Physicochemical Aspects of Reactions in Ironmaking and Steelmaking Processes

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Synopsis
This is a critical review of the physical chemistry of selected aspects of ironmaking and steelmaking processes. The equilibrium data from gas-slag-metal reactions are presented in a form suitable for easy application in the study of the state of reactions in ironmaking and steelmaking. Plant data indicate departures from equilibrium for most reactions in the blast-furnace bath and hearth. In steelmaking, most reactions are close to equilibrium at the time of furnace tapping. Comments are made on reaction equilibria in relation to the ladle refining of hot metal. A summary is made of new equilibrium data for desulfurization of liquid steel with calcium aluminate slags. Various examples are given of the role of vapor species in pyrometallurgical processes, e.g., silicon- and sulfur-bearing species and alkali cyanide vapors in the blast furnace, causes of fume emission during furnace tapping, and consequences of fume emission in coal gasification using liquid iron as the reaction medium.

I. Introduction
Studies of the physical chemistry of gas-slag-metal reactions and measurements of the physicochemical and thermochemical properties of materials pertinent to ironmaking and steelmaking processes have gone through many interesting stages of evolution during the past six decades or more. The first textbook written on the physical chemistry of steelmaking was the classical work by Schenck, "Einführung in die Physikalische Chemie der Eisenhüttenprozesse," published in the years 1932 and 1934. Related English translation of this book in 1945 was of much value to steelmakers in many countries and stimulated the birth of a new era of research on the physical chemistry of metallurgical reactions. The symposium on physical chemistry organized by the Faraday Society in 1948 set the main theme of research for the subsequent two decades on the fundamentals of pyrometallurgical processes.

Accumulated knowledge of the physical chemistry of gas-slag-metal reactions and the physicochemical properties of solid and liquid metallic solutions, molten slags, and refractory materials have been critically assessed and compiled by Kubaschewski and Alcock, Richardson, and Turkdogan. These reference books are used for the background scientific and technical information in the preparation of the present paper.

Upon kind invitation by the Iron and Steel Institute of Japan, a critical assessment is presented in this paper of some aspects of the present state of knowledge of the physicochemical aspects of ironmaking and steelmaking processes. For the paper to be technically comprehensive, the subject of discussion is confined to a few selected topics of process metallurgy in ironmaking and steelmaking that are of current interest:

1. General Considerations
Gas-slag and metal-slag reactions are redox reactions which are accompanied by exchange of electrons between the reacting species as they are transferred to and from nonpolar gaseous or metallic phase and ionic molten slag. For example, the transfer of sulfur from metal to slag is a reduction reaction involving exchange of electrons between sulfur and oxygen atoms:

\[ S + (O^{2-}) = O^+ + (S^{2-}) \]  \hspace{1cm} (1)

where underscore indicates solute in solution in the metal and ( ) species dissolved in the slag. In most cases, the transfer of a reactant from metal to slag is an oxidation process, such as:

\[ P^{5+} + \frac{5}{2} O + \frac{3}{2} (O^{2-}) = (POI^+)^{3+} \]  \hspace{1cm} (2)

Although the reactions as formulated above are conceptually correct, their equilibrium constants cannot be evaluated because the thermodynamic activity or activity coefficient of an individual ion cannot be determined experimentally. However, numerous attempts have been made in the past, following the work of Herasymenko, to represent the equilibrium constants of slag–metal reactions in terms of assumed ionic concentrations. Although the derivation of reaction equilibrium relations from the ionic structural models are of theoretical interest, their application to gas-slag–metal reaction equilibria in multicomponent systems has not been particularly rewarding when compared with the conventional methods of representing the reaction equilibria in terms of the measured thermodynamic quantities.

The solution models of slags, either constitutional or structural, have been much exploited in pursuit of a rationale for the composition dependence of the activity of constituent oxides in slags. No matter what major differences there might be between assumed solution models, they all yield activity vs. composition relations in reasonable agreement with the same set of data for binary and ternary silicate melts, because of the empirically adjustable parameters involved in

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the formulations. However, although the solution models may be fictitious, the formalisms derived therefrom are helpful in the extrapolation of data to other composition ranges. For example, Ban-ya et al$^{11,12}$ have shown that the composition dependence of the activity coefficient of ferrous oxide in complex silicate and phosphate melts can be represented by an empirical formalism based on the regular solution model for polymeric melts proposed by Lumsden.$^{13}$

Because of lack of activity data for complex slags and limited applicability of empirical solution models, the slag–metal equilibrium relations are often represented in terms of the concentrations of reactants and products by adopting the mass-action law. The isothermal equilibrium constant $K$ thus expressed varies with the slag composition, on account of omission of the activity coefficients of oxide reactants and products in the expression of the equilibrium constant $K$.

The mass-action law has been applied in the past in a variety of ways to represent the state of slag–metal reaction equilibria. The apparent disparities sometimes seen in the experimental data of different investigators on slag–metal equilibria are often attributable to the format of representing the state of equilibrium for slags of varying compositions. In an attempt to develop a relatively simple rationale, Turkdogan$^b$ proposed a method of application of phase rule to describe the slag–metal reaction equilibria as discussed below.

Let us consider in a general way the equilibrium distribution of an element $X$ between slag and metal.

$$X \text{ (in metal)} = (X) \text{ (in slag)} \quad (3)$$

The independent state variables which determine the solubility of $X$ in the slag (in a simple or complex ionic form) coexistent with the metallic phase may be deduced by invoking the Gibbs phase rule:

$$p + f = e + 2 \quad (4)$$

where, $p$: the number of phases
$f$: the number of degrees of freedom
$e$: the number of components of the system.

For the phosphorus reaction between liquid iron and slag, the system may be described by the following six components: Fe, P, O, (CaO), (SiO$_2$) and (MO), where MO represents MgO plus other minor slag components, e.g., MnO, Al$_2$O$_3$, CaF$_2$, ... For isobaric and isothermal conditions, we now have from Eq. (4) $p + f = 6$. With the assumption that phosphorus has virtually no effect on its activity coefficient in the metal and slag phase, the equilibrium distribution ratio ($\%P$/[$\%P$]) between slag and metal may be described by the following functional relations, depending on the number of phases present$^*$:

2 phases: slag and metal,

$$\left[ \frac{[\%P]}{[\%P]} \right]_{p,f} = \phi \left( \frac{[\%O]}{[\%SiO_2]}, \frac{[\%SiO_2]}{[\%SiO_2]} \right) \quad (5)$$

3 phases: MgO-saturated slag and metal,

$$\left[ \frac{[\%P]}{[\%P]} \right]_{p,f} = \phi \left( \frac{[\%O]}{[\%SiO_2]}, \frac{[\%SiO_2]}{[\%SiO_2]}, \frac{[\%SiO_2]}{[\%SiO_2]} \right) \quad (6)$$

4 phases: MgO- and CaO-saturated slag and metal,

$$\left[ \frac{[\%P]}{[\%P]} \right]_{p,f} = \phi \left( \frac{[\%O]}{[\%SiO_2]}, \frac{[\%SiO_2]}{[\%SiO_2]} \right) \quad (7)$$

Although qualitative, the slag basicity defined by the concentration ratio (oxides of network modifiers)/(oxides of network formers) gives a general indication of the extent of depolymerization of the melt, hence is a simple indicator of the trend in changes of oxide activities with composition. Consequently, the equilibrium constants for slag–metal reactions expressed in terms of concentrations of slag components are often simple functions of slag basicity, at least for composition ranges of practical interest.

The concept of slag basicity appears to have been first introduced by Herty for steelmaking slags in the mid 1920's; he proposed a simple concentration ratio, so-called the $V$ ratio:

$$V = \frac{\%CaO}{\%SiO_2} \quad (8)$$

The definition of slag basicity is somewhat arbitrary. For example, if we were to assume that in steelmaking-type slags the concentrations of CaO and MgO are equivalent on a molar basis, and similarly on a molar basis 1/2 P$_2$O$_5$ is equivalent to SiO$_2$, in terms of mass concentrations of oxides, the slag basicity $B$ may be defined by the ratio:

$$B = \frac{\%CaO + 1.4(\%MgO)}{\%SiO_2 + 0.84(\%P_2O_5)} \quad (9)$$

The basic steelmaking slags are saturated with magnesia and dicalcium (magnesium) silicate. For such slags containing less than about 3 % P$_2$O$_5$, the basicity $B$ given by the above expression is essentially a linear function of the $V$ ratio with a proportionality factor of about 1.17.

$$B = 1.17 \frac{\%CaO}{\%SiO_2} \quad (10)$$

For blast furnace slags, which contain 10 to 20 % Al$_2$O$_3$, the basicity is often represented by the mass concentration ratio:

$$B' = \frac{\%CaO + \%MgO}{\%SiO_2} \quad (11)$$

2. Ironmaking Reactions

The state of equilibrium in metallurgical reactions involving three or more phases cannot be evaluated accurately without giving due consideration to interrelations among different reactions occurring simultaneously. In conventional laboratory experiments with blast-furnace-type systems at unit activities of carbon and carbon monoxide, many hours of reaction

$^*$ It should be noted that the argument presented here is the corrected version of that given by the author in Ref. 6).
The equilibrium distributions of manganese and silicon between slag and metal shown by dotted curves in Fig. 1 are consistent with the functional relation (21) deduced from the general thermodynamic considerations. Since CaO is one of the reactants as given by Eq. (14), the sulfur distribution ratio has to be a function of both the slag basicity $B'$ and the concentration of CaO in the slag; the dotted curves in Fig. 1 for $[%S]/[%S]$ are for 40 % CaO in the slag. The dotted equilibrium curves in Fig. 1 for graphiteseaturated melts at 1 bar CO pressure were derived from the appropriate free energy data, oxide activities, and experimentally determined equilibrium relations given by Eqs. (18) and (19).

In his 1978 Howe Memorial Lecture, Turkdogan discussed the state of slag–metal reactions in the blast furnace hearth, based on the analysis of the daily average plant data for various blast furnaces of U.S. Steel Corporation and those reported by Okabe et al. for Chiba Works of Kawasaki Steel Corporation. The data analyzed are typical for most blast furnace operations. The melt temperatures at tap are in the range 1450 to 1550 °C, mostly in the range 1475 to 1525 °C. The average slag compositions in mass percent are in the range: 38 to 44 % CaO, 8 to 10 % MgO, 34 to 38 % SiO2, 10 to 12 % Al2O3, 0.5 to 1.0 % MnO, 1 to 2 % S, 0.1 to 0.6 % K2O, <0.2 % FeO, and minor amounts of other oxides. The sum of the concentrations of four major constituent oxides CaO, MgO, SiO2, and Al2O3 is in the range 95 to 97 %.

The basicity of these slags, defined by the ratio ($\%$CaO+$\%$MgO)/$\%$SiO2, is in the range 1.25 to 1.55. The hot metal compositions from these blast furnaces are in the range: 0.4 to 0.8 % Mn, 0.5 to 1.5 % Si, 0.02 to 0.05 % S and other usual impurities, the amount of carbon (~5 %) in graphite-saturated metal depending on temperature and the concentration of the other solutes.

The plant data are scattered, irrespective of the hot metal temperature at tap, within the shaded areas shown in Fig. 1 for silicon, manganese, and sulfur distribution ratios. However, for a given blast furnace, the scatter in the data is usually much less and the effect of slag basicity on the distribution ratios is qualitatively in accord with the equilibrium data. That is, for any given blast furnace, the daily average plant data give the ratio $[%S]/[%S]$ that decreases with increasing slag basicity; $[%Mn]/[%Mn]$ and $[%S]/[%S]$ increase with increasing slag basicity. Of the three reactions considered, the distribution of silicon between metal and slag is closer to equilibrium for the three-phase gas–slag–metal reaction (12) in the blast furnace hearth.

If there is approach to equilibrium for the manganese–sulfur coupled reaction (17), for small changes in the concentration of CaO in slags, the sulfur-distribution ratio should be directly proportional to the manganese-distribution ratio. The plant data are scattered, irrespective of temperature, within the shaded
area shown in Fig. 2 (top diagram); the equilibrium lines (dotted) are from Eq. (20)) for 40 % CaO. However, for a given blast furnace there is much less scatter in the data which show the expected linear relation between (\%S)/[\%S] and [\%Mn]/(\%MnO).

Values of \(K_{\text{MnSi}}\) from plant data scattered within the shaded area in Fig. 2 (bottom diagram) are below the equilibrium line (dotted). This observation from the plant data may indicate that as the metal droplets pass through the slag layer in the blast furnace, the direction of the reaction might be

\[
2(\text{MnO}) + \text{Si} \rightarrow 2\text{Mn} + (\text{SiO}_2) \quad \text{(22)}
\]

Such an intuitive deduction, however, may not be correct. Observed departure from equilibrium for reaction (15) may be attributed to competition between FeO and MnO in the slag for oxidation of silicon. It is a generally accepted view that with a blast-furnace burden of low basicity, the residual iron oxide in the melting zone of the bosh is higher than with a burden of high basicity. In slags of low basicity, the higher concentration of iron oxide in the upper part of the slag layer would be in competition with MnO for reaction with both silicon and carbon. Consequently, departure from equilibrium for reactions (13) and (14) is expected to be greater in slags of low basicity. The trend seen from the plant data in Figs. 1 and 2 substantiate the deductions made from the foregoing argument. A study of plant data from a ferromanganese blast furnace\textsuperscript{20} also show departures from equilibrium for reaction (15) in a manner similar to that for the iron blast furnace.

Delve et al.\textsuperscript{21} have studied the titanium–silicon reaction in graphite-saturated melts using blast-furnace-type slags:

\[
(\text{TiO}_2) + \text{Si} = (\text{SiO}_2) + \text{Ti} \quad \text{(23)}
\]

Their experimental results, for temperatures of 1 500 and 1 600 °C and basicities of 1 to 2, may be summarized by the following equation.

\[
K_{\text{TiSi}} = \frac{[\%\text{Ti}]}{[\%\text{Si}]} \quad \text{(24)}
\]

From the blast-furnace-plant data compiled by Delve et al.\textsuperscript{21} and by Hess et al.,\textsuperscript{22} it is noted that the values of \(K_{\text{TiSi}}\) are two to three times lower than those given by Eq. (24), which presumably represents the equilibrium relation. Observed departure from equilibrium for reaction (23) in the blast furnace hearth is similar to the state of silicon–manganese reaction (15) in iron- and ferromanganese-blast furnaces.

3. Steelmaking Reactions

Many equilibrium measurements have been made of reactions between liquid iron alloys and slags relevant to steelmaking processes. The equilibrium rela-
tions for the key reactions given below are taken from the author’s critical assessment of the experimental data of various origin.

The recommended value of the equilibrium constant for the carbon–oxygen reaction in liquid iron is that obtained by Fuwa and Chipman:

\[
\begin{align*}
\text{CO} &= \text{C} + \text{O} \\
K &= \frac{[a_0][a_0]}{P_{\text{CO}}} \\
\log K &= -\frac{1168}{T} - 2.076
\end{align*}
\]

where \( P_{\text{CO}} \) is in bar and the activities \( a_0 \) and \( a_0 \) are taken equivalent to [\%C] and [\%O], respectively, at low solute concentrations. It should be noted that the ratio \( \text{CO}_2/\text{CO} \) in the gas increases with decreasing concentration of carbon. For a total pressure of \( P_{\text{CO}_2} + P_{\text{CO}} = 1 \text{ bar}, \) the \( \text{CO}_2 + \text{C} = 2\text{CO} \) equilibrium gives for 1600 °C: 0.05 bar \( \text{CO}_2 \) for 0.03 % C and 0.14 bar \( \text{CO}_2 \) for 0.01 % C in iron.

From the known oxygen solubility in liquid iron and the iron oxide activities in the quaternary melts \( \text{CaO-MgO-FeO}_\text{t}-\text{SiO}_2 \), the following relation is obtained for \( \text{CaO(MgO)} \)-saturated simple slags in equilibrium with iron–carbon melts (<1 % C) at 1600 °C and \( \text{CO}_2 + \text{CO} = 1 \text{ bar}. \)

\[
[\%C]/[\%\text{FeO}_t] \simeq 0.33 
\]

where the subscript \( t \) indicates the total iron in the slag as oxides represented as \( \text{FeO} \), i.e., \( \%\text{FeO}_t = \%\text{FeO} + 0.9 \times \%\text{Fe}_2\text{O}_3 \).

For the slag basicity \( V > 1 \), the equilibrium relation for the manganese reaction is reduced to a simple form for temperatures of 1550 to 1700 °C.

\[
\begin{align*}
\text{Mn}^{+}(\text{FeO}) &= (\text{MnO}) + \text{Fe} \\
\frac{\%\text{MnO}}{(\%\text{Mn})} &= \frac{K_{\text{MnFe}}}{(%\text{CaO}) \left( \%\text{SiO}_2 \right)} = 6
\end{align*}
\]

For slags saturated with \( \text{CaO} \) and \( \text{Ca}_4\text{P}_2\text{O}_9 \), the following equilibrium relation was obtained by Ban-ya and Matoba for the phosphorus oxidation at low concentrations in iron.

\[
\begin{align*}
4\text{CaO(s)} + 2\text{P} + 5\text{O} &= \text{Ca}_4\text{P}_2\text{O}_9(s) \\
K_F &= \frac{1}{[\%\text{P}] \left( \%\text{O} \right)^5} \\
\log K_F &= \frac{75660}{T} - 31.77
\end{align*}
\]

The temperature dependence of \( K_F \) determined in an earlier study by Fischer and vom Ende differs considerably from the above equation. However, for the temperature range 1530 to 1585 °C investigated by Ban-ya and Matoba, the values of \( K_F \) in these in-
dependent determinations agree within a factor of about 1.5. It should be noted that the enthalpy change accompanying reaction (28) estimated from the thermochemical data is closer to that given by the above equation.

Various formalisms have been used in the past to represent the slag–metal equilibrium with respect to the phosphorus reaction. Using the slag–metal equilibrium data and thermochemical data available in the early 1950’s, Pearson and Turkdogan derived an empirical equation for the effect of temperature and slag composition on the activity coefficient of $P_2O_5$ in the slag, relative to the hypothetical pure liquid $P_2O_5$. A similar formalism was adopted by Suito et al. to interpret their recent results for phosphorus distribution between liquid iron and slags saturated with magnesia. These different formalisms of varying complexity do not fit all the experimental data on the phosphorus reaction.

A new formalism proposed recently by the author is based on the functional relations given by Eqs. (5) to (7). Using all the available experimental data, including the recent work of Suito et al., it was found that for slags not saturated with lime or dicalcium silicate, the following functional relation described the data reasonably well:

$$K_{PS} = \frac{\text{[P]} \times \text{[oxide]}}{\text{[P]} \times \text{[P]}} = \phi [\% \text{FeO}, V]$$

$$........................(29)$$

For double saturation of the slag with lime and magnesia, when the basicity $V > 2.5$, the isothermal equilibrium relation $K_{PS}$ is a function of FeO and essentially independent of basicity, in accord with the derivation of the functional relation (7).

For slags of the system CaO–FeO–SiO$_2$–P$_2$O$_5$ saturated with either CaO or Ca$_4$P$_2$O$_9$, the phosphorus distribution ratio would be a function of both % FeO and % SiO$_2$. However, the data of Fischer and vom Ende and of Knüppel and Oeters in Fig. 3 for these singly saturated phosphate melts may be represented by a single curve. The scatter in the data masks the apparently small effect of % SiO$_2$ on the relation:

$$\frac{\text{[P]} \times \text{[oxide]}}{\text{[P]} \times \text{[P]}} = \phi [\% \text{FeO}]$$

$$........................(30)$$

for singly saturated slags containing less than 8 % SiO$_2$.

From the analysis of available experimental data, the relations in Fig. 4 were obtained for steelmaking-type slags saturated with both dicalcium silicate and magnesio-wustite, for general guidance in evaluating the state of the phosphorus reaction in steelmaking.
The representation of the experimental data in the manner described did not show any effect of CaF₂ on the phosphorus distribution ratio, indicating that CaF₂ in moderate proportions is equivalent CaO. This subject is discussed further later in the paper in relation to the ladle refining of hot metal.

For the low oxygen potentials sustained in the presence of metallic iron, the sulfur dissolves in the slag as a sulfide ion. For the slag–metal reaction (1), the equilibrium relation may be represented by

$$K_S = \frac{[S]}{[S]} \cdot \frac{[\text{FeO}_4]}{[\text{FeO}_4]}$$

where, $K_S$: a function of temperature and slag composition.

Various schemes were proposed in the past to represent the variation of $K_S$ with slag composition. As suggested by the author in an earlier study of the available data, the simplest form of the composition dependence of $K_S$ is that shown in Fig. 5 for wide ranges of slag compositions and temperatures of 1 530 to 1 730 °C; the relation is well represented by a single curve for the concentration of acidic oxides above 5%. Lorscher studied the sulfur reaction using slags saturated with tricalcium phosphate. For melts containing about 42% P₂O₅ and 3 to 6% FeO₄, remainder being CaO, the $K_S$ is in the range 2 to 4 which is in general accord with other data in Fig. 5. The greater scatter of the data points at low concentrations of acidic oxides is attributed to the greater sensitivity of $K_S$ at very high basicities to the relative concentrations of basic oxides. For CaO–FeO₄ melts, the curve intercepts the ordinate at $K_S \approx 540$.

Although the steelmaking methods and practices differ to varying degrees, the same fundamental principles of gas–slag–metal reactions apply to them all. In keeping with the theme of the present discourse, the deliberation here is confined to the discussion of the state of reactions during steel refining as affected by slag composition. For low phosphorus in the furnace charge, i.e., <0.2% P in the hot metal, the compositions of slags at the time of furnace tapping are in the following ranges: 40 to 60% CaO, 2 to 8% MgO, 3 to 8% MnO, 4 to 30% FeO₄, 12 to 28% SiO₂, 1 to 5% P₂O₅, 1 to 2% Al₂O₃, 1 to 2% CaF₂, 0.1 to 0.2% S, and minor amounts of other oxides.

Most industrial basic slags are saturated with magnesia and dicalcium (magnesium) silicate and, for the low-phosphorus practice, the sum of the concentrations of CaO, FeO₄, and SiO₂ is in the range 87 to 90%. In this pseudo-ternary system, the composition of the melt is that given by the univariant equilibrium for dicalcium silicate saturation at a constant temperature. When the slag composition is adjusted to account for entrained metallic iron and undissolved lime particles, the total iron oxide content of the finishing slag at tap decreases with increasing concentrations of SiO₂+P₂O₅ and dissolved CaO as indicated by the shaded areas in Fig. 6 for basic-open hearth (BOH), oxygen-top blowing (BOF), and oxygen+lime-bottom.
blowing (Q-BOP) steelmaking practices. Variations in composition within the shaded areas suggest that some basic steelmaking slags may not be saturated with dicalcium (magnesium) silicate, despite the fact that BOF and Q-BOP slags always contain entrained particles of undissolved lime. The Q-BOP slags usually contain more CaO than BOF slags. For the range 1550 to 1650 °C, the tap temperature has no detectable effect on the distribution of data points in this composition diagram.

The dotted line in each diagram is for dicalcium (magnesium) silicate saturation in the simple CaO-6%MgO-FeO-SiO2 melts in equilibrium with liquid iron at 1600 °C. There is a pronounced shift in the position of the univariant equilibrium in the composition diagram for the saturated-steelmaking slags to higher concentrations of CaO and to the corresponding lower concentrations of SiO2 as compared to the quaternary system CaO-6%MgO-FeO-SiO2 in equilibrium with liquid iron. This change in the melt composition to higher concentrations of lime is due to the presence of P2O5, MnO, Fe2O3, MgO, and small amounts of other oxides which shift the saturation isotherm to higher concentrations of CaO. Another rationale is that the slag basicity changes from low to high levels as the iron oxide content of the saturated slag increases, e.g., the V ratio is 2.0 to 2.5 for slags containing 4 to 6 % FeO and increases to 3.4 to 3.6 for slags containing 28 to 30 % FeO. That is, in saturated slags the basicity is fixed by the concentration of iron oxide, hence by the concentration of carbon in the steel.

The oxygen activity in liquid steel measured with the EMF-oxygen sensor gives the concentration of oxygen in solution in the steel (for low-alloy plain carbon steels). The BOF and Q-BOP data for concentrations of oxygen in steel and total iron oxide in slag at tap, for temperatures of 1550 and 1650 °C and for carbon contents in the range 0.01 to 0.8 %, are distributed within the shaded area in Fig. 7(A). The dotted curve is calculated from the data on the solubility of oxygen in liquid iron and the activity of iron oxide36> along the lime-saturation isotherm for relatively simple slags CaO(MgO)-SiO2-FeO. The position and shape of the shaded area (where the plant data are distributed), relative to the dotted line for the simpler saturated slags, indicate that the activity coefficient of iron oxide in steelmaking slags decreases with increasing concentration of iron oxide and with the corresponding increase in slag basicity.

From the compositions of slag and metal samples taken at tap in BOF and Q-BOP steelmaking at temperatures of 1590 to 1610 °C, a plot is made in Fig. 7(B) of the product \((\%\text{MnO})/\%\text{Mn})\text{CaO/}\%\text{SiO2}\) against the concentration of iron oxide. The broken line drawn with the slope of six represents the slag-metal equilibrium for the manganese reaction as given in Eq. (27). It is self evident that there is close approach to the slag-metal equilibrium with respect to the manganese reaction in oxygen-steelmaking processes, over wide ranges of carbon content of steel at tap.

In oxygen-lime bottom blowing as in Q-BOP, the slag formation begins in the melt near the tuyere zone where the oxides of iron, manganese, silicon, and phosphorus react rapidly with the lime powder. As the
slag particles traverse the bath with CO bubbles, they react with carbon. Because of the secondary reaction with carbon in the bath, the concentrations of iron oxides and manganese oxide in Q-BOP slags are lower than those in BOF (or BOP) slags. That is, for a given concentration of carbon in the bath, the metal/slag manganese-distribution ratio in Q-BOP is higher than in BOF.

The plant data plotted in Fig. 8 show the relation between the concentrations of oxygen and carbon in steel at tap. With the exception of low-carbon melts in the Q-BOP, the oxygen contents of steel at all carbon levels for BOF and Q-BOP steelmaking are close to the equilibrium values for a pressure of 1.5 bar CO which is an average total gas pressure in the bath. The lower oxygen contents of steel in Q-BOP at low carbon levels suggests that oxidation of CO to CO$_2$ in the bath is well above the equilibrium values for the reaction:

$$\text{CO}_2 + \text{C} = 2\text{CO} \quad \text{(32)}$$

That is, when the rate of oxygen-bottom blowing exceeds the rate of consumption of oxygen by carbon, manganese, and iron, the excess oxygen will oxidize the CO generated in the bath near the tuyere zone to CO$_2$, thus diluting CO and allowing the decarburization to proceed at lower levels of residual oxygen in the steel.

On the basis of the foregoing process analysis, which was discussed elsewhere in more detail, certain advantages are anticipated in the use of argon+oxygen mixtures in the later stages of refining of steel in both the top and bottom blowing practices, particularly for steels containing less than 0.02% C. In fact, these anticipated advantages have been realized in recent developments of combined top and bottom blowing practices in steelmaking, e.g., LBE and K-BOP.

Many previous studies of plant data have shown that at the time of furnace tapping in all types of steelmaking processes, the sulfur-distribution ratio between slag and metal is close to the equilibrium relation shown in Fig. 5.

The BOF and Q-BOP plant data for temperatures of about 1600 °C are plotted in Fig. 9(A) showing the variation of log $K_{eq}$ with the total iron oxide content of the slag. For low P$_2$O$_5$ contents in slags saturated with dicalcium silicate and magnesia, the concentrations of iron oxide and silica or lime in the slag are interrelated. Therefore, for doubly saturated slags, the phosphorus-distribution ratio alone will be a single function of the concentration of iron oxide. The equilibrium relation for doubly saturated, low-phosphorus slags is shown by the dotted curve in Fig. 9(B). The points for Q-BOP are scattered about the...
dotted curve representing the equilibrium relation. The data for BOF, for slags containing more than about 15 % FeO, show departures from equilibrium in favor of high phosphorus in the steel. The same plant data are plotted in Fig. 10 showing the variation of the phosphorus-distribution ratio with the carbon content of the steel at tap. For steels containing 0.03 to 0.05 % C at turndown, the slag/metal phosphorus distribution ratio for Q-BOP is about twice that for BOF. Furthermore, lower levels of carbon attainable by oxygen-bottom blowing brings about more extensive dephosphorization of the metal.
As was noted in previous studies, the analysis of the plant data substantiates the view that at the time of furnace tapping there is close approach to slag-metal equilibrium for most reactions. Therefore, the equilibrium data for slag-metal reactions in conjunction with plant data will provide a reliable basis for static and dynamic process control in steelmaking, with certain adjustments in the charge control model to accommodate small differences in melt-shop practices.

III. Ladle Refining

Prior to the 1970's, the ladle treatment of hot metal was confined almost entirely to desulfurization when it was considered necessary. In the case of liquid steel, the ladle refining has been practiced for a much longer time. However, prior to the 1950's, the ladle refining of steel meant deoxidation, recarburization, resulfurization for free machinability of steel and moderate additions of alloying elements. The advent of continuous casting and an increase in customer demand for high-strength, low-alloy steels with improved transverse mechanical properties made it necessary to develop increasingly more sophisticated methods of treating steel in the ladle for deoxidation, desulfurization, degassing, and shape control of inclusions. In recent years, there has been a growing demand for cleaner steels, i.e., steels containing very low concentrations of nonmetallic inclusions, low sulfur steels (<10 ppm S), alloy steels low in interstitial elements H, N, C, O, and S, and for other quality steels for special applications. Such high levels of steel refinement can be achieved only by a suitable method of ladle treatment.

Since the late 1970's, there has been a rapid growth of technology for ladle refining of both hot metal and steel, the so-called secondary steelmaking or ladle metallurgy. There is an overwhelming volume of publications of research and development on ladle metallurgy. Regretably, many of the publications, both from the academia and the industry, are on repetitive work. A critical assessment of the accumulated knowledge and technical information on ladle metallurgy in a comprehensive, yet in a condensed form, would be a worthwhile undertaking. In the present discussion of a few selected areas of ladle refining, with particular emphasis on slag-metal reactions, no attempt is made to cite in a chronological order the large volume of repetitive publications on the subject. References to almost all the publications related to ladle metallurgy can be found in the proceedings of three series of symposia, \textit{"Scaninject"}, held in Luleå, Sweden, in 1977, 1980, and 1983,\textsuperscript{37–39} and in other publications cited in this paper.

1. Rate of Refining in Stirred Melts

To enhance the rate of refining of steel with the overlaying slag, with the injected powder reactants and the flotation of reaction products out of the steel bath, various methods of stirring have been developed in the steel industry: electromagnetic, mechanical, and argon injection. References may be made to re-
Mori and Sano\textsuperscript{44} proposed the following equation
\[ C_t = C_0 \exp(-kt) \] ............... (33)
where, \( C_0 \): the initial concentration of reactant in the steel
\( C_t \): the concentration at time \( t \)
\( k \): the apparent volumetric rate constant for a given type and intensity of stirring.

The mixing time, \( \tau \), to achieve about 95 \% homogenization in stirred melts is a good measure of the rate of ladle refining. From measurements of the rate of solute homogenization in 50 t argon stirred melts in the ladle, 50 t ASEA-SKF, 200 t RH and 65 kg water model experiments, Nakaniishi \textit{et al.}\textsuperscript{43} derived the following empirical relation for mixing time \( \tau \) as a function of the rate of dissipation of energy, \( z \), in the stirred melt.
\[ \tau = (600 \pm 100)z^{-0.40} \] ............... (34)
where \( z \) is in second and \( \tau \) in W/t liquid steel. For gas stirred melts, \( z \) is due essentially to the buoyancy energy of the injected gas, the contributions of the kinetic energy of the gas, and the thermal expansion of gas to the circulating flow are small enough to be neglected.
\[ z = 6.18 \times 10^{-9} V T W \ln \left(1 + \frac{\rho g H}{10^2 P}\right) \] ............... (35)
where, \( V \): the gas flow rate (nm\(^3\)/min)
\( T \): the melt temperature (K)
\( W \): the mass of the melt (t)
\( \rho \): the density of the melt (kg/m\(^3\))
\( g \): the gravity acceleration (m/s\(^2\))
\( H \): the depth of the gas inlet (m)
\( P \): the gas pressure at inlet (bar).
For \( \rho = 7000 \text{ kg/m}^3 \) and \( g = 9.81 \text{ m/s}^2 \), \( z \) is given by
\[ z = 0.014 V T W \log \left(1 + \frac{H}{1.46 P}\right) \] ............... (36)

Mori and Sano\textsuperscript{46} proposed the following equation for time of mixing for the purpose of scale-up
\[ \tau = F \left(\frac{W/\rho}{\dot{E}}\right)^{1/3} \] ............... (37)
where, \( F \) (dimensionless): a proportionality factor that depends on the geometry of the melt container.

In model experiments of solute homogenization in aqueous solutions, Haida and Brimacombe\textsuperscript{45} used torpedo- and ladle-shaped vessels, and found that \( F \) increases with an increase in the diameter/height ratio, \( D/H \), for the cylindrical ladle and length/height ratio, \( L/H \), for the torpedo ladle. The following relation may be obtained from their results
\[ F = 150 \left(\frac{D}{H}\right)^{0.85} = 150 \left(\frac{L}{H}\right)^{0.85} \] ............... (37-a)

Haida and Brimacombe\textsuperscript{46} also found that their results on mixing time in aqueous solutions as represented by Eq. (37), agree well with those of Nakaniishi \textit{et al.}\textsuperscript{43} for stirred liquid steel mentioned earlier. Another formulation of the mixing time given below is that derived by Sano and Mori\textsuperscript{43} from a mathematical model that describes circulating flow in a molten steel bath with inert gas injection.
\[ \tau = 100 \left[\frac{(D/\rho H^2)}{\dot{E}}\right]^{0.237} \] ............... (38)

This derived formula is also found to agree well with the measured values of mixing time in stirred steel baths and in water-model experiments.

Kikuchi \textit{et al.}\textsuperscript{37} measured the rate of dephosphorization of low-carbon steels in stirred melts. They found that the volumetric rate constant, \( k' \), for dephosphorization increased with an increase in the intensity of stirring. Their results may be approximated by the relation:
\[ k' (\text{min}^{-1}) = 0.007z^{0.4} \] ............... (39)
which, in combination with Eq. (34), gives \( k'\tau \approx 0.07 \). That is, as one would expect from the rate of mass transfer considerations, the volumetric rate constant is inversely proportional to the mixing time.

2. Hot-metal Refining
Since the late 1970’s there has been an intensified R & D effort, particularly in Japan, to explore the uses of fluxes in the refining of molten pig iron to low levels of silicon, sulfur, and phosphorus. The objectives—with an economic and environmental bias—are two-fold:
(i) to increase the recycling of steelmaking slags (low in phosphorus) to the blast furnace for the recovery of iron and manganese; and
(ii) to develop slagless steelmaking from hot-metal low in sulfur, phosphorus, and silicon, thus minimizing slag disposal.

In his 1981 Howe Memorial Lecture, Fuwa\textsuperscript{48} presented a detailed account of research and development in Japan on the ladle treatment of hot metal. This subject will not be pursued further here with the exception of citing a few selected interesting examples of slag-metal reactions pertaining to the desulfurization and dephosphorization of hot metal by ladle treatment.

In practice, the hot metal is desulfurized and dephosphorized by injecting with nitrogen and/or oxygen a mixture of sinter fines, burnt lime, calcium fluoride, and some calcium chloride. In some practices, sodium carbonate alone is injected. At low temperatures and with fluxes having high capacities for phosphorus and sulfur, the hot
metal can be refined to the residual levels of 0.005 \% \( P \) and 0.002 \% \( S \). It is well to remember that the hot metal thus refined contains hardly any silicon, therefore there is severe limitation to the amount of scrap steel that can be melted during decarburization in the converter.

At sufficiently low oxygen potentials, the phosphorus dissolves in molten slags and fluxes as a phosphide ion (\( \text{P}^3^- \)). Tabuchi et al.49) studied the following phosphide and phosphate reactions in CaO–Al\(_2\)O\(_3\) and CaO–CaF\(_2\) melts.

\[
\frac{1}{2} \text{P}_2 + \frac{3}{2} (\text{O}^2-) = (\text{P}^3^-) + \frac{3}{4} \text{O}_2
\]

They found that the critical partial pressure of oxygen for transition from the phosphide to phosphate reaction at 1 550 °C is about 10\(^{-18}\) bar \( \text{O}_2 \) for the calcium aluminate melt and about 10\(^{-18}\) bar \( \text{O}_2 \) for the lime-saturated CaO–CaF\(_2\) melt. Their experimental data give for the phosphate capacity, in units of wt\%/

\[
C_P = \frac{\% \text{P}_2 \text{O}_5}{\% \text{P} \% \text{O}^{2.5}} \quad (42)
\]

C\(_P\)=4.1×10\(^{10}\) for the aluminate melt (41\%CaO+59\%Al\(_2\)O\(_3\)) and C\(_P\)=4.1×10\(^{11}\) for the lime-saturated CaO–CaF\(_2\) melt. To facilitate comparison with other slag–metal equilibria for the phosphate reaction, \( C_P \) may be converted to another formulation of the phosphate capacity.

\[
K_P = \frac{\% \text{P}_2 \text{O}_5}{\% \text{P} \% \text{O}^{2.5}} \quad (43)
\]

With the known free energy data for solution of gaseous oxygen in liquid iron\(^{39,40}\) and of gaseous phosphorus (\( \text{P}_2 \)) in liquid iron,\(^{41}\) the \( C_P \) values of Tabuchi et al.\(^{49}\) for 1 550 °C give \( K_P = 4.1 \times 10^{10} \) for the aluminate melt (\(~40\% \text{ CaO}\)) and \( K_P = 4.1 \times 10^{11} \) for the fluoridate melt (\(~20\% \text{ CaO}\)).

In the system CaO–FeO–P\(_2\)O\(_5\) saturated with CaO and Ca\(_3\)P\(_2\)O\(_8\), the melt contains about 28 \% \text{P}_2\text{O}_5 and 15 \% \text{FeO}.\(^{42}\) For this saturated slag, the equilibrium constant \( K_P \) in Eq. (28) gives \( K_P = 2.1 \times 10^8 \) for 1 550 °C and \( K_P = 0.6 \times 10^8 \) for 1 600 °C. The values of \( K_P \) derived from the results of Tabuchi et al.\(^{49}\) are two to three orders of magnitude higher than that for the lime- and phosphate-saturated melt.

In laboratory experiments, Kawai et al.\(^{49,50}\) measured the concentrations of oxygen and phosphorus in iron samples equilibrated with lime–fluoride- and lime–alumina-based slags at 1 600 °C. Their data give values of \( K_P \) increasing from about 10\(^4\) at 50 \% \text{CaO} + \text{CaF}_2 to about 10\(^8\) at 85 \% \text{CaO} + \text{CaF}_2 for the aluminate melts (with no \text{CaF}_2) containing 35 to 40 \% \text{CaO}, the value of \( K_P \) in the range 4 \times 10^4 to 1.3 \times 10^5. High values of \( K_P \) derived from the data of Tabuchi et al.\(^{49}\) are inconsistent with other slag–metal equilibrium data. This disparity may be due to the indirect method of estimating the oxygen potential in their experimental system.

Because of current interest on fluoride-based slags or fluxes for hot metal dephosphorization, numerous speculations have been made of the possible effect of CaF\(_2\) on the phosphate capacity of slags. An empirical equation proposed by Healy\(^{29}\) to describe the phosphorus distribution ratio as a function of slag composition when used for fluoride slags gives some unusual results. As shown by Kawai et al.\(^{42,51}\) for example, such an exercise would predict a distribution ratio \( \% \text{P}/\% \text{P} \) in an 80 \% CaF\(_2\)-based slag about four orders of magnitude greater than that in the CaF\(_2\)-free slag, an impossible situation.

As discussed elsewhere,\(^6\) and briefly mentioned earlier, for lime- and magnesia-saturated slags the \( K_{PS} \) in Eq. (29) for a given temperature is a single function of the concentration of iron oxide in the slag. On the basis of this reasoning, the data of Kawai et al.\(^{49,51}\) and Kikuchi et al.\(^{41,46}\) for 1 600 °C are plotted in Fig. 11 where the dotted curve represents the equilibrium relation for complex steelmaking-type slags (containing 0 to 5 \% \text{CaF}_2) assessed in a previous study.\(^6\) It should be noted that Kikuchi et al.\(^{40}\) gave their results in a graphical form as isoloeths of \( \% \text{P}/\% \text{P} \) in a pseudo-ternary system CaO–CaF\(_2–\)FeO, (total being 88 \% ) of MgO-saturated slags containing about 4 \% SiO\(_2\) and 1 to 2 \% \text{P}_2\text{O}_5. Considering the diversity in slag compositions, there is a general agreement between the results of vastly different types of experimental work.

The aluminate anions copolymerize with silicate and phosphate anions to form complex alumino-silico-phosphate anions. Therefore, in the functional relation \( K_{PS} \) we may include alumina. Assuming that 0.5 mol Al\(_2\)O\(_3\) is equivalent to 1 mol SiO\(_2\), the concentration of Al\(_2\)O\(_3\) as molar silica equivalence would be 1.18 \times \% \text{Al}_2\text{O}_3. In the lower diagram in Fig. 11, log \( (1+\% \text{SiO}_2+1.18 \times \% \text{Al}_2\text{O}_3)/(\% \text{P}_2\text{O}_5/\% \text{P}) \) is plotted against the total iron oxide content of the slag. It follows from the foregoing analysis that CaF\(_2\) has no particular effect on the phosphate capacity of the slag where CaF\(_2\) behaves much like CaO. The major role of CaF\(_2\) in slags for hot metal dephosphorization is to lower the liquidus temperature and lower the viscosity of the slag for use at hot metal temperatures. The highest distribution ratio \( \% \text{P}/\% \text{P} \) attainable is with lime-saturated slags containing 15 to 25 \% \text{FeO}, and low concentrations of SiO\(_2\) and Al\(_2\)O\(_3\).

As would be anticipated from the thermodynamic properties of phosphate melts, the ratio \( \% \text{P}/\% \text{P} \) obtained with soda-based slags is higher than that with lime-based slags. For example, Marukawa et al.\(^{43}\) have found that in the dephosphorization of liquid iron, essentially saturated with graphite, the ratio \( \% \text{P}_2\text{O}_5/\% \text{P} \) is about 1 000 at 1 300 °C for slag basicity of Na\(_2\)O/SiO\(_2\)=3; a similar distribution ratio is obtained at a lower basicity of 1.5 when the temperature is decreased to 1 200 °C.\(^{44}\) It should be noted, however, that carbon increases the activity coefficient of phosphorus dissolved in iron; for hot metal compositions the activity coefficient of phosphorus...
the pattern of liquid flow. The metal was dephosphorized at 1300 °C from about 0.1 to 0.01% P with carbon remaining at about 4.4%. From the compositions of metal and slag samples and measured oxygen activities near the slag layer, they estimated the phosphorus capacity of the slag. For CaF₂-fluxed slags with basicity $V^{-1}$, they obtained values in the range 10⁴₅ to 10⁴⁸ for $K_p$ at 1300 °C; this corresponds to $K_p = 10^{10}$ which is close to the value estimated by extrapolating the data for steelmaking slags from 1600 to 1300 °C, with due adjustment of $K_p$ for the activity coefficient $f_C$ ~ 5 in graphite saturated iron.

Compared to dephosphorization, it is much easier to desulfurize hot metal by various means, e.g., injection of magnesium, calcium carbide, burnt lime, and fluoride- or soda-based slags used for dephosphorization. In a recent publication, Turkdogan and Martonik presented some equilibrium data for the gas-slag-metal reaction:

$$\text{CaO(s)} + \text{S} + \text{C} = \text{CaS(s)} + \text{CO}$$

It will suffice for the present to state that at 1 bar pressure of CO and for graphite-saturated melts coexistent with solid CaO and CaS, the equilibrium concentration of sulfur in liquid iron is about 4 ppm at 1600 °C and increases to about 8 ppm at 1400 °C. With injection of burnt lime, the hot metal can, in practice, be desulfurized to about 20 ppm S. Emi and Iida, however, were able to desulfurize hot metal to 20 ppm S at about 1400 °C by injection of powdered limestone into hot metal in the transfer ladle. Improved efficiency of desulfurization close to the equilibrium levels of sulfur is attributed to the higher reactivity of finely dispersed CaO that is formed upon in situ dissociation of injected limestone powder. Another advantage is that the CO₂ generated reacts exothermically with silicon in the hot metal, thus compensates for the heat losses.

### 3. Liquid Steel Refining

In the ladle refining of steel we are concerned primarily with deoxidation, desulfurization and degassing of steel. Recently, the author presented a critical evaluation of current knowledge on ladle deoxidation, desulfurization, and inclusions in steel, both fundamental and practical aspects. The present discussion of this subject, which does not include degassing, is an addendum to the author's previous paper.

Calcium aluminate-based slags play a key role in the ladle deoxidation and desulfurization of steel. To ensure the attainment of isotropic mechanical properties in the steel, the sulfide inclusions that form during solidification of the steel should be in the form of evenly dispersed globules of sizes in the micron range. The presence of alumina inclusions in the steel is undesirable in continuous casting and in many applications of the steel; the calcium aluminate, as finely dispersed particles, is the preferred form of oxide inclusions in killed steels. These objectives can be fulfilled for killed steels containing less than a total of 25-ppm sulfur + oxygen by achieving a fine dispersion of minute particles of molten calcium aluminate in
liquid steel during the ladle treatment.

In the ladle desulfurization of steel with aluminum and prefused calcium aluminate slag, the following reaction prevails.

\[
(CaO) + \frac{2}{3} Al + S = (CaS) + \frac{1}{3}(Al_2O_3)
\]  

The equilibrium constant for this reaction determined experimentally by Schürmann et al. \(^{60}\) for 1 600 °C is about three-fold of the value computed \(^{59}\) from thermochemical data and reliable equilibrium data for various gas–slag–metal reactions. To resolve this discrepancy, Ozturk and Turkdogan \(^{61}\) have recently determined, under closely controlled experimental conditions, the equilibrium distribution of sulfur between calcium aluminate melts and liquid iron containing aluminum. Also, the measurements were made of the solubility of CaS at 1 550 and 1 600 °C over the composition range of the liquid phase from the aluminate to the lime saturation. The results of these equilibrium measurements were found to be in close agreement with those computed previously \(^{59}\) from other equilibrium data.

As is seen from the equilibrium relation in Fig. 12(A) for steel containing 0.04 % Al in solution, the sulfur-distribution ratio increases appreciably with increasing ratio CaO/Al_2O_3. Obviously, the lime-saturated aluminate slag should be used for effective desulfurization of steel. The effect of aluminum concentration in steel on the sulfur-distribution ratio is shown in Fig. 12(B) for the lime-saturated aluminate melts in which the solubility of CaS increases from 1.8 % S at 1 500 °C to 2.2 % S at 1 650 °C. These equilibrium data indicate that the steel containing 0.03 to 0.05 % Al can be desulfurized to the levels of a few ppm S by interacting the argon-stirred liquid steel with the lime-saturated aluminate slag. In fact, in a well-controlled ladle refining practice, \(^*\) it has been possible to desulfurize steel on industrial scale to levels below 10 ppm S.

If the ladle treatment of steel with calcium aluminate is intended to achieve cleaner steel, i.e., low in total oxygen as aluminate inclusions, without desulfurization, the ratio CaO/Al_2O_3 in the synthetic slag and the residual aluminum in the metal should be reduced as indicated by the equilibrium data. For example, for the steel to contain 0.02 % S and 0.02 % Al after the ladle treatment, the prefused calcium aluminate to be used should be saturated with sulfur, e.g., \(\approx 2\) % S, and have a mass ratio CaO/Al_2O_3 of about 1:1. This is in the middle of the liquid composition range; therefore, the slag has capacity to absorb alumina inclusions from the steel when mixed with the metal with argon stirring. For the particular case considered as an example, the equilibrium concentration of oxygen in solution in the steel would be about 2 to 3 ppm.

The aluminum-killed steel may be desulfurized also by injecting a mixture of burnt lime and fluor spar. The extent of desulfurization that can be achieved depends on the efficiency of fluxing of the deoxidation product alumina with the injected lime. Kor and Richardson \(^{62}\) determined the sulfide capacity, C_s, of CaO–CaF_2–Al_2O_3 melts at 1 500 °C. Their data are

---

\* (a) No slag carry-over during furnace tapping
(b) Basic refractory lining for the ladle
(c) High argon flow using porous plug
(d) Ladle cover to avoid air oxidation of the melt

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presented in a different form in Fig. 13 as a plot of \( \log K_s \) against the concentration of CaF\(_2\) for indicated mass ratios of \( \% \text{Al}_2\text{O}_3/\% \text{CaO} \). It is seen that CaF\(_2\) has only a small effect on the sulfide capacity of the aluminate slag. However, CaF\(_2\) fluxes both CaO and CaS; for the invariant equilibrium at 1 500 °C, the liquid phase contains about 60 \( \% \) CaF\(_2\), 20 \( \% \) CaS, and 20 \( \% \) CaO. Therefore, an addition of 5 to 10 \( \% \) CaF\(_2\) to the injected burnt lime would curtail the coating of lime particles with a layer of CaS, hence would improve the efficiency of lime usage in ladle desulfurization.

In the silicon-deoxidized steel, the desulfurization is governed by the reaction:

\[
(CaO) + \frac{1}{2} \text{Si} + S = (CaS) + \frac{1}{2} (\text{SiO}_2)
\]

The sulfide capacity, and the deoxidation capability with silicon, of calcium silicate melts is low even at lime saturation; therefore, desulfurization by reaction (46) is possible only when the activity of silica is lowered significantly by using a suitable flux such as pre-fused calcium aluminate. The relation shown in Fig. 14 for sulfur and silicon concentrations is for steels equilibrated with calcium aluminate+5\( \% \)SiO\(_2\) melts saturated with CaO and CaS. In this slag, the activity of silica is in the range 10\(^{-5}\) to 10\(^{-4}\) and the activity of alumina about 5\( \times \)10\(^{-3}\), both with respect to the pure solid oxides, for which the following are the equilibrium concentrations of silicon and aluminum in the steel at 1 600 °C: 0.01 \( \% \) Al for 0.07 \( \% \) Si and 0.03 \( \% \) Al for 0.3 \( \% \) Si. However, at these low oxide activities in the slag considered, the kinetics of Si-Al redox reaction would be sluggish, consequently at low solute concentrations, e.g., <0.05 \( \% \) Al and <0.5 \( \% \) Si, there may be little or no countercurrent transfer of silicon and aluminum between slag and metal by the redox reaction in a relatively short time of ladle refining. However, if the aluminate slag contains 8 to 10 \( \% \) SiO\(_2\), there could be appreciable loss of aluminum from metal to slag because of oxidation of aluminum in the steel by silica in the slag.

IV. Role of Vapor Species

Because of the high temperatures involved, vaporization plays a significant role in pyrometallurgical reactions. In a reactor such as a blast furnace, the formation and condensation of various vapor species is responsible for the recycle of some of the elements between the high and low temperature regions of the furnace. Familiar iron oxide fumes emitted in steel-making operations is a consequence of enhanced vaporization of iron under certain conditions. In the nonferrous industry, the slag fuming is used in the recovery of, for example, tin and zinc from slags. Vaporization in high-temperature manufacturing processes (i) can be an asset for the operation of the process, (ii) may impede the smooth operation of the process, or (iii) may cause pollution of the environment. Many aspects of vaporization studied in the past few decades have been of much value in the development of special processing techniques, a better understanding of the workings of the high-temperature processes and in curtailing vaporization-related pollution problems.

1. Vaporization in the Blast Furnace

The countercurrent flow in the blast furnace of solids from low- to high-temperature zones and of gases from high- to low-temperature zones brings about a cyclic process of vaporization and condensation which has a decisive influence on the overall operation of the furnace. It is now well established that the silicon and sulfur in the coke are transferred to the slag and iron in the blast furnace \textit{via} the vapor species SiO, SiS, CS, and other minor sulfur-bearing species. The earlier and recent studies of quenched
blast furnaces have revealed that while the sulfur content of the slag increases with the descent of the burden in the bosh, the sulfur and silicon contents of the metal droplets reach maxima and then decrease as they pass through the slag layer.\textsuperscript{19,62,64} This phenomenon of vapor-phase mass transfer has been substantiated by the experimental work of Tsuchiya et al.\textsuperscript{65} and Tukr doctrines et al.\textsuperscript{14} under conditions partly simulating the bosh region of the blast furnace.

In the presence of carbon and depending on temperature and activity of silica in the slag or coke, the SiO vapor is generated by one of the following reactions:

\[
\text{SiO}_2 \rightarrow \text{SiO} + \text{CO} \quad (47)
\]

\[
\text{SiO} + \text{C} \rightarrow \text{Si} + \text{CO} \quad (48)
\]

At 1 bar pressure of CO, \( a_{\text{SiO}_2} = 1 \) and above about 1 500 °C, SiO\(_2\) is converted to SiC and SiO is generated by reaction (48); for \( a_{\text{SiO}_2} = 0.1 \), reaction (48) applies only at temperatures above about 1 610 °C. In the experiments cited,\textsuperscript{10} the SiO generated by passage of CO through a coke bed at temperatures of 1 600 to 1 900 °C, were found to be close to the equilibrium values for reaction (48). Volatile SiS is generated by reactions of the type with the coke ash:

\[
\text{CaS} \rightarrow \text{SiS} + \text{CaO} \quad (49)
\]

\[
\text{FeS} \rightarrow \text{SiS} + \text{CO} + \text{Fe} \quad (50)
\]

The reaction of these vapor species with metal and slag may be represented by the equations:

Metal

\[
\text{SiO} + \text{C} = \text{Si} + \text{CO} \quad (51)
\]

Slag

\[
\text{SiO} + 0.5(\text{O}^2-) + 0.5\text{C} = (\text{Si} - \text{O}^2-) + 0.5\text{CO} \quad (52)
\]

Experiments have been made to simulate the events in the upper part of the blast-furnace hearth where metal droplets pass through the slag layer.\textsuperscript{14} Within a short residence time (1 to 2 s) of metal droplets in the slag, appreciable changes occurred in the composition of the metal droplets: manganese oxide in the slag oxidized silicon in metal droplets from 1.0 % Si to about 0.2 % Si and the metal was desulfurized from 0.1 % S to about 0.02 % S.

Coke samples taken from the tuyere zone of the blast furnace usually contain 12 to 16 % ash which has a basicity (CaO + MgO)/SiO\(_2\) of about 0.6; for a typical blast furnace slag, the basicity is about 1.5. Therefore, the partial pressures of SiO and sulfur-bearing species in the gas near the coke surface are expected to differ from those interacting with the slag. For the purpose of comparison, calculations are made for assumed local equilibrium at 1 500 °C for the systems gas–slag and gas–coking coke ash at 1 500 °C and 1 bar pressure of CO.

\[
\begin{align*}
B' &= 1.5, \quad a_{\text{SiO}_2} = 0.05, \quad B' &= 0.6, \quad a_{\text{SiO}_2} = 0.3 \\
2\% (\text{Si}), \ C_0 &= 3 \times 10^{-4}, \quad 5\% (\text{Si}), \ C_0 &= 10^{-4}, \\
\text{(wt)} & \quad \text{(wt)}
\end{align*}
\]

\[
\begin{align*}
\text{SiO} &= 2.6 \times 10^{-4} \quad 1.5 \times 10^{-3} \\
\text{SiS} &= 3.9 \times 10^{-3} \quad 1.7 \times 10^{-2} \\
\text{S}_2 &= 8.6 \times 10^{-8} \quad 4.9 \times 10^{-3} \\
\text{CS} &= 5.5 \times 10^{-5} \quad 4.3 \times 10^{-3} \\
\text{COS} &= 5.5 \times 10^{-6} \quad 1.2 \times 10^{-4}
\end{align*}
\]

Table 1. Calculated equilibrium vapor pressures in bar for the systems gas–slag and gas–coking coke ash at 1 500 °C and 1 bar pressure of CO.

To calculate the equilibrium vapor pressure of potassium for the reduction reaction:

\[
(\text{K}_2\text{O}) + \text{C} = 2\text{K(g)} + \text{CO(g)} \quad (53)
\]

The computed equilibrium values in Table 2 are for a blast furnace slag containing 0.5 % K\(_2\)O and having a basicity of \( B' = 1.5 \): \( K \) is the equilibrium constant for reaction (53) from the thermochemical data and \( a_{\text{K}_2\text{O}} \) is the activity of K\(_2\)O in the slag, relative to the hypothetical solid K\(_2\)O, from the experimental data of Steiler.\textsuperscript{66}

Table 2. Equilibrium vapor pressure of potassium for reaction (53) with slag having 0.5 % K\(_2\)O and \( B' = 1.5 \).

\[
\begin{array}{|c|c|c|}
\hline
\text{Temperature} & K, \text{bar}^3 & a_{\text{K}_2\text{O}} \\
\hline
1 200 & 3.10 \times 10^4 & 2.1 \times 10^{-12} \\
1 300 & 2.69 \times 10^4 & 5.5 \times 10^{-13} \\
1 400 & 1.81 \times 10^4 & 1.4 \times 10^{-11} \\
1 500 & 9.78 \times 10^3 & 3.5 \times 10^{-11} \\
\hline
\end{array}
\]
carried away by the furnace gas. For a typical total gas volume of 2,300 nm³/t-HM, the partial pressure of the total potassium vapor species would be 7.2×10⁻⁴ bar (for a total gas pressure of 3.6 bar in the bosh region). Comparison of this total potassium pressure in the gas with those in Table 2 for the gas-slag equilibrium indicates that the slag particles will pick up potassium from the gas only at temperatures below 1,200 °C. The ash in the coke samples taken from the tuyere zone contains 2 to 4% (Na₂O+K₂O) which is several fold of that in the original coke ash. Because of the low basicity of coke ash, the amount of alkali therein is expected to be 5 to 10 times greater than that found in the slag. In the upper part of the bosh, the slag and coke will pick up alkalis from the gas. As the temperature of the slag and coke increases during descent in the bosh, they will emit alkali vapors to the gas phase. However, the partial pressure of potassium vapor in the gas would probably be below that given in Table 2 for the gas-slag equilibrium. Nevertheless, the numerical examples cited suggest that much of the alkali accumulated in the bosh and hearth zone of the blast furnace, via recycling, are in the gas phase.

According to a mass spectrometric study of vaporization of potassium cyanide by Simmons et al.,⁶⁹ the equilibrium pressures of vapor species are in the order $p_{(KCN)₂} > p_{KCN} > p_{K}$. For atmospheric pressure of nitrogen and at graphite saturation, the following are the equilibrium ratios of the vapor species: at the melting point of KCN (635 °C), (KCN)₂: KCN: K = 2: 1: 0.76 and at the boiling point (1,132 °C), (KCN)₂: KCN: K = 4.6: 1: 0.19. It is all too clear that (KCN)₂ is the dominant alkali-bearing species in the blast furnace. The sodium in the burden underg oes cyclic reactions similarly to potassium; however, the concentration of sodium-bearing species are about one-tenth of the potassium-bearing species.

In addition to the well-known problems associated with alkali accumulation in the blast furnace stack, the alkali cyanides are also responsible for the generation of ammonia and hydrogen cyanide in the upper part of the stack by the reactions:

$$2\text{KCN} + 3\text{H}_2\text{O} = \text{K}_2\text{CO}_3 + 2\text{NH}_3 + \text{C} \quad \text{(54)}$$
$$\text{NH}_3 + \text{CO} = \text{HCN} + \text{H}_2\text{O} \quad \text{(55)}$$

These and other organic volatile matters thus generated in the stack end up in the wash water of the blast furnace off-gas. Recent experimental work of Turkdogan and Josephic,⁷⁰ under conditions partly simulating the blast furnace stack, substantiated the validity of this mechanism of generation of ammonia and hydrogen cyanide in the stack.

2. Iron Oxide Fumes

Evolution of iron oxide fumes is a common occurrence in all steelmaking operations, e.g., in melting, in refining with oxygen blowing, and during furnace tapping. The mechanism of this interesting phenomenon was resolved in an earlier study by Turkdogan et al.,⁷¹ based on the concept of diffusion-limited enhanced vaporization of metals in an oxidizing environment. In this counterflux-transport process, at some short distance from the surface of the metal, the oxygen and metal vapor react to form a metal oxide mist (fume). The formation of an oxide in the gas phase provides a sink for the metal vapor and oxygen resulting in the counterflux of these two gaseous species. An increase in the oxygen partial pressure, and/or an increase in the gas-film mass-transfer coefficient for oxygen, decreases the thickness of the sub-boundary layer through which the metal vapor is diffusing, hence increases the rate of fuming. Also, the higher the vapor pressure, or higher the temperature, the faster would be the rate of fuming. For given temperature and conditions of gas flow over the metal surface, the rate of vaporization is represented in a general form by the relation:

$$\text{Rate of fuming} = \Phi(1-\theta) \exp \left(-\frac{E}{RT}\right)$$

where, $E$: is the energy of vaporization
$\Phi$, $\phi$: constants for given conditions of steady-state vaporization
$(1-\theta)$: the fraction of metal surface exposed to the oxidizing gas stream.

When the flux of oxygen toward the surface of the metal is greater than the equivalent countercurrent diffusive flux of the metal vapor, the metal surface becomes oxidized, i.e., $(1-\theta) \rightarrow 0$, and consequently the fuming ceases. Just before this cutoff, the rate of fuming will be close to the maximum rate of vaporization that is attainable is vacuo. These theoretical expectations have been well substantiated experimentally.

During furnace tapping, the metal stream is exposed to air, consequently the iron oxide fumes are emitted by the mechanism described. The fume emission is particularly intensive in the blast furnace metal runner, because of the high vapor pressure of manganese at the concentrations present in the hot metal. Furthermore, the metal droplets ejected by gas evolution from the hot metal in the runner increase the gas–metal interfacial area, consequently intensify the fume emission. It follows from the basic concept of the mechanism of fuming that the extent of fume emission can be suppressed by either eliminating gaseous oxygen from the exposed surface of the metal or by covering the metal surface with a layer of slag. Depletion of oxygen near the metal surface can be achieved by shrouding the metal runner with a gas

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* It should be noted that in the free energy tables in p. 12 of Ref. 5), the value given for the vaporization of liquid KCN is incorrect; it should have been, according to the data of Simmons et al.⁶⁹:

$$2\text{KCN} (l) = (\text{KCN})₂(g)$$
$$\Delta G° = 52.180 - 36.64T \text{ (cal)}$$
White fumes emitted from the blast furnace slag runner is another example of vaporization-induced occurrence. Samples of white fumes collected over the slag runner have been characterized recently by Simon and Kelly,72 in U.S. Steel Research Laboratory, using the scanning electron microscope. The X-ray scan spectra revealed that the potassium and sulfur were the most dominant elements in the fume samples. Such a finding is consistent with the expected reaction of slag with air during tapping.

The blast furnace slag contains 1.5 to 2.0 % S, and as discussed earlier, the potassium vapor pressure of the slag is relatively high. Therefore, upon exposure to air, the potassium and sulfur will be evolved from the slag as potassium sulfate by the reaction:

$$2(K^+)+(S^{2-})+2O_2 = K_2SO_4 \text{(white fume)}$$

In addition, there is SO$_2$ evolution, readily evidenced by the characteristic odor in the casthouse,

$$S^{2-} + \frac{3}{2}O_2 = (O^2-) + SO_2$$

In the oxidizing atmosphere over the slag, the sulfur dioxide is partly oxidized to sulfur trioxide. In the cooler ambient atmosphere away from the slag surface, SO$_3$ and K$_2$SO$_4$ will react with moisture in the air and form a sulfate complex xK$_2$SO$_4$.yH$_2$SO$_4$ which appears as white fume. The X-ray scan spectra indicated an atom concentration ratio K/S of about one in the collected fume samples, which apparently has the composition of K$_2$SO$_4$.H$_2$SO$_4$. The higher the slag temperature, the greater the extent of fuming caused by the above reactions.

The emission of white fumes can be suppressed by spreading a thin layer of sand over the slag surface in the runner. This simple remedy works for two reasons: added sand, or other inert powder, chills the salg surface and also reduces the surface area of slag exposed to air.

Yamamoto and Harashima73 studied changes in chemical composition of slag during the refining of hot metal with sodium carbonate and oxygen-top blowing. They deduced from the composition of slag and fume collected that there was preferential vaporization of sulfur and sodium from the slag. This observation can be explained also in terms of reaction (57) written for Na$^+$ in the slag and Na$_2$SO$_4$ in the fume.

Vaporization in Coal Gasification

Certain vapor species that are generated in some coal gasification processes may cause side reactions which could affect the industrial application of the gasification process. Because such processes are still in the early stages of development, technical information available is meagre, therefore we can at present only speculate on the possibility of vaporization-induced side reactions and consequences thereof.

In the coal gasification processes that are now being developed, e.g., CGS, COIN, KR, the pulverized or granular coal is partially combusted with oxygen and steam in a bath of liquid iron to generate a reducing gas for use in the ore reduction and smelting processes. In his doctorate dissertation, Fukagawa74 presented a comprehensive review of much of the work done to date on coal gasification using liquid iron as the reduction medium. Technical developments made to date on direct usage of coal in the steel industry are presented in a series of papers published recently in *Ironmaking and Steelmaking*.

Bench scale experiments and pilot plant tests have shown that about 15 to 30 % of the sulfur in coal is absorbed by the molten iron and slag in the gasifier and the remainder transferred to the gas and iron dust (fume) emitted. The gas-metal interaction in the combustion zone is conducive to enhanced vaporization of iron by the mechanism already described. Away from the combustion zone, the iron oxide fume is reduced to metallic iron dust which interacts with sulfur-bearing vapor species in the reducing gas. As the temperature of the dust-laden gas decreases, more sulfur is absorbed by the iron dust. Upon cooling and dedusting, the reducing gas generated contains less than 300 vol-ppm H$_2$S. The iron oxide fume emitted during gasification of coal is an efficient gas desulfurizer contained in the system only when the reducing gas is cooled and dedusted. The dust removed from the cooled reducing gas contains up to about 8 % S, a material not suitable for recycle.

The sulfur and dust-related problems with these coal gasifiers have to be surmounted for direct usage of hot reducing gas in the shaft or fluidized bed reduction of iron ore. Noting that the hot reducing gas enters the ore reducer at about 900 °C, the gas has to be dedusted at a relatively high temperature, for which a new technology is needed. In a reducing gas containing 25 vol% H$_2$, the entrained iron dust will not desulfurize the gas below 800 vol-ppm H$_2$S at 900 °C. Such a high sulfur-bearing gas is not suitable for the reduction of iron ore. Hot dedusting and desulfurization may be achieved by passing the gas, for example, through a bed of calcined dolomite at about 950 °C. In such a process, the sulfided doloma has to be removed periodically from the reactor and be treated for disposal. Of course, other methods of hot dedusting and desulfurization can be visualized; the subject will not be pursued further here.

Another problem to be resolved is that involving alkalies in the coal. Since coal contains some nitrogen, most of the alkalies will be contained in the gas generated as alkali cyanide vapors, which will eventually condense in the ore reducer. Obviously, measures have to be taken to prevent the accumulation of alkali carbonates and cyanides in the upper part of the shaft reducer.

We see from the examples cited, there are many ramifications to the role of vapor species in pyrometal-
lurgical or other high temperature processes. The vapor species generated may cause pollution problems, may impede the operation of the process or may assist the process reactions.

V. Concluding Remarks

Scope of the physical chemistry of ironmaking and steelmaking is, of course, much greater than what has been presented in this discourse. Therefore, the concluding remarks are confined to the subjects discussed in this paper. The state of reactions in pyrometallurgical processes can be evaluated with confidence from accumulated knowledge of the physicochemical and thermodynamic properties of materials and of the process engineering concepts pertinent to high temperature technology. The analysis of plant data indicates departures from equilibrium for various gas–slag–metal reactions in the bosh and hearth zones of the blast furnace. The least departure from equilibrium is for the distribution of silicon between metal and slag. Departure from equilibrium for the manganese-silicon reaction is greater for slags of low basicity. Despite departures from equilibrium, the silicon and sulfur contents of the hot metal change in a systematic manner for a given blast furnace, i.e., high silicon/low sulfur and low silicon/high sulfur.

In oxygen steelmaking processes, most reactions approach slag–metal equilibrium at the time of furnace tapping. However, some differences are seen in the behavior of phosphorus reaction in the oxygen-top and -bottom blowing processes. The salg/metal phosphorus distribution is closer to equilibrium in Q; BOP than in BOF steelmaking, particularly for low carbon contents at tap.

A greater use is being made of the gas–slag–metal equilibrium data in recent developments of ladle refining of hot metal and steel. At temperatures of about 1 300 °C and with fluxed-basic slags of low melting temperatures, it is now possible to dephosphorize hot metal to the levels of 0.005 % P at carbon contents in the range 4.0 to 4.5 %. The aluminum-killed steel can be desulfurized to levels below 10 ppm S by interacting liquid steel with a line-saturated aluminate slag using argon stirring for slag-metal mixing.

Vapor species are now known to play various roles in pyrometallurgical processes. The alkali cyanide vapors are responsible for alkali recycle and accumulation in the blast furnace and also for the generation of ammonia and hydrogen cyanide in the upper part of the stack. The silicon and sulfur-bearing vapor species are responsible for the transfer of silicon and sulfur from coke to metal and slag in the bosh region of the blast furnace. Fumes emitted upon exposure of liquid steel, hot metal or blast furnace slag to air are consequences of some vaporization phenomenon.

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