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Abstract

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ON THE DIFFUSION COEFFICIENT IN LIQUIDS

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In our works on the theory of the viscosity of liquids (^{1}), we proceeded from the idea that, when "coupled" molecules are moved away from one another to a distance greater than the equilibrium distances r_0, corresponding to the minimum of the potential energy, attractive forces act between the molecules. If, in this case, the total kinetic energy of two molecules belonging to two layers of a liquid proves to be less than the binding energy, then, under certain additional conditions, a bond may arise between these molecules, and for a certain time (not more than half the period of oscillation) such a system begins to behave as one "kinetic unit."

If, however, the total kinetic energy of the pair of molecules under consideration, when they move in opposite directions, is greater than the binding energy, then no bond can arise between the molecules, and the molecules will move independently of one another. Under a certain condition, indicated below, these molecules have the possibility of passing from one layer of the liquid into the nearest one, i.e., diffusion will be observed. Thus, the average kinetic energy per molecule capable of diffusion will be

$$\varepsilon_{\mathrm{d}} > \frac{1}{2}\varepsilon_0, \tag{1}$$

where ε_0 is the energy of one bond of liquid molecules.

As was shown in our works (^{1}),

$$\varepsilon_0 = 2\lambda_{i0}/\gamma, \tag{2}$$

where λ_{i0} is the internal latent heat of evaporation of the liquid in vacuum at absolute zero; γ is the coordination number of the liquid.

Since the average distance between liquid molecules is smaller than their linear dimensions, one more condition is necessary for a molecule to pass from one layer to another: it is necessary that two nearby molecules of the layer into which the given molecule passes be at a distance permitting the penetration of the new molecule, i.e., at a distance greater than the equilibrium one.

Let us denote the probability of such a favorable arrangement of molecules by W. From the considerations discussed, it follows that the process of diffusion in liquids differs from the process of diffusion in gases in that, in gases at low pressures, all molecules take part in the diffusion process, whereas in liquids only those do whose energy is greater than ε_d and opposite which a free place is formed. For the process of "self-diffusion" in gases, kinetic theory leads to the following

equation for the diffusion coefficient:

$$D = \frac{1}{8}\pi\lambda\bar{c}, \tag{3}$$

where λ is the distance over which mass transfer occurs in one elementary act, and $\bar{c}$ is the mean velocity of the molecules.

For liquids, in accordance with what was said above, one must write

$$D = 2Wr_0\bar{c}, \tag{4}$$

where r_0 is half the equilibrium distance between the centers of the molecules, which, for simplicity, we shall regard as spherical. Since real molecules are not spherical, in the indicated method of calculation we replace them by spheres with an effective radius, which behave in the same way as the real molecules. The coefficient $\pi/8$ has been omitted, because the motion of the molecules must be considered only in two directions (toward the next layer and away from it). The quantity λ in liquids cannot exceed the mean distance between the centers of the molecules. Transitions over a greater distance have a very small probability. The quantity r_0 is readily determined as

$$r_0 = \sqrt[3]{\frac{3v_m}{4\pi N_0}}, \tag{5}$$

where v_m is the volume of a gram-molecule of the liquid, and N_0 is Avogadro' s number. The mean velocity is

$$\bar{c} = \int_{c_\mathrm{d}}^{\infty} c\,\frac{dN}{N}, \tag{6}$$

where c_d is the velocity of molecules whose kinetic energy is equal to ε_d. Substituting into expression (6) the value of dN/N from Maxwell' s velocity distribution law, integrating, and passing from velocities to energies, we obtain

$$\bar{c} = \frac{2}{\sqrt{\pi}}\sqrt{\frac{2RT}{M}}\, e^{-\varepsilon_0/2RT}\left[\frac{\varepsilon_0}{2RT}+1\right]. \tag{7}$$

Since the process of molecules moving away from one another, and thereby freeing space for the diffusing molecule, is analogous to the process of evaporation, the quantity W may be written in the form

$$W = e^{-2\lambda_i T/\gamma RT}, \tag{8}$$

where λ_{iT} is the internal latent molecular heat of evaporation at the given temperature.[*]

Substituting (5), (7), and (8) into (4), we obtain the final equation

$$D = 4\,\frac{\sqrt[3]{3}\sqrt{2R}}{\sqrt[3]{4\pi N_0}\sqrt{\pi}}\,\frac{v_m^{1/3}T^{1/2}}{M^{1/2}}\, e^{-2\lambda_i T/\gamma RT}\, e^{-\varepsilon_0/2RT}\left[\frac{\varepsilon_0}{2RT}+1\right]. \tag{9}$$

Since expression (4) is written for the process of "self-diffusion," all quantities characterizing the properties of the molecules (v_m, M, λ_{iT}, ε_0) must be taken as averages for the substances composing such a system.

[*] Obviously, this expression is valid only under the condition that the attractive forces decrease sharply with distance, i.e., when they can be neglected at distances between molecules equal to their diameter. Otherwise the exponent will include the quantity $\lambda < \lambda_{iT}$.

Expression (9) gives the dependence of the diffusion coefficient on temperature, concentration, and pressure, since the quantities v_m, $\lambda_i T$ are functions of temperature, concentration, and pressure, while ε_0 is a function of concentration and pressure.

Under the condition that only neighboring molecules interact and that their relative concentrations around any one of them are identical, for a solution consisting of two components (2):

$$\varepsilon_0 = \varepsilon_{011}c_1^2 + 2\varepsilon_{012}c_1c_2 + \varepsilon_{022}c_2^2, \tag{10}$$

where ε_{0ij} is the binding energy between molecules of the i-th and j-th kinds, and c_1 and c_2 are the mole fractions of the two components in the solution. Depending on the relation among the quantities ε_{011}, ε_{022}, and ε_{012}, the diffusion coefficient, with changing concentration, will vary either linearly or pass through a maximum, a minimum, or a point of inflection. The quantity ε can readily be found from the temperature dependence of the density and viscosity of liquids (1).

The quantity λ_{iT} for a given system of two liquids must be calculated from an analogous equation.

How well formula (9) agrees with experiment can be seen from Table 1.

The diffusion coefficients of *o*-xylene in *n*-xylene were measured in our laboratory by the diffraction micromethod by T. S. Makareva and V. V. Erchenkov. The values of the binding energies ε_0 needed for the calculations, found from the temperature dependence of the density and viscosity of liquids (^{6}), proved to be as follows:

System	*o*-xylene —*n*-xylene
ε_0, cal/mole	2117.7
$C_2H_5OH—C_2H_5OD$	3393.6
$C_6H_6—C_6H_5D$	2343.1

For calculating the diffusion coefficients it is necessary to know the coordination number γ for the given system. This quantity was calculated from equation (9), using the diffusion coefficient for a temperature of 15 or 20°.

As is seen from Table 1, the calculated diffusion coefficients for the systems *o*-xylene —*n*-xylene and benzene —monodeuterobenzene, with increasing temperature, regularly all exceed the experimentally found values. This is explained, on the one hand, by inaccuracies in determining the latent heats of evaporation at different temperatu- pores, and on the other hand, by the fact that as the temperature rises the coordination numbers of liquids decrease. A small change in the coordination

Table 1

Calculated and experimental values of diffusion coefficients and coordination numbers of liquids

T, °K	d_4^t, $\frac{\text{g}}{\text{cm}^3}$	λ_{iT}, $\frac{\text{cal}}{\text{mole}}$ (4)	$D_{\text{calc}}\cdot 10^5$, $\frac{\text{cm}^2}{\text{sec}}$	$D_{\text{exp}}\cdot 10^5$, $\frac{\text{cm}^2}{\text{sec}}$	coord. number	d_4^t, $\frac{\text{g}}{\text{cm}^3}$	λ_{iT}, $\frac{\text{cal}}{\text{mole}}$ (5)	$D_{\text{calc}}\cdot 10^5$, $\frac{\text{cm}^2}{\text{sec}}$	$D_{\text{exp}}\cdot 10^5$, $\frac{\text{cm}^2}{\text{sec}}$ (5)	coord. number	d_4^t, $\frac{\text{g}}{\text{cm}^3}$	λ_{iT}, $\frac{\text{cal}}{\text{mole}}$ (4)	$D_{\text{calc}}\cdot 10^5$, $\frac{\text{cm}^2}{\text{sec}}$	$D_{\text{exp}}\cdot 10^5$, $\frac{\text{cm}^2}{\text{sec}}$ (3)	coord. number
288.2	–	–	–	–	–	0.7936	7387	0.800	0.800	6.436	0.88408	7619	1.88	1.88	6.136
293.2	0.8704	9702	1.122	1.124	7.790	0.7851	7324	1.040	1.050	6.452	0.87340	7078	2.52	2.15	5.910
298.2	–	–	–	–	–	0.7764	7261	1.229	1.310	6.410	0.86268	7336	3.31	2.40	5.670
303.2	0.8627	9515	1.482	1.397	7.678	0.7677	7176	1.692	1.700	6.444	0.85190	7188	4.29	2.67	5.444
308.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
318.2	–	–	–	–	–	–	–	–	–	–	–	–	–	–	–
323.2	0.8462	9296	2.323	2.026	7.512	–	–	–	–	–	–	–	–	–	–
343.2	0.8297	8990	3.540	2.848	7.320	–	–	–	–	–	–	–	–	–	–

number leads to a significant change in the calculated diffusion coefficient. The values of the coordination numbers calculated from formula (9) using experimentally found values of the diffusion coefficients are given in Table 1.

As is seen from the data presented above, the coordination numbers for the systems *o*-xylol—*n*-xylol and C_6H_6—C_6H_5D decrease only slightly with temperature; however, if for calculations of the diffusion coefficients one uses a coordination number found for some one temperature, this leads to discrepancies between the calculated diffusion coefficients and the experimental data. In the case of the system C_2H_5OH—C_2H_5OD the coordination number practically does not change with temperature, and if any of its values in the given temperature interval is used, the calculated values of the diffusion coefficients are in good agreement with the experimental values.

Calculations of the same type were carried out by us for a number of other systems and likewise showed good agreement between theory and experiment.

The quantity

$$-2\lambda_i\tau/\gamma T = \Delta S, \tag{11}$$

where ΔS is the change in entropy upon bond formation, calculated per 1 mole. The temperature dependence of this quantity is determined by the expression

$$\frac{\partial \Delta S}{\partial T} = \frac{2}{\gamma}\,\frac{\Delta C}{T}, \tag{12}$$

where ΔC is the difference between the heat capacities of the liquid and the vapor that are in equilibrium. If, approximately, it is assumed that the quantity ΔC does not depend on temperature, then

$$\Delta S = \alpha \ln T + \beta. \tag{13}$$

where α and β are constants.

Substituting (11), with (14) taken into account, into (9), we obtain

$$D = 4\,\frac{\sqrt[3]{3}\sqrt{2R}}{\sqrt[3]{4\pi N_0}\sqrt{\pi}}\,\frac{v_m^{1/3}T^{1/2}}{M^{1/2}}\,e^{\beta l/R}\left[\frac{\varepsilon_0}{2RT}+1\right]e^{(\alpha T\ln T-\varepsilon_0)/RT}. \tag{14}$$

According to calculations, for many liquids

$$v_m^{1/3}T^{1/2}\left[\frac{\varepsilon_0}{2RT}+1\right] \simeq \text{const.} \tag{15}$$

Therefore expression (15) may be written in the following form

$$D = Ae^{(\alpha T \ln T - \varepsilon_0)/RT}, \tag{16}$$

where

$$A = \frac{4\sqrt[3]{3}\sqrt{2R}\, v_m^{1/3} T^{1/2}}{\sqrt[3]{4\pi N_0}\sqrt{\pi}} \left[\frac{\varepsilon_0}{2RT} + 1\right] e^{\beta l/R}.$$

Equation (16), as calculations show, agrees well with experimental data.

If expression (16) is logarithmized, we obtain

$$\ln D = \ln A + \frac{\alpha \ln T}{R} - \frac{\varepsilon_0}{RT}, \tag{17}$$

from which it is evident that over a broad temperature interval $\ln D$ is not linear with respect to the variable $1/T$. In narrow temperature intervals it may be consid-

state that $\ln T = a - b/T$, where a and b are constant coefficients, and, consequently, the dependence of $\ln D$ on $1/T$ in narrow temperature intervals will be linear.

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