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On Activities of Coexisting Elements in Molten Iron. II

The Activity of Silicon in Molten Fe-Si System.*

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Synopsis

Constructing the following electrode concentration cell, the authors measured electromotive force corresponding to the change of silicon content in iron by potentiometer.

Fe-Si | silicate slag | pure Si

The temperature range of the experiment was 1,520~1,540°C and for the measurement of temperature Pt-Pt·Ph thermocouple was used. As preliminary experiments, the reversibility and thermoelectromotive force were investigated. The theoretical relation between electromotive force E and the activity of silicon a_{Si} is as follows:

$$E = RT/nF \times \ln a^{i}_{Si}/a_{Si} - RT/nF \times \ln a^{i}_{Si}/a'_{Si} \cdots\cdots\cdots\cdots (1)$$

where a^{i}_{Si} : the activity of silicon ion in the molten slag.
a'_{Si} : the activity of pure silicon.
n : the number of Faradays required for the cell reaction.

Because pure silicon is selected as a standard state, then the following equation is obtained from eqn. (1):

$$E \fallingdotseq -0.0002T/n \times \log a_{Si} \cdots\cdots\cdots\cdots (2)$$

n is approximately determined as $n=4$ by the calculation from authors' data. The activity of silicon has been obtained by substituting the values E, n and T in eqn. (2)

Judging from this result, Fe-Si binary solution is recognized to be semi-regular solution and obeys Henry's law up to about $N_{Si}=0.08$, where N_{Si} represents the mole fraction of silicon in Fe-Si binary solution. Furthermore, the free energy change ΔG^{0}_{1803} of the following reaction at 1,530°C has been calculated from authors' data,

$$\text{Si(liquid)} = \text{Si(in Fe)} \cdots\cdots\cdots\cdots (3)$$

ΔG^{0}_{1803} represents the free energy of solution of silicon at unit activity on a scale in which the activity is equal to percentage at infinite dilution.

To convert this to activity on a mole fraction scale which the activity of pure liquid silicon is unity requires the following eqn. (4):

$$\Delta G^{0}_{1803} = \mu^{0}_{Si}(\text{dil. soln.}) - \mu^{0}_{Si}(\text{pure}) = RT \ln a_{Si}(\text{dil. soln.})/a_{Si}(\text{pure}) \cdots\cdots (4)$$

From the relation between $\log a_{Si}/N_{Si} = \gamma_{Si}$ and square of the mole fraction of iron N^{2}_{Fe}, activity coefficient γ^{0}_{Si} which represents γ_{Si} at $N_{Fe}=0$ is obtained as 0.013 and the mole fraction of silicon in dilute solutions is 0.0199 times its weight percentage. From these two values, the ratio of the activities of silicon on the two scales is obtained as 0.00026. Substituting this value to eqn. (4), authors have been obtained the following value: $\Delta G^{0}_{1803} = -29{,}700$ cal.

I. Introduction

The behavior of silicon in molten iron has been discussed from the results obtained by usual chemical equilibrium(1~4) or by calculations,(5) and Fe-Si binary

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* The 53rd. report of the Research Institute of Mineral Dressing and Metallurgy.

(1) Z. Shibata and I. Taziri: J. Japan Inst. Metals, **2** (1942), 44.

(2) K. Sanbongi and M. Ohtani: Sci. Rep. RITU, A **4** (1952), 59, 409.

(3) C. A. Zapffe and C. E. Sims: Trans. Amer. Inst. Min. Met. Eng., **154** (1943), 192.

(4) N. A. Gokcen and J. Chipman: J. Metals, **4** (1952), 172.

(5) A.I.M.E.: Basic Open Hearth Steelmaking. (1951), Chap. 16. p. 639.
J. Chipman: Discussions. Faraday Soc., No. 4. (1948), 45.

solution is regarded to conform with Henry's law in low concentration of silicon. Since no measurement has yet been made as to how Fe-Si binary solution behaves in the whole range of concentration, it still remains to be the matter of inference. The authors had previously observed by the measurement of chemical equilibrium(2) that about 8% of Si behaves in conformity with Henry's law in Fe-Si binary solution.

The present experiment was performed with a view to further investigate the behavior of Si in the range mentioned above and to clarify it in high concentration. By constructing a concentration cell as in the case of the experiment on Fe-C system(6), the authors found the electromotive force between the two electrodes, from which the activity of the consitituents was calculated.
For example, according to the former method,(1~4) it is possible to observe the behavior of Si from the reaction:

$$(SiO_2)_{sat.} + 2H_2 = \underline{Si} + 2H_2O,$$

but many difficulties are brought into the experiment by remarkable increase in the ratio p_{H_2}/p_{H_2O} as Si is concentrated. On the other hand, the ionization of molten slag has been verified, by an application of which it would be possible to find electrochemically the activity of coexisting elements in molten iron. From this standpoint of view, the authors performed experiments electrochemically in distinction from usual method and clarified the behavior of the Fe-Si binary solution in the whole range.

II. Experimental Apparatus and Operations

Being almost the same as in the case of the measurement of Fe-C system(6) previously reported, the detailed description of the apparatus is omitted, with the exception of a few items which are new. As for electrodes, pure Si was used as the standard electrode, various alloys of Fe-Si as the other electrode and diammeter 1 mm Mo. rod as lead wire. The same type of crucible as used in the measurement of Fe-C system was used in the early stage of the experiment, but the crucible of type shown in Fig. 1 (a) was used from half-way down the experiment. The crucible of this type is useful in adding and connecting with molten slag.

(a) Method of extracting samples

On completing the measurement, samples are immediately extracted by the method shown in Fig. 1 (b); they can be sucked up in proper amounts by means of scale on the syringe. At the tip of the rubber tube is fixed

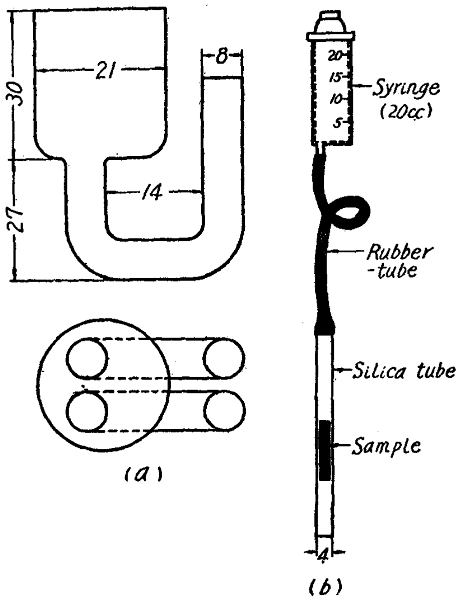

Fig. 1. (a) Crucible.
(b) Sampling method.

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(6) K. Sanbongi and M. Ohtani: Sci. Rep. RITU, A 5 (1953), 263.

a silica tube 4 mm in inner diameter, which can be changed with a new one after breaking it on completion of suction of samples.

(b) Revised Pt-Pt·Rh thermocouple was used for the measurement of temperature.

(c) The slag used was SiO_2-CaO-Al_2O_3 ternary system, which was dissolved for many hours in a graphite crucible having less than 1 % of ashes. When the release of gas no longer observed, it was poured in the mold. It must broken in to pieces before it is used.

The result of analysis of the slag after it was dissolved during the experiment is as shown in the following table:

SiO_2%	Al_2O_3%	CaO%
43.45	5.61	50.94

(d) The spectrographic analysis showed the purity of silicon attached on the standard electrode to be with Al, Mg, and Cu and with negligible amount of Fe, C, Ca, and Mo. Microscopic photographs were taken of them, but they will be omitted from the present description. Although Mo rod was used as lead wire, the mixture of Mo was not observable because of the shortness of time for the measurement.

In the way of preliminary experiments, investigations were made of thermoelectromotive force and reproducibility. No thermoelectromotive force was observed, but it was reproducible and observed as reversible cell.

III. Results of experiment

The results of the experiments are summarized in Table 1. The temperature at which the measurements were made was fixed principally at 1,530°C, but no

Table 1. Experimental data at 1,733～1,813°K.

No.	$\underline{Si}$ (%)	N_{Si}	E·M·F (V)	T°K	a_{Si}
12	23.01	0.37	0.080	1,773	0.12
13	23.48	0.38	0.060	1,773	0.21
14	25.18	0.40	0.063_4	1,788	0.19_5
15	25.18	0.40	0.064_5	1,773	0.18_7
16	25.18	0.40	0.064_5	1,763	0.18_6
17	2.5	0.049	0.260	1,793	0.001
18	2.5	0.049	0.265	1,793	0.001
22	20.27	0.33	0.085	1,773	0.11
23	20.27	0.33	0.110	1,793	0.06
28	5.68	0.107	0.250	1,813	0.0018
29	7.56	0.145	0.246_3	1,813	0.0019
30	6.65	0.134	0.240_9	1,813	0.0022
31	2.32	0.045	0.325_6	1,813	0.00026
32	0.04	0.0008	0.477_6	1,818	0.000006
34	3.89	0.075	0.286	1,803	0.00067
35	4.06	0.078	0.250	1,803	0.0017
36	23.10	0.37	0.090	1,793	0.10
37	64.96	0.785	0.013	1,793	0.716
39	37.15	0.551	0.033	1,793	0.43
6	54.20	0.70	0.016	1,733	0.67
7	47.14	0.64	0.030	1,743	0.46
8	39.86	0.57	0.035	1,723	0.39
9	43.21	0.60	0.035	1,733	0.39
10	47.09	0.63	0.030	1,743	0.45
11	47.91	0.645	0.025	1,753	0.52
38	pure	1	$0.0000 \sim 0.0001_5$	1,733～1,813	1

remarkable effect was observed in the measurements made at different temperature for the purpose of seeing the effect of temperature. The relation between electomotive force and mole fraction of silicon is shown in Fig. 2.

As was described in the last report⁽⁶⁾, the relation between electromotive force E (volt) and the activity of silicon a_{Si} can be expressed by the following equation:

$$E=-0.000198T/n\times\log a_{Si} \quad (1)$$

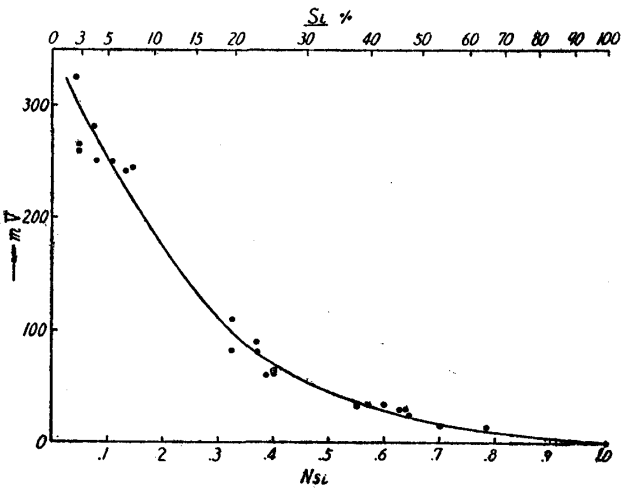

Fig. 2. Relation between electromotive force and mole fraction of silicon.
Mark, ⊙ means overlaped point of two experimental values.

Strictly speaking, it is

$$E=RT/nF\times\ln a^{i}_{Si}/a_{Si}-RT/nF\times\ln a^{i}_{Si}/a'_{Si}$$
$$=RT/nF\times\ln a'_{Si}/a_{Si} \quad (2)$$

Where, a'_{Si}: activity of pure Si
a_{Si}: activity of silicon in Fe-Si binary solution
a^{i}_{Si}: activity of Si ions in molten silicate slag

By choosing pure silicon as the standard state, $a'_{Si}=1$ and from the eqn. (2),

$$E=-RT/nF\times\ln a_{Si}$$

In eqn. (1), n can be calculated as follows: that is, in low concentration of Si, the following equation (3) can be obtained without much error by using mole fraction of Si in stead of a_{Si}.

$$E_1-E_2$$
$$=-0.0002T/n\times\log N_{Si}/N_{Si} \quad (3)$$

From Fig. 2, $N^1{}_{Si}=0.05$, $E_1\fallingdotseq 0.290$, $N^2{}_{Si}=0.10$, $E_2\fallingdotseq 0.265$, $T=1{,}800$, and substituting them in eqn. (3), $n\fallingdotseq 4.32$. Accordingly, by taking $n=4$, subsequent calculation were made.

Substituting E, T, and $n=4$ obtained from the experiment, values of a_{Si} were obtained as shown in Fig. 3 (a). In the Fig. 3 (a) those calculated by Chipman⁽⁵⁾ were plotted by the dotted line.

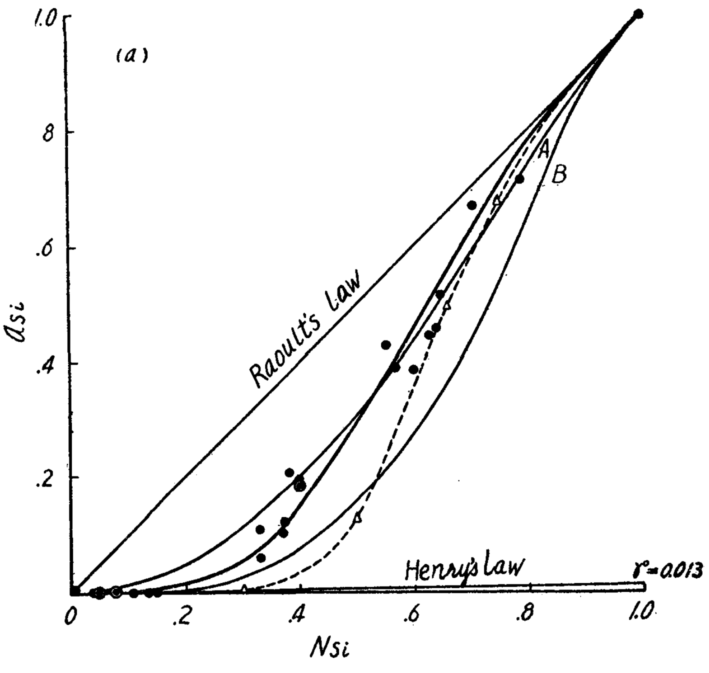

Fig. 3. (a) The activity of silicon in molten Fe-Si system at 1,530°C (average)

The effect of temperature

being almost unobservable, they may be regarded as showing the activity at the temperature of 1,530°C, for the average temperature for the experiment was fixed at that temperature.

IV. Consideration

(1) Although it is not clear how the Fe-Si binary alloys behave in molten state, the authors tried, through the application of the equation already solved, to find their behavior in the regular solution.

Fowler and Guggenheim⁽⁷⁾ introduced the following equation for their behavior in the regular solution.

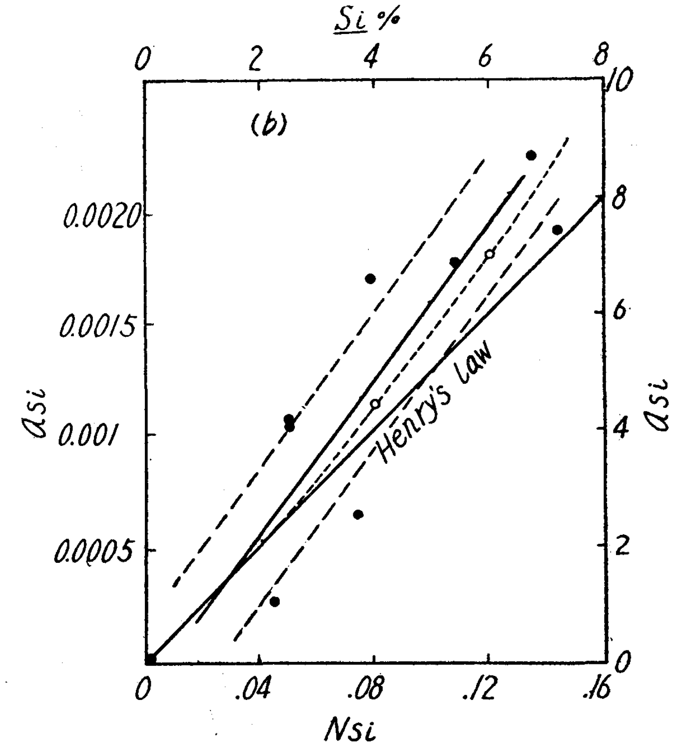

Fig. 3. (b) Relation between a_{Si} and N_{Si} in low concentration of silicon.
○ : from Basic Open Hearth Steelmaking⁽⁵⁾

$$P_A = P_A^0 \left(\frac{N_A}{N_A+N_B}\right)\exp\left\{\frac{\omega_{AB}}{kT}\left(\frac{N_B}{N_A+N_B}\right)^2\right\} \qquad (4)$$

Where, P_A: partial vapour pressure

P_A^0 : vapour pressure of pure liquid

N_A,N_B: mole number of A, B elements respectively

ω_{AB}: interaction energy of A-B atoms.

Assuming the Fe-Si binary system to be the the regular solution, and, in eqn. (4), taking N_{Si} to be the mole fraction of Si and a_{Si} to be the activity of Si, eqn. (5) wll be obtained at once as follows:

$$a_{\mathrm{Si}} = N_{\mathrm{Si}}\ \exp\left\{\frac{\omega_{\text{Fe-Si}}}{kT}(1-N_{\mathrm{Si}})^2\right\} \qquad (5)$$

In eqn. (5), $\omega_{\text{Fe-Si}}/kT$ is not clear, but it should be of minus value since the experimental value appears below the straight line shown in Raoult's law; by putting $\omega_{\text{Fe-Si}}/kT = -2$, -5 and inserting proper numerical value in N_{Si}, values of a_{Si} are calculated from eqn. (5), the result of which is the line $A.B$ in Fig. 3(a).

By modifying eqn. (5), eqn. (6). is obtained

$$\log a_{\mathrm{Si}}/N_{\mathrm{Si}} = 2.303\omega_{\text{Fe-Si}}/kT + 2.303(1-N_{\mathrm{Si}})^2 \qquad (6)$$

By substituting in eqn. (6) the results obtained by the authors, various points apearing in Fig. 4 were obtained. Their relation is not in a straight line, but in a curve. If the Fe-Si binary solution were regular solution, this relation should be a straight line. Consequently, the assumption made above is not correct, and

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(7) R. Fowler and E. A. Guggenheim: Statistical thermodynamics, (1941), 356.

the Fe-Si binary solution is regarded to be what Chipman⁽⁵⁾ called semi-regular solution. In Fig. 4. those shown with white circles are the calculated values obtained by Chipman⁽⁵⁾ from the phase diagram.

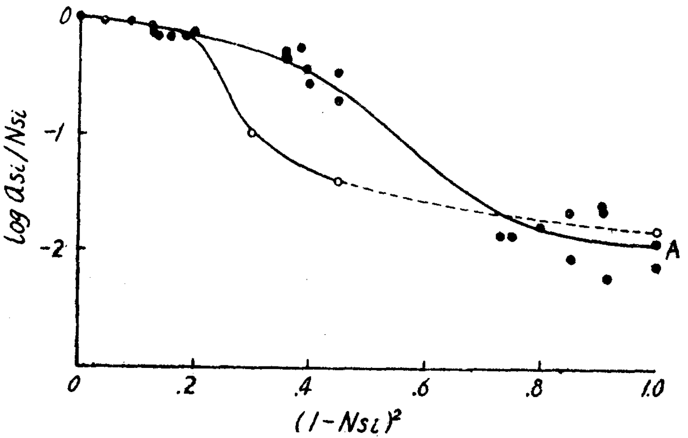

Fig. 4. Relation between log a_{Si}/N_{Si} and $(1-N_{Si})^2$.

(2) As shown in Fig. 3 (b), there seems to be two scales to expreses a_{Si}, the activity of Si, namely, Henry's activity and the activity which might as well be defined as Raoult's activity.

Assuming P_γ to be the partial pressure of γ constituent of vapor which is in equilibrium with the solution under consideration now, and P^R_γ to be the vapor pressure of the solution only pure constituent, Raoult's activity may be expressed as follows:

$$a_R = P_\gamma / P^R_\gamma$$

while, if we assume P^H_γ to be the vapor pressure of γ constituent which is in equilibrium which is in equilibrium with the solution when diluted, Henry's activity may be expressed by the following equation:

$$a_H = P_\gamma / P^H_\gamma$$

Let us now convert the activity one from other of the two scales and find out some thermodynamic values. In low concentration, 1% Si, converted into mole fraction, corresponds to 0.0199 N_{Si}. Then let us consider the following formula for the reaction at 1,530°C:

$$\text{Si(liquid)} = \text{Si (in Fe)} \qquad (7)$$

If we take ΔG^0_{1803} as the change in free energy in the above reaction formula, then

$$\mu^0_{Si}(\text{dil.soln.}) - \mu^0_{Si}(\text{pure}) = \Delta G^0_{1803} = RT\ln a_{Si}(\text{dil.soln.})/a_{Si}(\text{pure})$$
$$= 4.575 \times 1{,}803 \log a^R_{Si} \qquad (8)$$

From eqn. (8), $\Delta G^0_{1803} = 4{,}575 \times 1{,}803\ (\log N_{Si} + \log \gamma^0_{Si})$ (9)

Henry's law states that in a dilute solution the activity of the solute is proportional to its concentration. Within the range of composition for which Henry's law is valid the activity coefficient is constant and its value is designated. In other words, γ^0 is the slope of the Henry's law line.

The value of γ^0_{Si} can be calculated from the point, A at which it cuts the coordinate $N_{Fe}=1$ in Fig. 4, and putting approximately $\log \gamma_{Si} = -1.90$ and $N_{Si} = 0.0199$, it may be found from eqn. (9),

$$\Delta G^0_{1803} \fallingdotseq -29{,}700\text{cal.}$$

According to Chipman⁽⁵⁾, ΔG^0 in the reaction (7) has been calculated as follows:

$$SiO_2=Si(\text{in Fe})+2O\ (\text{in Fe}) \tag{a}$$
$$\Delta G^0{}_{1873}=38{,}100\text{cal}$$
$$Si(\text{liquid})+O_2(\text{gas})=SiO_2(\text{solid}) \tag{b}$$
$$\Delta G^0{}_{1873}=-126{,}300\text{cal}$$
$$O_2(\text{gas})=2O\ (\text{in Fe}) \tag{c}$$
$$\Delta G^0{}_{1873}=-58{,}500\text{cal}$$

From equations (a), (b), (c)

$$Si(\text{liquid})=Si(\text{in Fe})$$
$$\Delta G^0{}_{1873}=-29{,}700\text{cal}$$

Eqn. (10) is given as the function of temperature

$$\Delta G^0=-29{,}000-0.30T \tag{10}$$

In eqn. (10), if we look for $\Delta G^0{}_{1803}$ when $T=1{,}803$ we find

$$\Delta G^0{}_{1803}=-29{,}500\text{cal}$$

which is in good agreement with the results of the authors.

As to the conversion of the two scales, $\gamma^0_{Si}=0.013$ is obtained from $\log\gamma^0_{Si}=-1.9$ and the mole fraction of silicon in dilute solutions is 0.0199 times its weight percentage. From this two values, the ratio of the activities of silicon on the scales is obtained as 0.00026.

Fig. 3 (b) represents the relation between a_{Si} and N_{Si} or $\underline{Si}\%$ in lower concentration of Si in Fe-Si system enlarged, showing the two scales being simultaneously graduated with $\gamma^0_{Si}=0.013$ as converted value. For example, 0.10 N_{Si} corresponds to 5% Si, that is Henry's activity $a_{Si}=5$, while Raoult's activity $a_{Si}=0.0013$. These data were treated by statistical calculation. Correlation coefficient γ between a_{Si} and N_{Si} was obtained as follows: $\gamma \fallingdotseq 0.918$. This value is highly significant statistically. Regression line and deviation, which were shown in Fig. 3 (b) as follows:

$$a_{Si} \fallingdotseq 0.0179\ N_{Si}-0.00016$$
$$S \fallingdotseq 0.0003$$

Judging from this result, it may be say that it is in conformity with Henry's law approximately up to 0.08 N_{Si} under the level of significance 5%. Beyond this point, it gradually slips upward.

(3) When measurements were with the addition of Fe-Si alloys, the experimental values would be fragmentary if measured at the same interval of time as in the case of Fe-C system⁽⁶⁾, and it was necessary to increase the interval after the addition of Fe-Si alloys. In other words, it was observed in the performance of experiment that the diffusion velocity of Si was slower than that of C in molten iron. In examining the diffusion velocity of each element to molten iron, the diffusion velocity of Si was found to be 1/10 of that of C, as shown in Table 2.

Dr. Sano⁽⁹⁾ gives examples of the melting of spring steel of Si-Mn type as shown in Table 3; our results are in good agreement with these instances.

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(8) W. F. Holbrook, C. C. Furnas and T. L. Joseph: Ind. Eng. Chem., **24** (1932), 993.

(9) K. Sano: J. Iron and Steel Inst. Japan., **38** (1952), No. 2. p. 1-11.

(4) Construction of molten slag

The present experiment has given us an idea that such a reaction as Si→Si^{+4} and that Si ion exists in ternary slag SiO_2-CaO-Al_2O_3, of which the experiment consisted. Matushita and Sakagami(10) recognized also Si^{+4} in the molten SiO_2-CaO system. The construction of molten slag, however, should be considered with the results of experiments on electro-conductivity, viscosity and others, and so our ideas on it will be given in another paper.

Table 2. Diffusion velocity of several elements in liquid iron.

Element	cm^2/sec at 1,600°C
C	0.004
S	0.001
Si	0.0004
Mn	0.0005
P	0.0006

Table 3. Segregation of silicon and carbon.

No.	Si%		C%	
	Before Tap	Ladle	Before Tap	Ladle
1	2.92	1.69	0.54	0.58
2	2.64	1.55	0.58	0.62
3	2.29	1.60	0.56	0.57
4	2.33	1.34	0.60	0.60

V. Conclusion

Constructing the following electrode concentration cell, the authors measured the electromotive force between the electrodes, from which they calculated the activity of silicon in molten iron and the change in free energy in the reaction in eqn. (2) from the result of the experiment.

$$\text{Fe-Si} \mid SiO_2\text{-CaO-}Al_2O_3 \mid \text{pure Si} \qquad (1)$$

$$\text{Si (liquid)} = \text{Si(in Fe)} \qquad (2)$$

The activity of silicon in molten iron is in conformity with Henry's law in low concentration of silicon, showing complicated features on the way, and it is in conformity with Raoult's law in high concentration.

And for the change in free energy in eqn. (2), authors obtained the following value:

$$\Delta G^0_{1803} = -29{,}700 \text{ cal}$$

The change in the activity a_{Si} against temperature was not pronounced.

In concluding our report, we wish to express their hearty thanks to Mr. N. Nishida for his assistance.

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(10) Y. Matushita and R. Sakagami: J. Iron and Steel Inst. Japan, **39** (1953), 295.