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PHENOMENOLOGICAL COEFFICIENTS OF THE VISCOSITY FOR LOW-MOLECULAR ELEMENTARY LIQUIDS AND SOLUTIONS

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Abstract. The shear forces and corresponding strains appearing in the flow under the action of chemical potential gradient have been analyzed. The ratios for determination of the viscosity coefficient for low-molecular pure liquids and solution components were established. It was proved that the viscosity of the low-molecular solution can be expressed *via* the terms of the viscosity coefficients of its components and *via* their concentration.

Keywords: chemical potential, viscosity of pure liquids, characteristic time of the viscous flow.

1. Introduction

The temperature dependence of the viscosity coefficient for the low–molecular elementary liquids is well described by the Arrhenius empirical equation:

$$h = A\exp\{E/RT\} \qquad (1)$$

where E is the activation energy of the viscous flow. However, the theoretical interpretation of the pre-exponential factor A faces considerable difficulties which have not been overcome till the present time.

Among the molecular-kinetic theories of low-molecular liquids complying with the Newton's equation, let us mark out two main formulated by Frenkel [1, 2] and by Eyring [3-5].

In accordance with the Frenkel's theory under the presence of a shear strain σ the rapid layer of liquid entrains the slow one with the velocity rate ΔJ :

$$\Delta \quad = usd^2 \qquad (2)$$

where u is the mobility of particle and δ is the interparticle distance.

Substituting of ΔJ by $\frac{dJ}{dy}d$, where dJ/dy is the velocity gradient of the hydrodynamic flow along y axis, which is normal to the flow, and using the *Newton's* equation in a form $h\frac{dJ}{dy} = s$, the following ratio was obtained by Frenkel:

$$h = (ud)^{-1} \qquad (3)$$

Substitution of the Einstein's equations into (3)

$$u = D/kT \qquad (4)$$

$$D = d^2/6t \qquad (5)$$

leads to the final result

$$h = 6kTt/d^3 \qquad (6)$$

where D is the coefficient of the diffusion; τ is the characteristic time of the particles transport from the one equilibrium state into another, which can be also called as the characteristic time of the viscous flow.

According to Frenkel t is determined by the oscillation frequency in the quasi-lattice of liquid and by the probability of the hole formation, *i. e.* corresponding free volume needed for the particle transport:

$$t = t_0\exp\{E/RT\} \qquad (7)$$

Therefore, here t_0 is the characteristic time of the oscillating movement of a particle in the quasi-lattice of liquid; E is energy of hole formation or of the free volume in liquid, which is necessary to pass the particle from one position of equilibrium into another.

After the integration of (6) and (7) the Frenkel's equation becomes as follows:

$$h = \frac{6kT}{d^3} t_0 \exp\{E/RT\} \qquad (8)$$

In the calculations Frenkel assumed that $t_0 = 10^{-13}$ s, which is equal to the determination

$$t_0 = h/kT \qquad (9)$$

However, the calculations of the pre-exponential multiplier in (8) sometimes give the values exceeding the experimental ones by 2-3 orders. These divergences were explained by Frenkel by the dependence of E on temperature; however, such phenomenon is observed very seldom.

In molecular-kinetic theory of Eyring the starting principle consists in the fact that the action of force causing the liquid flow decreases the height of the energy barrier at the movement of particle in the forward direction and increases it in the backward direction. The rate constant κ of the particles transfer *via* the potential barrier is described by the standard equation of the theory of absolute rates of chemical reactions:

$$\kappa = \frac{kT}{h} \frac{Q^*}{Q} \exp\{-E/RT\} \qquad (10)$$

where Q and Q^* are the statistical sums of the particle per unit of volume in main and activated states respectively.

Under considerable following simplifications the force of shift disappears from the equation of transfer. As a result, the expression for the viscosity coefficient according to Eyring becomes as follows:

$$h = \frac{hN_A}{V} \frac{Q}{Q^*} \exp\{E/RT\} \qquad (11)$$

where V is the molar volume of liquid.

Assuming that the statistical sum Q^* of particle in the activated state is devoid of one freedom degree of the transitional movement, Eyring writes:

$$\frac{Q}{Q^*} = \frac{(2p\,mkT)^{1/2}}{h} u_f^{1/3} \qquad (12)$$

where υ_f is free volume per one particle.

Let us note, however, that in accordance with the starting Eq. (10) Q^* is already devoid of one freedom degree of the oscillating movement, otherwise the co-multiplier kT/h would not appear in Eq. (10). Making Q^* devoid of another freedom degree, ***namely***, the transitional one, would be absolutely physically unjustified.

Although the expression (12) in the presented case is fitting of theory to the result, let us use it for determination of characteristic time of the translational movement:

$$t_0 = \left(\frac{2p\,m}{kT}\right)^{1/2} u_f^{1/3} \qquad (13)$$

By combining of (12) and (13) into (11) we can obtain:

$$h = \frac{kN_A T}{V} t_0 \exp\{E/RT\} \qquad (14)$$

In accordance with the Frenkel's equation (7) such expression can be written as follows:

$$h = RTt/V \qquad (15)$$

Taking d^3 as the volume falling per one particle, we will obtain from the expression (6) the equation analogous to (15):

$$h = 6RTt/V \qquad (16)$$

Thus, in spite of the difference in molecular-kinetic approaches of Frenkel and Eyring to the analysis of the viscosity coefficient for simple liquids, they lead to the ratios containing the same phenomenological value RTt/V. The difference between (15) and (16) is visualized in numerical coefficient and physical interpretation of t_0 determined by the expressions (9) and (13). This difference is quite substantial, since t_0 of the translational movement is two orders higher than t_0 of the oscillating movement. At the analysis of the solution viscosity Eyring and Frenkel do not use the notion "*coefficient of solution component viscosity*", preferring to describe the viscosity of solution *via* the coefficients of viscosity for pure liquids. Here it is assumed that the viscosity of solution can be described by the equations analogous to (8) and (11), but at the same time, free activation energy (according to Eyring) or an activation energy (according to Frenkel) is declared as the function of the solution composition. This leads Eyring to the equation:

$$\ln h = N_1 \ln h_1 + N_2 \ln h_2 \qquad (17)$$

which was proposed by Arrhenius and Kendall earlier [6].

A more complicated equation for the binary solution was proposed by Frenkel:

$$\ln h = \frac{1}{2}N_1^2 \ln h_1 + \frac{1}{2}N_2^2 \ln h_2 + N_1 N_2 \ln h_{12} \qquad (18)$$

In these equations N_i is molar part of the component; η_i is its coefficient of viscosity in pure liquid state; η_{12} is additional viscosity, which, in accordance with Frenkel, reflects the difference in energies of interaction of particles by the first and the second kinds between themselves and between the particles of the same kind.

In conclusion of the presented short review let us note that the molecular-kinetic analysis of Frenkel and Eyring as to viscosity coefficients for pure liquids leads to the ratios (15) and (16) containing the general phenomenological factor RTt/V, which requires the substantiation from more general considerations. Coefficients of viscosity of the solution components in this approach are not revealed. The characteristic time of the viscous flow remains undefined. We will solve these problems in the following chapters.

2. Coefficient of Viscosity for Low-Molecular Pure Liquid

Let us accept phenomenological determination of the stationary flow J of substance, the moving force of which is the gradient of the chemical potential μ [7, 8] as the starting point for the analysis. Let us write these flows along the direction of the x and y axes:

$$J_x = -\frac{L}{RT}c\frac{\partial m}{\partial x}, \; J_y = -\frac{L}{RT}c\frac{\partial m}{\partial y} \qquad (19)$$

where L is the transfer coefficient having the dimension of the diffusion coefficient; c is the molar-volumetric concentration of particles.

For pure liquid at $T = const$ the chemical potential μ is the function only of pressure P. That is why it can be written as $\partial m/\partial x = V\partial P/\partial x$, where V is molar volume. Since $Vc = 1$, instead of the (19) we will get

$$J_x = -\frac{L}{RT}\frac{\partial P}{\partial x}; \qquad J_y = -\frac{L}{RT}\frac{\partial P}{\partial y} \qquad (20)$$

The flows can be expressed also via the transfer rate u and concentration c: $J_i = cu_i$. Then, with taking into account Eq. (20) we will have:

$$u_x = -\frac{LV}{RT}\frac{\partial P}{\partial x}; \quad u_y = -\frac{LV}{RT}\frac{\partial P}{\partial y} \qquad (21)$$

By differentiating of u_x upon y, and u_y upon x, we will obtain

$$\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x} = -2\frac{LV}{RT}\frac{\partial^2 P}{\partial x \partial y} \qquad (22)$$

If η is the coefficient of the liquid viscosity, then according to the *Newton's* equation

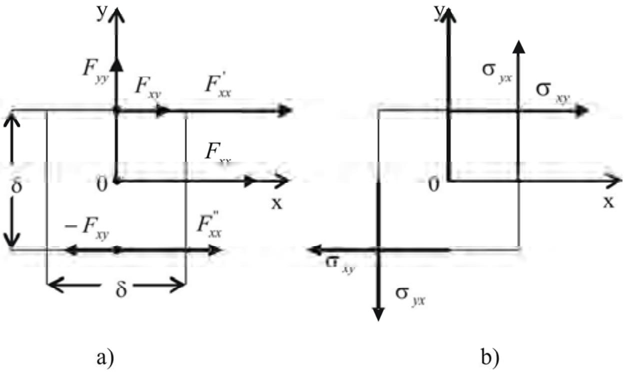
$$h\left(\frac{\partial u_x}{\partial y} + \frac{\partial u_y}{\partial x}\right) = s_{xy} = s_{yx} \qquad (23)$$

where $s_{xy} = s_{yx}$ are the shift components of the stress tensor; the first index points out direction of the component of force, and the second one points out direction of the normal to the plate of the application of force.

From the comparison of (22) and (23) follows:

$$-2h\frac{LV}{RT}\frac{\partial^2 P}{\partial x \partial y} = s_{xy} = s_{yx} \qquad (24)$$

Next, in liquid let us separate the elementary cube with the edges δ. The sectional elevation of this cube by the plate xy is shown in Fig. 1a.



a) b)

Fig. 1. Scheme of the formation of shear forces F_{xy} (a) and tensions σ_{xy} (b) under dependence of normal force F_{xx} on coordinate y

Let is assume that in the center of the cube the gradient of pressure in direction x is equal to $-\partial P/\partial x$.

Since $-\partial P/\partial x$ is the force acting on a unit of the volume of liquid, full force F_{xx}, acting on the whole volume d^3 of cube in the direction of the x axe will be equal to

$$F_{xx}(x=0, y=0) = -\frac{\partial P}{\partial x}d^3 \qquad (25)$$

Tangential or shear forces appeared as a result of the dependence of F_{xx} on y. Let us write the new forces F_{xx} at $x = 0$ as $y = \frac{d}{2}$ and $y = -\frac{d}{2}$:

$$F_{xx}^{'}\left(x=0, y=\frac{d}{2}\right) = -\frac{\partial P}{\partial x}d^{3} - \frac{\partial^{2}P}{\partial x\partial y}d^{4}/2 \quad (26)$$

$$F_{xx}^{''}\left(x=0, y=-\frac{d}{2}\right) = -\frac{\partial P}{\partial x}d^{3} + \frac{\partial^{2}P}{\partial x\partial y}d^{4}/2 \quad (27)$$

The difference in these forces creates the shear forces F_{xy}, applied to the top and the bottom of cube faces, normal to the axe y (see Fig. 1a):

$$F_{xy}\left(x=0, y=\frac{d}{2}\right) = F_{xx}^{'} - F_{xx}^{''} = -\frac{\partial^{2}P}{\partial x\partial y}d^{4} \quad (28)$$

$$F_{xy}\left(x=0, y=-\frac{d}{2}\right) = F_{xx}^{''} - F_{xx}^{'} = \frac{\partial^{2}P}{\partial x\partial y}d^{4} \quad (29)$$

These forces create the shear tensions $s_{xy} = F_{xy}/d^{2}$:
on the top face

$$s_{xy} = -\frac{\partial^{2}P}{\partial x\partial y}d^{2} \quad (30)$$

and on the bottom face

$$s_{xy} = \frac{\partial^{2}P}{\partial x\partial y}d^{2} \quad (31)$$

As follows from this, under the chosen direction of force F_{xx}

$$-\frac{\partial^{2}P}{\partial x\partial y} = \frac{s_{xy}}{d^{2}} \quad (32)$$

The stress tensor is symmetrical, that can be easily demonstrated by the analogous analysis of force F_{yy} depending on x, that is why $s_{xy} = s_{yx}$, as it is shown in Fig. 1b.

By substituting of (32) in (24), we obtain:

$$h = \frac{1}{2}\frac{RT}{LV}d^{2} \quad (33)$$

Next using the Einstein's ratio for the transfer coefficient

$$L = d^{2}/6t \quad (34)$$

which takes into account the randomness of the particle wandering in all three directions of space, we finally find:

$$h = 3RTt/V \quad (35)$$

3. Partial Coefficients of the Components of Low-Molecular Solution

Let us determine the flows of ***i***-component of the solution along x and y axes according to the formula (19):

$$J_{ix} = -\frac{L_i}{RT}c_i\frac{\partial m_i}{\partial x}, \qquad J_{iy} = -\frac{L_i}{RT}c_i\frac{\partial m_i}{\partial y} \quad (36)$$

Due to the difference in the transfer coefficients L_i of the solution components it can be formally supposed that the conditions similar to the components separation in the baromembrane process can appear in the hydrodynamic flow [8]. In the last case these conditions are realized at the expense of a high gradient pressure upon membrane layer and a great difference in transfer coefficients L_i and L_j ***via*** the membrane.

However we suppose that at the viscosity change the hydrodynamic flows are weak enough and the effect of the components separation can be neglected. Consequently, a liquid solution is homogeneous upon composition and all derivatives by ***dc_i/dx*** type are equal. Then, although the chemical potential μ_i is the function of the solution composition ***via*** the thermodynamic activity of the component, the derivatives $\partial m_i/\partial x$ are the function only of the gradient of pressure. Therefore, at *T = const* and presented composition of solution, $\partial m_i/\partial x = \bar{V}_i\partial P/\partial x$, where $\bar{V}_i$ is the partial-molar volume of solution ***i***-component. Since:

$$c_i\bar{V}_i = j_i \quad (37)$$

where φ_i is the volumetric part of the presented component, the expressions (36) can be rewritten as:

$$J_{ix} = -\frac{L_i}{RT}j_i\frac{\partial P}{\partial x} \qquad J_{iy} = -\frac{L_i}{RT}j_i\frac{\partial P}{\partial y} \quad (38)$$

Expressing these flows in a form $J_{ix} = c_i u_{ix}$, $J_{iy} = c_i u_{iy}$, and taking into account (37) and (38) we will obtain:

$$\frac{\partial u_{ix}}{\partial y} + \frac{\partial u_{iy}}{\partial x} = -2\frac{L_i\bar{V}_i}{RT}\frac{\partial^{2}P}{\partial x\partial y} \quad (39)$$

Since $\partial P/\partial x$ is a force applied to the unit of the volume of solution then $j_i\partial P/\partial x$ is a force applied to the presented component in the unit of the volume. Consequently, it can be supposed, that the contribution of the presented component into general viscosity of solution η depends not only on the partial coefficient of viscosity η_i, but also on volumetric part φ_i. That is why we postulate the dependence:

$$h = \sum_i h_i j_i \quad (40)$$

Thus, the contribution of *i* component into the viscosity of solution is determined by the value $h_i j_i$, that is why it is necessary to write the Newton's equation for each component of the solution as:

$$h_i j_i \left(\frac{\partial u_{ix}}{\partial y}+\frac{\partial u_{iy}}{\partial x}\right)= s_{ixy} = s_{iyx} \qquad (41)$$

Here $s_{ixy} = s_{iyx}$ is the contribution of *i* component into corresponding full shear stresses $s_{xy} = s_{yx}$, so:

$$s_{xy} = \sum_i s_{ixy} \qquad (42)$$

From the comparison of (41) and (39) it follows that:

$$2h_i j_i \frac{L_i \bar{V}_i}{RT}\frac{\partial^2 P}{\partial x \partial y} = s_{ixy} = s_{iyx} \qquad (43)$$

Let us again refer to the elementary cube of volume δ^3 (Fig. 1). In the center of this cube the force acts on the presented component along the *x* axe; this force, as it was noticed, is equal to $-j_i \partial P/\partial x$. Taking into account the volume of cube, we have:

$$F_{ixx}(x=0, y=0) = -j_i \frac{\partial P}{\partial x} d^3 \qquad (44)$$

The force F_{ixx} depends on coordinate *y*, that is why we write the new forces at *x* = 0, but at $y = d/2$ and $y = -d/2$:

$$F_{ixx}(x=0, y=\frac{d}{2}) = -j_i \frac{\partial P}{\partial x} d^3 - j_i \frac{\partial^2 P}{\partial x \partial y} d^4/2 \qquad (45)$$

$$F_{ixx}(x=0, y=-\frac{d}{2}) = -j_i \frac{\partial P}{\partial x} + j_i \frac{\partial^2 P}{\partial x \partial y} d^4/2 \qquad (46)$$

The difference in these forces creates the shearing forces F_{ixy}, applied to the cube faces, normal to *y* axe, which determine the shear stresses $s_{ixy} = F_{ixy}/d^2$. In particular, in the direction of F_{ixx} the shear stress on the top face of cube will be equal to:

$$s_{ixy} = -j_i \frac{\partial^2 P}{\partial x \partial y} d^2 \qquad (47)$$

Using this ratio in (43), we obtain:

$$h_i = \frac{1}{2}\frac{RT}{L_i \bar{V}_i} d^2 \qquad (48)$$

Expressing the transfer coefficient L_i *via* corresponding Einstein's ratio $L_i = d^2/6t_i$ we finally obtain:

$$h_i = 3RTt_i/\bar{V}_i \qquad (49)$$

Thus, postulated dependence (40) leads to the expression (49) for the coefficient of the viscosity of solution in the same form as for the pure liquid. However, the viscosity coefficient η_i is the function of the solution composition.

Substitution of (49) into (40) and taking (37) into account permits to express the viscosity of solution by the ratio more convenient from the practical point of view:

$$h = 3RT\sum_i c_i t_i \qquad (50)$$

For binary solution it can be written as:

$$h = 3RT(c_1 + c_2)(N_1 t_1 + N_2 t_2) \qquad (51)$$

where N_i is molar part of the component.

Since $c_1 + c_2 = V^{-1}$, where *V* is a molar volume of the solution, equal to $(M_1 N_1 + M_2 N_2)/r$, it follows from the (51) that

$$h = 3RT\left(\frac{r}{M_1 N_1 + M_2 N_2}\right)\left(t_1 + N_2(t_2 - t_1)\right) \qquad (52)$$

where M_i are molar masses of components, ρ is a density of solution at presented composition.

An expression (52) permits to find the numerical values of τ_i and their dependence on composition of the solution based on the experimental values of viscosity η.

4. Characteristic Time of the Viscous Flow

As it can be seen from the phenomenological expressions (35) and (49), the main problem at the viscosity coefficient calculation is the determination of the characteristic time τ of the viscous flow. According to Frenkel τ can be described by the expression (7), in which τ_0 is determined either by vibration freedom degree of liquid particles or by the translational one, in others words by the ratios (9) or (13), respectively.

In order to compare the experimental values of τ_0 with the calculated ones according to (9) and (13), we described the temperature dependence of viscosity for a series of ***n***-alkanes and ***n***-alcohols, and also for water on the basis of referenced data ***via*** the Arrhenius equation in the following form:

$$\ln h = \ln A + E/RT \qquad (53)$$

Coefficients of this equation are represented in the Table. On the basis of viscosity values at temperature 293 K, according to (35) the values τ_{293}, and after that according to (7) the values τ_0 were calculated. The results of the calculations are represented in the Table.

At *T* = 293 K the characteristic time of the oscillating movement is equal to $h/kT = 1.63 \cdot 10^{-13}$ s, and of the translational motion $(2p\,m/kT)^{1/2} u_f^{1/3}$ is approximately two orders greater.

That is why, the experimental values $t_0 << (2p\,m/kT)^{1/2} u_f^{1/3}$. At the same time, for the *n*-alkanes τ_0 is somewhat greater than h/kT, although is of the same order, but for the associated liquids, *n*-alcohols and water, τ_0 is considerable less than h/kT. Besides, in a series of the *n*-alcohols a well-defined slope opposition of the dependence between the activation energy of the viscous flow and τ_0 is observed: the greater is E, the less is τ_0. Both factors, *i.e.* $t_0 << h/kT$ and observed slope opposition compensation effect, cannot be explained using the approximations of Eyring and Frenkel.

In the Eyring's theory of the absolute reactions rates there are three essential drawbacks: a) the concentration of the activated complexes can be found from the consideration of condition of their equilibrium with the initial (or final) substances; b) the activated complex is devoid of one freedom degree along the coordinate of the reaction; c) the transmission coefficient is the empirical co-multiplier.The approach that preserves the main advantages of the theory of absolute reactions rates but eliminates the listed above drawbacks is described in detail in [9]. Here let us only shortly touch upon it with the specific aim of the analysis of characteristic time of viscous flow.

Let the elementary reversible reaction

$$A \underset{\overleftarrow{\kappa}}{\overset{\overrightarrow{\kappa}}{\rightleftarrows}} B \qquad (54)$$

proceeds *via* the activated complex C, general for initial and final substances. Then it can be written as:

$$A \underset{\nu_1}{\overset{\kappa_1}{\rightleftarrows}} C \underset{\kappa_2}{\overset{\nu_2}{\rightleftarrows}} B \qquad (55)$$

In accordance with (55), the activated complex C has a right to roll back from the top of the potential barrier into both potential holes with the frequencies ν_1 and ν_2, which are not the activation parameters. Parameters κ_1 and κ_2 are activation parameters. In other words, they depend on the value of the potential barrier, and determine the frequencies of the activated complexes formation from the initial and final substances respectively.

Let a, b and c be the concentrations A, B and C. The rate of the elementary reaction (54) according to the law of mass action

$$u = \overrightarrow{k}a - \overleftarrow{k}b \qquad (56)$$

is strictly defined, *i.e.* has the physical sense only under condition $dc/dt = 0$, to which the stationary concentration of activated complexes c_s corresponds:

$$c_s = (k_1 a + k_2 b)/(n_1 + n_2)\,. \qquad (57)$$

In this case, in accordance with the scheme (55):

$$u = k_1 a - \nu_1 c_s = \nu_2 c_s - k_2 b \qquad (58)$$

By substituting of (57) into (58), we obtain:

$$u = \frac{k_1 \nu_1}{\nu_1 + \nu_2} a - \frac{k_2 \nu_1}{\nu_1 + \nu_2} b \qquad (59)$$

Table

Referenced and calculated data on to the viscosity of some liquids

Liquid	M, g/mol	$\rho\cdot 10^6$, g/m^3	ΔH_{ev}, kJ/mol	$\eta_{293K}\cdot 10^{-3}$ Pa·s	$-\ln A$, Pa·s	$\frac{E}{R}$, K	$\tau_{293K}\cdot 10^{-12}$, s	$\tau_0\cdot 10^{-13}$, s	$\frac{\Delta S^*}{R}$	T^*, K	$D\cdot 10^9$, m^2/s
pentane C_5H_{12}	72	0.626	26.43	0.229	11.29	851	3.61	1.98	0.50	—	15.4
hexane C_6H_{14}	86	0.655	31.55	0.320	11.12	900	5.75	2.67	0.20	—	10.6
heptane C_7H_{16}	100	0.684	36.55	0.409	11.10	970	8.21	3.04	0.07	—	8.0
octane C_8H_{18}	114	0.702	41.48	0.540	11.19	1070	12.03	3.10	0.05	—	5.8
nonane C_9H_{19}	128	0.718	39.92	0.710	11.32	1195	17.37	2.94	0.11	—	4.3
methanol CH_3OH	32	0.793	38.45	0.584	11.83	1285	3.23	0.40	2.10	612	8.6
ethanol C_2H_5OH	46	0.789	42.01	1.190	12.63	1725	9.52	0.26	2.53	682	3.7
propanol C_3H_7OH	60	0.804	48.12	2.256	13.38	2135	23.10	0.16	3.02	707	1.8
buthanol C_4H_9OH	74	0.810	52.3	2.950	13.74	2315	37.00	0.14	3.15	735	1.3
pentanol $C_5H_{11}OH$	88	0.814	56.94	4.140	15.88	3045	61.42	0.019	5.15	591	0.9
water H_2O	18	0.997	40.66	1.005	13.22	1865	2.49	0.043	4.33	431	6.5

If an equilibrium *Maxwell–Boltzmann* distribution of the energy between the particles and their freedom degrees is kept in the system, then in accordance with the law of mass action the following ratios should be performed:

$$k_1/n_1 = K_1, \qquad k_2/n_2 = K_2 \tag{60}$$

where K_1 and K_2 are equilibrium constants of the activated complexes formation from the initial and final substances respectively.

By substituting these ratios in (59) and comparing them with (56) we will obtain the following expressions for the constants rates of direct and reverse elementary reaction (54):

$$\overrightarrow{k} = \frac{\nu_1\nu_2}{\nu_1+\nu_2}K_1, \overleftarrow{k} = \frac{\nu_1\nu_2}{\nu_1+\nu_2}K_2 \tag{61}$$

With respect to the analysis of the characteristic time of viscous flow the constant rate κ of the particles transfer *via* the potential barrier can be presented by analogous (61) expression:

$$k = \frac{\nu_1\nu_2}{\nu_1+\nu_2}K^* \tag{62}$$

where K^* is the constant of equilibrium of activated complex with particles in the main state. It can be described by usual thermodynamical ratio *via* the standard entropy ΔS^* and enthalpy ΔH^* of activation:

$$K^* = \exp\left\{\Delta S^*/R\right\}\exp\left\{\text{-}\Delta H^*/RT\right\} \tag{63}$$

Let us admit that the movement of the activated complex in the both directions of the transfer is determined by the oscillating freedom degree in such a way that $n_1 = n_2 = kT/h$. Then:

$$k = \frac{1}{2}\frac{kT}{h}\exp\left\{\Delta S^*/R\right\}\exp\left\{\text{-}\Delta H^*/RT\right\} \tag{64}$$

Here the value of the transmission coefficient is well defined. Characteristic time of the transfer is inversely proportional to κ, that is why:

$$t = 2\frac{h}{kT}\exp\left\{\text{-}\Delta S^*/R\right\}\exp\left\{\Delta H^*/RT\right\} \tag{65}$$

and for τ_0 we have the following expression:

$$t_0 = 2\frac{h}{kT}\exp\left\{\text{-}\Delta S^*/R\right\} \tag{66}$$

In accordance with the data of Table the experimental values of τ_0 for *n*-alkanes are practically agreement with the value $2h/kT = 3.27\cdot10^{-13}$ s.

For the associated liquids $t_0 << 2h/kT$, which indicates essentially greater value of positive entropy of activation ΔS^*. These values $\Delta S^*/R$, calculated according to (66), are represented in the Table. For the homologous series of the *n*-alcohols the symbate dependence of ΔS^* on E is clearly observed. For the *n*-alkanes such relationship is not observed, since the values of ΔS^* for them are little and stay within the ranges of the inaccuracy of their determination based on the experimental values of τ_0.

In accordance with the conclusion (62) the activated complex has not only the same number, but also the same freedom degree as the particles in the main state. That is why in the presented case we cannot obtain $\Delta S^* > 0$ at the expense of freedom degrees redistribution at the particle transfer from the main state into the activated one. Since at given P and T the activation is accompanied by the energy increasing, the entropy should also increase like it increased at the phase transition of the first kind at $\Delta H > 0$.

Thus, we suppose, that in the activation process at viscous flow of liquid the change of ΔS^* can be expressed *via* ΔH^* similarly as at the phase transition of the first kind. Activation process at the given P and T is non-equilibrium, however theoretically at a given P a hypothetic temperature T^* at which the activation transition would be equilibrium can be always found. Consequently, at this temperature T^*:

$$\Delta S^* = \Delta H^*/T^* \tag{67}$$

Then the expression (66) can be rewritten as:

$$t_0 = 2\frac{h}{kT}\exp\left\{\text{-}\frac{\Delta H^*}{RT^*}\right\} \tag{68}$$

Calculated values of T^* according to (67) for the *n*-alcohols and water are represented in the Table. For homological series of *n*-alcohols the values of T^* are not considerably different from one another, which explains the experimentally observed the slope-opposition dependence of τ_0 on $\Delta H^* \approx E$.

In conclusion of the presented section it is necessary to note that the activation entropy by (67) type occurs also in chemical processes as one of the elements of the general activation entropy. This fact is proved both by rapidly observed compensation effects in a range of the single-type chemical reactions, and by the presence of so called quick reactions, description of which is beyond the Eyring's theory.

5. Calculation of the Diffusion Coefficients Based on the Coefficients of Viscosity

Experimental determination of the diffusion coefficients D is a quite complicated and labour intensive process, whereas the experimental determination of the coefficients of viscosity is not so complicated.

The long ago established empirical Walden's rule

$$\eta D \approx const \tag{69}$$

does not offer an estimation of the value *const* and is approximate, however it points on the possibility of D calculation based on the experimental values η.

For pure liquids the relationship between the transfer coefficient L or coefficient of self-diffusion D is determined *via* the ratio (33), which can be rewritten in a form of the Walden's rule (*L=D*)

$$hD = \frac{1}{2}\frac{RT}{V}d^2 \qquad (70)$$

Expressing the transfer area δ^2 *via* the molar volume of liquid

$$d^2 = (V/N_A)^{2/3} \qquad (71)$$

for the coefficient of the self-diffusion we obtain the expression:

$$D = \frac{1}{2}\frac{RT}{h N_A^{2/3}}\left(\frac{r}{M}\right)^{1/3} \qquad (72)$$

The calculated values of *D* according to (72) with the use of experimental data of η at T = 293 K are represented in the Table. As we can see, the calculated data of *D* have a typical order for the liquids by similar kind, clearly reflect the dependence of *D* on molar mass in the presented homolytical range and on the nature of homolytical range.

For the solutions the determination of coefficients of diffusion of components on the viscosity is a more complicated task. In accordance with (48) and (71) we have:

$$D_i = \frac{1}{2}\frac{RT}{h_i \overline{V}_i}\left(\frac{V}{N_A}\right)^{1/3} \qquad (73)$$

where *V* is molar volume of the solution. Thus $V = M/r$, $M = \sum_i M_i N_i$ is molar mass of the solution.

As we can see, the calculation of the coefficient of diffusion of the solution's component according to (73) needs the knowledge, first of all, of the coefficient of the viscosity of the presented component and its partial-molar volume.

6. Conclusions

An analysis of the molecular-kinetic theories of Frenkel and Eyring leads to the expressions for the coefficients of viscosity of low-molecular pure liquids, containing the RTt/V ratio. From the general phenomenological determinations of the substances flow under the action of the gradient of chemical potential and analysis of the shear forces and corresponding tensions appearing in the flow it was proved that the viscosity coefficient of pure liquid is ordered to the ratio $h = 3RTt/V$, and in the case of the component of solution it is ordered to the ratio $h_i = 3RTt_i/\overline{V}_i$.

Comparison of the experimental values of the characteristic times τ of the viscous flow and the calculated ones shows that the pre-exponential multiplier τ_0 is determined not only by the frequency of the oscillating movement of the particles in the quasi-lattice of the liquid but also by the entropy factor. This leads to the conclusion that the activation entropy at the viscous flow of the liquid can be found via the same expression as in the case of the entropy at the phase transition by the first kind. The obtained expression for the activation entropy $\Delta S^* = \Delta H^*/T$ allows to explain the low values of $t_0 << 2h/kT$ for the associated liquids and the observed slope opposition for the dependence between τ_0 and the activation energy of the viscous flow.

The expressions were proposed, according to which the coefficients of the self-diffusion and diffusion based on corresponding coefficients of the viscosity of low-molecular pure liquids and melts can be calculated.

An analysis of the Maxwell's equation and the deformation rates of the conformational volumes of polymeric chains and their rotation allowed to separate the frictional and elastic coefficients of the viscosity of high-molecular single-component liquid. It was shown that exactly the elastic coefficient of the viscosity is gradiently depended value. At the same time, the so called maximal Newton viscosity at $g \to 0$ is not such value and it is represented by a sum of frictional and elastic components. On the contrary, at $g \to \infty$ the effective viscosity is wholly determined only by the frictional component.

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ФЕНОМЕНОЛОГІЧНІ КОЕФІЦІЄНТИ В'ЯЗКОСТІ НИЗЬКОМОЛЕКУЛЯРНИХ ПРОСТИХ РІДИН ТА РОЗЧИНІВ

Анотація. *В роботі проведено аналіз сил зсуву та відповідних напружень, що виникають в потоці під дією градієнта хімічного потенціалу. Встановлені співвідношення для визначення коефіцієнта в'язкості низькомолекулярних чистих рідин та компонентів розчину. Доведено, що в'язкість низькомолекулярного розчину може бути виражена через коефіцієнти в'язкості його компонентів та їх концентрацію.*

Ключові слова: *хімічний потенціал, в'язкість чистих рідин, характеристичний час в'язкої течії.*