

From Eq. (3.15)

\[
\ln(Q_i/K_i) = -\frac{A_i}{RT}
\]

so

\[
\frac{1}{RT} (Z_j A_1 - Z_i A_j) = -Z_j \ln(Q_i/K_i) + Z_i \ln(A_j/K_j)
\]

\[
= \ln\left(\frac{Q_i}{Q_j} / K_i / K_j\right) = \ln(Q_{ij} / K_{ij})
\]

where

\[
Q_{ij} = Q_i^{+Z_j} Q_j^{-Z_i}, \quad K_{ij} = K_i^{-Z_j} K_j^{+Z_i}
\]
are defined as concentration ratio and pair equilibrium constants for the exchange reaction as follows:

\[ Z_i Z_j M_i + Z_i M_j + Z_j M_i \]  \hspace{1cm} (3.23)

Then the equation for \( \omega_i \) becomes:

\[ \omega_i = \sum_j \left( \frac{Z_j (k_{ij} a_i a_j)}{\sum_{s} Z_s k_s a_s} \right) \ln \left( Q_{ij} / K_{ij} \right) \]  \hspace{1cm} (3.24)

Here the reactions rate is expressed in terms of rate constants, interfacial activities and equilibrium constants. To make the expression simpler, the transference number \( B \) is introduced defined by the following equation.

\[ B_{ij} = \frac{Z_j (k_{ij} a_i a_j)}{\sum_{s} Z_s k_s a_s} \]  \hspace{1cm} (3.25)

Then,

\[ \omega_i = \sum_j B_{ij} \ln \left( Q_{ij} / K_{ij} \right) \]  \hspace{1cm} (3.26)

in a special case where the interfacial concentrations are not far from equilibrium, the transference numbers could be expressed with constants:

\[ B_{ij} = \frac{Z_j (k_{ij} a_i^*) (k_{ij} a_j^*)}{\sum_{s} Z_s k_s a_s^*} \]  \hspace{1cm} (3.27)

where \( a_i^* \) stands for the equilibrium activity at the interface. The exchange reactions rate is introduced as follows:
\[ \omega_i^0 = \frac{k_i}{\omega_i^{ch}} a_i \]  

(3.28)

Then,

\[ B_{ij} = \frac{Z_j^{1/2} \omega_j^{1/2}}{\sum Z_j^{1/2} \omega_j^{1/2}} \]  

(3.29)

3.1.2.3 Mathematical Analysis of Conditions for Cooperative and Competitive Coupling

From Eq. (3.22),

\[ \omega_i = \frac{k_i a_i}{RT} \frac{1}{\sum Z_j^{1/2} \omega_j^{1/2}} \sum Z_j^{1/2} \frac{k_j a_j (Z_j A_i Z_j A_j)}{} \]

\[ = \frac{k_i a_i}{RT} \frac{A_i}{RT} \frac{1}{\sum Z_j^{1/2} \omega_j^{1/2}} \sum Z_j^{1/2} \frac{k_j a_j (1 - \frac{Z_j A_j}{Z_j A_i})}{\sum Z_j^{1/2} \omega_j^{1/2}} \]

\[ = \frac{k_i a_i A_i}{RT} \frac{1}{\sum Z_j^{1/2} \omega_j^{1/2}} \sum Z_j^{1/2} \frac{k_j a_j (1 - \frac{Z_j A_j}{Z_j A_i})}{\sum Z_j^{1/2} \omega_j^{1/2}} \]  

(3.30)

Now the following coupling factor \( \xi_i \) and partial coupling factor \( \theta_{ij} \) are introduced:

\[ \xi_i = \sum \left( \frac{Z_j^{1/2} k_j a_j (1 - \frac{Z_j A_j}{Z_j A_i})}{\sum Z_j^{1/2} k_j a_j} \right) \]  

\[ = \sum \theta_{ij} \]  

(3.31)

In Eq. (3.30) \( \frac{k_i a_i A_i}{RT} \) is a term which excludes the electrochemical contribution to the reaction rate, so this can be defined as chemical reaction rate denoted by \( \omega_i^{ch} \). Then,
electro-chemical reaction rate $\omega_i$ is expressed as

$$\omega_i = \xi_i \cdot \omega_i^{ch}$$

Depending on the magnitude of coupling factor $\xi_i$, the character and strength of the coupling differ as follows:

- $\xi_i > 1$: cooperative coupling or reaction (i) will be speeded up,
- $\xi_i = 1$: no coupling effect,
- $0 < \xi_i < 1$: competitive coupling or reaction (i) will be slowed down,
- $\xi_i < 0$: up-hill reaction will be followed by the reversal of reaction.

This coupling factor $\xi$ is a function of interfacial concentrations, therefore it is time dependent.

3.2 Phenomenological Diffusion Equations for Metallic and Ionic Phases

3.2.1 General Expression for Metallic Phase

The generalization of Fick's first equation is the set of the following equation,

$$J_i = - \sum_{k=1}^{n-1} D_{ik} \frac{\partial C_k}{\partial x} \quad (i = 1, \ldots, n-1)$$

In a source free system and in the absence of chemical reaction in the region concerned, that is in the bulk
metal, molar mass of each component should be conserved, so,
\[ \frac{\partial}{\partial x} (J_i) + \frac{\partial C_i}{\partial t} = 0 \]  \hspace{1cm} (3.34)

Hence, \((n-1)\) independent partial differential equations yield general expressions for the metallic diffusion.

It is reported\(^{(31)}\) that if the relative range of concentration difference is not more than about 20\% then the diffusion may be approximated by average constants. Eq. (3.34) then simplifies to
\[ \frac{\partial C_i}{\partial t} = \sum_{k=1}^{n-1} D_{ik} \frac{\partial^2 C_k}{\partial x^2} \]  \hspace{1cm} (3.35)

In the diffusion process, the diffusion flux is dependent on the frame of the reference, so are the diffusion coefficients.

In general, the diffusivities of individual species in the system are not equal to one another, the inert marker imbedded into the diffusion system is known to move with the movement of each species. This is called Kirchendall effect. When the reference frame is fixed in the inert marker, the intrinsic diffusivities are obtainable.
However in usual diffusion experiments the reference frame is not the inert marker, instead the reference frame is not fixed at all, so that every diffusion flux is relative to each other. Thus, experimentally obtainable diffusivities are mutual or chemical diffusivities.

In addition, the self diffusivity is defined as such that using a tracer, a radio isotope, the diffusivity is measured from the concentration profile analyzed by Eq. (3.35) for one component:

In the present numerical analysis only chemical diffusivities are used in the metallic phase, and assumed to be constant.

3.2.2 General Expression for Slag Phase

Ionic diffusion in the slag phase is described by the Nernst-Plank equation:

\[ J_i = -D_i \left( \frac{\partial C_i}{\partial x} + \frac{Z_i F C_i}{RT} \frac{\partial \phi}{\partial x} \right) \quad i = 1, 2, \ldots, n \]  

(3.36)

where \( J_i \) is the ionic flux, \( D_i \) is the self-diffusivity and \( C_i \) is the concentration, \( \phi \) is the electrostatic potential, and \( \frac{\partial \phi}{\partial x} \) is the electric field strength which is acting on the ionic species (i).
When the electroneutrality is assumed in the form of zero net current production in every space and time,

$$\sum_i z_i J_i = 0$$

(3.37)

This condition determines internal electric field \( \frac{\partial \phi}{\partial x} \):

$$\frac{\partial \phi}{\partial x} = \frac{RT}{F} \frac{\sum_i z_i D_i \frac{\partial C_i}{\partial x}}{\sum_i z_i^2 C_i D_i}$$

(3.38)

Therefore, Nernst-Plank equation turns out to be:

$$J_i = -D_i \frac{\partial C_i}{\partial x} + z_i C_i \frac{\sum_i z_i D_i \frac{\partial C_i}{\partial x}}{\sum_i z_i^2 D_i C_i}$$

(3.39)

From the definition of concentrations,

$$\sum_i C_i = \text{const.}$$

So,

$$\frac{\partial C_i}{\partial x} = - \sum_{j \neq i} \frac{\partial C_j}{\partial x}$$

(3.40)

Eqs. (3.39), (3.40) give the general expression for coupled ionic diffusion. Phenomenological mutual diffusion coefficients, which are usually defined \( (n-1)^2 \) in its number for \( n \) component system, can be formulated as functions of self diffusivities \( D_i \), concentrations \( C_i \) (assumed to be representing chemical activity) and valencies \( Z_i \).

For ternary systems, interdiffusivities are formulated as follows:
\[ D_{11} = \Omega (z_1 z_3 D_{11} D_3 + z_2 D_{12} D_2 + z_3 D_{13} D_3) \]
\[ D_{12} = \Omega (z_3 D_3 - z_2 D_2) z_1 D_1 C_1 \]
\[ D_{21} = \Omega (z_3 D_3 - z_1 D_1) z_2 D_2 C_2 \]
\[ D_{22} = \Omega (z_1 D_1 D_2 C_1 + z_2 z_3 D_2 D_3 C_2 + z_3 D_2 D_3 C_3) \]

where \( \Omega = 1/\sum_{i=1}^{3} z_i^2 C_i D_i \) \hspace{1cm} (3.41)

Fick's second law for this system is:
\[
\begin{align*}
\frac{\partial C_1}{\partial t} &= \frac{\partial}{\partial x} \left( D_{11} \frac{\partial C_1}{\partial x} \right) + \frac{\partial}{\partial x} \left( D_{12} \frac{\partial C_2}{\partial x} \right) \\
\frac{\partial C_2}{\partial t} &= \frac{\partial}{\partial x} \left( D_{21} \frac{\partial C_1}{\partial x} \right) + \frac{\partial}{\partial x} \left( D_{22} \frac{\partial C_2}{\partial x} \right) \\
\end{align*}
\]

(3.42)

Since \( D_{ij} \) is no more constant, Eq. (3.42) is a non-linear partial differential equation to be solved by numerical method.

3.2.3 Cooperative and Competitive Coupled Diffusion

From Eq. (3.39),
\[
J_i = -D_i \frac{\partial C_i}{\partial x} + Z_i C_i D_i \left[ \sum_j \frac{\partial C_j}{\partial x} \right]
\]
\[
= -D_i \frac{\partial C_i}{\partial x} \left[ 1 - \frac{\sum_j Z_j C_j D_j \frac{\partial C_j}{\partial x} / (\partial x)}{\sum_j Z_j C_j D_j} \right] \hspace{1cm} (3.43)
\]
In Eq. (3.43), the term $-D_i \frac{\partial C_i}{\partial x}$ excludes the electro-chemical coupling features while the second term represents the coupling so it can be denoted as a diffusion coupling factor $\zeta_i$ as follows:

$$\zeta_i = 1 - \frac{\sum_{j=1}^{Z_c} \frac{\partial C_j}{\partial x}/(D_j C_j)}{\sum_{j=1}^{Z_c} D_j C_j}$$

(3.44)

The first term is denoted as $J_{ch}^i$, thus,

$$J_{ch}^i = -D_i \frac{\partial C_i}{\partial x}$$

(3.45)

$$J_i = \zeta_i \cdot J_{ch}^i$$

(3.46)

The coupling factor $\zeta$ is a function of not only time but also location.

Depending on the magnitude of the coupling factor $\zeta$, the character and strength of the coupling in diffusion differs as follows:

- $\zeta_i > 1$, cooperative coupling; diffusion of component (i) is speeded up,
- $\zeta_i = 1$, coupling effect is zero,
- $0 < \zeta_i < 1$, competitive diffusion, diffusion of component (i) is slowed down,
- $\zeta_i < 0$, up-hill diffusion should occur in component (i).
This coupling factor depends on valencies, concentrations, self diffusivities and concentration gradients of all the species. Thus numerical evaluation of Eq. (3.44) cannot be attained quantitatively. However, qualitative evaluation for \( \zeta \) can be done as follows. For the weak diffusing species in which \( |\partial C_i/\partial x| \approx 0 \), one could see that the coupling factor \( \zeta \) should be away from 1.0, because
\[
| (\partial C_j/\partial x)/(\partial C_i/\partial x) | \text{ becomes much greater than unity.}
\]
On the other hand, for the strong diffusion species in which
\( |\partial C_i/\partial x| >> 0 \), since the ratios of individual concentration gradients
\( |(\partial C_j/\partial x)/(\partial C_i/\partial x)| \) becomes smaller than unity, one could see that the coupling factor \( \zeta \) should be very close to 1.0.

3.3 Boundary Value Problems for the Diffusion Equations

It is known that the solutions of any differential equations (especially partial differential equations) depends on the boundary conditions. For the present diffusional processes, there are two kinds of boundary conditions, (1) one of them describes the situation at the open end of phases of slag and metal, (2) the other one describes the condition at the slag-metal interface.

The former one is expressed as follows:
\[
\frac{\partial C_i}{\partial x} = 0 \quad (i = 1, 2, 3)
\]

This condition is reasonably valid if the size of the sample is large enough to vanish the concentration gradients as \( x \) approaches the open end of phases of slag and metal.

The latter one should be determined by the mass flux continuous equation, which means that the diffusional flux in either metal or slag is equal to the interfacial reaction flux;

\[
J_i \text{ (metallic)} = \omega_i
\]

\[
J_i \text{ (slag)} = \omega_i \quad (i = 1, 2, 3)
\]

For consistency, both flux expressions for diffusion and for reactions in the continuity expression, Eq. (3.48) must be expressed in the same concentration units. The usual concentration unit in the diffusion expression is amount per unit volume (commonly mol/cm\(^3\)), whereas those for the interfacial reaction rate involves molar fraction which is dimensionless. Therefore, care must be exercised to ensure that the same concentrations are used in both expressions. It is apparent that from the concentration units indicated, the densities of both phases will enter into the continuity expression.
It is convenient to use mol fraction unit for both expressions. It is necessary to review the definition of mol fractions, molar density and so on.

Mol fraction \( N_i \),

\[
N_i = \frac{n_i}{\sum_i n_i} \quad (3.49)
\]

where \( n_i \) represents the number of mols of species \( i \).

Molar density \( \rho \) of phase \( j \);

\[
\rho_j = \frac{\sum_i n_i}{\text{unit volume}} = \left[ \frac{\text{mol}}{\text{unit volume}} \right] \quad (3.50)
\]

Concentration \( C_i \),

\[
C_i = \frac{n_i}{\text{unit volume}} = \left[ \frac{\text{mol}}{\text{unit volume}} \right] \quad (3.51)
\]

From Eqs. (3.49)-(3.51),

\[
C_i = N_i \rho_i \quad (3.52)
\]

Once this condition is taken into the flux continuity expression, Eq. (3.48), no other cases are necessary. Thus, after converting the Eq. (3.48) into as follows,

\[
J_i \text{ metallic} = \frac{\omega_i}{\rho_i \text{ metallic}}
\]

\[
J_i \text{ slag} = \frac{\omega_i}{\rho_i \text{ slag}} \quad (i = 1, 2, 3) \quad (3.53)
\]
then, notations for concentration becomes unimportant. For convenience, notation \( C \) is used for both diffusion equations and reaction rate expressions with a unit of molar fraction.

Under the assumption that during the reaction and diffusion processes for any species molar density of metallic phase and slag phase does not change appreciably, those molar densities are to be approximately evaluated by the data of iron and steel making systems. It is considered that the density of metal is approximately 7.0 (gm/cm\(^3\)) and for slag it is approximately 3.0 (gm/cm\(^3\)). As an additional assumption, metal is supposed to consist mainly of Fe, Ni, Mn, whose molar weight is approximately 56 (gm/mol) and slag is supposed to consist mainly of FeO, NiO, MnO, SiO\(_2\), CaO, whose accumulated molar weight is approximately 60 gm/mol. Therefore, the molar densities for those phases are approximated as follows:

\[
\rho_{\text{metal}} = \frac{7.0 \text{ (gm/cm}^3\text{)}}{56 \text{ (gm/mol)}} = 0.125 \text{ (mol/cm}^3\text{)}
\]

\[
\rho_{\text{slag}} = \frac{3.0 \text{ (gm/cm}^3\text{)}}{60 \text{ (gm/mol)}} = 0.05 \text{ (mol/cm}^3\text{)}.
\]
4.1 Review of Numerical Techniques

It is necessary to review the numerical techniques which are employed in the present work. Firstly the finite difference methods for the second order of partial differential equations are reviewed. Secondly, some problems of numerical techniques inherent in the present analysis are discussed especially about the boundary value problems.

4.1.1 Finite Difference Method

It is essential for the numerical method to make discrete points, which is called grid, in x-space coordinate and examine the relationship among the functions of x on the grid for the numerical analysis (Fig. 4.1).

According to the Taylor expansion theory,
\[ f(x+h) = f(x) + hf'(x) + \frac{h^2}{2!} f''(x) + \ldots \]  
(4.1)

Thus the first derivative of \( f(x) \) is,
\[ f'(x) = \frac{f(x+h)-f(x)}{h} - \frac{h}{2!} f''(x) + \ldots \]  
(4.2)

The polynomials \( \frac{h}{2!} f''(x) + \ldots \) is called a truncation error denoted by \( \sigma(h) \) when \( f'(x) \) is approximated as follows:
Fig. 4.1 Spacing in x-coordinate with a grid space h for the numerical analysis of function $f(x)$. 
\[ f'(x) = \frac{f(x+h) - f(x)}{h} + o(h) \] \hspace{1cm} (4.3)

By convention the following notation is used:
\[
\begin{align*}
  f(x-h) &= f_{j-1}, \\
  f'(x) &= f_j, \\
  f(x+h) &= f_{j+1} \text{ and so on.}
\end{align*}
\]

So,
\[
\begin{align*}
  f'(x) &= \frac{f_{j+1} - f_j}{h} + o(h) \hspace{1cm} (4.4)
\end{align*}
\]

In the same manner, from the expansion of \( f(x-h) \),
\[
\begin{align*}
  f'(x) &= \frac{f_j - f_{j-1}}{h} + o(h) \hspace{1cm} (4.5)
\end{align*}
\]

Eq. (4.4) is called forward representation, and Eq. (4.5)
is called backward representation.

For the second-order differentials, by expanding
\( f(x+h) \) and \( f(x+2h) \) as follows:
\[
\begin{align*}
  f(x+h) &= f(x) + hf'(x) + \frac{h^2}{2} f''(x) + \frac{h^3}{6} f'''(x) + \ldots \hspace{1cm} (4.6)
  f(x+2h) &= f(x) + 2hf'(x) + 2h^2 f''(x) + \frac{4}{3} h^3 f'''(x) + \ldots \hspace{1cm} (4.7)
\end{align*}
\]

Eliminating the term of \( f'(x) \) from Eqs. (4.6) and (4.7),
\[
\begin{align*}
  f''(x) &= \frac{f(x+2h) - 2f(x+h) + f(x)}{h^2} - hf'''(x) + \\
  \text{or} \hspace{1cm} f''(x) &= \frac{f_{j+2} - 2f_{j+1} + f_j}{h^2} + o(h) \hspace{1cm} (4.8)
\end{align*}
\]
Eq. (4.8) is a forward representation and the backward representation is as follows:

\[ f''(x) = \frac{f_j - 2f_{j-1} + f_{j-2}}{h^2} + \cdots \]  

(4.9)

For the more accurate calculation, the second order approximation becomes necessary. For the first derivative,

\[
\begin{align*}
    f'(x) &= \frac{f(x+h) - f(x)}{h} - \frac{h}{2} f''(x) - \frac{h^2}{6} f'''(x) + \cdots \\
    &= \frac{f(x+h) - f(x)}{h} - \left\{ \frac{h}{2} f'(x+2h) - 2f'(x+h) + f'(x) - h f''(x) + \ldots \right\} \\
    &= \frac{f(x+2h) + 4f'(x+h) - 3f'(x)}{2h} - \frac{h^2}{3} f''(x) + \cdots \\
    \text{or } f'(x) &= \frac{f_{j+2} - 4f_{j+1} + 3f_j}{2h} + o(h^2). 
\end{align*}
\]

(4.10)

for the forward representation and in the same manner,

\[
\begin{align*}
    f'(x) &= \frac{f_{j-2} - 4f_{j-1} + 3f_j}{2h} + o(h^2) 
\end{align*}
\]

(4.11)

for the backward representation.

4.1.2 Finite Difference Method for Second Order Partial Differential Equations

Basic diffusion equations are as follows for metallic phase,

\[
\frac{\partial \text{CM}_1}{\partial t} = \text{DM}_{11} \frac{\partial^2 \text{CM}_1}{\partial x^2} + \text{DM}_{12} \frac{\partial^2 \text{CM}_2}{\partial x^2} 
\]

(4.12)
\[
\frac{\partial CM2}{\partial t} = DM21 \frac{\partial^2 CM1}{\partial x^2} + DM22 \frac{\partial^2 CM2}{\partial x^2},
\]

for slag phase,

\[
\frac{\partial CS1}{\partial t} = \frac{\partial}{\partial x} (DS11 \frac{\partial CS1}{\partial x}) + \frac{\partial}{\partial x} (DS12 \frac{\partial CS2}{\partial x}),
\]

\[
\frac{\partial CS2}{\partial t} = \frac{\partial}{\partial x} (DS21 \frac{\partial CS1}{\partial x}) + \frac{\partial}{\partial x} (DS22 \frac{\partial CS2}{\partial x}).
\]

The initial condition is,

\[
CM1(x,0) = CM10
\]
\[
CM2(x,0) = CM20
\]
\[
CS1(x,0) = CS10
\]
\[
CS2(c,0) = CS20
\]

One of the boundary conditions for the open end of the system is,

\[
\left( \frac{\partial CM1}{\partial x} \right)_{x=0} = 0
\]
\[
\left( \frac{\partial CM2}{\partial x} \right)_{x=0} = 0
\]
\[
\left( \frac{\partial CS1}{\partial x} \right)_{x=x_0} = 0
\]
\[
\left( \frac{\partial CS2}{\partial x} \right)_{x=x_0} = 0
\]

The other boundary condition for slag-metal interface is,

\[
\omega_1 = \rho_m \overline{J}_1 = \rho_m \left( -DM11 \frac{\partial CM1}{\partial x} - DM12 \frac{\partial CM2}{\partial x} \right)_{x=x_i}.
\]
\[ \omega_2 = \rho_m \frac{\partial m_2}{\partial x} = \rho_m \left( -Dm_{11} \frac{\partial \rho_{11}}{\partial x} - Dm_{12} \frac{\partial \rho_{12}}{\partial x} \right) \bigg|_{x=x_i} \]

\[ \omega_1 = \rho_s \frac{\partial s_1}{\partial x} = \rho_s \left( -Dsl_{11} \frac{\partial \rho_{11}}{\partial x} - Dsl_{12} \frac{\partial \rho_{12}}{\partial x} \right) \bigg|_{x=x_i} \]

\[ \omega_2 = \rho_s \frac{\partial s_2}{\partial x} = \rho_s \left( -Dsl_{21} \frac{\partial \rho_{11}}{\partial x} - Dsl_{22} \frac{\partial \rho_{12}}{\partial x} \right) \bigg|_{x=x_i} \]  

(4.18)

where \( \rho \) represents the molar density of slag and metal, and \( x_i \) and \( x_0 \) represent the interfacial and the slag end coordinates respectively.

In order to solve the above set of equations (Eqs. (4.12) to (4.18)) numerically, the following time and space grids are employed as shown in Fig. 4.2. In the finite difference usage, central representation is also used in addition to the forward and the backward representation.

From the initial conditions, all the concentrations on any space grid points at \( t = 0 \) (or \( i = 1 \)) are known values. By either forward or backward representation of first and second derivatives, any three continuing grid points on the time coordinate \( t = 1 \), are to be used to calculate one of the unknowns on time coordinate \( t = 2 \). In Fig. 4.2, the points A, B, C are used to calculate the values on point D. A, B, C represent any grid points on \( t = 1 \) and D represents any grid points on \( t = 2 \) except at \( x = 0 \), \( x_i \) and \( x_0 \). This set of points A-B-C-D is called the inverse T cell.
Fig. 4:2 Location and time coordinate grids employed for the present numerical analysis. Inverse T-cell, AEDCD, is used to obtain unknown values at point D from known values on A, B and C.
By sweeping this inverse T cell from \( x = 0 \) to \( x = x_0 \), the unknown concentrations for both metallic and slag phase on \( t = 2 \) are to be obtained except at points \( x = 0, x_1 \), and \( x_2 \). The values on those three points are to be calculated from the boundary conditions.

Once all the unknowns on \( t = 2 \) grid are obtained, those values are completely displaced on \( t = 1 \) grid. Then by the same sweeping procedure, all the unknowns for the next time step \( (t = 2 + \Delta t) \) are to be obtained on time \( t = 2 \).

By repetitions of these procedures, any values at \( t = t \) are to be calculated from the values at one time step before or from the values on \( t = t - \Delta t \).

For the present diffusion problem, Fick's second law may be represented by Eq. (4.19):

\[
\frac{\partial f}{\partial t} = F \left( \frac{\partial f}{\partial x}, \frac{\partial^2 f}{\partial x^2} \right) \tag{4.19}
\]

Eq. (4.19) may be rewritten in terms of finite difference as Eq. (4.20):

\[
\frac{\Delta f}{\Delta t} = \frac{1}{\Delta x^2} G(\Delta f, \Delta^2 f) \tag{4.20}
\]

When the inverse T-cell \( A-B-C-D \) is applied to this equation the following two equations should be obtained:
\[ f = f_D - f_B \]  \hspace{1cm} (4.21)

\[ f_D = f_B + \frac{\Delta t}{\Delta x^2} \cdot F(\Delta f, \Delta^2 f) \]  \hspace{1cm} (4.22)

\( \Delta f \) and \( \Delta^2 f \) in the function \( F \) in Eq. (4.22) are the space finite differences at \( t = 0 \) (or \( i = 1 \)), therefore they are the functions of \( f_A, f_B \) and \( f_C \). Thus,

\[ f_D = f_B + \frac{\Delta t}{\Delta x^2} \cdot G(f_A, f_B, f_C) \]  \hspace{1cm} (4.23)

One of the examples will be shown in Eq. (4.35), and some others are seen in the computer program attached in the Appendix.

4.2 Computer Program

In this section, an outline of the present computer program for the pseudo-ternary slag-metal system is presented in terms of a flow chart, boundary value problem and stability conditions.

4.2.1 Flow Chart

Fig. 4.3 shows the block diagram type of flow chart which is employed in the present analysis.

It starts from data input which consists of valencies, anodic reaction rate constants, equilibrium constants, diffusivities, molar densities, \( \Delta x, \Delta t \) initial concentrations and so on. After the data input, initial concentrations are
Fig. 4.3 Flowchart employed in the numerical analysis of semi-rotal reaction kinetics.
fed into the individual space mesh points on the time coordinate 1.

Based on the interfacial concentrations, the electro-chemical reaction rates are to be calculated; then the new set of interfacial concentrations for time coordinate 2 is calculated. Bulk concentrations for time coordinate 2 follows this. Upon this stage all the new concentrations on every point of the grid for time coordinate 2 are determined for every species 1, 2 and 3.

Thereafter, the space averages of concentrations are calculated in both phases. At this stage, if the conditions \( \text{NEED} = 0 \) is satisfied, then all the results are to be printed out.

After this step, time space must step up by \( \Delta t \), so all the values on the coordinate 2 is transcribed on the coordinate 2, followed by the return to the position 1000 in Fig. 4.3 to repeat the whole calculation again.

This sweeping procedure in time and space grid continues until the following condition fulfills,

\[ II > \text{LIMIT}. \]
4.2.2 Finite Difference Equations

Before the deduction of finite difference equations from differential equations, basic nomenclatures have to be presented here. Other nomenclatures can be referred to in the Appendix.

As basic indexing principles, numbers 1; 2, 3 are used for species and for coordinates of time and space, M represents metallic, S represents slag, D represents diffusivity, C represents molar fraction and W represents the interfacial reaction rate.

For combinations of those indexing the following conventions are used:

[example] --- molar concentration representation,

\[ C_{3, M, 2} \]

represents the molar fraction of metallic component 3 on time coordinate 2 and on space coordinate 9.

\[ C \quad \text{molar concentration} \]
\[ 1, 2, 3 \quad \text{number of component} \]
\[ M, S \quad \text{metallic or slag} \]
\[ 0, 1, 2 \quad \text{time coordinate} \]
\[ 1 \text{ to } LE \quad \text{space coordinate} \]
4.2.2.1 Interfacial Concentration Calculation

In order to determine the interfacial concentrations, flux continuity condition is used as a boundary condition. If the interfacial reaction rate is approximated by the rate of one time step before, the flux continuous equation is solved explicitly for the interfacial concentrations.

The diffusional fluxes of component 1 and 2 in the metallic interface are:

\[
J_{1}^{m} = - \left( \frac{\partial C_{1}}{\partial x} \right)_{x=L} - \left( \frac{\partial C_{2}}{\partial x} \right)_{x=L}
\]

\[
= - \frac{DM_{11}}{2\Delta x} \times \left( C_{1}M_{2}(LM) - 4*C_{1}M_{2}(LM) + 3*C_{1}M_{2}(L) \right)
\]

\[
J_{2}^{m} = - \left( \frac{\partial C_{1}}{\partial x} \right)_{x=L} - \left( \frac{\partial C_{2}}{\partial x} \right)_{x=L}
\]

\[
= - \frac{DM_{12}}{2\Delta x} \times \left( C_{2}M_{2}(LM) - 4*C_{2}M_{2}(LM) + 3*C_{2}M_{2}(L) \right) \quad (4.24)
\]

\[
J_{1}^{m} = - \left( \frac{\partial C_{1}}{\partial x} \right)_{x=L} - \left( \frac{\partial C_{2}}{\partial x} \right)_{x=L}
\]

\[
= - \frac{DM_{12}}{2\Delta x} \times \left( C_{1}M_{2}(LM) - 4*C_{1}M_{2}(LM) + 3*C_{1}M_{2}(L) \right)
\]

\[
J_{2}^{m} = - \left( \frac{\partial C_{1}}{\partial x} \right)_{x=L} - \left( \frac{\partial C_{2}}{\partial x} \right)_{x=L}
\]

\[
= - \frac{DM_{21}}{2\Delta x} \times \left( C_{2}M_{2}(LM) - 4*C_{2}M_{2}(LM) + 3*C_{2}M_{2}(L) \right) \quad (4.25)
\]

The underlined parts in Eqs. (4.24) and (4.25) are already determined by the diffusion equation (see the following section). Since the flux continuous equations are,
\[ J_1^m = \omega_1 \]  
\[ J_2^m = \omega_2 \]  

The interfacial concentration is to be solved by Eqs. (4.24) to (4.27) as follows,

\[ C_{1M2}(L) = \frac{(4.0*C_{1M2}(LM) - C_{1M2}(LMM))}{3.0} - \text{MEPSI}_1 \]  
\[ C_{2M2}(L) = \frac{(4.0*C_{2M2}(LM) - C_{2M2}(LMM))}{3.0} - \text{MEPSI}_2 \]  

Where,  
\[ \text{MEPSI}_1 = \frac{(W_1*DM_{22}-W_2*DM_{12})\Delta x}{(DM_{11}*DM_{22} - DM_{12}*DM_{21})*\text{MDENSI}} \]  
\[ \text{MEPSI}_2 = \frac{(W_2*DM_{11}-W_1*DM_{21})\Delta x}{(DM_{11}*DM_{22} - DM_{12}*DM_{21})*\text{MDENSI}} \]  

\[ \text{MDENSI} = \text{metallic molar density} = 0.125 \text{ (mol/cm}^3) \].

In the same manner, similar expressions are obtained for slag phase interfacial concentrations.

It is noteworthy that second order approximations (Eqs. (4.24) and (4.25)) are employed for the first partial differentials so that the truncation errors are to be in the order of \((\Delta x)^2\). This second order approximation is essentially important because the MEPSI1 or 2 could have the magnitude of \(\Delta x\) and if the expression of diffusion flux has a first order truncation error, that is \(\Delta x\), then the whole calculation becomes disastrous.
Approximation of \( \omega_i(t+\Delta t) \) by \( \omega_i(t) \), could be exactly justified in the limit \( \Delta t \to 0 \). In the real calculation where \( \Delta t \) is small but finite, so under a certain \( \Delta t \), the error must be considered. Since the theoretical error estimation is difficult, the following way has been followed. That is, a comparison method between the first approximation method and the more exact iteration method which is shown below (Fig. 4.4):

Supposing all concentration are determined at \( t = t \) and the solutions at \( t = t+\Delta t \) are going to be determined. \( \omega_i(t+\Delta t) \) and \( J_i^S(t+\Delta t) \), \( J_i^m(t+\Delta t) \) comprise the boundary conditions which are implicitly related to each other, so there is no way to get the solution explicitly. This problem may be solved by the following chart method. (See Figure 4.4.)

This iterative method has been examined and the results are compared to the results of a first approximation method in which \( \omega_i(t+\Delta t) = \omega_i(t) \). They are found to be almost identical to each other within four digits of calculation under a certain \( \Delta t \) value. Thus all the results are obtained by the first order approximation method not resorting to the time consuming iteration method.
Fig. 4.4 Flow chart for the iteration to obtain the interfacial quantities, \( C_i, C'_i, \omega_i \).

\( T \) stands for truth and \( F \) stands for false.
4.2.2.2 Bulk Concentration Calculation

The metallic bulk concentrations are calculated by the Fick's second law with constant diffusivities. The following numerical finite difference expression is directly obtained by Eqs. (4.12) and (4.13),

\[
C_{1M2}(J) = C_{1M1}(J+1) + AA * (D_{11} * C_{1M1}(J) + D_{12} * C_{M1}(J)) \quad (4.32)
\]
\[
C_{2M2}(J) = C_{2M1}(J+1) + AA * (D_{21} * C_{1M1}(J) + D_{22} * C_{M1}(J)) \quad (4.33)
\]

where

\[
AA = \frac{\Delta t}{(\Delta x)^2}
\]

\[
C_{1M1}(J) = C_{1M1}(J+1) - 2 * C_{1M1}(J) + C_{1M1}(J-1),
\]
\[
C_{M1}(J) = C_{M1}(J+1) - 2 * C_{M1}(J) + C_{M1}(J-1),
\]

and \( J \) runs from 2 to \( LM_1 \).

The finite difference expression for slag phase is more complicated because the diffusivities are not be constant.

For the component 1, Eq. (4.14) is,

\[
\frac{\partial C_1}{2t} = \frac{1}{\Delta x} (D_{11} \frac{\partial C_1}{\partial x}) + \frac{1}{\Delta x} (D_{12} \frac{\partial C_2}{\partial x})
\]

\[
= \frac{2D_{11}}{\Delta x} \frac{\partial C_1}{\partial x} + D_{11} \frac{\partial^2 C_1}{\partial x^2} + \frac{2D_{12}}{\Delta x} \frac{\partial C_2}{\partial x} + D_{12} \frac{\partial^2 C_2}{\partial x^2} \quad \text{(4.34)}
\]
Finite difference expression for this equation (4.34) is,
\[
\frac{\text{C1S2}(J) - \text{C1S1}(J)}{\Delta t} = \frac{1}{(\Delta x)^2} \left\{ \text{D11}(J) \cdot \text{D11}(J-1) \cdot (\text{C1S1}(J) - \text{C1S1}(J-1)) \\
+ \text{D11}(J) \cdot (\text{C1S1}(J+1) - 2\text{C1S1}(J) + \text{C1S1}(J-1)) \\
+ (\text{D12}(J) - \text{D12}(J-1)) \cdot (\text{C2S1}(J) - \text{C2S1}(J-1)) \\
+ \text{D12}(J) \cdot (\text{C2S1}(J+1) - 2\text{C2S1}(J) + \text{C2S1}(J-1)) \right\}
\]
(4.35)

In such a way, one can get the final expressions for \text{C1S2}(J)
and \text{C2S2}(J) as follows:
\[
\text{C1S2}(J) = \text{C1S1}(J) + AA \cdot (\text{D11}(J) \cdot \text{C1S1}(J) + \text{D11}(J) \cdot \text{C1S1}(J-1)) +
\text{D12}(J) \cdot \text{C1S1}(J) + \text{D12}(J) \cdot \text{C1S1}(J-1))
\]
(4.36)
\[
\text{C2S2}(J) = \text{C2S1}(J) + AA \cdot (\text{D21}(J) \cdot \text{C2S1}(J) + \text{D21}(J) \cdot \text{C2S1}(J-1)) +
\text{D22}(J) \cdot \text{C2S1}(J) + \text{D22}(J) \cdot \text{C2S1}(J-1))
\]
(4.37)

where \text{D11}(J), \text{D12}(J), \text{D21}(J), \text{D22}(J) and \text{C1}(J), \text{C2}(J), \text{C3}(J),
\text{C4}(J)$ are formulated in the main program (Appendix).

4.2.3 Criterion for Numerical Stability

There are two criteria for stability of the numerical solution. Here stability means that under some numerical parametric condition, the solutions are obtainable no matter how the solution is close to the exact solution or not. On the other hand, non-stability means that the solution is not obtainable yielding some variables far from reality.
Even after a stable condition is attained (by good combination of $\Delta x$ and $\Delta t$) one still ought to examine whether the solution is the converged solution or not. It would be a truly trial and error type examination. The method to find out the accurate solution is explained by the following procedure:

**Step 1. (stability test):**
Set the first trial $\Delta x_1$ and $\Delta t_1$ based on the reasons which would be detailed in the following, and if the result yields negative concentrations reduce the increments $\Delta x_2$ and $\Delta t_2$ (with keeping $\Delta t_2/(\Delta x_2)^2 = \Delta t_1/(\Delta x_1)^2$). If it does not give any negative concentrations go to Step 2.

**Step 2. (convergency test):**
Set a few other combinations of $\Delta x$ and $\Delta t$ varying small values of $\Delta x$ and $\Delta t$ from the final combination in Step 1, and see the trends of the solution. Try to reduce the values little by little until the solution does not change within a certain digits (in the present analysis it is 4 digits).

**Step 3. (economy test):**
Keeping the $\Delta x$ in the final set of Step 2, increase
\[ \Delta t \text{ alone and see the trend. Maximize the value of } \Delta t \text{ within the allowance mentioned in step 2.} \]

First trial \( \Delta x_1 \), and \( \Delta t_1 \) could be estimated by two criteria shown in the following as functions of the system parameters such as diffusivities, rate constants, concentrations and so on.

**Criteria 1. (Diffusion Criteria):**

\[
\left| C_{LS2}(J) - C_{LS1}(J) \right| = \left| \frac{\Delta t}{\Delta x^2} \right| \left[ (DS_{11}(J) - DS_{11}(J-1) + (C_{LS1}(J) - C_{LS1}(J-1) + DS_{11}(J) \cdot C_{LS1}(J) \cdot C_{LS1}(J-1)) \right]
\]

\[
\sim \frac{\Delta t}{\Delta x^2} \cdot DS_{11}(J) \cdot C_{LS1}(J) \cdot \frac{1}{10} < C_{LS1}(J)
\]

Thus, \[ \frac{\Delta t}{(\Delta x)^2} < \frac{10}{DS_{11}(J)} \quad (4.38) \]

**Criteria 2. (Interfacial Reaction Criteria):**

\[ C_{LS2}(L) = \frac{4.0 \cdot C_{LS2}(LS) - C_{LS2}(LSS)}{3.0} \]
Thus, \[ \Delta x < \left| \frac{3 \times \text{DENSI1} \times \text{DENSI1}^*(L)}{2 \times W1} \right| \] (4.39)

It should be noted that those two criteria give only an indication about the appropriate combination of \( \Delta x \) and \( \Delta t \) for a particular system. Final \( \Delta x \) and \( \Delta t \) must be determined by the procedures described before (from step 1. to 3.).

4.3 Selecting Values of Parameters for Numerical Calculations

Since many metallurgical parameters have not been obtained from the experimental works for the applications of the present theoretical analysis related to the real slag-metal systems, hypothetical slag-metal systems are taken into consideration. In the real iron and steelmaking processes, slag-metal systems consist of more than five components. However, at present, only pseudo-ternary slag-metal systems are examined as a first step of numerical analysis for this problem.
In order to proceed the numerical calculation, some numbers for individual metallurgical parameters are ought to be fed into the formula. Since hypothetical systems are assumed, all kinds of freedom for the parametric selection are available. They are classified into three kinds of selection:

1. initial and final composition of the system,
2. specific rate constants for individual reactions,
3. chemical diffusivities in metal and tracer diffusivities in slag.

Among the various combinations of those selections, only some of them are examined based on such conditions that the system could show (1) a prominent feature of coupled reaction which means the reversal of reaction (one of the coupling factors $\xi_i$ should be negative), and (2) just competitive or cooperative feature of coupled reaction (none of the coupling factors should be negative).

4.3.1 Initial and Final Concentrations

The hypothetical system consists of $m_1-m_2-m_3$ (metallic phase) and $m_1^{Z1+} - m_2^{Z2+} - m_3^{Z3+} - m_4^{Z4-}$ (slag phase) where $Z_1=Z_2=Z_3=-Z_4=2$. The component four is assumed to exist only in slag phase as $m_4^{2-}$ which is immobile. Under this condition the molar fraction of $M_4^{2-}$ or $C_4^1$ must be 0.5.
for any time and any location in the slag. Thus the system becomes pseudo-ternary.

The initial and final compositions of metal and slag are arbitrarily chosen as shown in Table 4.1.

<table>
<thead>
<tr>
<th>(a) initial composition</th>
<th>(b) final composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>i</td>
<td>C_i</td>
</tr>
<tr>
<td>1</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>0.20</td>
</tr>
<tr>
<td>3</td>
<td>0.60</td>
</tr>
<tr>
<td>4</td>
<td>0.00</td>
</tr>
</tbody>
</table>

(C_i represents metallic and C_i' represents slag)

Table 4.1 Compositions of slag and metal

Following this combination of final compositions, equilibrium constants become as follows,

for individual electrodic reactions

\[ K_1 = 2.500, \]
\[ K_2 = 0.682, \]
\[ K_3 = 0.076; \]

for exchange reactions

\[ K_{12} = 7.4 \times 10^{-2} \]
\[ K_{13} = 9.0 \times 10^{-4} \]
4.3.2 Self-Diffusivities and Chemical Diffusivities

Even for hypothetical system, self and chemical diffusivities are employed from the iron and steelmaking data (special report No. 12 of I.S.I.J., "Properties of liquid iron and slag").

Most of the reported chemical diffusivities in the metal are in the range from $5 \times 10^{-4}$ to $10^{-5}$ cm$^2$/sec at iron and steelmaking temperature (1300°C - 1600°C). For slag, the data is fairly poor in number and in accuracy, however chemical diffusivities of Fe, Al, Ni, O, Si, etc. in the blast furnace type slag are in the range from $5 \times 10^{-5}$ to $10^{-6}$ cm$^2$/sec at around 1500°C.

For the present calculation, chemical and tracer diffusivities are arbitrarily selected as follows within the above mentioned range:

for metal,

$$D_{11} = 1. \times 10^{-4}$$
$$D_{12} = 1 \times 10^{-6}$$
$$D_{21} = 1. \times 10^{-6}$$
$$u_{22} = 5 \times 10^{-5} \text{ (cm}^2/\text{sec})$$

for slag,

$$D_1 = 2 \times 10^{-5}$$
$$D_2 = 1.5 \times 10^{-5}$$
\[ D_3 = 1 \times 10^{-5} \text{(cm}^2/\text{sec)} \]

4.3.3 Specific Reaction Rates and Exchange Reaction Rates

In the rate expression, one of the most important kinetic constants is a specific reaction rate (anodic reaction rate) constant or an exchange reaction rate for a particular interfacial concentration. There is few reported values for these parameters simply because of a lack of analysis along with the electroodic theory in pyrometallurgical systems.

Tkuda\(^{(32)}\) reported some values of exchange current density which could be converted to specific reaction rate constants. The converted specific reaction rate constant ranges from \(3 \times 10^{-4}\) to \(1 \times 10^{-5}\) mol/cm\(^2\) sec. depending on the reaction and the activity involved in the system.

(Surveyed reactions are Fe → Fe\(^{2+}\) + 2e\(^-\), Mn → Mn\(^{2+}\) + 2e\(^-\), Si → Si\(^{4+}\) + 4e\(^-\) etc.)

It may be estimated that those values could be ranged more widely than the above variations, since in aqueous electrodics the exchange current ranges from \(10^{-3}\) to \(10^{-13}\) am/cm\(^2\) \(^{(33)}\). So in this work, selected range for the exchange reaction rate constant is from \(10^{-2}\) to \(10^{-6}\) mol/sec/cm\(^2\).
CHAPTER 5

COMPUTATIONAL RESULTS

The slag-metal systems which were analyzed in the present work were of finite dimension, i.e., 0.1 mm thickness for both phases. Concentrations in terms of molar fractions were calculated for both phases as a function of reaction time and location. Seven systems, as shown in Table 5.1, which can be divided into two groups, have been studied.

In the first group of five systems, the competitive couplings which may cause the reversal of reaction were investigated. Besides, the comparison between the interfacial reaction rate and the diffusion rates has been done to see the rate controlling step.

In the second group of two systems, competitive and cooperative reaction coupling were investigated as well as coupled diffusion phenomena.

The systems under consideration do not involve gaseous phases and they are under isothermal and isobaric conditions. The selected values of kinetic parameters and initial concentrations are shown in Table 5.1.
5.1 Concentration Profiles and Their Time Dependency

Differential equations (3.35) and (3.42) for pseudo-ternary systems have been solved by the numerical method presented in Chapter 4 with thermodynamic and kinetic parameters shown in Table 5.1. The computed results in the form of concentration profiles at different times of reaction have been obtained.

For each system A to G, there are three diagrams, one for each chemical element. Individual concentration profiles for each system are labelled for reaction time, for example, $t = 0$ for initial state and $t = \infty$ is for final equilibrium state. The profiles are shown in Figs. (5.1) to (5.21). In each diagram, the slag-metal interface is located at $x = 0$ and the region $x \leq 0$ is for metal and $x > 0$ for slag phase. All concentrations shown in the profiles are expressed in atom or ion fractions.

In order to illustrate the changes in profiles due to the variation in the values of kinetic parameters, the profiles for each component from the various systems should be compared with each other. For this purpose all the available concentration profiles are shown in Fig. 5.22.

It is seen that there is an uphill reaction in the component 2 in systems B, C, D, E and F. The uphill
diffusion is seen in the component 2 in every system except A. Reactions 2 and 3 are seen to proceed rather monotonically toward the equilibrium state.

It is obvious that the concentration gradients throughout the space for each component are different from one system to another. Generally the profiles in the metallic phase are flatter than in the slag phase, and they become flatter as the system changes from A to B, C, D and E.

From Table 5.1 the parameters \( k_i/D_i \) are seen to vary by three orders of magnitude among the first 5 systems and it is seen that as this ratio \( k_i/D_i \) reduces the concentration profiles become flatter.

In the last two groups, there is an uphill diffusion in the slag component (2), without an uphill reaction to induce it. Especially in system F, even though the absolute amount is small, component 2 accumulates in the interfacial region when the mass flux is from the slag phase to the metallic phase.

5.2 Interfacial Concentrations

Since interfacial reactions are the primary concern in slag metal reaction kinetics, interfacial concentration's
are analyzed as a function of reaction time. They have been given in Figs. (5.1) to (5.21) for both slag and metal phases. To simplify the discussion in the next chapter, the interfacial concentrations on the slag side in systems A to E as functions of time are shown in Figs. (5.23.a) to (5.23.e):

In Figs. (5.23.a) to (5.23.e) there are two common features:

(1) the reversal of reactions 2 (or uphill reaction),
(2) monotonic changes of $C_1$ and $C_3$ as functions of reaction time.

From Figs. (5.23.b) to (5.23.d), the reaction reversal point of component 2 correspond to a characteristic concentration of $C'_3$, i.e. about 0.10. Below this value, the effect of reaction 3 seems to be insufficient to make the coupling between 2 and 3 strong.
Table 5.1 Selected Values of Kinetic Parameters and Initial Concentrations

<table>
<thead>
<tr>
<th>System</th>
<th>Rate Constant, ( \frac{\text{mole}}{\text{cm}^2\cdot\text{sec}} )</th>
<th>( \bar{\xi}_1 )</th>
<th>( \bar{\xi}_2 )</th>
<th>( \bar{\xi}_3 )</th>
<th>Coupling factor (at ( t = 0 ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>5x10^{-3}</td>
<td>5x10^{-3}</td>
<td>1.822x10^{-2}</td>
<td>250</td>
<td>333</td>
</tr>
<tr>
<td>B</td>
<td>5x10^{-4}</td>
<td>5x10^{-4}</td>
<td>1.822x10^{-3}</td>
<td>25</td>
<td>33.3</td>
</tr>
<tr>
<td>C</td>
<td>5x10^{-5}</td>
<td>5x10^{-5}</td>
<td>1.822x10^{-4}</td>
<td>2.5</td>
<td>3.33</td>
</tr>
<tr>
<td>D</td>
<td>2.25x10^{-5}</td>
<td>2.25x10^{-5}</td>
<td>8.33x10^{-5}</td>
<td>1.75</td>
<td>1.67</td>
</tr>
<tr>
<td>E</td>
<td>5x10^{-6}</td>
<td>5x10^{-6}</td>
<td>1.822x10^{-6}</td>
<td>0.25</td>
<td>0.33</td>
</tr>
<tr>
<td>F</td>
<td>5x10^{-5}</td>
<td>1x10^{-5}</td>
<td>1x10^{-5}</td>
<td>2.5</td>
<td>0.67</td>
</tr>
<tr>
<td>G</td>
<td>5x10^{-5}</td>
<td>1x10^{-5}</td>
<td>5x10^{-6}</td>
<td>2.5</td>
<td>0.67</td>
</tr>
</tbody>
</table>

Diffusivities in metal, cm²/sec
- \( \bar{D}_{11} = 1.0x10^{-4} \)
- \( \bar{D}_{12} = \bar{D}_{21} = 1.0x10^{-6} \)
- \( \bar{D}_{22} = 5.0x10^{-5} \)

Self-diffusivities in slag, cm²/sec
- \( D_{11}^S = 2.0x10^{-5} \)
- \( D_{22}^S = 1.5x10^{-5} \)
- \( D_{33}^S = 1.0x10^{-5} \)

Equilibrium Constants, dimensionless
- \( K_1 = 2.50 \)
- \( K_2 = 0.682 \)
- \( K_3 = 0.076 \)

Initial Concentrations, mole fraction
- in metal: \( C_{10} = C_{20} = 0.2, C_{30} = 0.6 \)
- in slag: \( C_{10}^I = 0.1, C_{20}^I = C_{30}^I = 0.2, C_{40}^I = 0.5 \)
Fig. 5.1 Concentration profiles as a function of time

Numbers:
1: 0.005
2: 0.010 sec.
Fig. 5.2 Concentration profiles as a function of time

Numbers: 1: 0.005
2: 0.010 sec.
Fig. 5.3 Concentration profiles as a function of time
Numbers 1: 0.005
2: 0.010 sec.
Fig. 5.4 Concentration profiles as a function of time
Numbers:
1: 0.024
2: 0.080
3: 0.640 sec.
Fig. 5.5 Concentration profiles as a function of time

Numbers
1: 0.003
2: 0.024
3: 0.080
4: 0.640 sec.
Fig. 5.6 Concentration profiles as a function of time

Numbers
1: 0.024
2: 0.080
3: 0.640 sec.
Fig. 5.7 Concentration profiles as a function of time
Numbers:
1: 0.5
2: 2.0
3: 5.0 sec.
Fig. 5.8 Concentration profiles as a function of time
Numbers:
1: 0.5
2: 2.0
3: 5.0
4: 10.0 sec
Fig. 5.9 Concentration profiles as a function of time
Numbers 1: 0.5
2: 2.0
3: 5.0 sec.
Fig. 5.10 Concentration profiles as a function of time
Numbers 1: 1.0
2: 2.0
3: 5.0 sec.
Fig. 5.11 Concentration profiles as a function of time

- Concentration numbers:
  1: 1.0
  2: 2.0
  3: 5.0
  4: 10.0 sec.
Fig. 5.12 Concentration profiles as a function of time

Numbers:
1: 1.0 s
2: 2.0 s
3: 5.0 s
Fig. 5.13 Concentration profiles as a function of time
Numbers: 1: 2.0
2: 5.0
3: 10.0 sec.
Fig. 5.14 Concentration profiles as a function of time

Numbers:
1: 2.0
2: 5.0
3: 10.0 sec.
Fig. 5.15 Concentration profiles as a function of time

Numbers:
1: 2.0
2: 5.0
3: 10.0 sec.
Fig. 5.16 Concentration profiles as a function of time.

Numbers:
1: 0.5 sec.
2: 5.0 sec.
3: 19.5 sec.
SYSTEM F
REACTION 2

Fig. 5.17 Concentration profiles as a function of time

Numbers: 1: 0.5
2: 5.0
3: 19.5 sec.
Fig. 5.18 Concentration profiles as a function of time

Numbers
1: 0.5
2: 5.0
3: 19.5 sec.
Fig. 5.19 Concentration profiles as a function of time

Numbers 1: 0.5
2: 5.0
3: 10.5 sec.
Fig. 5.20 Concentration profiles as a function of time
Numbers 1: 0.5
2: 5.0
3: 19.5 sec.
Fig. 5.21 Concentration profiles as a function of time

Numbers 1: 0.5
2: 5.0
3: 19.5 sec.
Fig. 5.22  Concentration profiles in systems A to G and in reaction 1 to 3. Arrows indicate up-hill diffusion. Details should be referred to Figs. 5.1 to 5.21.
Fig. 5.23.a: Change of interfacial concentrations in slug phase
Fig. 5.23.1: Change of interfacial concentrations in sloop phase
Fig. 5.23.c Change of interfacial concentrations in slp phase.
Fig. 3.23.b Change of interfacial concentrations in slag phase.
Fig. 5.23. Change of interfacial concentrations in slag phase.
CHAPTER 6

DISCUSSION

The interdependency of simultaneous slag-metal reactions is electro-chemical in nature. A theoretical analysis has been presented in Chapter 3 and computational results shown in Chapter 5.

In this Chapter, firstly coupled interfacial reactions are discussed in terms of coupling factor $\zeta$. Then coupled diffusion is discussed in terms of coupling factor $\zeta$, as well as coupled interfacial reactions.

This is followed by a discussion of rate-controlling steps of over-all reaction kinetics.

Finally, the following will be discussed: the physical significance of the calculated results, their possible impact on future experimentations, and the potential and limitation for the industrial application.

6.1 Coupled Interfacial Reactions

It has been shown that in general the rate of interfacial reactions may be expressed as follows:

$$\omega_i = \omega_i^{ch} \zeta_i$$  \hspace{1cm} (3.26)
where \( \omega^\text{ch}_i = k_1 a_i \Lambda_i / RT \) (3.27)

\( \omega^\text{ch}_i \) is the reaction rate in the forward direction involving the \( i \)-th element in the absence of coupling due to other reactions.

For individual reactions, the reaction path, i.e., whether the reaction approaches equilibrium asymptotically or whether it moves away from equilibrium for a period of time, can be estimated by the initial coupling factor \( \xi_i \).

From the argument in Section 3.1.2.3, the coupling factor for the \( i \)-th reaction, \( \xi_i \), may be positive or negative. The physical meaning of these values is given below:

\( \xi_i > 1.0 \).

It means that the presence of other reactions would speed up this \( i \)-th reaction.

\( 0 < \xi_i < 1.0 \).

It means that the presence of other reactions would slow down this \( i \)-th reaction.

\( \xi_i = 0 \).

Reaction rate is zero but it may not be the equilibrium state. It may be the moment when the reversible electrodic reaction reverses its direction.
The influence of other simultaneously occurring reactions is so overwhelming that this i-th reaction proceeds in a direction opposite to that dictated by its own driving force $\Lambda_i$.

For example, from the definition of coupling factor (Eq. (3.31)), $\xi_2$ for the pseudo-ternary system under consideration which consists of ideal solutions may be written as follows:

$$\xi_2 = \frac{z_1^2 k_1 C_1 (1 - \frac{z}{z_1} \frac{\Lambda_1}{\Lambda_2})}{z_1^2 k_1 C_1 + z_2^2 k_2 C_2 + z_3^2 k_3 C_3} + \frac{z_3^2 k_3 C_3 (1 - \frac{z}{z_3} \frac{\Lambda_3}{\Lambda_2})}{z_1^2 k_1 C_1 + z_2^2 k_2 C_2 + z_3^2 k_3 C_3}$$

$$= \xi_1 + \xi_3$$ (6.1)

The signs of $\frac{z_i}{z_j} \frac{\Lambda_j}{\Lambda_i}$ depends on the characteristics of the coupled reactions and its magnitude varies mainly due to $\frac{\Lambda_j}{\Lambda_i}$. It is easy to see that the weakest reaction which has the smallest value of $|\Lambda_i|$ would have a value $\xi_i$ farthest away from unity, provided that the ability to carry the electric current $z_i k_i C_i$ is not insignificant.

That is to say, even though the coupling between two reactions are of the same magnitude in the absolute value, the net effect on rate of individual reactions may be different. The mutual effect of two reactions that the
the same order of magnitude is also interesting. The rate of the stronger reaction may be altered less, i.e., the coupling factor for the stronger one is closed to unity.

In the present analysis in its relation to reaction (2) which is the weaker one, reactions (1) and (3) both satisfy this description as the dominating reaction as shown in Fig. (5.22). The contribution of reaction (1) to $i_2, \theta_{21}$ is positive and that of reaction (3) to $i_2, \theta_{23}$, is negative at least at the beginning of the reactions.

The up-hill reaction shown in Fig. (5.5) and Fig. (5.8) for reaction (2) is certainly due to reaction 3. In order to illustrate the points mentioned above, as an example, the interfacial concentrations, $\theta_{21}$, $\theta_{23}$ and $i_2$ of system D are listed in Table 6.1.

In order to see the cooperative and competitive coupling, without reversal of reaction, in which all coupling factors are positive, the systems F and G are analysed with the same thermodynamic and kinetic parameters except $k_3$ (see Table 5.2).

Since systems F and G have different values of $k_3$, it is certain that the value of $\omega_3$ will also be different. In addition to this, $\omega_1$ and $\omega_2$ should also be different for
<table>
<thead>
<tr>
<th>TIME (SEC)</th>
<th>$C_1$</th>
<th>$C_2$</th>
<th>$C_3$</th>
<th>$C_4$</th>
<th>$C_5$</th>
<th>$C_6$</th>
<th>$C_7$</th>
<th>$C_8$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0</td>
<td>0.200</td>
<td>0.200</td>
<td>0.600</td>
<td>0.100</td>
<td>0.200</td>
<td>0.200</td>
<td>0.397</td>
<td>0.225</td>
</tr>
<tr>
<td>1.0</td>
<td>0.190</td>
<td>0.190</td>
<td>0.612</td>
<td>0.152</td>
<td>0.220</td>
<td>0.128</td>
<td>0.238</td>
<td>0.003</td>
</tr>
<tr>
<td>2.0</td>
<td>0.184</td>
<td>0.197</td>
<td>0.619</td>
<td>0.167</td>
<td>0.222</td>
<td>0.111</td>
<td>0.208</td>
<td>0.609</td>
</tr>
<tr>
<td>3.0</td>
<td>0.179</td>
<td>0.197</td>
<td>0.624</td>
<td>0.177</td>
<td>0.222</td>
<td>0.101</td>
<td>0.199</td>
<td>0.436</td>
</tr>
<tr>
<td>4.0</td>
<td>0.175</td>
<td>0.196</td>
<td>0.626</td>
<td>0.186</td>
<td>0.220</td>
<td>0.094</td>
<td>0.175</td>
<td>0.303</td>
</tr>
<tr>
<td>5.0</td>
<td>0.171</td>
<td>0.196</td>
<td>0.633</td>
<td>0.194</td>
<td>0.218</td>
<td>0.088</td>
<td>0.164</td>
<td>0.191</td>
</tr>
<tr>
<td>6.0</td>
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<td>0.196</td>
<td>0.637</td>
<td>0.201</td>
<td>0.216</td>
<td>0.082</td>
<td>0.154</td>
<td>0.093</td>
</tr>
<tr>
<td>7.0</td>
<td>0.164</td>
<td>0.197</td>
<td>0.640</td>
<td>0.208</td>
<td>0.214</td>
<td>0.078</td>
<td>0.147</td>
<td>0.006</td>
</tr>
<tr>
<td>8.0</td>
<td>0.161</td>
<td>0.197</td>
<td>0.643</td>
<td>0.213</td>
<td>0.212</td>
<td>0.074</td>
<td>0.140</td>
<td>0.070</td>
</tr>
<tr>
<td>9.0</td>
<td>0.158</td>
<td>0.197</td>
<td>0.645</td>
<td>0.219</td>
<td>0.210</td>
<td>0.071</td>
<td>0.134</td>
<td>0.133</td>
</tr>
<tr>
<td>10.0</td>
<td>0.156</td>
<td>0.198</td>
<td>0.647</td>
<td>0.223</td>
<td>0.208</td>
<td>0.069</td>
<td>0.129</td>
<td>0.200</td>
</tr>
</tbody>
</table>

Table 6.1 The Evolution of Interfacial Concentrations and Coupling Factors in System D
F and G, even though both \( k_1 \) and \( k_2 \) are the same in each system, because of coupling. Since the coupling between reaction (1) and (3) is cooperative and that between reaction (2) and (3) is competitive, coupling factor \( f_1 \) would decrease and \( f_2 \) would increase if \( k_3 \) decreases.

The shift from system F to G by halving the value of \( k_3 \) yields the reduction of \( f_1 \) and the increase of \( f_2 \), so reaction 1 is faster and reaction 2 is slower in system F than in system G as shown in Fig. 6.1. In this figure, normalized interfacial concentrations are used, which are defined by Eq. (6.2), in order to compare the progress of individual reactions with respect to each other.

\[
\bar{C}_1 = \frac{C_1(t=\tau) - C_1(t=0)}{C_1(t=\infty) - C_1(t=0)}
\]

where \( 0 < \bar{C}_1 < 1 \).

6.2 **Coupled Diffusion in Slag Phase**

There is no concentration gradient in either slag or metal phase initially, before the commencement of slag-metal reactions. The diffusional field is induced and maintained by interfacial reactions. The presence of up-hill diffusion is generally accepted as undisputable evidence of coupling among diffusional fluxes.
Fig. 6.1 Comparison of normalized concentrations between system F and G, where $I_{1,2}^F$ in system F are equal to $I_{1,2}^G$ in system G.
As an example, the results of system B will be discussed. Fig. 5.5 shows that in every profile in the slag phase except in line (4), there is an up-hill diffusion (up-hill region is shown below).

For line (1); \( t = 0.008 \text{ sec.}, \ 0.09 < x < 0.20 \text{ mm.} \)
For line (2); \( t = 0.024 \text{ sec.}, \ 0 < x < 0.09 \text{ mm.} \)
For line (3); \( t = 0.080 \text{ sec.}, \ 0 < x < 0.15 \text{ mm.} \)

Among the three up-hill diffusions, there are two different types. One of them does not involve the interfacial reaction directly, but the others do in such a way that the reversal of the direction of the interfacial reaction results in a flow against the concentration gradient. Line (1) corresponds to the former case and lines (2) and (3) correspond to the latter case. Since there is an up-hill reaction for component (2), in a short period \( (0 < t < 0.01 \text{ sec.}) \), its concentration builds up near the slag interface. After this period the up-hill reaction ceases and down-hill reaction starts while the concentration build-up remains. Therefore in this stage there must be up-hill diffusion.

Even without an up-hill reaction, up-hill diffusion could be observed when the concentration gradient of that component is smaller than others. For instance, one can see the up-hill diffusion of component (2) in systems F and G (Fig. (5.17) and (5.20)).
In both systems \( t_2 \) is positive, so there is no up-hill reaction at the interface, however there is up-hill diffusion as follows:

In system F, for line (1) \( 0 < x < 0.035 \) (mm),

for line (2) \( 0 < x < 0.090 \) (mm).

In system G, for line (2) \( 0 < x < 0.100 \) (mm),

for line (3) \( 0 < x < 0.100 \) (mm).

Basic argument for ionic diffusion can be done in terms of ionic diffusion coupling factor \( \zeta_i \) for individual components.

The coupling factor \( \zeta_i \) is,

\[
\zeta_i = 1 - \frac{\sum_j z_j z_i c_i D_j \frac{\partial c_j}{\partial x}}{\sum_j z_j^2 D_j c_j}
\]  \hspace{1cm} (3.12)

In the present analysis, since \( |\Lambda_1| \sim |\Lambda_3| >> |\Lambda_2| \) and \( |\omega_1| \sim |\omega_3| >> |\omega_2| \) for most of the reaction time, the transfer of component 2 should be generally small both in bulk phases and at the interface. This means that in the slag bulk phase the following relationship may exist when the product \( c_i D_i \) are not very different one from the other,

\[
\left| \frac{\partial c_1}{\partial x} \right| \sim \left| \frac{\partial c_3}{\partial x} \right| >> \left| \frac{\partial c_2}{\partial x} \right|
\]

in an appreciable region in the slag phase except near the open end of the phase. Therefore \( \zeta_2 \) could have negative value but \( \zeta_1 \) and \( \zeta_3 \) should be positive and close to unity.
6.3 **Considerations on the Rate Controlling Step**

As shown in Fig. 5.22, the shape of the concentration profile differs from system to system. It should be pointed out that the flatness of the profile depends on the value of $k_1/D_1^S$ because it is a reasonable measure of the relative intrinsic capability of chemical reaction and diffusion to result in fluxes responding to the externally-imposed driving forces, provided the molar densities of slag and metal and the size of the specimen do not change during the course of reaction. It is certain that if the ratio, $k_1/D_1^S$, increases, ionic diffusion process contributes more resistance to the overall system. In the extreme case in which the ratio is exceedingly large, the overall reaction kinetics is essentially rate controlled by the diffusion process in the slag phase. On the other hand when the ratio decreases interfacial reaction gains its importance, the extreme case of this is the interfacial reaction rate control scheme.

The ratio $k_1/D_1^S$ has a dimension which may be identified in the following way:

$$\frac{k_1}{D_1^S} = \frac{\text{mol}}{\text{cm}^2 \text{sec}} \cdot \frac{\text{cm}^2}{\text{sec}} = \frac{\text{mol}}{\text{cm}^4}$$

If one takes a characteristic length $L_s$ which is a slag phase thickness in the present one dimensional system, modified Sherwood Number for slag phase mass transfer is
introduced here with taking the molar density into the consideration:

\[ \frac{\dot{V}_1}{L_s} \cdot \frac{L_s}{D_1} \cdot \frac{[\text{mol}]}{[\text{cm}^2 \cdot \text{cm}]} = [1] \quad (6.3) \]

For a general discussion about the rate controlling step this modified Sherwood Number should be taken into considerations. The modified Sherwood Number for metallic phase can also be defined as follows:

\[ Sh^*_m = \frac{\dot{V}_1}{L_m} \cdot \frac{L_m}{D_1} \cdot \frac{[\text{mol}]}{[\text{cm}^2 \cdot \text{cm}]} \quad (6.4) \]

Since generally \( Sh^*_m < Sh^*_s \), \( Sh^*_s \) is important to describe the general features of slag-metal reaction kinetics.

In the present analysis these numbers vary as follows:

\[ 5.0 \times 10^{-2} < Sh^*_s < 3.6 \times 10^2, \]

\[ 4 \times 10^{-3} < Sh^*_m < 1.5 \times 10^3 \]

From Fig. 5.22 with this consideration one could conclude that in slag-metal diffusion and reaction kinetics of iron and steelmaking systems, if

\[ Sh^*_s > 3.6 \times 10^2 \text{ (system A-3) } \]
the kinetic system can be considered to be essentially controlled by the diffusion in the slag phase as shown in Fig. 5.3, on the other hand, if

\[ \text{Sh}^* = 5.0 \times 10^{-2} \text{ (system L-1)} \]

the overall rate of reaction can be considered to be essentially controlled by interfacial reaction as shown in Fig. 5.13. The modified Sherwood Number could be named as the Damköhler Number, Da, as suggested by Rudolf Jeschar (Kinetics of Metallurgical Processes in Steelmaking, edited by W. Dahl et. al.).

6.4 Physical Significance of the Calculated Results

As mentioned in the literature review, the conventional theory of slag-metal reaction kinetics does not properly take the multiple reactions into their consideration. Multi-component coupled diffusion process has been theoretically investigated\(^{(24,25)}\) and the theory has been experimentally confirmed\(^{(25)}\). The combined kinetics of the interfacial reaction and the diffusion processes has been formulated by Lu' and Okongwu\(^{(3,25)}\) but never been solved except in pseudo-binary systems\(^{(3)}\). In pseudo-binary systems, coupling features such as reaction acceleration, deceleration and up-hill reaction, or up-hill diffusion are not expected to be seen.

Through the investigation of theoretical formalisms in the kinetics of slag-metal reactions, two coupling factors, i.e., \( \xi \) and \( \zeta \) are introduced in the present work. Former is
for chemical reaction and the latter is for diffusion process. Those coupling factors have made it clear to illustrate the existence of reaction acceleration, deceleration, up-hill reactions and up-hill diffusions semiquantitatively based on the initial conditions.

However, it would be very difficult to see the details of the coupling phenomena and the contributions to the control of overall rate by various steps at different reaction times in the absence of solutions.

In this work, pseudo-ternary systems are selected as the simplest but meaningful systems to investigate theoretically the simultaneous slag-metal interfacial reactions inco- operated with simultaneous metallic and ionic diffusions. Numerical solutions of a set of properly formulated equations have been obtained for a kinetic system of slag-metal reaction for the first time.

The results have clarified the features of (1) coupled interfacial reactions such as reaction acceleration, deceleration and up-hill reaction and (2) coupled ionic diffusion such as diffusion acceleration, deceleration and up-hill diffusion and (3) the reaction-diffusion combined effect in which relative contributions of the electro-chemical reactions and mass
transport in both phases to the over-all reaction rate are to be seen.

Even though numerical results have shown several features of slag-metal kinetics theoretically, there will be no attempt to make the comparison of experimental data in the literature and the results of the present work. Since this was the first attempt to obtain the solution of a set of properly formulated equations, there was not enough experimental facts to make an adequate calculation for the comparison with the experiment. In order to simplify the system to carry out theoretical calculation, the following were assumed; (1) slag and metal phases both behave as ideal solutions, (2) combination of ionic species whose valencies are such as \( Z_1 = Z_2 = Z_3 = -Z_4 = 2 \) may exist, (3) the fourth ionic specy is immobile. Those assumptions should be corrected to obtain more realistic solution in future, however at present it seems to be significant to obtain some solutions of this problem in order to have some ideas of the coupled reaction kinetics.

In addition to those assumptions, there is another kind of limitations in the present results due to the choice of the values of the parameters. In the investigated systems, from A to G, all the kinetic, thermodynamic and geometrical parameters are fixed except the anodic rate constant. Among
those parameters, geometrical or dimensional parameters is
considered to be very influential to the solutions for the
systems with same kinetic and thermodynamics constants.

When the systems with different dimensions are to
be compared, it becomes a basic desire to see the dynamic
similarity among the behavior of different systems. Since
combinations of dimensional, kinetic parameters with respect
to some thermodynamical parameters, could yield too numerous
systems to seek all the solutions of those system kinetics,
the dynamic similarity is desirable to obtain.

Therefore, in the following, an attempt will be made
to pursue the criteria for the dynamic similarity among
slag-metal systems. In the usual dimensional analysis,
thetical equations are to be made dimensionless by the
introduction of characteristic length and time and of dimen-
sionless groups such as Reynolds number, Schmidt number and
so on.

The fundamental difficulty for the dimensional
analysis in the present study lies in the complexity of the
theoretical equations which seems to defy the introduction
of dimensionless quantities.
In the previous section it is indicated that the modified Sherwood number may serve as a criteria to determine the rate controlling step for the slag-metal reaction kinetics.

If the diffusion process can be described by the following simple equation,
\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}
\]  
(6.4)
such non-dimensional distance and time as
\[
x = \frac{x}{x_o},
\tau = \frac{Dt}{x_o^2}
\]  
(6.5)
where \(x_o\) is a characteristic length of the system, can be introduced to yield a non-dimensional diffusion equation as follows,
\[
\frac{\partial C}{\partial \tau} = \frac{\partial^2 C}{\partial \chi^2}
\]  
(6.6)
Therefore, as long as the initial and boundary conditions are maintained, the solution of the Eq. (6.6) is unique, so the system can be described by this equation and a characteristic length \(x_o\).

For a general multiple component system, however, Eq. (6.4) is not expected to represent the diffusional phenomena exactly. Even then, since the diffusivities of any
CHAPTER 7
CONCLUDING REMARKS

First of all, it should be stated that this work is the first numerical solutions of the equations for the kinetics of multiple-component slag-metal systems. The interfacial reactions serve a part of boundary conditions for diffusion in both phases. In the present work, 7 pseudo-ternary systems are numerically analysed and the following conclusions may be reached:

(1) Coupling factor $\xi_1$ for $i$-th electroodic reaction which is defined in the present work, clarifies the influence due to the presence of other reactions and may be used to predict the resultant effect such as: (a) acceleration of the $i$-th reaction ($\xi_1 > 1.0$) (b) deceleration ($0 < \xi_1 < 1.0$) and (c) up-hill reaction ($\xi_1 < 0$).

(2) Diffusion coupling factor $\zeta_1$ for $i$-th component which is defined in the present work clarifies the influence of other simultaneous diffusional fluxes of ionic species and may be used to predict the resultant
effect such as: (a) acceleration of the \(i\)-th diffusional flux \( \psi_i \), 1.0) (b) deceleration \( \psi_i \), 1.0) and (c) up-hill diffusion \( \psi_i \), 0).

(3) The modified Sherwood Number for slag phase, 
\[
\text{Sh}_S^* = \frac{k^{*}_{S} L_S}{D_S^{*}}
\]
could serve as a measure to estimate the rate controlling step as follows:

- \( \text{Sh}_S^* \geq 360 \): diffusion control,
- \( 0.05 \leq \text{Sh}_S^* < 360 \): mixed control,
- \( \text{Sh}_S^* < 0.05 \): interfacial electro-chemical reaction control.

(4) The variation of interfacial concentrations with time relates to the modified Sherwood Number. The interfacial reactions are further from their equilibrium state and the interfacial concentrations change faster with time when the \( \text{Sh}_S^* \) is smaller and vice versa.

(5) Further advance in the studies of kinetics of slag-metal reactions; at present stage of development would be promoted by experimental measurements of \( k^*_{S} \) by isotope exchanges, carefully planned slag-metal experiments and improvements in mathematical modelling.
References


(6) S. Ramachandran, T.B. King, N.J. Grant: Trans. AIME, 266, p. 1549 (1956).


(33) Fontana and Greene: Corrosion Engineering, p. 309.
Appendix

In this appendix, one of the computer programs which is used in the present work is attached and a list of nomenclatures in the program is also attached.
PROGRAM TST (INPUT,OUTPUT,TAPE1=INPUT,TAPE6=OUTPUT)

NUMERICAL SOLUTION OF COUPLED DIFFUSION EQUATIONS FOR A PSEUDO-
TERNARY SLAG/METAL SYSTEM BY A FINITE DIFFERENCE METHOD

10 COMMON (C15/5001,C21/5001,C31/5001,
C12/1000,C22/1000,C32/1000),
C1/1000,C2/1000,C3/1000),
CH1(1000),CH2(1000),CH3(1000),
CM1(500),CM2(500),CM3(500),
CM1(1000),CM2(1000),CM3(1000),
CM1(1000),CM2(1000),CM3(1000),
CM1(1000),CM2(1000),CM3(1000),
CH1(1000),CH2(1000),CH3(1000),
TH3(1000),TH4(1000)

30 READ(5,10) LIMIT,IELT,KK1,KK2
READ(5,12) XI,DELTAX,DELTA
READ(5,14) ED12,ED13,ED21,ED23
READ(5,16) D01,D02,D03,D04
READ(5,18) DELTA,DELTA
READ(5,11) MDEN1,MDEN2
READ(5,19) LSPEC

10 INDEX FOR THE INTERFACE, LE=LHJ INDEX FOR THE SYSTEM SO THAT 1 TO L
IS THE SOFT SLAG, THE SIZE OF BOTH PHASES IS NOT RESOLV-
ABLE EQUAL EACH OTHER

20 LIMIT=COMPUTATIONAL TIME LIMIT,INDEX,KK=PRINT OUT FREQUENCY INDEX

30 I=COMPUTATIONAL TIME STEP INDEX

40 J=EXCHANGE REACTION RATE

50 DENS1=DENS2 DENSITY TOTAL ATOM OR ION NUMBERS PER UNIT VOLUME)

60 WRITE(6,10) LE,LIMIT,IELT,KK1,KK2
WRITE(6,12) XI,DELTAX,DELTA
WRITE(6,14) MDEN1,MDEN2,DELTA,DELTA

70 EQUIL=100/(DELTAX**2)

80 REAL-1

90 REAL-2

100 REAL-3
CALCULATE THE INTERFACIAL ELECTRO-CHEMICAL REACTION FLUXES.
WHERE DIMENSION ARE (ATOMS OR IONS/CH--2/SEC).

115 1601 CONTINUE

120 1601 CONTINUE

125 1601 CONTINUE

130 1601 CONTINUE

135 1601 CONTINUE

140 1601 CONTINUE

145 1601 CONTINUE

150 1601 CONTINUE

155 1601 CONTINUE

160 1601 CONTINUE

165 1601 CONTINUE

170 1601 CONTINUE

175 1601 CONTINUE

180 1601 CONTINUE

185 1601 CONTINUE

190 1601 CONTINUE

195 1601 CONTINUE

200 1601 CONTINUE

205 1601 CONTINUE

210 1601 CONTINUE

215 1601 CONTINUE

220 1601 CONTINUE

225 1601 CONTINUE

230 1601 CONTINUE

235 1601 CONTINUE

240 1601 CONTINUE

245 1601 CONTINUE

250 1601 CONTINUE

255 1601 CONTINUE

260 1601 CONTINUE

265 1601 CONTINUE

270 1601 CONTINUE

275 1601 CONTINUE

280 1601 CONTINUE

285 1601 CONTINUE

290 1601 CONTINUE

295 1601 CONTINUE

300 1601 CONTINUE

305 1601 CONTINUE

310 1601 CONTINUE

315 1601 CONTINUE

320 1601 CONTINUE

325 1601 CONTINUE

330 1601 CONTINUE

335 1601 CONTINUE

340 1601 CONTINUE

345 1601 CONTINUE

350 1601 CONTINUE

355 1601 CONTINUE

360 1601 CONTINUE

365 1601 CONTINUE

370 1601 CONTINUE

375 1601 CONTINUE

380 1601 CONTINUE

385 1601 CONTINUE

390 1601 CONTINUE

395 1601 CONTINUE

400 1601 CONTINUE

405 1601 CONTINUE

410 1601 CONTINUE
L1 = LE-1
L2 = LE-2
L3 = LE-3

SPECIFY THE INITIAL CONDITIONS FOR THE SYSTEM

DO 100 J = 1, L
C1(J) = C140
C2(J) = C240
C3(J) = C340

100 CONTINUE
J = J + 1
C1(J) = C150
C2(J) = C250
C3(J) = C350

101 CONTINUE

SPECIFY THE LOCATION VARIABLE

X(1) = 0,
JC 102 J = 2, L
X(J) = DELTAX * FLCAT(J - 1)

102 CONTINUE

SET IS CALCULATED INSIDE THE II LOOP BECAUSE IT IS TIME DEPENDENT

T = T + DE/2

103 CONTINUE

T = T + DE/2

104 CONTINUE

START COMPUTING THE CONCENTRATION DISTRIBUTIONS FOR BOTH PHASES

IT = 1
105 CONTINUE

T = T + DE/2

110 CONTINUE

IT = IT + 1
175

\[ C_t(J) = \text{C}_1S_1(J) - \text{C}_1S_1(J-1) \]
\[ C_{t+1}(J) = \text{C}_1S_1(J+1) - \text{C}_1S_1(J) \]
\[ C_{t+2}(J) = \text{C}_1S_1(J+2) - \text{C}_1S_1(J) \]

180

\[ \text{CO} = \text{C}_1S_1(J+1) + \text{C}_1S_1(J) + \text{C}_1S_1(J-1) \]
\[ \text{CD} = \text{C}_1S_1(J+1) + \text{C}_1S_1(J) - \text{C}_1S_1(J-1) \]

185

**CONTINUE**

\[ \text{C} = \text{C}_1S_1(J) \]

190

**CONTINUE**

**CALCULATE THE CONCENTRATION DISTRIBUTIONS AT TIME \( t + 2 \)** IN BOTH PHASES BASED ON THE CONCENTRATIONS AT TIME \( t \).

**METALIC PHASE**

\[ C_{105} = 0.2 \text{I}_4 \]
\[ C_{105}(J) = C_{105}(J) + \text{C}_1S_2(J) + \text{C}_1S_2(J) \]
\[ C_{105}(J) = C_{105}(J) + \text{C}_2S_2(J) + \text{C}_2S_2(J) \]

**CONTINUE**

**JOINT JAIY VALUES FOR METALIC PHASE**

\[ C_{202}(J) = \text{C}_2S_2(J) + \text{C}_2S_2(J) \]
\[ C_{202}(J) = \text{C}_2S_2(J) + \text{C}_2S_2(J) \]

**CONTINUE**

**SLAG PHASE**

\[ C_{210} = \text{SL}_S \]
\[ C_{210}(J) = C_{210}(J) + \text{C}_1S_2(J) + \text{C}_1S_2(J) \]
\[ C_{210}(J) = C_{210}(J) + \text{C}_2S_2(J) + \text{C}_2S_2(J) \]

**CONTINUE**

**JOINT JAIY VALUES FOR SLAG PHASE**

\[ C_{220} = \text{SL}_S \]
\[ C_{220}(J) = C_{220}(J) + \text{C}_1S_2(J) + \text{C}_1S_2(J) \]
\[ C_{220}(J) = C_{220}(J) + \text{C}_2S_2(J) + \text{C}_2S_2(J) \]

**CONTINUE**

\[ C_{220}(J) = C_{220}(J) + \text{C}_1S_2(J) + \text{C}_1S_2(J) \]
\[ C_{220}(J) = C_{220}(J) + \text{C}_2S_2(J) + \text{C}_2S_2(J) \]
CALCULATE THE ELECTRO-CHEMICAL AND THE CHEMICAL AFFINITIES
AND THE ELECTRIC POTENTIAL DIFFERENCE AT THE INTERFACE
FOR METAL IN VOLT AT 1600 DEGREES C.

IF (I.EQ.1 .AND. J.EQ.0) GO TO 2349

LCAF3 = (X1/(X1*X1))*R1
LCAF2 = (X2/(X2*X2))*R1
LCAF1 = (X3/(X3*X3))*R1

(1) = LCAF3
(2) = LCAF2
(3) = LCAF1

IF (I.EQ.1) THEN

WRITE (6,333) LCAF1, LCAF2, LCAF3
WRITE (8,693) AFFIN1, AFFIN2, AFFIN3
WRITE (8,693) AFFIN1, AFFIN2, AFFIN3

CONTINUE

COMPUTE THE SPACE AVERAGE ***** METAL *****

COMPUTE THE SPACE AVERAGE ***** SLAG *****
150, 3.140, *DELTA T = +3E-10, 3.180, *DELTA X = +1DE-10, 3.170
100 = CX-T(14), 1X-1502, 3, 3.7214X*, 3.18X*, ADD2X, 3.15X*, AVG1*, 3.13X*, AVG2*, 3.12X*,
1.9Y, 1.8Y, 1.7Y, 1.6Y, 1.5Y, 1.4Y, 1.3Y, 1.2Y, 1.1Y, 1.0Y, 0.9Y, 0.8Y, 0.7Y, 0.6Y, 0.5Y, 0.4Y, 0.3Y,
1.2X, 1.1X, 1.0X, 0.9X, 0.8X, 0.7X, 0.6X, 0.5X, 0.4X, 0.3X, 0.2X, 0.1X, 0.0X, *C1S(J)*, *C2S(J)*,
1.35X*, 1.25X*, 1.15X*, 1.05X*, 0.95X*, 0.85X*, 0.75X*, 0.65X*, 0.55X*, 0.45X*, 0.35X*, 0.25X*, 0.15X*,
0.05X*, 0.0X, 0.1X, 0.2X, 0.3X, 0.4X, 0.5X, 0.6X, 0.7X, 0.8X, 0.9X, 1.0X, 1.1X, 1.2X, 1.3X, 1.4X,
1.5X, 1.6X, 1.7X, 1.8X, 1.9X, 2.0X, 2.1X, 2.2X, 2.3X, 2.4X, 2.5X, 2.6X, 2.7X, 2.8X, 2.9X, 3.0X,
3.1X, 3.2X, 3.3X, 3.4X, 3.5X, 3.6X, 3.7X, 3.8X, 3.9X, 4.0X, 4.1X, 4.2X, 4.3X, 4.4X, 4.5X, 4.6X,
4.7X, 4.8X, 4.9X, 5.0X, 5.1X, 5.2X, 5.3X, 5.4X, 5.5X, 5.6X, 5.7X, 5.8X, 5.9X, 6.0X, 6.1X, 6.2X,
6.3X, 6.4X, 6.5X, 6.6X, 6.7X, 6.8X, 6.9X, 7.0X, 7.1X, 7.2X, 7.3X, 7.4X, 7.5X, 7.6X, 7.7X, 7.8X,
7.9X, 8.0X, 8.1X, 8.2X, 8.3X, 8.4X, 8.5X, 8.6X, 8.7X, 8.8X, 8.9X, 9.0X, 9.1X, 9.2X, 9.3X, 9.4X,
9.5X, 9.6X, 9.7X, 9.8X, 9.9X, 10.0, 10.1, 10.2, 10.3, 10.4, 10.5, 10.6, 10.7, 10.8, 10.9, 11.0, 11.1,
11.2, 11.3, 11.4, 11.5, 11.6, 11.7, 11.8, 11.9, 12.0, 12.1, 12.2, 12.3, 12.4, 12.5, 12.6, 12.7, 12.8,
14.6, 14.7, 14.8, 14.9, 15.0, 15.1, 15.2, 15.3, 15.4, 15.5, 15.6, 15.7, 15.8, 15.9, 16.0, 16.1, 16.2,
16.3, 16.4, 16.5, 16.6, 16.7, 16.8, 16.9, 17.0, 17.1, 17.2, 17.3, 17.4, 17.5, 17.6, 17.7, 17.8, 17.9,
18.0, 18.1, 18.2, 18.3, 18.4, 18.5, 18.6, 18.7, 18.8, 18.9, 19.0, 19.1, 19.2, 19.3, 19.4, 19.5, 19.6,
21.4, 21.5, 21.6, 21.7, 21.8, 21.9, 22.0, 22.1, 22.2, 22.3, 22.4, 22.5, 22.6, 22.7, 22.8, 22.9, 23.0,
23.1, 23.2, 23.3, 23.4, 23.5, 23.6, 23.7, 23.8, 23.9, 24.0, 24.1, 24.2, 24.3, 24.4, 24.5, 24.6, 24.7,
26.5, 26.6, 26.7, 26.8, 26.9, 27.0, 27.1, 27.2, 27.3, 27.4, 27.5, 27.6, 27.7, 27.8, 27.9, 28.0, 28.1,
28.2, 28.3, 28.4, 28.5, 28.6, 28.7, 28.8, 28.9, 29.0, 29.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8,
FUNCTION F(Y,K,PAR)
DIMENSION Y(I)
IR=1,0
FTP=7.3
GOTO (1,1,1,1,
1 F=(B12*(Z2*Y(1)-Z1*Y(2))+B13*(Z3*Y(1)-Z1*Y(3)))/FTP-W1
2 RETURN
3 F=(B11*(Z1*Y(2)-Z2*Y(1))+B23*(Z3*Y(2)-Z2*Y(3)))/FTP-W2
4 RETURN
5 F=(B11*(Z1*Y(3)-Z3*Y(1))+B32*(Z2*Y(3)-Z3*Y(2)))/FTP-W3
6 RETURN
7 END
NOMENCLATURE IN COMPUTER PROGRAM

\( \Delta t/(\Delta x)^2 \)

\( \text{AFFM}_i \) CHEMICAL AFFINITY FOR REACTION \( i \)

\( \text{AVCMI}_1 \) SPACE AVERAGE OF \( \text{CiM}_1 \)

\( \text{AVCMI}_2 \) SPACE AVERAGE OF \( \text{CiM}_2 \)

\( \text{AVCIS}_1 \) SPACE AVERAGE OF \( \text{CiS}_1 \)

\( \text{AVCIS}_2 \) SPACE AVERAGE OF \( \text{CiS}_2 \)

\( \text{CiM}_0 \) INITIAL CONCENTRATION OF METALLIC COMPONENT \( i \)

\( \text{CiS}_0 \) INITIAL CONCENTRATION OF SLAG COMPONENT \( i \)

\( \text{CiM}_1 \) CONCENTRATION OF METALLIC COMPONENT \( i \) AT \( t = t \)

\( \text{CiM}_2 \) CONCENTRATION OF METALLIC COMPONENT \( i \) AT \( t = t + \Delta t \)

\( \text{CiS}_1 \) CONCENTRATION OF SLAG COMPONENT \( i \) AT \( t = t \)

\( \text{CiS}_2 \) CONCENTRATION OF SLAG COMPONENT \( i \) AT \( t = t + \Delta t \)

\( \text{Bij} \) TRANSMISSION COEFFICIENT

\( \text{DELFAI} \) \( \Delta \phi \), POTENTIAL DIFFERENCE ACROSS METAL TO SLAG

\( \text{DELTAX} \) \( \Delta x \) (CM.)

\( \text{DELTAT} \) \( \Delta t \) (SEC.)

\( \text{DMij} \) \( D_{ij} \) IN METAL

\( \text{DSi} \) \( D_i \) IN SLAG

\( \text{ELCAFI} \) ELECTRO-CHEMICAL AFFINITY OF REACTION \( i/j \)

\( \text{EQKij} \) PAIR EQUILIBRIUM CONSTANT \( K_{ij} \)

\( \text{LIMIT} \) CALCULATION LIMIT INDEX

\( \text{RI} \) \( k_i \), ANODIC REACTION RATE CONSTANT FOR REACTION \( i \)
SDENSI \( \omega_s \), MOLAR DENSITY OF SLAG
MDENSI \( \rho_M \), MOLAR DENSITY OF METAL
\( \omega_i \), ELECTRO CHEMICAL REACTION RATE
ZSYSTM McMaster Library Sub-Routine