Kinetics of Evaporation of Manganese, Copper and Sulfur from Iron Alloys in Vacuum Induction Melting*

By Reichi OHNO**

Synopsis

The evaporation-rate constant $K_i$ (kg m$^{-2}$ s$^{-1}$) for each of manganese, copper and sulfur in the vacuum induction melting of iron alloys has been determined. The rate constant $K_m$ or $K_i^*$ (kg m$^{-2}$ s$^{-1}$) for the vaporization of these elements at the vacuum-melt interface is calculated. In each of the Fe–C–Mn, Fe–C–Cu and Fe–C–Si–S systems, the value of $K_i$ at a lower stirring rate is about one half of that at a higher stirring rate; hence mass transfer in the melt must be involved in the rate-determining step for their evaporation at the lower stirring rate. In the Fe–C–Cu and Fe–Mn systems, the value of $K_{Cu}$ at 1 973 K is obviously greater than that at 1 873 K, but those of $K_{Mn}$ at both temperatures are close to each other. The rates of evaporation of manganese must be determined predominantly by the rate of its transfer in the melt in view of the values of $\rho K_m$ at both temperatures, which were calculated on the basis of the equation $K_i = \rho K_m K_i^* (\rho K_m + K_i^*)$, where $\rho$ (kg m$^{-3}$) is the density of the melt and $K_m$ (m$^{-1}$) is the mass-transfer coefficient in the melt. In the Fe–Mn, Fe–Cu and Fe–Sn systems at 1 873 K, most of the reported experimental values of $K_{Mn}$, $K_{Cu}$ and $K_{Sn}$ agree well with their respective calculated values from the equation by taking $\rho K_m = 6.8 \times 10^{-1}$ (kg m$^{-2}$ s$^{-1}$), but the present experimental values of $K_{Cu}$ are smaller than the calculated value. The plots of $K_i$ vs. $a_0$ in the Fe–Si–S system are linear at two different stirring rates. The rate constants $k_1$ and $k_2$ given by this linear relation at a lower stirring rate are smaller than those at a higher stirring rate, respectively, and must involve $K_m$. In the desulfurization of Fe–S, Fe–C–S, Fe–Si–S and Fe–C–Si–S alloys at temperatures in the range 1 688 to 1 873 K, the relation between $K_0$ and $K_i^*$ is represented by a curve calculated from the equation by taking $K_0 = 0.24 K_i^*$ and $\rho K_m = 2.5$ regardless of the temperatures and the alloy systems. This value of $\rho K_m$ is much greater than the value of $\rho K_m$ for Fe–Mn, Fe–Cu and Fe–Sn systems. Oxygen and sulfur hardly affect the rate of evaporation of copper from molten iron at 1 873 K.

II. Experimental

1. Apparatus and Procedure

Various iron alloys were vacuum-melted in an induction furnace. Heating was carried out by a 430 kHz induction current and evacuation was carried out by a rotary pump (500 l/min), an oil-diffusion pump (400 l/s), and an oil-ejector pump (650 l/min). After each of the alloys (140–170 g) was heated to a desired temperature under argon at 0.10 MPa, it was vacuum-melted for a definite time, and then argon was readmitted into the furnace; the sample was taken out from the melt by suction with a silica tube (5 mm in 1D) and was subjected to the elemental analysis. Temperature of the melt was measured with an optical pyrometer and controlled within $\pm 20 \text{K}$ by manually adjusting the input power. The time of vacuum melting was 5 to 20 min. Pressure during vacuum melting was measured by an ionization gage, being in the range $10^{-1}$ to 1 Pa. Tables 1 and 2 show the experimental con-

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Table 1. Experimental conditions and the evaporation-rate constants ($K_i$) of manganese, copper and sulfur

<table>
<thead>
<tr>
<th>Series</th>
<th>Run No.</th>
<th>System</th>
<th>%C</th>
<th>%Si</th>
<th>($%i)_0$</th>
<th>Temperature (K)</th>
<th>Heating condition</th>
<th>Crucible</th>
<th>$K_i$ (kg.m(^{-2}).s(^{-1}))</th>
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<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>Fe-C-Mn</td>
<td>4.25-4.31</td>
<td>—</td>
<td>0.99</td>
<td>1773</td>
<td>HC-A</td>
<td>AL-1</td>
<td>3.8×10(^{-1})</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>Fe-C-Mn</td>
<td>4.13-4.15</td>
<td>—</td>
<td>0.99</td>
<td>1773</td>
<td>HC-B</td>
<td>AL-1</td>
<td>1.9×10(^{-1})</td>
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<tr>
<td></td>
<td>3</td>
<td>Fe-C-Cu</td>
<td>3.60-3.68</td>
<td>—</td>
<td>2.06</td>
<td>1773</td>
<td>HC-A</td>
<td>AL-1</td>
<td>2.1×10(^{-1})</td>
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<tr>
<td></td>
<td>4</td>
<td>Fe-C-Cu</td>
<td>3.98-4.04</td>
<td>—</td>
<td>2.03</td>
<td>1773</td>
<td>HC-B</td>
<td>AL-1</td>
<td>1.0×10(^{-1})</td>
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<td></td>
<td>5</td>
<td>Fe-C-Si-S</td>
<td>3.83-3.91</td>
<td>0.88-0.99</td>
<td>0.23</td>
<td>1773</td>
<td>HC-A</td>
<td>AL-1</td>
<td>4.7×10(^{-1})</td>
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<td>6</td>
<td>Fe-C-Si-S</td>
<td>3.69-3.82</td>
<td>0.86-0.93</td>
<td>0.22</td>
<td>1773</td>
<td>HC-B</td>
<td>AL-1</td>
<td>1.9×10(^{-1})</td>
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<td>2</td>
<td>7</td>
<td>Fe-Mn</td>
<td>0.046</td>
<td>—</td>
<td>0.95</td>
<td>1873</td>
<td>HC-A'</td>
<td>AL-2</td>
<td>5.8×10(^{-1})</td>
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<td></td>
<td>8</td>
<td>Fe-Mn</td>
<td>0.049</td>
<td>—</td>
<td>0.91</td>
<td>1973</td>
<td>HC-A'</td>
<td>AL-2</td>
<td>6.1×10(^{-1})</td>
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<td>9</td>
<td>Fe-Cu</td>
<td>0.046</td>
<td>—</td>
<td>2.02</td>
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<td></td>
<td>10</td>
<td>Fe-Cu</td>
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<td>—</td>
<td>2.00</td>
<td>1973</td>
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<td>AL-2</td>
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<td>11</td>
<td>Fe-C-S</td>
<td>4.15-4.28</td>
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<td>0.93-1.00</td>
<td>0.23</td>
<td>1693</td>
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<td>AL-1</td>
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<td>4.39-4.46</td>
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<td>AL-1</td>
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<td>Fe-C-Si-S</td>
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<td>HC-A</td>
<td>AL-1</td>
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<td>16</td>
<td>Fe-Si-S</td>
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<td>0.92-1.0</td>
<td>0.23</td>
<td>1873</td>
<td>HC-A'</td>
<td>AL-2</td>
<td>1.7×10(^{-1})</td>
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<td>17</td>
<td>Fe-Si-S</td>
<td>0.053</td>
<td>1.90-2.02</td>
<td>0.28</td>
<td>1873</td>
<td>HC-A'</td>
<td>AL-2</td>
<td>3.0×10(^{-1})</td>
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<td>18</td>
<td>Fe-Si-S</td>
<td>0.044</td>
<td>2.80-2.96</td>
<td>0.22</td>
<td>1873</td>
<td>HC-A'</td>
<td>AL-2</td>
<td>6.0×10(^{-1})</td>
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<td>19</td>
<td>Fe-Si-S</td>
<td>0.044</td>
<td>0.94-1.01</td>
<td>0.26</td>
<td>1873</td>
<td>HC-A'</td>
<td>AL-3</td>
<td>1.3×10(^{-1})</td>
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<td>20</td>
<td>Fe-Si-S</td>
<td>0.036</td>
<td>1.85-1.99</td>
<td>0.23</td>
<td>1873</td>
<td>HC-A'</td>
<td>AL-3</td>
<td>3.3×10(^{-1})</td>
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<td>21</td>
<td>Fe-Si-S</td>
<td>0.039</td>
<td>2.87-3.04</td>
<td>0.25</td>
<td>1873</td>
<td>HC-A'</td>
<td>AL-3</td>
<td>5.1×10(^{-1})</td>
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<td>Fe-Si-S</td>
<td>0.027</td>
<td>0.95-1.04</td>
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<td>1873</td>
<td>HC-B'</td>
<td>AL-3</td>
<td>8.1×10(^{-2})</td>
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<td>Fe-Si-S</td>
<td>0.038</td>
<td>1.92-2.07</td>
<td>0.22</td>
<td>1873</td>
<td>HC-B'</td>
<td>AL-3</td>
<td>1.8×10(^{-1})</td>
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<td>24</td>
<td>Fe-Si-S</td>
<td>0.053</td>
<td>1.88-2.02</td>
<td>0.23</td>
<td>1873</td>
<td>HC-B'</td>
<td>AL-3</td>
<td>3.5×10(^{-1})</td>
</tr>
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<td>25</td>
<td>Fe-Si-S</td>
<td>0.045</td>
<td>2.91-3.05</td>
<td>0.24</td>
<td>1873</td>
<td>HC-B'</td>
<td>AL-3</td>
<td>3.5×10(^{-1})</td>
</tr>
</tbody>
</table>

Notes:
- $i$: an evaporating element, i.e., manganese, copper or sulfur
- ($\%i)_0$: the initial concentration of $i$ (wt%)

Table 2. Experimental conditions and the evaporation-rate constants of copper ($K_{Cu}$) at 1873 K

<table>
<thead>
<tr>
<th>Run No.</th>
<th>System</th>
<th>($%Cu)_0$</th>
<th>%S</th>
<th>($%O)_0$</th>
<th>Crucible</th>
<th>$K_{Cu}$ (kg.m(^{-2}).s(^{-1}))</th>
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<tbody>
<tr>
<td>26</td>
<td>Fe-Cu</td>
<td>2.06</td>
<td>—</td>
<td>0.0006-0.0016</td>
<td>AL-1</td>
<td>2.3×10(^{-1})</td>
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<td>27</td>
<td>Fe-Cu-S</td>
<td>2.16</td>
<td>0.11-0.12</td>
<td>0.0012-0.0018</td>
<td>MG</td>
<td>2.1×10(^{-1})</td>
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<td>28</td>
<td>Fe-Cu-O</td>
<td>1.76</td>
<td>—</td>
<td>0.047-0.049</td>
<td>MG</td>
<td>1.9×10(^{-1})</td>
</tr>
</tbody>
</table>

Notes:
- ($\%Cu)_0$: the initial concentration of copper (wt%)
A: induction heating coil
B: silica tube (7.5 cm in ID)
C: outer alumina crucible (5.5 cm in ID, 12 cm in height)
D: alumina crucible (AL-1; 3.8 cm in ID, 2.5 cm in depth) or magnesia crucible (MG; 3.8 cm in ID, 2.6 cm in depth)
E: molten iron alloy
F: silica tube (8.5 cm in ID)
G: outer alumina crucible (6.5 cm in ID, 15 cm in height)
H: graphite crucible (5.3 cm in ID, 6.0 cm in OD, 11 cm in height)
I: alumina crucible (D)
J: alumina crucible (AL-3; 3.0 cm ID, 6.0 cm in depth)
K: alumina crucible (AL-2; 2.7 cm ID, 10 cm in depth)
L: graphite cylinder (4.2 cm in ID, 4.7 cm in OD, 5.8 cm in length)
M: molybdenum ribbon
N: magnesia plate

(a) Heating condition HC-A
(b) Heating condition HC-B
(c) Heating condition HC-A'
(d) Heating condition HC-B'

Fig. 1. Crucible arrangements

ion was analyzed on the basis of the rate equation:

\[- \frac{d(\%i)}{dt} = K_i \frac{A}{W} \{(\%i) - (\%i)_i\} \quad \text{(1)}\]

giving the integrated form:

\[\log \frac{(\%i)_0 - (\%i)_i}{(\%i) - (\%i)_i} = K_i \frac{1}{2.3} \frac{A}{W} t \quad \text{(2)}\]

where,

\[
\begin{align*}
(\%i)_0 & : \text{the concentration of } i \text{ in the melt at time } t (\text{wt} \% ) \\
(\%i)_i & : \text{the concentration of } i \text{ at } t = 0 \text{ (wt} \% )
\end{align*}
\]

\[
\begin{align*}
(\%i) & : \text{the finally attainable concentration of } i \text{ (wt} \% ) \\
A & : \text{the surface area of the melt (m}^2 \text{)} \\
W & : \text{the weight of the melt (kg)} \\
K_i & : \text{the evaporation-rate constant of } i \text{ (kg} \cdot \text{m}^{-2} \cdot \text{s}^{-1} \text{)}
\end{align*}
\]

In Figs. 2 to 7 (p.p. 734-737), the left side of Eq. (2) or \( \log \left( \frac{(\%i)_0}{(\%i)_i} \right) \) is plotted against \( \left( \frac{A}{W} \right)t \). Values of \( K_i \) calculated from the slopes of the straight lines are presented in Tables 1 and 2. The values of \( (\%S) \), in the Fe-C-Si-S system of Series 3 were estimated at 0.006 for Run No. 14 and 0.0049 for Run No. 15 by extrapolating the plots of \( (\%S) \) vs. \( t \).

IV. Rate Equations

The evaporation of one alloying element from a liquid metal under a reduced pressure involves the following three processes: (a) transfer of the element through the metal phase to the metal–gas interface, (b) vaporization at the interface, and (c) transfer through the gas phase to the condensing surface.

If the rate of evaporation of the alloying element \( i \) is determined by the processes (a), (b) and (c), it is expressed by the following form: \(^{13}\)
Fig. 3. Evaporation of manganese from Fe-Mn alloys and copper from Fe-Cu alloys at 1873 and 1973 K under HC-A.

Fig. 4. Desulfurization of Fe-C-S alloys at 1688 and 1873 K under HC-A.

\[
- \frac{d(\%i)}{dt} = \frac{A}{W} \frac{1}{\rho K_m + K_v + K_g} \times (\%i), \quad \text{(3)}
\]

where \(\rho\) is the density of the melt (kg\cdot m^{-3}), \(K_m\) is the mass-transfer coefficient in the melt (m\cdot s^{-1}), \(K_v\) is the rate constant for the vaporization of \(i\) at the interface (kg\cdot m^{-2}\cdot s^{-1}), being given by \(\alpha \sqrt{M_i} / (2\pi RT)^{\frac{1}{2}} P_v^e k\) where \(\alpha\) is the condensation coefficient of the evaporating species \(i\), \(M_i\) is the molecular weight of \(i\) (kg\cdot mol^{-1}), \(R\) is gas constant (kg\cdot m^{2}\cdot s^{-2}\cdot K^{-1}\cdot mol^{-1}), \(T\) is absolute temperature (K), \(\gamma^o_i\) is the Raoultian activity coefficient of \(i\) at infinite dilution, \(P_v^e\) is the equilibrium vapor pressure of pure \(i\) (kg\cdot m^{-1}\cdot s^{-2}), and \(k\) is the proportionality constant in the relation \(N_i = k(\%i)\) where \(N_i\) is the mole fraction of \(i\), and \(K_g\) is the rate constant for the transfer of \(i\) through the gas (kg\cdot m^{-2}\cdot s^{-1}), being given by \((100k_g M_i \gamma^o_i P_v^e k) / RT\) where \(k_g\) is the mass-transfer coefficient in the gas (m\cdot s^{-1}).

If the rate of formation of an evaporating species is so slow that the chemical reaction for its formation is not in equilibrium, this process must be taken into consideration.

When \((\%i)_{\text{eq}} < (\%i)\), Eqs. (1) and (3) give

\[
K_i = \frac{1}{\rho K_m + K_v + K_g} \quad \text{(4)}
\]

When \(K_g \gg \rho K_m\) and \(K_g \gg K_v\), Eq. (4) gives

\[
K_i = \frac{\rho K_m K_v}{\rho K_m + K_v} \quad \text{(5)}
\]

When mass transfer occurs by diffusion across the interface from a small element of liquid brought up to the interface by induction stirring, \(K_m\) is expressed by the following equation based on the rigid flow model:\(^{34}\)

\[
K_m = 2 \sqrt{\frac{D}{\tau'}} \quad \text{(6)}
\]

where, \(D\): the diffusion coefficient (m^{2}\cdot s^{-1})

\(\tau'\): the life time of the element moving along the interface(s).

If each element brought to the interface is itself fully turbulent and the rate of mass transfer will...
depend solely on the rate at which new elements are brought to the interface, $K_m$ is expressed by the form\cite{10}

$$K_m = \bar{v} \text{................(7)}$$

where, $\bar{v}$: the mean velocity of the element normal to the interface.

Equations (6) and (7) show that $K_m$ at a higher stirring rate is greater than the value at a lower stirring rate. The values of $K_m$ may be decreased by the presence of surface active substances in the interface\cite{11,13} or increased by the interfacial turbulence which can occur when they evaporate from the interface\cite{12}.

According to the mass spectrometric analysis by Kato and Fukube,\cite{15} the desulfurization of iron alloys

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under vacuum occurs by the formation of various sulfur-bearing species, i.e., S and \( \text{S}_2 \) in the Fe–S system; S, \( \text{S}_2 \), CS and \( \text{CS}_2 \) in the Fe–C–S system; and S, \( \text{S}_2 \), CS, \( \text{CS}_2 \) and SiS in the Fe–C–Si–S system. When the rate of desulfurization is determined by the process (b) and the value of \( a \) for each species is taken as unity, the rate of desulfurization of the Fe–C–Si–S system is expressed in the form:

\[
-d(\% S)/dt = 100 A \frac{W}{k_1 \alpha_{\text{Si}} + k_2 \alpha_{\text{S}}} \left[ \sqrt{\frac{M_{\text{Si}}}{2\pi RT} P_{\text{Si}} + \sqrt{\frac{M_{\text{S}}}{2\pi RT} P_{\text{S}}}} + \sqrt{\frac{M_{\text{CS}}}{2\pi RT} P_{\text{CS}} + \frac{2\sqrt{M_{\text{CS}}/M_{\text{Si}}}}{\sqrt{2\pi RT} P_{\text{SiS}}}} + \sqrt{\frac{M_{\text{SiS}}}{2\pi RT} P_{\text{SiS}}} \right]
\]

where, \( M_i \) (i' = S, \( \text{S}_2 \), CS, \( \text{CS}_2 \) or SiS): the molecular weight of i' (kg·mol\(^{-1}\))

\( P_{i'} \) (i' = S, \( \text{S}_2 \), CS, \( \text{CS}_2 \) or SiS): the equilibrium vapor pressure of i' (kg·m\(^{-2}\)·s\(^{-1}\))

\( f_{\text{S}} \): the Henrian activity coefficient of sulfur in the alloy

\( \alpha_{\text{C}}, \alpha_{\text{Si}} \): the activities of carbon and silicon in the alloy when the standard states are pure graphite and liquid silicon, respectively

\( K'_{\text{S}}, K'_{\text{S}_2}, K'_{\text{CS}}, K'_{\text{CS}_2}, \text{and } K'_{\text{SiS}} \): the equilibrium constants for the reactions \( S = S(g), \ 2S = S_2(g), C + S = CS(g), C + 2S = CS_2(g), \) and \( S + Si = SiS(g) \), respectively.

Therefore, if the value of \( a \) for each species is unity, the rate constant for the process (b), which is defined by the equation \( -d(\% S)/dt = k_3(A/W)(\% S) \), is given by:

\[
k_3 = 100 \sqrt{\frac{M_{\text{Si}}}{2\pi RT} f_{\text{Si}} + 2\sqrt{\frac{M_{\text{S}}}{2\pi RT} f_{\text{S}}}} + \sqrt{\frac{M_{\text{CS}}}{2\pi RT} f_{\text{CS}} + \frac{2\sqrt{M_{\text{CS}}/M_{\text{Si}}}}{\sqrt{2\pi RT} f_{\text{SiS}}}} + \sqrt{\frac{M_{\text{SiS}}}{2\pi RT} f_{\text{SiS}}} \]

On the basis of the study of Kato and Fukube,\(^{15}\) it is reasonable to consider that the desulfurization of Fe–Si–S alloys occurs predominantly by the reactions \( \text{Si} + S = \text{SiS}(g) \) and \( S = S(g) \). Assuming that the rate of desulfurization of the alloys is determined by the formation of SiS and S on the melt surface, Fruehan and Turkdogan\(^{6}\) derived the following equation:

\[
-d(\% S)/dt = 100 A \frac{W}{k_1 \alpha_{\text{Si}} + k_2 \alpha_{\text{S}}} \left[ \sqrt{\frac{M_{\text{Si}}}{2\pi RT} f_{\text{Si}} + \sqrt{\frac{M_{\text{S}}}{2\pi RT} f_{\text{S}}}} + \frac{2\sqrt{M_{\text{CS}}/M_{\text{Si}}}}{\sqrt{2\pi RT} f_{\text{SiS}}}} + \frac{M_{\text{SiS}}}{2\pi RT} K'_{\text{SiS}} \alpha_{\text{Si}} f_{\text{SiS}}(\% S) \right] \]

where, \( k_1 \) (kg·m\(^{-2}\)·s\(^{-1}\)): the rate constant for the formation of SiS

\( k_2 \) (kg·m\(^{-2}\)·s\(^{-1}\)): the rate constant for the formation of S.

When \( \% S_i = 0 \), Eqs. (1) and (10) give

\[
k_{\text{SiS}} f_{\text{S}} = 100(k_1 \alpha_{\text{Si}} + k_2) \]

They demonstrated the plot of \( K_{\text{SiS}} f_{\text{S}} \) vs. \( \alpha_{\text{Si}} \) to be linear.

V. Thermodynamic Quantities and Rate Constants for Vaporization

Values of the activity coefficients of manganese, copper and tin, which were used for the evaluation of \( K'_{\text{S}} \), are presented in Table 3. The activity coefficients except \( \gamma_{\text{Na}} \) and \( \gamma_{\text{Ca}} \) at 1 873 K were evaluated by means of the Darken’s quadratic formalism.\(^{22}\) Data for the Fe–Mn system at 1 873 K\(^{19}\) the Fe–Cu system at 1 873 K\(^{21}\) and the Fe–Sn system at 1 820 K\(^{23}\) were adjusted to the temperatures shown in Table 3 by taking \( a_{\text{Fe}} \) so as to be inversely pro-

Table 3. Activity coefficients of manganese, copper and tin at infinite dilution in liquid iron alloys (Standard state is pure liquid)

<table>
<thead>
<tr>
<th>System</th>
<th>Temperature (K)</th>
<th>Mn</th>
<th>Cu</th>
<th>Sn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–i</td>
<td>1 873</td>
<td>1.3(^{(1)})</td>
<td>8.0(^{(1)})</td>
<td>2.8</td>
</tr>
<tr>
<td>Fe–C–Cu (3.6%C)</td>
<td>1 973</td>
<td>1.2</td>
<td>7.4</td>
<td>—</td>
</tr>
</tbody>
</table>

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portional to the absolute temperature as suggested by Darken and Gurry.\textsuperscript{24} The value of $\gamma_{Fe}^c$ in the Fe–
C–Cu alloy was calculated from $\gamma_{Fe}^c$\textsuperscript{23} in the Fe–Cu
system at 1 873 K and the interaction coefficient $\varepsilon_{FeCu}^c = 4.27$\textsuperscript{21} at 1 873 K.

Table 4 shows the vapor pressures of pure manganese, copper and tin, and the values of $K_v$ of evaporating species. The values of $K_v$ were calculated by taking $a = 1$ from the values of $\gamma_{Fe}^c$ and $P^0$ on the basis of the expression for $K_v$ given in section IV. The value of $K_v$ for the Fe–C–Mn alloy (Run No. 1) was estimated at 0.8 by the use of $\varepsilon_{FeMnCu}^c = -4.47$\textsuperscript{20} at carbon saturation.

Thermodynamic quantities used for the evaluation of $K_v$ are presented in Tables 5 and 6. The activities of silicon in the Fe–Si–S alloys are based on the results of an investigation by Fruehan.\textsuperscript{31} Those in the Fe–C–Si–S alloys were calculated on the basis of the Darken's formalism\textsuperscript{32} representing the activity coefficient of the component $X$ in the graphite-saturated Fe–C–X system. The value of $\alpha_{FeSi}$ in this formalism was calculated from the data of Rist and Chipman\textsuperscript{30} on the activity coefficients of carbon.

The activities of carbon in the Fe–C–S system (Run Nos. 11 and 12) are based on the data compiled by Elliott, et al.,\textsuperscript{19} the activity coefficients of carbon in the Fe–C–Si–S system (Run Nos. 13 to 15) were evaluated from the solubility of graphite in Fe–Si alloys,\textsuperscript{20} and the values of the activity coefficient of sulfur are based on the study at 1 873 K by Sherman and Chipman.\textsuperscript{34} Each value of $K_v$ given in Table 6 is the average of the values of $K_v$ at the maximum and minimum sulfur concentrations investigated.

### VI. Discussion

The results obtained by Ward\textsuperscript{11} for the evaporation of manganese from inductively stirred iron at 1 853 K show that at pressures below 9 Pa the values of $K_v$ are independent of pressure. This fact suggests that under these conditions the rate-determining step for this evaporation does not involve the process (c). On the basis of this fact, it is assumed in the present discussion that Eq. (5) holds.

In each alloy system of Series I, the experimental value of $K_v$ for HC–B is about one half of that for HC–A. Hence the process (a) must be involved in the rate-determining step for the evaporation of $i$ at the lower stirring rate. Values of $\rho K_v$ for HC–A were calculated as 0.35 for the Fe–C–Cu system and 0.7 for the Fe–C–Mn system from the calculated values of $K_v$ and the experimental ones of $K_v$ on the basis of Eq. (5). Since the value of $\rho K_v$ is smaller than the value of $K_v$ in each system, even at a higher stirring rate the process (a) is possibly involved in the rate-determining step for the evaporation.

### Table 5. Standard free energies of formation of sulfur-bearing species. For the reaction as written, $\Delta G^\circ = A - BT$

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$A$ (J)</th>
<th>$B$ (J·K$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\frac{1}{2}S_2(g) = S(g)$</td>
<td>131 910</td>
<td>22.05</td>
<td>18</td>
</tr>
<tr>
<td>$(\frac{1}{2}S_2(g) + \frac{1}{2}CO(g)) = CO_2(g)$</td>
<td>99 940</td>
<td>16.57</td>
<td>27</td>
</tr>
<tr>
<td>$\frac{1}{2}S_2(g) = S(g)$</td>
<td>213 400</td>
<td>58.26</td>
<td>28</td>
</tr>
<tr>
<td>$C(l) + \frac{1}{2}S_2(g) = CS(g)$</td>
<td>246 900</td>
<td>95.4</td>
<td>29</td>
</tr>
<tr>
<td>$C(l) + \frac{1}{2}S_2(g) = CS_2(g)$</td>
<td>-13 800</td>
<td>6.7</td>
<td>30</td>
</tr>
<tr>
<td>$Si(l) + \frac{1}{2}S_2(g) = SiS(g)$</td>
<td>2 680</td>
<td>50.30</td>
<td>8</td>
</tr>
</tbody>
</table>

$S$: the hypothetical 1% solution of sulfur in liquid iron or an Fe–C (4.35%) alloy (g), (l) and (s): the pure gaseous, liquid and solid states at 101 325 Pa (1 atm pressure), respectively

### Table 6. Activities of carbon and silicon, activity coefficient of sulfur, and $K_v$ in iron alloys containing sulfur

<table>
<thead>
<tr>
<th>System</th>
<th>Run No.</th>
<th>Temperature (K)</th>
<th>$a_i$</th>
<th>$a_{Si} \times 10^4$</th>
<th>$f_S$</th>
<th>$K_v$ (kg·m$^{-2}$·s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe–S</td>
<td>—</td>
<td>1 873</td>
<td>—</td>
<td>—</td>
<td>1.0</td>
<td>$4.4 \times 10^{-2}$</td>
</tr>
<tr>
<td>Fe–C–S</td>
<td>11</td>
<td>1 688</td>
<td>0.669</td>
<td>—</td>
<td>—</td>
<td>$2.0 \times 10^{-1}$</td>
</tr>
<tr>
<td>Fe–C–S</td>
<td>12</td>
<td>1 873</td>
<td>0.542</td>
<td>—</td>
<td>3.5</td>
<td>1.2</td>
</tr>
<tr>
<td>Fe–Si–S</td>
<td>16, 19, 22</td>
<td>1 873</td>
<td>—</td>
<td>1.05</td>
<td>1.15</td>
<td>$6.1 \times 10^{-1}$</td>
</tr>
<tr>
<td>Fe–Si–S</td>
<td>17, 20, 23, 24</td>
<td>1 873</td>
<td>—</td>
<td>2.64</td>
<td>1.35</td>
<td>1.7</td>
</tr>
<tr>
<td>Fe–Si–S</td>
<td>18, 21, 25</td>
<td>1 873</td>
<td>—</td>
<td>4.45</td>
<td>1.55</td>
<td>3.2</td>
</tr>
<tr>
<td>Fe–C–Si–S</td>
<td>13</td>
<td>1 693</td>
<td>0.941</td>
<td>1.96</td>
<td>4.2</td>
<td>2.0</td>
</tr>
<tr>
<td>Fe–C–Si–S</td>
<td>14</td>
<td>1 773</td>
<td>0.926</td>
<td>2.75</td>
<td>4.3</td>
<td>4.2</td>
</tr>
<tr>
<td>Fe–C–Si–S</td>
<td>15</td>
<td>1 873</td>
<td>0.949</td>
<td>7.28</td>
<td>4.9</td>
<td>$1.9 \times 10$</td>
</tr>
</tbody>
</table>

The standard states of $a_i$ and $a_{Si}$: pure graphite and liquid silicon, respectively $f_S$: the Henrian activity coefficient of sulfur in the liquid iron alloys

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...
tion of copper and manganese.

In Series 2, the experimental value of $K_{eq}$ at 1 973 K is obviously greater than that at 1 873 K, but those of $K_{eq}$ at both temperatures are close to each other. In both alloy systems, the experimental value of $K_i$ is smaller than that of $K_w$. The values of $\rho K_w$ calculated from those of $K_i$ and $K_w$ by Eq. (5) are 6.5 x 10^{-1} at 1 973 K and 6.3 x 10^{-1} at 1 973 K for the Fe-Mn system, and 4.3 x 10^{-1} at 1 873 K and 5.1 x 10^{-1} at 1 973 K for the Fe-Cu system. In the Fe-Mn system, the experimental value of $K_{eq}$ is close to the value of $\rho K_w$ at each temperature and hence the rates of evaporation of manganese may be determined predominantly by the rate of process (a). The small temperature dependence of $K_{eq}$ may be explained on the basis of this idea. If $K_w$ is expressed in Eq. (6) and $t'$ is independent of temperature, the experimental data on the diffusion coefficient of the Fe-Mn system give 1.1 for the ratio of $K_w$ at 1 873 K to that at 1 773 K. In the Fe-Cu system, the values of $K_{eq}$ and $\rho K_w$ differ from each other and hence the processes (a) and (b) are possibly involved in the rate-determining step for the evaporation of copper.

The curve in Fig. 8 represents the relation between $K_i$ and $K_w$ defined by Eq. (5) at a fixed value of $\rho K_w$, i.e., 6.8 x 10^{-1}; this value was obtained from $K_M$, and $K_w$ in the Fe-Mn system on the basis of Eq. (5). Most of the experimental points of $K_{eq}$, $K_{Cu}$ and $K_{Sn}$ obey this curve, but those of $K_{eq}$ in the present study are lower than the value of $K_{eq}$ indicated by this curve.

In the present study of the Fe-Si-S system, the plot of $K_{eq}[Fe]/a_{eq}$ is also linear for both HC-A' and HC-B' as represented in Fig. 9. The slope of each line gives $k_1$ and the intercept $k_2$. The values of $k_i$ are shown in Fig. 9 and those of $k_2$ are 5.5 x 10^{-2} for HC-A' and 1.8 x 10^{-2} for HC-B'. Thus the values of $k_i$ and $k_2$ for HC-B' are smaller than those for HC-A', respectively. Hence the rate constants $k_i$ and $k_2$ for HC-B' must involve the mass-transfer coefficient in the melt.

The plots of the experimental values of $K_s$ vs. $K_i$ in Series 3 and 4 are shown in Fig. 10. The value of $K_s$ for the Fe-S system, i.e., 4.8 x 10^{-2} is close to that of $K_i$, but in each of the other systems, $K_s$ is smaller than $K_i$; the ratio $K_s/K_i$ decreases with an increase in $K_i$. The relation between $K_s$ and $K_i$ up to $K_i$=3 can be represented by a straight line for each of HC-A or HC-A', and HC-B'. This fact means that the plot of $K_{eq}[Fe]/a_{eq}$ can be a straight line for each heating condition. However, most of the experimental points of $K_s$ for HC-A or HC-A' obey the curve $A$ regardless of the temperatures and the alloy systems. This curve was calculated from the following equation corresponding to Eq. (5):

$$K_s = \frac{2.5 \times 0.24 k_i}{2.5 + 0.24 k_i}$$

where the numerical value 2.5 corresponds to the value of $\rho K_w$ and another numerical value 0.24 seems to be associated with the condensation coefficient,
which may depend on the sulfur-bearing species. It should be noted that a factor by which \( K_s \) is multiplied is calculated as 1.1 for the Fe-S system and 0.34 for the Fe-C-S system (Run No. 11) from \( K_s \) and \( K_i \) in each system and the numerical value 2.5, being greater than the numerical value 0.24 in both systems. The curve B was calculated from the equation of the same type:

\[
K_s = \frac{0.6 \times 0.24 K_i}{0.6 + 0.24 K_i} \quad \text{..........................(13)}
\]

where the numerical value 0.6 corresponds to the value of \( \rho K_m \) for HC-B, being much smaller than the numerical value 2.5 for HC-A or HC-A'. Process (a) must be involved in the rate-determining step for the desulfurization in which \( K_s \) is smaller than 0.24 \( K_i \). The numerical value 2.5 is much greater than the values of \( \rho K_m \) for HC-A or HC-A' in the Fe-Mn, Fe-Cu and Fe-Sn systems. This greater value of \( \rho K_m \) may be due to the interfacial turbulence which can occur when surface active sulfur evaporates from the interface. The present study suggests that \( K_m \) may be expressed in terms of \( K_i \) and \( \rho K_m \) on the basis of Eq. (5).

As may be seen from Fig. 7 and the values of \( K_{Cu} \) given in Table 2, sulfur and oxygen hardly affect the rate of evaporation of copper.

**VII. Summary**

1. In each of the Fe-C-Mn, Fe-C-Cu and Fe-C-Si-S systems at 1773 K, the experimental value of \( K_i \) for HC-B is about one half of that for HC-A. Hence the process (a) must be involved in the rate-determining step for the evaporation of \( i \) under HC-B. Even under HC-A this process is possibly involved in the step for the evaporation of manganese and copper.

2. In the Fe-Cu and Fe-Mn systems under HC-A', the experimental value of \( K_{Cu} \) at 1773 K is obviously greater than that at 1783 K, but those of \( K_{Mn} \) at both temperatures are close to each other. The rates of evaporation of manganese must be determined predominantly by the process (a). Both the processes (a) and (b) can be involved in the rate-determining step for the evaporation of copper.

3. In the Fe-Mn, Fe-Cu and Fe-Sn systems at 1783 K, most of the reported experimental values of \( K_{Mn} \), \( K_{Cu} \) and \( K_{Sn} \) agree well with their respective values calculated from Eq. (5) on the assumption of a fixed value of \( \rho K_m \), but the present experimental values of \( K_{Cu} \) are smaller than the calculated one.

4. The plot of \( K_{Cu}/K_i \) vs. \( a_{Cu} \) in the Fe-Si-S system is linear for both HC-A' and HC-B'. The rate constants \( k_1 \) and \( k_2 \) for HC-B' are smaller than those for HC-A', respectively, and must involve the mass-transfer coefficient in the melt. In the desulfurization of Fe-S, Fe-C-S, Fe-Si-S and Fe-C-Si-S alloys at temperatures in the range 1688-1783 K, most of the experimental points of \( k_{Cu} \) for HC-A or HC-A' obey the curve calculated from Eq. (5) by taking \( K_s = 0.24 K_i \) and \( \rho K_m = 2.5 \) regardless of the tempera-

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