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# Diffusion of Sulfur in Liquid Iron. I

## Diffusion in Pure Iron\*

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### Synopsis

The diffusion coefficient of sulfur in liquid iron has been measured at the temperature range from 1,560° to 1,670°C. Since the concentration of sulfur was low in the present investigation, the diffusion coefficient was calculated by assuming as constants independent of the concentration. The result was expressed as follows:

$$D = 4.9 \times 10^{-4} \exp(-4350/T).$$

The diffusion coefficient and the activation energy are nearly the same as those of carbon, cobalt and phosphorus in liquid iron. The activation energy is about one-tenth of the heat of vaporization and this shows that the holes in liquid iron are small.

The theoretical values derived from the absolute reaction rate theory and the diffusion coefficient calculated by the Stokes-Einstein equation are compared with the experimental results.

### I. Introduction

The rate of desulfurization of iron by slag under reducing condition was studied for the last few years. The results of the studies on the diffusion of sulfur in liquid  $\text{CaO-SiO}_2\text{-Al}_2\text{O}_3$  slag<sup>(1)</sup> and the rate of transfer of sulfur across a metal-slag interface<sup>(2)</sup> were already reported.

The data of diffusion in liquid metal will be of use not only to the study of the kinetics of refining reaction, but also to the study of the structure of liquid metal. Nevertheless, investigations on the diffusion in liquid metal are few except for the case of metals of low melting point.

Diffusion coefficients of various elements in liquid iron saturated with carbon had been measured by Holbrook, Furnas and Joseph<sup>(3)</sup> and Paschke and Hauttmann<sup>(4)</sup>, but their results seem to be erroneous because of the method of experiment and the scattering of values of the diffusion coefficient.

Recently, Morgan and Kitchener<sup>(5)</sup> measured the diffusion coefficients of carbon and cobalt in liquid iron by using radioactive carbon,  $\text{C}^{14}$ , and cobalt,  $\text{Co}^{60}$ . Saitô and Maruya<sup>(6)</sup> measured the diffusion coefficients of silicon and manganese in liquid

\* The 79th Report of the Research Institute of Mineral Dressing and Metallurgy.

(1) T. Saitô and Y. Kawai, Science Repts. RITU, A5 (1953), 460.

(2) T. Saitô and Y. Kawai, Science Repts. RITU, A7 (1955), 402; Y. Kawai, ditto, A8 (1956), 352.

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

(4) M. Paschke and A. Hauttmann, Arch. Eisenhüttenw., 9 (1935), 305.

(5) D. W. Morgan and J. A. Kitchener, Trans. Faraday Soc., 50 (1954), 51.

(6) T. Saitô and K. Maruya, Bulletin Research Inst. Mineral Dress. Metall., 9 (1953), 271; 10 (1954), 167; 12 (1956), 27.

iron saturated with carbon. According to these investigations, diffusion coefficients of these elements in liquid iron are  $2 - 8 \times 10^{-5}$  cm<sup>2</sup>/sec and the activation energy for diffusion is of the order of 10,000 cal.

Maekawa and Nakagawa<sup>(7)</sup> measured the diffusion coefficient of sulfur in liquid iron, but the result was larger than those mentioned above, therefore, it seems to be necessary to perform further experiments.

## II. Experimental procedure

An iron rod containing sulfur was joined with a pure iron rod into a couple in an alumina tube, as shown in Fig. 1, and was melted for diffusion at a desired temperature in a Tamman furnace.

The iron rod specimen containing sulfur was prepared by melting a mixture of electrolytic iron powder (C 0.03%, Si 0.02%, Mn 0.005%, P 0.06%, S 0.01%) and pure sulfur powder in a magnesia crucible and by suctioning the melt into a silica tube 4 mm in diameter by an injector. The concentration of sulfur of the specimen was intended to be about 1%.

The diffusion specimen (a couple of iron rod containing sulfur with a pure iron rod) was introduced into an alumina tube, the bottom of which was closed by a magnesia plug, and was melted in a Tamman furnace at a desired temperature for two hours for diffusion.

The clearance between the diffusion specimen and the alumina tube was so small that the liquid iron-sulfur metal melted initially would not drop into the clearance between the solid pure iron specimen and the tube. (When copper was melted on a solid iron rod in an alumina tube, it was observed that liquid copper did not drop into the clearance.)

A carbon tube heating element of the Tamman furnace was made thick at the middle part and a carbon block with a bore was introduced on the diffusion specimen to improve the uniformity of temperature distribution in the furnace.

Before the diffusion run, temperature distribution in the furnace was always measured and the diffusion specimen was introduced into a proper portion of the furnace. An example of temperature distribution in the furnace is illustrated in Fig. 1.

An alumina tube was introduced into a bore of the carbon block on the diffusion specimen so that carbon powder might not fall on the surface of the metal.

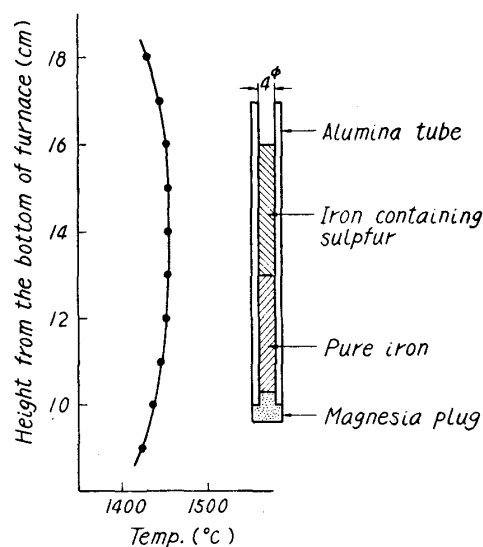


Fig. 1 Sample for diffusion run and uniformity of furnace temperature.

(7) S. Maekawa and Y. Nakagawa, Reported at the Tōkyō Meeting of the Japan Institute of Metals, April, 1955.

Temperature was measured by a disappearing-filament optical pyrometer sighted on the surface of liquid metal. The pyrometer was calibrated by comparison with a Pt-Pt-Rh thermocouple.

The diffusion specimen melted in two minutes and reached a desired temperature in about another five minutes. After being held at this temperature for two hours, the specimen was cooled by switching off the power of the furnace. The time required for solidification was about two minutes.

The solid specimen was extracted by breaking the alumina tube and was cut into pieces 5 mm in length. And, by the chemical analysis of sulfur content of each pieces, the concentration-penetration curves were obtained.

In this experiment the diffusion specimen was melted under carbon monoxide atmosphere, so the specimen might be carburized to some extent. But, the examination of the structure of pure iron melted under the same condition as the diffusion experiment showed that the degree of carburization was negligibly small.

### III. Result and discussion

Some concentration-penetration curves are shown in Fig. 2. A diffusion run at 1,615°C for two minutes was intended to serve as a blank to examine the influence of melting and freezing on the shape of interface.

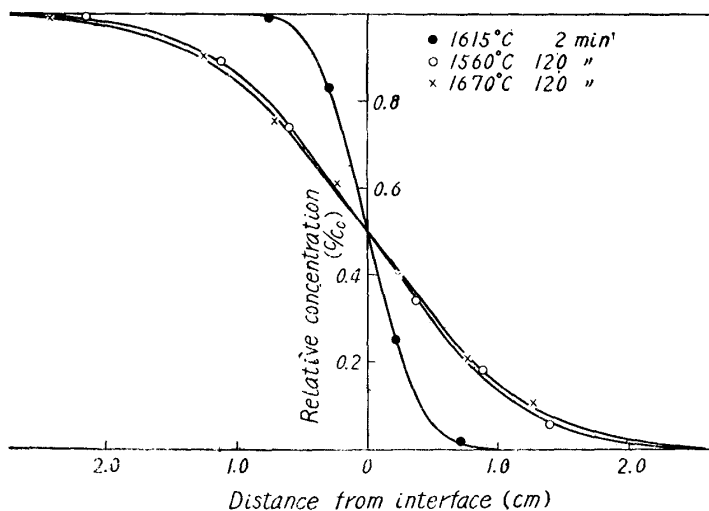


Fig. 2. Concentration-penetration curves after diffusion run.

From the comparison of the blank run with others, it was found that the penetration of sulfur in the blank run was greater than that predicted by the diffusion coefficient of sulfur. This shows that the shape of interface was changed during melting and freezing for some reasons (stir during melting, difference of surface tension between liquid iron and liquid iron-sulfur metal, and shrinkage during solidification.) Therefore, it was necessary to correct the concentration-penetration curves of diffusion run of two hours. The correction was done based on the result of the blank run as follows:

Assuming that the shape of interface was unchanged, the diffusion coefficient was calculated from the concentration-penetration curve of the diffusion of two hours and the penetration of sulfur during melting and freezing was estimated by applying this diffusion coefficient to the blank run. Next, the penetration of sulfur during melting and freezing was eliminated from the concentration-penetration curve of the diffusion of two hours and more accurate value of the

diffusion coefficient of sulfur was calculated. Further, more accurate value of penetration of sulfur during melting and freezing was estimated by applying this diffusion coefficient to the blank run. By repeating this procedure, the accurate value of the penetration of sulfur during melting and freezing was determined and the correction for the concentration-penetration curve of the diffusion of two hours was done. Blank run was carried out at another temperature, but the penetration of sulfur during melting and freezing was the same.

In this experiment the concentration of sulfur of metal was low, so the diffusion coefficients of sulfur were calculated as constants independent of sulfur concentration by the second equation of Fick's law. The particular solution of the equation which satisfies the initial and boundary conditions of this experiment is as follows :

$$C = \frac{C_0}{2} \left\{ 1 - \psi \left( \frac{x}{2\sqrt{Dt}} \right) \right\}, \quad (1)$$

where  $C$  is the concentration of sulfur at some distance  $x$  from the interface after diffusion time  $t$ ;  $C_0$  is the difference between initial concentration of sulfur in high and low-sulfur iron;  $D$  is the diffusion coefficient,  $\text{cm}^2/\text{sec}$ ;  $\psi$  is the Gauss' error integral.

The calculated diffusion coefficients are given in Table 1 where initial concentration of sulfur of iron-sulfur specimen are also shown.

Table 1. Diffusion coefficients of sulfur in liquid iron.

Experiment No.	No. 1	No. 2	No. 3	No. 4	No. 5	No. 6	No. 7
Temperature ( $^{\circ}\text{C}$ )	1560	1565	1610	1615	1630	1660	1670
Sulfur (%)	0.96	1.13	0.96	0.96	1.24	1.13	1.24
$D \times 10^5$ ( $\text{cm}^2/\text{sec}$ )	4.6	4.6	4.9	4.8	5.1	5.2	5.2

Temperature dependency of the diffusion coefficient is expressed by Arrhenius equation as follows :

$$D = A \exp(-Q/RT), \quad (2)$$

where  $A$  is the constant independent with temperature and  $Q$  is the activation energy for diffusion. Plotting the logarithms of the diffusion coefficients of sulfur to the reciprocals of absolute temperature, a linear relation was observed, as shown in Fig. 3, which can be expressed as follows :

$$D = 4.9 \times 10^{-4} \exp(-4350/T) \quad (3)$$

Thus, the activation energy for diffusion of sulfur in liquid iron is 8,600 cal.

According to the result of Maekawa and Nakagawa<sup>(7)</sup>, the diffusion coefficient of sulfur in liquid iron is  $11.6 - 15.4 \times 10^{-5} \text{ cm}^2/\text{sec}$  and the activation energy is 21,000 cal. These values are about twice the present values and greater than those

of diffusion of carbon<sup>(5)</sup>, cobalt<sup>(5)</sup> and phosphorus<sup>(8)</sup> in liquid iron. In Table 2 diffusion coefficients of these elements at 1,550°C and the activation energy are given for comparison.

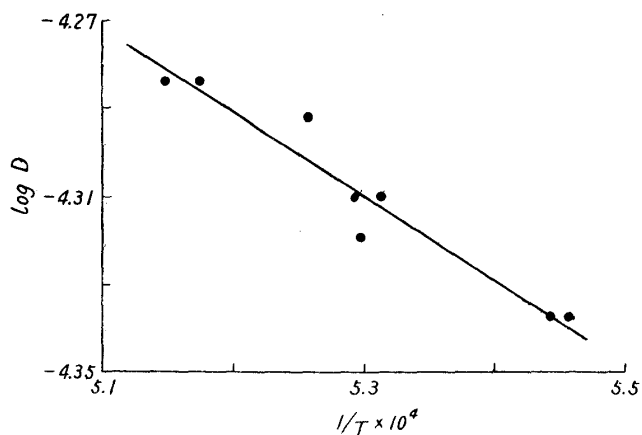


Fig. 3. Variation of diffusion coefficient with temperature.

The activation energy of diffusion is ordinarily of the same order as the activation energy for viscous flow. Recently, Barfield and Kitchener<sup>(9)</sup> measured the viscosity of liquid iron containing sulfur and determined the activation energy for viscous flow as 7,150 cal. This value is nearly the same as the value of activation energy for diffusion.

Table 2. Diffusion coefficients in liquid iron at 1,550°C and activation energy.

Element	C	Co	P	S
$D_{1550} \times 10^5 (\text{cm}^2/\text{sec})$	6.0	4.6	4.7	4.5
$Q$ (cal/mol)	10,000	11,000	8,000	8,600

The activation energy for diffusion is supposed to be about the same as the energy of forming a hole to allow the atom to move from one equilibrium position to the next in the adjoining hole. Therefore, the size of a hole may be estimated by comparing the activation energy with the heat of vaporization,  $L_v$ , which is nearly the same as the energy required to make a hole equal to atomic (molecular) size in liquid. The heat of vaporization of liquid iron is about 87,000 cal<sup>(10)</sup>.

Then,

$$\frac{L_v}{Q} \doteq 10. \quad (4)$$

Therefore, the size of the hole necessary for diffusion of sulfur in liquid iron is small (about one-tenth of atomic volume of iron).

Modern theories of molecular diffusion attempt to relate the diffusion coefficient to a model of liquid structure, but, unfortunately, in every case they employ a number of ill-defined quantities which are not directly measurable. Therefore, the concordance between the experimental value and the theoretical one is not satisfactory at the present stage. For example, according to the absolute reaction rate

(8) S. Maekawa and Y. Nakagawa, Reported at the Kanazawa Meeting of the Japan Institute of Metals, October, 1955.

(9) N. Barfield and J. A. Kitchener, J. Iron Steel Inst., **180** (1955), 324.

(10) K. K. Kelley, U. S. Bureau Mines, Bull. 383 (1935).

theory developed by Eyring and his school<sup>(11)</sup>, the constant  $A$  of the Arrhenius equation (2) is as follows:

$$A = \frac{\lambda^2}{V_f^{1/3}} \left( \frac{kT}{2\pi m} \right)^{1/2}, \quad (5)$$

where  $\lambda$  is the average jump distance for the action of diffusion. If the number of atoms in volume  $V$  is  $N$ ,  $\lambda$  is equal to  $(V/N)^{1/3}$ .  $V_f$  is the free volume which may be estimated in several ways (from the heat of vaporization, the frequency of elastic oscillation etc.);  $k$  is the Boltzmann constant;  $m$  is the mass of the atom. The value of  $A$  calculated from this equation is about  $2 - 7 \times 10^{-3}$  which is much greater than the experimental result,  $4.9 \times 10^{-4}$ .

Frequently, the Stokes-Einstein equation given below is used to relate the diffusion coefficient with the viscosity:

$$D = \frac{kT}{2\pi r \eta}, \quad (6)$$

where  $\eta$  is the viscosity and  $r$  is the radius of a sphere. Using the value of viscosity of iron-sulfur liquid measured by Barfield and Kitchener<sup>(9)</sup> and the atomic radius of sulfur, the diffusion coefficient of sulfur in liquid iron was calculated to be  $1.5 \times 10^{-5} \text{cm}^2/\text{sec}$  at  $1,550^\circ\text{C}$ . This is smaller than the present result. (Use of the ionic radius of sulfur gives a much smaller diffusion coefficient.) The Stokes-Einstein equation is not valid for the movement of spheres of size comparable with that of the liquid molecules, so it gives only a rough estimate of the value of the diffusion coefficient.

### Summary

Diffusion coefficient of sulfur in liquid iron was measured at the temperature range from  $1,560^\circ\text{C}$  to  $1,670^\circ\text{C}$ . The result can be expressed as follows:

$$D = 4.9 \times 10^{-4} \exp(-4350/T).$$

The activation energy for diffusion is 8,600 cal.

The diffusion coefficient and the activation energy are nearly the same as those of carbon, cobalt and phosphorus in liquid iron. Also, the activation energy for diffusion is nearly the same as the activation energy for viscous flow.

By a comparison of the activation energy with the heat of vaporization it was found that the size of the hole necessary for diffusion is small.

The value of the diffusion coefficient calculated by the absolute reaction rate theory was greater than that of the present result and the value calculated by the Stokes-Einstein equation was smaller.

In conclusion the author expresses his hearty thanks to Prof. T. Saitô for his suggestions and encouragement in the course of this study.

(11) S. Glastone, K. J. Laidler and H. Eyring, *The Theory of Rate Process*, (1941), 477.