# DETERMINATION OF THE DIFFUSION COEFFICIENTS OF ELEMENTS IN LIQUID CAST IRON BY OSCILLOGRAPHY AT CONSTANT CURRENT

1962

SovietRxiv

## Abstract

## Full Text

## PHYSICAL CHEMISTRY

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# DETERMINATION OF THE DIFFUSION COEFFICIENTS OF ELEMENTS IN LIQUID CAST IRON BY OSCILLOGRAPHY AT CONSTANT CURRENT

*(Presented by Academician A. N. Frumkin, April 11, 1962)*

The study of diffusion coefficients ($D$) in liquid cast iron provides certain information on the structure of this technically important melt. In addition, the values of $D$ and their dependence on temperature are of substantial interest for metallurgy. In the few recent works ($^{1-3}$) devoted to this question, the distribution of the diffusing substance along the length of a capillary was investigated. In this case, the low viscosity of liquid cast iron could have caused appreciable distortions due to convection. Errors associated with volume changes of the capillaries and samples during melting and solidification are also unavoidable. Thus, for example, for silicon the values of $D_{\mathrm{Si}}$ differ among various investigators by an order of magnitude. In view of the above, it was of interest to measure diffusion coefficients by another independent method, in particular by using oscillography at constant current. In this method, by determining the time ($\tau$) required to reach the limiting current at known concentration ($C_0$, mol/cm$^3$) and current density ($i$), the diffusion coefficients were calculated by formula (4):

$$D^{1/2} = \frac{2i\tau^{1/2}}{\pi^{1/2}nFC_0}, \tag{1}$$

where $n$ is the number of electrons participating in the electrode reaction, and $F$ is the Faraday constant. By varying the concentration and the current, one can vary the time required to reach the limiting current. The latter must be such that convection does not affect the diffusion process. In practice this is achieved when $\tau$ does not exceed several minutes ($^5$). In our experiments $\tau$ amounted to tenths of a second.

In the experiments an anode 1.5 mm in diameter was used. It consisted of Armco iron saturated with carbon and containing a small addition (0.1—0.4%) of the element (Me) whose diffusion was being studied. The added element (Si, V, Ti, and Nb) was selected so that the anodic process would be the transfer of its ions into a slag containing difficult-to-reduce oxides: CaO, MgO, $Al_2O_3$, $B_2O_3$, and also the oxide of Me.

Fig. 1. Cell schematic

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Fig. 2. Dependence of the logarithm of the diffusion coefficients ($\lg D$) of silicon (1), vanadium (2), titanium (3), and niobium (4) on $1/T$

Figure 2: Fig. 2. Dependence of the logarithm of the diffusion coefficients ($\lg D$) of silicon (1), vanadium (2), titanium (3), and niobium (4) on $1/T$

**Fig. 1. Cell schematic**

The scheme of the cell is shown in Fig. 1. Into a graphite cup **1** with the alloy under investigation there was inserted a corundum or zirconium crucible **2** with an opening in the bottom **3** of diameter 1.5 mm. The metal that flowed into it through the opening was removed. Then slag was charged and melted, and the electrodes 4. The measuring circuit did not differ from that described earlier ($^6$). X-ray photographs of the electrode in contact with slags of different compositions at various temperatures and current densities showed ($^1$) that the radius of the metallic meniscus is close to that for the tube. Therefore, the current density ($i$) was calculated under the assumption that the working surface of the anode has the shape of a hemisphere. In determining $C_0$ (mole/cm$^3$), the densities of liquid cast iron were taken from work ($^7$).

**Fig. 2.** Dependence of the logarithm of the diffusion coefficients ($\lg D$): silicon (1), vanadium (2), titanium (3), and niobium (4) on $1/T$

As is seen from Fig. 2, on which the obtained results are plotted, the temperature dependences of the diffusion coefficients can be expressed by the equations:

$$D_{\mathrm{Si}} = 12.7 \cdot 10^{-4} \exp(-9100/RT), \tag{2}$$

$$D_{\mathrm{Ti}} = 18.1 \cdot 10^{-4} \exp(-11400/RT), \tag{3}$$

$$D_{\mathrm{V}} = 6.2 \cdot 10^{-4} \exp(-7200/RT), \tag{4}$$

$$D_{\mathrm{Nb}} = 4.5 \cdot 10^{-4} \exp(-7600/RT). \tag{5}$$

Here the diffusion activation energies ($E$) of silicon, titanium, vanadium, and niobium in cast iron are apparent, owing to the change in the solubility of carbon in iron with temperature.

**Table 1**

**Diffusion coefficients of elements in iron melts saturated with carbon at 1350° according to data of various authors**

| Diffusing element | $D_2 \cdot 10^5$, cm$^2$/sec | Activation energy, kcal/g-ion | Diffusing element | $D_2 \cdot 10^{-5}$, cm$^2$/sec | Activation energy, kcal/g-ion |
|---|---|---|---|---|---|
| Ti (3) | 4.4 | 6.4 | Ni (3) | 2.7 | 3.9 |
| Ti * | 5.2 | 11.4 | P (3) | 9.9 | 11.0 |
| Si (3) | 13.9 | 7.2 | S (3) | 1.1 | 21.0 |
| Si * | 7.6 | 9.1 | S (1) | 2.7 | 7.5 |
| Si (2) | 1.9 | 8.2 | Fe (13) | 9.6 | 12.2 |
| V * | 6.6 | 7.2 | Alloy with 4.6% C | – | – |
| Nb | 4.3 | 7.6 | Fe (13) | 7.4 | 15.7 |
| Mn (2) | 3.2 | 5.8 | Alloy with 2.5% C | – | – |
| Mn (3) | 6.5 | 8.8 | | | |

* Experimental data.

In Table 1 our experimental data are compared with those available in the literature. The values of $D_{\mathrm{Ti}}$ are in good agreement with the results obtained by Grace and Derge (3). The values of $D_{\mathrm{Si}}$ lie between those found in works (3) and (4). Data on the diffusion of niobium and vanadium in liquid cast irons are absent from the literature.

The values $E_{\mathrm{a}}$ of the elements in iron-carbon melts are close to the activation energy of viscous flow of cast iron ($E_\eta = 10.2$ kcal/mole) (8). Apparently, the mechanisms of these processes in the melts studied are identical. Since the viscosity of cast irons has been measured (8), and small additions of Si, Nb, Ti, V are unlikely to change it appreciably, it is of interest to estimate the sizes of the diffusing particles. If the size of the latter ($r$) is greater than the radius ($r_c$) of the solvent particle, the applicability of the Stokes-Einstein relation should be expected:

$$D = \frac{kT}{6\pi\eta r}. \tag{6}$$

In the case where $r = r_c$, Eyring’ s expression is valid:

$$D = \frac{kT}{2\eta}. \tag{7}$$

Finally, if $r < r_c$, one may use equation (9):

$$D = \frac{kT}{6\pi\eta r}\frac{(1+3\eta/\beta r)}{2\eta/\beta r}, \tag{8}$$

in which $\beta$ is the coefficient of sliding friction between the diffusing particles and the medium. Relation (9) was recently applied [10] to the analysis of diffusion processes in tin. When the moving particles are much larger than the particles of the medium, then $\beta = \infty$ and expression (8) becomes (6). If the former are smaller than the latter, then $\beta = 0$ and

$$D = \frac{kT}{4\pi\eta r}. \tag{9}$$

**Table 2**

Results of calculations of the radius of diffusing particles

| Diffusing element | Atomic radius ($r_a$), Å | Ionic radius ($r_i$), Å | $r_{\text{calc}}$, Å by (6) | $r_{\text{calc}}$, Å by (7) | $r_{\text{calc}}$, Å by (9) |
|---|---|---|---|---|---|
| Si | 1.30 | 0.40 | 0.21 | 2.0 | 0.31 |
| V | 1.36 | 0.56 | 0.24 | 2.3 | 0.36 |
| Ti | 1.41 | 0.68 | 0.31 | 2.9 | 0.46 |
| Nb | 1.47 | 0.69 | 0.37 | 3.5 | 0.56 |

The sizes of the moving particles calculated from these equations are given in Table 2.

The rate of motion of the elements studied increases in the series Nb—Ti—V—Si. In the same sequence the atomic and ionic radii of these elements decrease. The values calculated by equation (7) prove to be considerably greater than the atomic radius, while those found from formulas (6), (9) are somewhat smaller than the ionic radius. Apparently, the elements dissolved in molten cast irons diffuse in the form of ions. A number of authors who have studied diffusion in tin [10] have arrived at a similar conclusion regarding the ionic form.

The best agreement with experiment is given by formula (9), which refers to the case where the moving particles are smaller than those of the medium (the radius of the $Fe^{2+}$ ion is 0.83 Å).

All the elements we studied have a rather large heat of dissolution in liquid iron. In this case, according to the fluctuation theory of self-diffusion proposed in [12], the coefficient $D$ of the dissolved substance should be close to that for the solvent, or somewhat smaller. Indeed, the coefficient of self-diffusion of iron in cast iron at 1350°, $(7.4—9.6) \cdot 10^{-5}$ cm$^2$/s [13], does not differ greatly from the corresponding values for the elements investigated.

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Received
9 IV 1962

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*Note: Figure translations are in progress. See original paper for figures.*

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