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Abstract

Full Text

PHYSICAL CHEMISTRY

I. A. NOVOKHATSKII, O. A. ESIN, and S. K. CHUCHMAREV

ON THE DIFFUSION OF HYDROGEN IN MOLTEN SLAGS

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The values available in the literature (^{1}) for the mass-transfer coefficient D_M of hydrogen in slags are very high ($10^{-3} \div 10^{-2}$ cm$^2 \cdot$ sec^{-1}). They were obtained under the conditions of an open-hearth furnace and reflect mainly not the molecular diffusion D_H, but convection, which inevitably arises in large volumes of liquid at high temperatures. In order to suppress convective flows as much as possible and to approach the value D_H, we experimentally carried out the case of nonstationary diffusion during the removal of gas from a membrane with one impermeable boundary (^{2}).

A thin ($\delta \simeq 1.5$ mm) layer of viscous ($\eta = 3 \div 100$ poise) liquid ($1410 \div 1600$°C) slag, containing $16.5 \div 53.0\%$ CaO; $8.2 \div 41.0\%$ Al_2O_3 and $6.0 \div 58.3\%$ SiO_2, was placed in a corundum boat located in a horizontal test tube made of Al_2O_3. By blowing thoroughly dried nitrogen through it, the water released from the slag was carried to a hygrometer. Upon reaching the dew (or frost) point, the mirror, initially dark, became luminous. Knowing the blowing intensity and the dew temperature, the rate V_{H_2O} of removal of water from the slag was determined.

Fig. 1. Kinetic curves for extraction of H_2O from slag No. 2 (27.3% CaO; 56.4% SiO_2 and 16.3% Al_2O_3) at 1410° for films of different thickness. Curves 1, 2, and 3 are for V_{H_2O} at $\delta = 1.3$ mm, 1.8 mm, and 2.6 mm, respectively; similarly, curves 4, 5, and 6 are for Q_τ/Q_0.

Figure 1 shows, for illustration, curves 1, 2, and 3 of the dependence of V_{H_2O} on time τ for three slag thicknesses. By graphical integration, the current Q_τ and initial Q_0 amounts of water dissolved in the slag were determined. Their ratios (curves 4, 5, and 6) were used to estimate the para-

meter θ, which under our conditions can be calculated with an accuracy of up to 1% from the formula:

Fig. 2. Dependence of the diffusion coefficient (1, 3) and viscosity (2) on temperature. 1, 2—for slag No. 2; 3—for slag No. 7 (53% CaO, 6% SiO_2, and 41% Al_2O_3)

Figure 2: Fig. 2. Dependence of the diffusion coefficient (1, 3) and viscosity (2) on temperature. 1, 2—for slag No. 2; 3—for slag No. 7 (53% CaO, 6% SiO_2, and 41% Al_2O_3)

$$Q_\tau / Q_0 \simeq 1 - 8/\pi^2 \left(e^{-\theta}\right). \tag{1}$$

Knowing θ, one can determine the value of the diffusion coefficient:

$$D_H = \frac{4\delta^2\theta}{\pi^2\tau}. \tag{2}$$

The values of D_H found for three slag thicknesses (1.3, 1.8, and 2.6 mm) proved to be very close: (1.0; 1.1; and 0.9) $\cdot 10^{-5}$ $\mathrm{cm}^2/\mathrm{sec}$. This confirms that, in our case, diffusion is the rate-limiting stage in the removal of water from the slag. If the slowed-down step were the transition across the slag-gas boundary, then for each given ratio Q_τ/Q_0 the concentration of water in the slag would be the same, and $V_{\mathrm{O_2H}}$ would not depend on the film thickness. As is seen from Fig. 1, this is not so.

Fig. 2. Dependence of the diffusion coefficient (1, 3) and viscosity (2) on temperature. 1, 2—for slag No. 2; 3—for slag No. 7 (53% CaO, 6% SiO_2, and 41% Al_2O_3)

To make sure that convective mixing was suppressed in our experiments, we used the relation obtained by Lin Tsya-tszyao[3]. Studying the onset of convection in a thin incompressible layer of liquid heated from below, he found the value of the instability threshold to be:

$$\mathrm{Re} = \frac{g\alpha(-\beta)\delta^4}{\varkappa\nu} = 1708. \tag{3}$$

In our case the temperature gradient $(-\beta) \leq 50^\circ/\delta$, the coefficient of thermal expansion $\alpha = 1.1 \cdot 10^{-5}$ deg^{-13}, $\delta < 0.3$ cm, the kinematic viscosity

$$\nu = \frac{3.2\ \text{(poise)}}{2.7\ (\mathrm{g} \cdot \mathrm{cm}^{-3})} \simeq 1.2\ \mathrm{cm}^2/\mathrm{sec}\ ^5,$$

and the thermal diffusivity

$$\varkappa = \frac{\lambda}{c\gamma} 1.53 \cdot 10^{-2}\ \mathrm{cm}^2/\mathrm{sec}\ ^6.$$

Hence Re $\simeq 0.8$, i.e., convection under our conditions could not play a noticeable role. Thus, the found values of D_H characterize predominantly the molecular diffusion of hydrogen in slags.

The following features of the results obtained attract attention. First of all, the value of the hydrogen diffusion coefficient is at least an order of magnitude greater than those obtained[7–9] for other ions (Ca, Fe, P, S, Si). It is unlikely that the anions OH^-, in the form of which water dissolves in slags[1,10], could move at such a high rate. For the viscosities of our melts at 1600°, lying within the range 3.2-75 poise[5,11], the value D, calculated by the Stokes-Einstein formula for the OH^- ion, is considerably smaller and amounts to 10^{-7}-10^{-8} cm^2/sec.

In connection with what has been said, it may be assumed, as was done by one of us[1], that hydrogen moves in slags (as in aqueous solutions[12–15]) in the form of a proton passing from one oxygen ion to another:

$$OH^- + O^{2-} \rightarrow O^{2-} + OH^-. \tag{4}$$

The next feature is the weak dependence of the coefficient D_H on temperature in melts rich in SiO_2. Thus, in slag No. 2, with an increase-

···temperature from 1410 to 1600° the value of D_H remains practically constant (see line 1 in Fig. 2), whereas the viscosity decreases sharply (line 2). A zero activation energy indicates that the diffusing particle moves in the absence of an energy barrier. This is hardly possible for the anion OH^-, but is quite probable for a proton. Indeed, as M. Huggins has shown (15), in the transfer of hydrogen from hydroxyl to oxygen the energy barrier is absent so long as the distance between the centers of neighboring O atoms does not exceed 2.65 Å. The latter value is very close to the distance (d = 2.64 Å) between oxygen ions in SiO_2 (16).

The third feature consists in the fact that, with increasing CaO concentration in the slag, the coefficient D_H increases (curves 1 and 2 in Fig. 3), but at the same time the activation energy also increases (line 3 in Fig. 2). According to the theory of absolute rates (12),

$$D = 2.72\,\frac{kT}{h}\lambda^2 \exp(\Delta S^*/R)\exp(-E/RT), \tag{5}$$

where k and h are the Boltzmann and Planck constants, ΔS^* is the activation entropy, which is usually small, and λ is the distance between neighboring equilibrium positions of the moving particle.

Fig. 3. Dependence of the diffusion coefficient (1, 2) and viscosity (3) on slag composition at 1600°.
1 –for 57% SiO_2, 2 –for 28% Al_2O_3

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From equation (5) it follows that a simultaneous increase in the values of D_H and E is possible when the value of λ increases. This does not contradict the assumption of proton transfer. Indeed, addition to the melt of CaO, in which the distance between oxygen ions in the lattice is $d = 3.41$ Å greater (16) than in SiO_2, leads to an increase in λ. An estimate of the latter from equation (5) and the experimentally found values of D_H and E gives acceptable values of λ. Thus, for slag No. 2, rich in SiO_2, at 1600° the value $D_H = 1.1 \cdot 10^{-5}$ cm^2/sec, $E = 0$; these correspond to a small distance $\lambda = 0.03$ Å. Conversely, for slag No. 7, rich in CaO, $D_H = 2.05 \cdot 10^{-5}$ cm^2/sec, $E = 20800$ cal/mol, whence $\lambda = 0.71$ Å. The plausibility of this value is confirmed by its closeness to the difference between the distance d in the CaO lattice and the diameter of the O^{2-} ion: $3.41 - 2 \cdot 1.32 = 0.77$ Å.

In conclusion, we note that the assumption of proton transfer requires additional experimental verification.

Ural Polytechnic Institute
named after S. M. Kirov
Sverdlovsk

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