On the Theory of Diffusion, Viscosity, and Electrolytic Conduction.

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In this report, problems on diffusion, viscosity, electrolytic conduction are treated as examples of the theory of reaction velocity. The results obtained are of a rather qualitative nature and require further developement.

1. Diffusion.(1) (2) The phenomena of diffusion and viscosity are very intimately connected with electrolytic conduction. In recent theory, particles in a liquid are always vibrating about an equilibrium position and occasionally jump from one place to another. This occurs when particles have sufficient energy to cross the potential barrier surrounding the vibrating particles. Let us first investigate the relation between the diffusion constant K, the number of jumps per unit time k_1 and the length of one jump λ.

According to Einstein's theory of diffusion(3) the probability dP that the particle in the solution will move from the original place and lie between x and $x+dx$ after a time t is as follows:

$$dP = \left(\frac{1}{4\pi Kt}\right)^{\frac{1}{2}} e^{-\frac{x^2}{4Kt}}\,dx \qquad (1).$$

When the above relation is extended to the case of three dimensions, the probability that the particle will lie between r and $r+dr$ is

$$dP = \left(\frac{1}{4\pi Kt}\right)^{\frac{3}{2}} e^{-\frac{r^2}{4Kt}}\,4\pi r^2 dr \qquad (2).$$

According to Rayleigh(4), when N lines of length λ are connected at random, the probability that the last point will lie at a distance of r to $r+dr$ from the initial point is as follows:

$$dP = 3\sqrt{\frac{6}{\pi}}\,\frac{N^{-\frac{3}{2}}}{\lambda^3}\,e^{-r^2/\frac{2}{3}N\lambda^2}\,r^2 dr \qquad (3).$$

Consequently, if we denote the length of one jump by λ and the number of jumps per unit time by k_1, the probability that the particle will lie, after a time t, between r and $r+dr$ is

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(1) S. Kaneko, *J. Chem. Soc. Japan*, **59** (1938), 673.
(2) S. Kaneko, *J. Chem. Soc. Japan*, **59** (1938), 1093.
(3) A. Einstein, *Ann. Physik.*, **17** (1905), 549.
(4) Lord Rayleigh, *Phil. Mag.*, **37** (1919), 321.

$$dP = 3\sqrt{\frac{6}{\pi}}\frac{(k_1t)^{-\frac{3}{2}}}{\lambda^3}e^{-r^2/\frac{2}{3}k_1t\lambda^2}r^2dr \qquad (4).$$

Comparing (2) and (4) we have the following:

$$K = \frac{k_1\lambda^2}{6} \qquad (5).$$

The above relation has been obtained by Eyring,⁽⁵⁾ but since his verification is not rigorous, the factor 1/6 is missing.

The value k_1 may then be calculated. Eyring calculated this value as the reaction velocity constant. Here k_1 is calculated by Horiuti's theory⁽⁶⁾ of reaction velocity, and the result is somewhat different from Eyring's. Horiuti's general formula of reaction velocity is expressed by

$$k_1 = kT\frac{\int^S\cdots\cdots\int e^{-\frac{E^*}{kT}}dq_2\,dq_3\cdots dq_n\,dp_2\,dp_3\cdots dp_n}{\int^V\cdots\cdots\int e^{-\frac{E}{kT}}dq_1\,dq_2\cdots dq_n\,dp_1\,dp_2\cdots dp_n} \qquad (6).$$

where k denotes Boltzmann's constant, T the absolute temperature, V the volume occupied by the initial system, S the surface of the transition state; q_1, q_2, q_3, ... are the coordinates of particles relating to position, and p_1, p_2, p_3, ... the coördinates relating to momentum. E the sum of the potential and kinetic energies of the particles, E^* the difference between the total energy E and the kinetic energy in the direction vertical to S. S in this case is a spherical surface of radius $\lambda/2$ surrounding the particle, and V is the so-called free volume per molecule v_f. Under this condition the integral of (6) becomes

$$k_1 = \sqrt{\frac{kT}{2\pi m}}\frac{\pi\lambda^2}{v_f}e^{-\frac{U^*}{kT}} \qquad (7)$$

where m is the mass of the particle and U^* the activation energy. If the particle is vibrating according to Hooke's law we have the relation

$$v_f = \iiint_{-\infty}^{\infty}\exp\left\{-\frac{f(x^2+y^2+z^2)}{2kT}\right\}dx\,dy\,dz = \left(\frac{2\pi kT}{f}\right)^{\frac{3}{2}} \qquad (8)$$

where f is the force constant. Between f and the number of vibrations ν there is the following relation:

$$(2\pi\nu)^2 = \frac{f}{m} \qquad (9).$$

Introducing (9) into (8) we have

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(5) H. Eyring, *J. Chem. Phys.*, **4** (1936), 283.
(6) J. Horiuti, this Bulletin, **13** (1938), 210.

$$v_f = \left(\frac{kT}{2\pi\nu^2 m}\right)^{\frac{3}{2}} \tag{10}$$

2. Viscosity. By definition the viscosity of a liquid is given by

$$\eta = \frac{f\lambda_1}{\Delta V} \tag{11}$$

where η is the viscosity, f the force acting between the neighbouring molecular layers sliding over each other per unit area, Δv the difference of velocity between these layers, and λ_1 the distance between them. If we denote the mean distance of molecules in the sliding direction by λ_2 and the mean distance of molecules in the direction vertical to λ_1, λ_2, by λ_3, then the force acting on a molecule from the neighbouring molecular layer is $f\lambda_2\lambda_3$. The value of ΔV is therefore given by

$$\Delta V = f\lambda_2\lambda_3\omega \tag{12}$$

where ω is the reciprocal of the friction coefficient of the molecule in the liquid. According to Einstein's theory⁽³⁾ of diffusion there is the relation

$$K = \omega kT \tag{13}$$

between K and ω.

From (11), (12), (13) and (5), we have

$$\eta = \frac{6\lambda_1 kT}{\lambda^2\lambda_2\lambda_3 k_1} \tag{14}$$

The above relation has been obtained by Eyring⁽⁵⁾ from a somewhat different standpoint, but the numerical coefficient 6 is lacking. By substituting (7) into (14), the value of η can be calculated. Considering that the factor $\exp(-U^*/kT)$ varies greatly with temperature as compared to the other factors, η can be approximately expressed by the following equation.

$$\log\eta = A + \frac{B}{T} \tag{15}$$

where A and B are constants.

3. Electrolytic Conduction.⁽¹⁾⁽²⁾⁽⁷⁾⁽⁸⁾ Ordinarily, the ions in a liquid are vibrating incessantly and jump occasionally from one place to another as already described. Since the jumps of ions occur uniformly in all directions, there is no current in the solution. But when an electric field is applied, the number of jumps increases in the direction of the field and decreases in the opposite direction, thus giving rise to an electric current. If we denote the strength of the field by E, the charge

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(7) S. Kaneko, *Bull. Electrotechn. Laboratory*, **2** (1938), 664.

(8) S. Kaneko, *Bull. Electrotechn. Laboratory*, **3** (1939), 99.

of an electron by ε, and the valency of the ions by z, then the activation energy is decreased in the direction θ by the amount

$$\frac{1}{2}\varepsilon z E \lambda \cos\theta$$

and the number of jumps increases in the following proportion:

$$\exp\left(\frac{1}{2}\varepsilon z E\lambda\cos\theta/kT\right).$$

Thus in a unit volume the number of jumps between θ and $\theta+d\theta$ is

$$d\nu = \frac{1}{2}nk_1\exp\left(\frac{\varepsilon z E\lambda\cos\theta}{2kT}\right)\sin\theta\, d\theta \tag{16}$$

where n is the number of ions per unit volume in the solution. The electricity transported by these ions is

$$\varepsilon z\lambda\cos\theta\, d\nu\ .$$

Summing up the above quantity we obtain the formula for specific conductivity

$$\kappa = \int_0^\pi \frac{1}{2}n\varepsilon z\lambda k_1\exp\left(\frac{\varepsilon z E\lambda\cos\theta}{2kT}\right)\sin\theta\cos\theta\, d\theta \tag{17}$$

Carrying out the integration, we have

$$\kappa = \frac{n\varepsilon^2 z^2\lambda^2 k_1}{6kT}\ \Xi(x) \tag{18}$$

$$\begin{aligned}\Xi(x) &= \frac{z}{x^2}\cosh x - \frac{3}{x^3}\sinh x\\ &= 1+\frac{3\cdot 4}{5\,!}x^2+\frac{3\cdot 6}{7\,!}x^4+\frac{3\cdot 8}{9\,!}x^6+\cdots\cdot\end{aligned} \tag{19}$$

$$x = \frac{\varepsilon z\lambda E}{2kT} \tag{20}$$

The value of k_1 is already given by (7).

When E is very small (18) may be simplified as follows.

$$\kappa = \frac{n\varepsilon^2 z^2\lambda^2 k_1}{6kT} \tag{21}$$

This is Ohm's law in electrolytic conduction. As in the case of viscosity log $\varkappa$ and $1/T$ have the linear relationship

$$\log\kappa = A - \frac{B}{T} \tag{22}$$

where A and B are empirical constants.

The above relation has been obtained by Rasch-Hinrichsen(9) from experiments on fused salts, glass, and other insulators.

When E is very large $\varkappa$ can be expressed by the following formula.

$$\log \kappa = a + bE \tag{23}$$

where a and b are constants. This is the empirical formula discovered by Poole(10) (11) from the measurement of the conductivities of mica, glass, and other solid dielectrics.

Equation (21) can be easily derived in another way. By definition the specific conductivity is given by

$$\kappa = n \varepsilon^2 z^2 \omega \tag{24}$$

Introducing (5) and (13) into (24) we obtain (21) at once.

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(9) E. Rasch and F. W. Hinrichsen, *Z. Elektrochem.*, **14** (1908), 41.
(10) H. H. Poole, *Phil. Mag.*, **32** (1916), 112.
(11) H. H. Poole, *Phil. Mag.*, **42** (1921), 488.