Diffusion of Vanadium, Copper, Silicon, Phosphorus and Sulfur in Molten Iron Saturated with Carbon

By Yōichi ONO** and SeisukeISHITOBI***

Synopsis

Diffusion coefficients of vanadium, copper, silicon, phosphorus, and sulfur in molten iron saturated with carbon were measured by the capillary-reservoir method in the temperature range from $1350^\circ$ to $1550^\circ$C. The results obtained are summarized by the following Arrhenius' equations:

$$D_v = (6.45 \pm 1.08) \times 10^{-4} \exp \left( -\frac{18700 \pm 600}{RT} \right) \text{cm}^2/\text{sec}$$

$$D_{Cu} = (4.15 \pm 7.5) \times 10^{-4} \exp \left( -\frac{21700 \pm 700}{RT} \right) \text{cm}^2/\text{sec}$$

$$D_{Mn} = (1.85 \pm 0.28) \times 10^{-4} \exp \left( -\frac{13500 \pm 500}{RT} \right) \text{cm}^2/\text{sec}$$

$$D_p = (7.05 \pm 0.95) \times 10^{-4} \exp \left( -\frac{17700 \pm 500}{RT} \right) \text{cm}^2/\text{sec}$$

$$D_S = (0.98 \pm 0.10) \times 10^{-4} \exp \left( -\frac{10000 \pm 300}{RT} \right) \text{cm}^2/\text{sec}$$

The present results were discussed together with the previous results on the diffusivities of chromium, manganese, cobalt, and nickel in molten iron saturated with carbon (Refer to Trans. ISIJ, 11 (1971), 275). A definite correlation was found between the diffusivity and the standard free energy of solution for the solute elements dissolved in molten iron saturated with carbon, i.e., the diffusivity increases with an increase of the standard free energy of solution.

I. Introduction

A knowledge of diffusivities of various elements in molten iron, combined with other properties such as viscosity and surface tension, is indispensable for the kinetic analyses of reactions in iron- and steelmaking processes. It is also important for the studies of the nature and the structure of molten iron, for the diffusivity of a solute element reflects the dynamic behavior of the element in molten iron.

Although the studies on the diffusion in molten iron have gradually become active in recent years, the results reported are not yet abundant nor sufficiently accurate, owing to the difficulties as encountered in high temperature measurements. Moreover, the solute element to be studied has been selected rather randomly for practical purposes, and systematic studies have scarcely been made on the diffusion in molten iron.31

Systematic research works directed toward the better understanding of diffusion phenomena in molten iron began several years ago in the present authors' laboratory. In the previous papers,2,40 it was shown that the diffusivity of chromium, manganese, cobalt, and nickel in molten iron saturated with carbon increased with increasing atomic number of the diffusing element, i.e., in the order of Cr, Mn, Co, and Ni. In the present paper, experimental results were described on the measurements of the diffusion coefficients of vanadium, copper, silicon, phosphorus, and sulfur in molten iron saturated with carbon. Vanadium and copper were selected as the elements belonging to the same fourth period in the Periodic Table of Elements as the elements studied in the previous work. Silicon, phosphorus, and sulfur were selected from the third period. The present results, together with the previous ones, were discussed in terms of the interaction of the diffusing element with the solvent iron.

II. Experimental Method

1. Principle

The capillary-reservoir method was applied to the measurement of diffusion coefficients in the present work.

In this method, a capillary tube with uniform diameter and one end sealed is filled with an alloy of an initial concentration $C_0$. The capillary is then immersed in a large reservoir melt of the same type of alloy with another concentration $C_s$. After a given period of time, the capillary is taken out of the reservoir, and the diffusion coefficient is determined according to the method described below.

If the diffusion coefficient $D$ is assumed to be constant in the concentration range between $C_0$ and $C_s$, Fick's second law is written

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

where $t$ is the diffusion time, and $x$ is the distance measured from the open end of the capillary along its axis. If the surface concentration at the mouth of the capillary is kept constant at $C_0$, and if the diffusion time $t$ and the capillary length $L$ are selected so that the changes of the concentration in the capillary resulting from diffusion should not penetrate the full length of the capillary, the initial and the boundary conditions will be as follows:

| L.C. | $C = C_0, \ t = 0, \ x \geq 0$ |
| B.C.1 | $C = C_0, \ t > 0, \ x > 0$ |
| B.C.2 | $C = C_0, \ t > 0, \ x > \infty$ |


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Under these conditions, the solution of Eq. (1) is given by

\[
\frac{C - C_0}{C_n - C_0} = 1 - \text{erf}\left(\frac{x}{2\sqrt{Dt}}\right) \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdot (3)
\]

in which \text{erf} refers to Gauss's error integral. Under the same conditions, the average concentration \( \bar{C} \) in the capillary after some short time \( t \) is related to the diffusion coefficient through the following equation:

\[
\frac{\bar{C} - C_0}{C_n - C_0} = 2\left(\frac{Dt}{\pi}\right)^{1/2} \quad \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdots \cdot (4)
\]

The diffusion coefficient can be evaluated either from Eq. (3) by measuring the distribution of concentration along the longitudinal direction of the capillary or from Eq. (4) by measuring the average concentration in the capillary. In the present work, the latter method was chosen, because this is simpler with respect to experimental technique and also is believed to yield more reliable results in liquid diffusion.

2. Apparatus

The diffusion apparatus is shown schematically in Fig. 1. In a capillary sample holder, made of high-purity graphite, are bored four to six capillaries of 2.5 to 3.0 mm in diameter and 20 to 35 mm in length, with their open ends directed upward. The sample holder is attached to the lower end of a graphite rod, and it is put into or taken out of the reservoir with the device consisting of a suspension wire, a chromatube, and the graphite rod. A graphite covering disk, together with a taper on the upper corner of the holder, helps to remove the excessive capillary sample resulting from thermal expansion and fusion, before the holder is dipped into the reservoir, and also to separate the reservoir melt from the capillary sample, when the holder is taken out of the reservoir.

The reservoir melt is contained in a graphite crucible, which is placed in the uniform temperature zone of a mullite reaction tube, 85 mm in I.D. and 900 mm in length, in a silicon carbide resistance furnace. The uniform temperature zone of \( \pm 5^\circ C \) extended over about 9 cm. To prevent thermal convection of the melt in the capillary, the temperature of the top of the capillary was kept about 3\(^\circ\)C higher than that of the bottom. The temperature of the capillary sample was calculated from the temperature measured by using a Pt-30%Rh-Pt-6%Rh thermocouple set under the graphite crucible with the aid of the temperature profile which had been determined beforehand. The temperature was maintained at a chosen temperature within \( \pm 5^\circ C \) during the experiments. The inside of the reaction tube was kept to non-oxidizing atmosphere by flowing argon into the reaction tube which has water-cooled vacuum seals at both ends.

3. Materials

In order to avoid the free convection due to the difference in density, an alloy of lower density was contained in the crucible and that of higher density was filled in the capillary. Silicon, phosphorus, sulfur, and vanadium were, therefore, added to the reservoir melt and allowed to diffuse into the capillary. On the other hand, copper was added to the capillary sample, and it diffused toward the reservoir.

If the diffusing element is contained at high concentration in molten iron, the interaction between atoms of the diffusing element may possibly influence the diffusivity and thus make the interpretation of results complicated. Hence, the concentration of the diffusing element was chosen as low as possible, as shown in Table 1.

The alloy was prepared by melting electrolytic iron in a graphite crucible and by adding the alloying element in case of a ternary alloy. The raw materials used and their purity were as follows; Si: metallic silicon (99.999%Si), P: ferrophosphorus (26.4%P), S: chemical reagent (>99.5%S), V: needle vanadium (99.76%V), and Cu: oxygen-free copper (>99.99% Cu).

The alloy for capillary sample was remelted in a graphite crucible in an argon atmosphere and was kept at the same temperature as that in the diffusion

![Fig. 1. Schematic cross section of the apparatus for measuring the diffusivity of elements dissolved in molten carbon-saturated iron by the capillary-reservoir technique](image)

<table>
<thead>
<tr>
<th>Diffusing element</th>
<th>Initial concentration in capillary, ( C_0 )</th>
<th>Concentration in reservoir, ( C_r )</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>wt %</td>
<td>at %</td>
</tr>
<tr>
<td>V</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Cu</td>
<td>1.00</td>
<td>0.75</td>
</tr>
<tr>
<td>Si</td>
<td>0.17</td>
<td>0.29</td>
</tr>
<tr>
<td>P</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>S</td>
<td>0.01</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Table 1. Concentrations of the diffusing element in the capillary and the reservoir melts
run in order to saturate the melt with carbon at that temperature. The capillary sample was taken out of the melt with silica tubes by suction. The sound sample without defects such as gas bubbles was inserted in the bore of the graphite holder.

4. Procedure

The graphite holder with filled capillaries was held just above the reservoir alloy of about 600 g in a graphite crucible which was placed in the uniform temperature zone of the reaction tube. After the reaction tube was degassed by a rotary pump, argon was introduced into the reaction tube, and the electric power was supplied to the furnace to heat the sample in argon atmosphere. When the reservoir alloy was melted down, the lower half of the holder was immersed into the reservoir melt and the system was further heated to the experimental temperature. The capillary holder was then immersed in the bath completely. After the given period of diffusion time, the holder was taken out of the reservoir and was plunged into water to quench. The temperature range of measurements was from 1 350°C to 1 550°C. The diffusion time was varied between 15 min and 1 hr.

The solidified capillary specimens were taken out of the graphite holder and were polished with emery paper to remove graphite powder attached to their surface. Finally, the metal specimen was chemically analyzed to determine the average concentration of the diffusing element. The chemical analyses were performed by using the spectrophotometric methods, except for the case of sulfur. The content of sulfur was determined by the combustion method.

III. Experimental Results

I. Experimental Results on Diffusion Coefficients

Diffusion coefficients of vanadium, copper, silicon, phosphorus, and sulfur in molten iron saturated with carbon were measured in the temperature range of 1 350°C to 1 550°C by the method described above. The results obtained are presented in Figs. 2 to 6, in which the logarithm of the diffusion coefficient is plotted against the reciprocal of the absolute temperature. In these figures a single point represents an average of nine to fifteen experimental values, and the vertical line through the point represents the spread in the experimental values. As seen in the figures, the temperature dependence of the diffusion coefficient is represented by the Arrhenius' equation:

\[ D = D_0 \exp(-Q/RT) \]  \hspace{2cm} (5)

in the temperature range of measurements. Values of the pre-exponential factor \( D_0 \) and the apparent activation energy \( Q \) obtained by the least square analysis of the experimental data are listed in Table 2. In Table 2, the values of the probable errors in \( D_0 \) and \( Q \) are also shown. The probable errors in \( D \) values are ±3.5\% to ±5.5\%.

2. Comparison of Present Results with the Results by Previous Authors

Some of the results by previous authors are also included in Figs. 2 to 6.

The diffusion coefficient of vanadium in molten iron saturated with carbon has been reported by Musikhin and Yesin,\(^5\) who measured the diffusivity by the chronopotentiometric method in the temperature range from 1 250°C to 1 400°C. Their results, as compared with the present results, are larger in the value of diffusion coefficient and smaller in the activation energy.

On the diffusion coefficient of copper in molten iron saturated with carbon, available data are not found in the previous literature.

The diffusion coefficient of silicon in molten iron saturated with carbon has been measured by a fairly large number of investigators. Their results are as follows; Investigators: Saito and Maruya\(^6\) (Method: diffusion-couple method, Temperature range: 1 400°C to 1 600°C, Diffusion coefficient at 1 400°C in cm²/sec: 2.0×10⁻²), Grace and Derge\(^7\) (capillary-reservoir method, 1 226°C to 1 412°C, 1.5×10⁻⁴), Musikhin and Yesin\(^8\) (chronopotentiometric method, 1 250°C to 1 450°C, 8.2×10⁻⁵), Kalunin, Yesin, and Toporishiev\(^9\) (chronopotentiometric method, 1 300°C to 1 500°C, 6.8×10⁻⁵), Shurygin and Shantaritin\(^10\) (measurement of dissolution rate of a rotating disk, 1 200°C to 1 400°C, 5.3×10⁻⁶), and Majdić, Graf, and Schenck\(^10\) (diffusion-couple method, 1 400°C to 1 500°C, 1.1×10⁻⁵). Among the previous results mentioned above, the results by Saito and Maruya, which are shown in Fig. 4, may be most reliable, considering from their elaborate experimental technique.\(^11\) Their results are, however, smaller in both diffusivity and activation energy in comparison with the present results. Their activation energy is particularly smaller, namely, 8.2 kcal/mol against the value of 13.3 kcal/mol by the present authors. Their data points are, as seen in Fig. 4, also represented by the broken line through the points in parallel with the straight line of the present work. A comparison of the number of data will put greater confidence in the activation energy obtained in the present work, for the number in the present work is about five times larger than that of Saito and Maruya.

The diffusion coefficient of phosphorus in molten iron saturated with carbon has been reported by Grace and Derge\(^7\) (capillary-reservoir method, 1 256°C to 1 412°C) and by Majdić, Graf, and Schenck\(^10\) (diffusion-couple method, 1 400°C to 1 600°C). As Fig. 5

<table>
<thead>
<tr>
<th>Diffusing element</th>
<th>( D_0 \times 10^N ) (cm²/sec)</th>
<th>( Q ) (cal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>V</td>
<td>6.45±1.08</td>
<td>18 700±600</td>
</tr>
<tr>
<td>Cu</td>
<td>41.5±7.5</td>
<td>21 700±700</td>
</tr>
<tr>
<td>Si</td>
<td>1.85±0.28</td>
<td>13 300±500</td>
</tr>
<tr>
<td>P</td>
<td>7.05±0.95</td>
<td>17 700±500</td>
</tr>
<tr>
<td>S</td>
<td>0.98±0.10</td>
<td>10 000±300</td>
</tr>
</tbody>
</table>
shows, the diffusion coefficient obtained by Majdić et al. agrees well with the value of the present work in the temperature range of measurements, while their activation energy is considerably larger than that of the present work.

The diffusion coefficient of sulfur in molten iron saturated with carbon has been obtained by Kawai\(^2\) (diffusion-couple method, 1 390° to 1 560°C, \(D\) value at 1 400°C in cm\(^2\)/sec: \(2.9 \times 10^{-5}\)), by Grace and Derge\(^3\) (capillary-reservoir method, 1 300° to 1 431°C, 1.3 \(\times 10^{-5}\)), and Majdić, Graf, and Schenck\(^4\) (diffusion-couple method, 1 350° to 1 450°C, 2.0 \(\times 10^{-5}\)). The results by Kawai, which seem to be most reliable, are compatible with the present results as to the temperature dependence, as shown in Fig. 6, in which the broken line is drawn through Kawai’s data in parallel with the straight line of the present work. On the other hand, the value of diffusion coefficient obtained by Kawai is considerably smaller than that of the present work.

As mentioned above, previous results are widely scattered by investigators. An exact evaluation of the reported results is, however, very difficult, because the literature is often lacking in detailed descriptions on experimental apparatus, materials, procedure, data, etc.

A number of unknown factors will make difficulties for the accurate determination of the "absolute" value of diffusivity at high temperature even in the present time. The present results may, nevertheless, be considered to adequately answer the purpose of examining at least the "relative" differences in diffusivity of diffusing elements, because the diffusion coefficients were measured under the very same experimental conditions in the present work.

3. Difference in Diffusivity among Solute Elements

Figure 7 shows a plot log \(D\) vs. atomic number of the diffusing element at the temperatures of 1 350° and 1 550°C for vanadium, copper, silicon, phosphorus, and sulfur studied in the present work, and chromium, manganese, cobalt, and nickel studied in the previous work.\(^5\) Comparison of the diffusion coefficients among silicon, phosphorus, and sulfur, which belong to the third period, shows that the dif-
fusion coefficient at 1550°C increases with an increase of atomic number, i.e., in the order of Si, P, and S, whereas at 1350°C phosphorus diffuses more slowly than silicon. As to the elements from the fourth period, the diffusion coefficient of copper is larger than that of nickel, which is expected from the order of atomic number. On the other hand, the diffusion coefficient of vanadium is larger than that of chromium, which is against expectation. In spite of a few irregularities such as mentioned above, it may be concluded that the diffusion increases as a general trend in the order of increasing atomic number for the elements belonging respectively to the third and the fourth period.

Figure 8 shows a plot of apparent activation energy vs. atomic number of diffusing element. Too much reliance will not be allowed to put on the values of activation energy, because they were obtained from the data of the narrow temperature range from 1350° to 1550°C. It may, however, be tentatively concluded that the correlation between the activation energy and the atomic number was not found.

**IV. Discussions**

The concentration of diffusing element was chosen at the sufficiently low range, which the experimental technique permitted, i.e., below about 1 atomic per cent, as shown in Table 1. It is, indeed, a question whether the concentration is considered to be so low that the interaction between atoms of the diffusing element can be completely neglected. However, the diffusion coefficient obtained may tentatively be regarded as representing approximately the self-diffusivity and consequently as being directly proportional to the mobility of the solute element in molten iron saturated with carbon.14)

For the theoretical interpretation of diffusion phenomena in liquid metals, various theories have been proposed15, 36-41) like Eyring’s hole theory, Cohen–Turnbull’s free-volume theory, and Swalin’s fluctuation theory. These theories have partially succeeded in the qualitative interpretation of the solute diffusion in relatively simple liquid metals like copper and silver, but they have not led to any satisfactorily quantitative agreement with experiments.15, 41-47)

In the present work, diffusion occurred in the three-component melt in which the concentration of carbon was the solubility limit of 20 atomic per cent, and that of the diffusing element was dilute. Moreover, the solvent iron is a transition metal. The structure and the atomic interaction of such a concentrated, ternary, transition metallic solution must be so complicated that the application of the above-mentioned theories to the present results would be impossible at the present time.

Experimental approaches to relate the solute diffusivity with its thermodynamic properties have recently been adopted by several investigators16-20) in parallel with the theoretical studies mentioned above. Based on an extensive literature survey, Suzuki and Mori,20) for example, suggested the correlation between the diffusion coefficient of an element j, \( D_j \), and the standard free energy of solution of the element in molten iron, \( \Delta F_j^\theta \); they found that \( D_j \) had a tendency to increase with an increase of \( \Delta F_j^\theta \).

This approach suggested by Suzuki and Mori seems to be most appropriate for the application to the present results. \( \Delta F_j^\theta \) must first be modified to evaluate the possible effect of coexisting carbon. In Fig. 9, the curve OP shows the activity of the component j in the binary Fe–j system based on Henry’s law with the standard state being the hypothetical 1% solution represented by the state A. \( \Delta F_j^\theta \) is the free energy change for one mole of the element j in the process that the pure substance j (the molar free energy = \( F_j^\theta \)) dissolves in molten iron to form the hypothetical 1% solution represented by the state A (the partial molar free energy = \( F_j^\theta \));
\[ \Delta F_j^* = \hat{F}_j^* - F_j^0 \] ...........................(6)

The value of \( \Delta F_j^* \) at 1550°C for various components is given in Table 3.

The curve OQ in Fig. 9 is the activity of the component \( j \) in the ternary Fe–j–C system, and the standard state is also the state A. The state B of the ternary system in the figure is the hypothetical point in carbon-saturated iron containing 1% of \( j \), and may now be regarded as the equivalent to the state A in the binary system. It is, therefore, reasonable to define the standard free energy of solution of the component \( j \) in liquid iron saturated with carbon, which is designated here as \( \Delta F_j^* \), as follows

\[ \Delta F_j^* = \hat{F}_j^* - F_j^0 \] ...........................(7)

where \( \hat{F}_j^* \) denotes the partial molar free energy of the component \( j \) in the state B. \( \hat{F}_j^* \) is related with \( F_j^0 \) through

\[ \hat{F}_j^* = F_j^0 + RT \ln f_j^{(C)} \] ...........................(8)

where \( f_j^{(C)} \) is the interaction coefficient between carbon and the element \( j \) at its infinite dilution in molten carbon-saturated iron;

\[ f_j^{(C)} = \left( \frac{f_j^{(Fe-j-C_{sat})}}{f_j^{(Fe-j)}} \right)_{\%C=0} \] ...........................(9)

Substitution of Eqs. (6) and (8) into Eq. (7) gives as the expression of \( \Delta F_j^* \)

\[ \Delta F_j^* = \Delta F_j^0 + RT \ln f_j^{(C)} \] ...........................(10)

As indicated by this equation, \( RT \ln f_j^{(C)} \) is the correction term that takes into account the effect of carbon on the standard free energy of solution of the element \( j \).

Since the experimental value of \( f_j^{(C)} \) at carbon saturation is not available, it must be estimated by any means. If Wagner’s formula,

\[ \log f_j^{(C)} = \epsilon_j^{(C)} \cdot [\%C] \]

is assumed to be applicable to the present case of carbon saturation, \( \Delta F_j^* \) will be calculated from

\[ \Delta F_j^* = \Delta F_j^0 + 4.575T \epsilon_j^{(C)} [\%C]_{sat.} \] ...........................(11)

where \( \epsilon_j^{(C)} \) denotes the interaction parameter between carbon and the element \( j \) at infinite dilution in Fe–j–C system. It is, however, doubtful whether Wagner’s formula is applicable or not to such a concentrated solution as carbon-saturated iron, for Wagner’s formula was originally introduced for dilute solutions.

If statistical thermodynamics is applied on the assumption that the Fe–j–C melt is a regular solution,24 the following equation will be obtained:

\[ \Delta F_j^* = \Delta F_j^0 + RT \epsilon_j^{(C)} N_{C_{sat.}} - \frac{1}{2} RT \epsilon_j^{(C)} N_{C_{sat.}}^2 \]

\[ + RT \ln \{100M_{Fe} \cdot N_{C_{sat.}} / [\%C]_{sat.}\} \] ...........................(12)

where \( \epsilon_j^{(C)} \) and \( \epsilon_j^{(C)} \) denote the interaction parameters of carbon on \( j \) and carbon, respectively, in molten iron for the reference of the pure substance and mole fractions. \( N_{C_{sat.}} \) is the solubility of carbon in molten iron in mole fraction.

The values of \( \Delta F_j^* \) at 1550°C calculated by using Eq. (11) and Eq. (12), respectively, are both included in Table 3. Despite the fact that both Eqs. (11) and (12) involve some assumptions about their bases, the values of \( \Delta F_j^* \) calculated from the two equations are in fairly good agreement with each other and may be regarded as approximations of the true value. The value estimated by using Eq. (12) will be used in the subsequent discussions.

Figure 10 shows a plot of the diffusion coefficients obtained in the previous and the present works against the respective values of the standard free energy of solution for the solute elements dissolved in molten carbon-saturated iron at the temperature of 1550°C. From this figure, a definite correlation seems to be noted between these two quantities. The diffusion coefficient \( D_l \) increases with an increase of the value of \( \Delta F_j^0 \) for the elements belonging to the same period in the Periodic Table. \( \Delta F_j^* \) represents the thermodynamic interaction of the solute element \( j \) with the solvent carbon-saturated iron. In other word, it can be considered to be a measure of the so-called stability of the element \( j \) in molten carbon-saturated iron; the element with smaller value of \( \Delta F_j^* \) or larger value of \( (-\Delta F_j^* \) may be regarded as having higher stability.

Table 3. Standard free energy of solution of various elements in molten carbon-free iron and in carbon-saturated iron at 1550°C

<table>
<thead>
<tr>
<th>( j )</th>
<th>Solution reaction</th>
<th>( \Delta F_j^0 ) (kcal/mol)</th>
<th>Ref. No.</th>
<th>( \epsilon_j^{(C)} )</th>
<th>( \epsilon_j^{(C)} )</th>
<th>Ref. No.</th>
<th>( \Delta F_j^* ) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>Si(l) = Si</td>
<td>-39.6</td>
<td>26</td>
<td>0.24</td>
<td>12.4</td>
<td>25</td>
<td>-29.0</td>
</tr>
<tr>
<td>P</td>
<td>1/2 P_2(g) = P</td>
<td>-37.6</td>
<td>26</td>
<td>0.24</td>
<td>12.8</td>
<td>25</td>
<td>-27.0</td>
</tr>
<tr>
<td>S</td>
<td>1/2 S_2(g) = S</td>
<td>-21.9</td>
<td>26</td>
<td>0.113</td>
<td>6.37</td>
<td>25</td>
<td>-16.9</td>
</tr>
<tr>
<td>V</td>
<td>V(s) = V</td>
<td>-23.2</td>
<td>26</td>
<td>-0.174</td>
<td>-7.88</td>
<td>25</td>
<td>-30.9</td>
</tr>
<tr>
<td>Cr</td>
<td>Cr(s) = Cr</td>
<td>-25.6</td>
<td>26</td>
<td>-0.118</td>
<td>-5.08</td>
<td>25</td>
<td>-30.8</td>
</tr>
<tr>
<td>Mn</td>
<td>Mn(s) = Mn</td>
<td>-15.4</td>
<td>26</td>
<td>-0.039</td>
<td>-1.9</td>
<td>24</td>
<td>-17.1</td>
</tr>
<tr>
<td>Co</td>
<td>Co(l) = Co</td>
<td>-16.9</td>
<td>26</td>
<td>0.042</td>
<td>2.86</td>
<td>25</td>
<td>-16.5</td>
</tr>
<tr>
<td>Ni</td>
<td>Ni(l) = Ni</td>
<td>-18.4</td>
<td>26</td>
<td>0.042</td>
<td>2.85</td>
<td>25</td>
<td>-15.0</td>
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<tr>
<td>Cu</td>
<td>Cu(l) = Cu</td>
<td>-8.8</td>
<td>26</td>
<td>0.066</td>
<td>4.06</td>
<td>25</td>
<td>-5.9</td>
</tr>
</tbody>
</table>

\* The following values25,40 are also used in the calculations: \( \epsilon_C^{(C)} = 9.9, [\%C]_{sat.} = 5.28, N_{C_{sat.}} = 0.206\)
It is, therefore, concluded from this plot that the element with greater stability has a smaller mobility and hence a smaller diffusion coefficient, and that smaller stability, on the contrary, leads to larger diffusivity.

On the other hand, the data of the elements in the third period and those of the elements in the fourth period seem to be shown by the different curves. It suggests the possibilities of the existence of another factors affecting the diffusivity, and they should be clarified by the future investigations.

In Fig. 11, the diffusion coefficients of silicon, phosphorus, and sulfur in molten iron binary alloys reported by the previous authors are plotted against the respective values of $\Delta F_j^*$. In this figure, a plot of the diffusivity in carbon-saturated iron obtained in the present work vs. $\Delta F_j^*$ are also shown on the same scale. Although the points for the binary systems are considerably scattered, it may be expected from this figure that there exists the same functional relationship between the diffusivity and the standard free energy of solution for the elements dissolved in molten iron, irrespective of whether carbon is contained in the solvent or not. If this relationship also applies to other elements, which is to be examined experimentally, it will be useful, for example, for the estimation of their diffusivities in molten carbon-free iron, which are very difficult to measure, from the observed values of diffusivity in molten carbon-saturated iron, where more reliable values may be obtained comparatively easily.

V. Conclusions

Diffusion coefficients of vanadium, copper, silicon, phosphorus, and sulfur in molten iron saturated with carbon were measured by the capillary-reservoir method in the temperature range from 1330°C to 1550°C.

(1) The experimental results obtained are summarized by the following Arrhenius' equations:

$$D_\text{v} = (6.45 \pm 1.08) \times 10^{-3} \times \exp \left( \frac{-18700 \pm 600}{RT} \right) \text{ cm}^2/\text{sec}$$

$$D_\text{Cu} = (41.5 \pm 7.5) \times 10^{-3} \times \exp \left( \frac{-21700 \pm 700}{RT} \right) \text{ cm}^2/\text{sec}$$

$$D_\text{h} = (1.85 \pm 0.28) \times 10^{-3} \times \exp \left( \frac{-13300 \pm 500}{RT} \right) \text{ cm}^2/\text{sec}$$

$$D_\text{f} = (7.05 \pm 0.95) \times 10^{-3} \times \exp \left( \frac{-17700 \pm 500}{RT} \right) \text{ cm}^2/\text{sec}$$

$$D_\text{s} = (0.98 \pm 0.10) \times 10^{-3} \times \exp \left( \frac{-10000 \pm 300}{RT} \right) \text{ cm}^2/\text{sec}$$

(2) The experimental results were discussed together with the previous results on the diffusivities of chromium, manganese, cobalt, and nickel in molten carbon-saturated iron. The following results were obtained:

a) The diffusion coefficient increases as a general trend in the order of increasing atomic number of the diffusing element, so far as the element belongs to a specified period in the periodic table of elements. On the other hand, no correlation has been found between the apparent activation energy of diffusion and the atomic number.

b) A definite correlation was found between the diffusion coefficient $D_j$ and the thermodynamic interaction of the diffusing element $j$ with the solvent carbon-saturated iron as expressed by the standard free energy of solution $\Delta F_j^*$, i.e., the diffusion coefficient $D_j$ increases with an increase of the value of $\Delta F_j^*$ for the elements belonging to the same specified period. It may be concluded from this finding that the element with greater stability in molten carbon-saturated iron has a smaller diffusivity in the medium, for the negative value of $\Delta F_j^*$ is considered as a measure of stability of the component $j$ in the solution.

c) The possibility of the same functional relationship was suggested between the diffusivity and the standard free energy of solution, irrespective of whether
carbon is contained in the solvent iron or not, provided that the due consideration is given to the effect of carbon.

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REFERENCES

11) Y. Ono: Report presented at the 6th Meeting of Bushi-Group (Subcommittee on the Properties of Melts), the 19th Committee (Steelmaking), Japan Society for the Promotion of Science, May 25, 1972.
12) Y. Kawai: *J. JIM*, 20 (1956), 517.
13) Y. Ono: Report presented at the 7th Meeting of Bushi-Group (Subcommittee on the Properties of Melts), the 19th Committee (Steelmaking), Japan Society for the Promotion of Science, Sept. 25, 1972.
21) The 19th Committee (Steelmaking) of Japan Society for the Promotion of Science: Recommended Equilibrium Constants of Reactions in Steelmaking, Nikkan Kogyō Press, Tokyo, (1968), 92.
33) Y. Kawai: *J. JIM*, 20 (1956), 514.