ON THE VISCOSITY OF PURE LIQUID.

By Mikio Tamura.

I) Derivation of the formula for the variation of viscosity with temperature.

Eyring and others[1] applied the theory of the absolute reaction rate to the problem of viscosity and obtained many interesting results. It is quite natural to expect similar results from the standpoint of the collision theory. Hence it is not of no interest to treat the problem of viscosity with this theory.

Let us first derive the expression for the coefficient of viscosity. Our treatment resembles as a matter of course that of Eyring and others, but there are some different points. The viscosity coefficent is given by the force necessary to shift a layer of liquid of unit area and of the thickness of one molecule past a second layer by the distance between two layers in unit time. For simplicity, let us assume that the molecules are arranged as shown in Fig. 1. In order to pass from
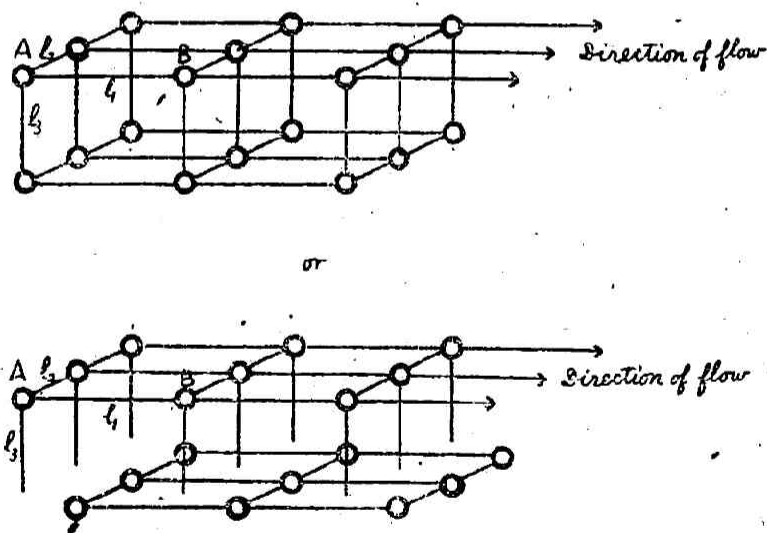

Fig. 1.

A to B it is necessary for a molecule at A to jump over a potential barrier which lies between A and B. In other words, the passage of the molecule at A to B requires the expenditure of energy. This energy of activation is considered to -

1) H. Eyring, *J. Chem. Phys.*, 4, 283 (1936); R. H. Ewell and H. Eyring, *ibid.*, 5, 726 (1937); J. O. Hirschfelder, D. P. Stevenson and H. Eyring, *ibid.*, 5, 856 (1937); etc. See also S. Glasstone, K. J. Laidler and H. Eyring, *The Theory of Rate Process*, (1941) p. 477.

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be required to push other molecules aside, to make a suitable hole and perhaps to break some bonds in the case of associated liquids as discussed below.
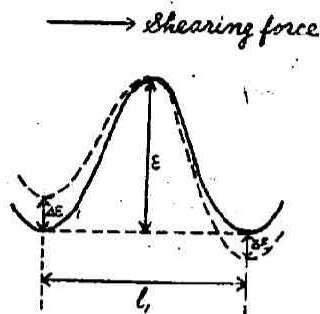

Fig. 2.

Let us assume that the potential barrier is symmetrical and has minima at A and B as shown in Fig. 2. Let f be the shearing force acting on a single molecule. The effect of the force causing the flow of liquid is to reduce the height of the energy barrier in the forward direction by an amount $\Delta\varepsilon$ and the height in the opposite direction will be raised by the same amount. $\Delta\varepsilon$ is given by the following relation : .

$$f l_1 = 2\Delta\varepsilon \tag{1}$$

The number of times a molecule passes over the barrier and moves in the forward direction per second is given by

$$k_1 = \nu e^{-\frac{(\varepsilon - \Delta\varepsilon)}{kT}} \tag{2}$$

where ν is the frequency factor, k the Boltzmann constant; and that in the opposite direction is given by

$$k_2 = \nu e^{-\frac{(\varepsilon + \Delta\varepsilon)}{kT}} \tag{3}$$

$k_1 - k_2$ gives the number of particles which pass from A to B in one second. The condition required to get the formula for the viscosity coefficient is the one which moves on molecule at A towards B by a distance equal to l_3 in one second, i. e.

$$k_1 - k_2 = \frac{l_3}{l_1} \tag{4}$$

Substituting Eqs. (2) and (3) in Eq. (4) gives

$$\frac{l_3}{l_1} = \nu\left(e^{-\frac{(\varepsilon - \Delta\varepsilon)}{kT}} - e^{-\frac{(\varepsilon + \Delta\varepsilon)}{kT}}\right) = \nu e^{-\frac{\varepsilon}{kT}} 2\sinh\frac{\Delta\varepsilon}{kT} \tag{5}$$

As in the ordinary condition $\frac{\Delta\varepsilon}{kT} \ll 1$, it follows that

$$2\nu e^{-\frac{\varepsilon}{kT}}\frac{\Delta\varepsilon}{kT} = \frac{l_3}{l_1} \tag{6}$$

Now Newton's law of viscous flow for stream line motion is

$$F = \eta A \frac{dv}{dx} \tag{7}$$

where F, η, A and $\dfrac{dv}{dx}$ have usual meanings. As in our case $A=1$, $\dfrac{dv}{dx}=1$ and $f=Fl_1l_2$, from Eqs. (1) and (7) we get

$$\eta=F=\frac{f}{l_1l_2}=\frac{2\Delta\varepsilon}{l_1^2l_2}\tag{8}$$

Substituting the relation (6) in Eq. (8) gives

$$'\eta=\frac{l_n^2}{l_1^2l_1l_2l_3}\frac{kT}{\nu}e^{\frac{\varepsilon}{kT}}\tag{9}$$

or

$$\eta=\left(\frac{l_3}{l_1}\right)^2\cdot\frac{1}{V}\cdot\frac{RT}{\nu}e^{\frac{E}{RT}}\tag{10}$$

where V is the molecular volume, E the activation energy per mole for viscous flow and R the gas constant. The relation (10) is similar to those obtained from somewhat different standpoint by the other authors[2]. Taking the logarithm of the both sides of Eq. (10), we get

$$\log\eta=2\log\left(\frac{l_3}{l_1}\right)-\log V+\log R+\log T-\log\nu+\frac{E}{RT}\tag{11}$$

II) The evaluation of E and $\log\nu$.

Assuming the relation (10) or (11) to be valid, we have calculated the values of E and $\log\nu$ for a) water, b) benzene and c) mercury. These values change
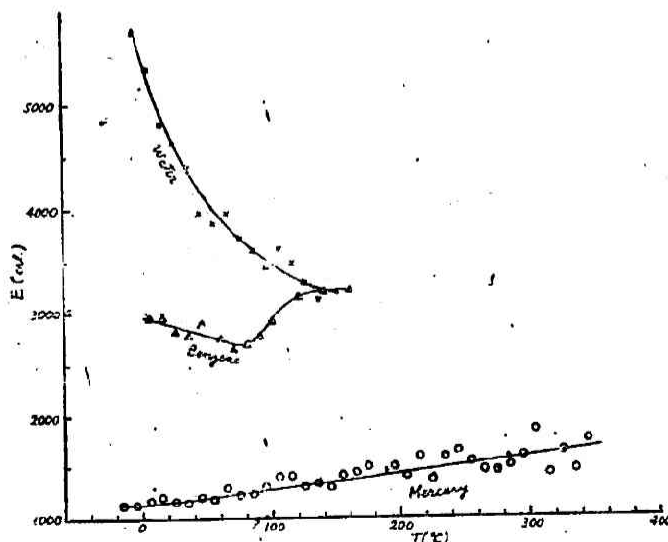

Fig. 3.

2) Eyring and others, see foot-note 1); S. Kaneko, *Bull. Chem. Soc. Japan*, 15, 276 (1940); R. Simha, *J. Chem. Phys.*, 7, 202 (1939); J. Frenkel, *Trans. Faraday Soc.*, 33, 58 (1936).

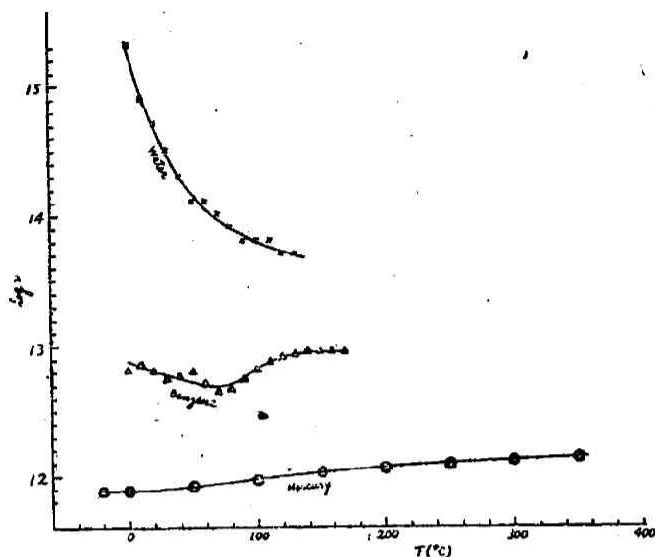ON THE VISCOSITY OF PURE LIQUID   61

Fig. 4.

with temperature as shown in Figs. 3 and 4. All the viscosity data have been taken either from the International Critical Tables or from Landolt-Börnstein's Physikalisch-Chemische Tabellen and the most probable values have been used. For mercury the data given in Ward's paper[3] have been also consulted. In the calculation it has been assumed that $l_1 = l_2$.

a) Water

As is pointed out by several authers, abnormally large viscosity of water may be due to the hydrogen bond structure. When a molecule in water flows, it must not only break van der Waals' and dipole "bonds", but also hydrogen bond. From Fig. 3 it is seen that the activation energy for the flow process in abnormally high at low temperatures. The activation energy at 0°C may be about 2800 calories higher than that of high temperature where almost all the hydrogen bonds may be considered to have been broken. If the energy of the hydrogen bond is assumed to be 3000 calories per mole[4], the breaking of the hydrogen bond seems to play an important rôle in the flow process of this liquid. And .this view does also elucidate the abnormally high value of log ν of water, as seen in Fig. 4, at low temperatures.

Judging from Fig. 4, let us assume log ν for water at high temperatures, where all the bonds are broken, to be 13.5. Then log ν at 0°C is 1.8 higher than this i. e. ν at 0°C is about 630 times as large as that at high ,temperatures. Now it

3) A. G. Ward., *ibid.*, 35, 91 (1936).
4) Burnham, Cross and Leighton, *J. Am. Chem. Soc.*, 59, 1134 (1937).

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it is reasonable to assume two or three water molecules to be associated on the average at 0°C. Then for such a large "molecule" we must, as is well known, use the following expression in Eq. (1).

$$e^{-\frac{E}{RT}}\left[\frac{(E/RT)^{s-1}}{(s-1)!}+\frac{(E/RT)^{s-2}}{(s-2)!}+\ldots\ldots\right] \qquad (12)$$

instead of $e^{\frac{E}{RT}}$. Let us assume that three molecules, for example, are associated. Then if the value in the brackets in the above expression is 3×630, we can explain the abnormally high value of $\log \nu$ at 0°C. If we consider the case at 0°C, since $E=5500$, the value in the brackets becomes about 1900 when s is taken to be 7. Since three water molecules contain 9 atoms, s must not exceed $3 \times 9 - 6 = 21$. While in our case s is equal to 7, it is not unreasonable. In a similar way, the high value of $\log \nu$ is explainable even if the value of association factor is assumed to be 2. It seems difficult to elucidate the high value of ν at low temperatures without assuming the association and the breaking of the hydrogen bond.

b) Benzene

At first sight it is striking that the curve for benzene has a minimum. Benzene cannot be considered to associate even at low temperatures, because the value of k in the Eötvös law, for example, does not become small at lower temperatures. But cybotactic groups may exist and the streaming process may help benzene molecule to arrange face to face contacting with the greatest area, and the rise of temperature may disturb this arrangement. Another point to be considered is the influence of the change of the value of $\frac{l_3}{l_1}$ in Eq. (11), which we have assumed to be constant and equal to 1, on the calculation of E and $\log \nu$. Probably $\frac{l_3}{l_1}$ is small at low temperatures and approaches to 1 with increasing temperature. This will raise the values of E and $\log \nu$ a little more at lower temperatures than those in Figs. 3 and 4. The increase of E and $\log \nu$ at higher temperatures may be due to the same causes that will be discussed later in the case of mercury. In short, for benzene it is necessary to make further searching inquiry.

c) Mercury

As in this case we can put $l_1 = l_3$, there is no ambiguity arising from the value of $\frac{l_3}{l_1}$. Here also we see that not only E but also $\log \nu$ increase obviously with temperature. For complex molecules the change of E with temperature is expected from the influence of the temperature on the shape of the molecule and of

orientation[5]. But for mercury, we cannot expect such a temperature dependence except at low temperatures where the existence of Hg_2 molecules cannot be neglected. For the lack of the viscosity data near the melting point, we cannot evaluate the value of E and $\log \nu$ near that point. But from the curve below 100°C, it is supposed that the curve below -10°C is parallel to the temperature axis or has a minimum. If this is true it may to due to the existence of Hg_2 molecules. Now let us consider what causes the value of E to increase with temperature. Since the increase in E when the interatomic distance is decreased by oscillation may be reasonably considered to exceed the decrease in E when the distance increases by the same amount, it is not strange that the mean value of the energy of activation for flow process increases with temperature, even if the average interatomic distance increases by thermal expansion.

Next we will consider the cause of the increase in $\log \nu$ with temperature. At low temperatures the atoms vibrate just as those in the solid state. But the amplitudes are so large that the ideal case of the harmonic oscillator can no longer be employed, and the restoring force may increase at a greater rate than the displacement. Thus the frequency will increase with rising temperature. This relation between the frequency of vibration of atoms and temperature must be closely connected with the change of heat capacity of this liquid with temperature, and indeed some authors[6] assumed the increase of ν with temperature in their attempts to calculate the molecular heat of liquids.

Further discussion must be deferred until the calculations are carried on for many other liquids, and it may possibly become necessary to modify somewhat the above considerations.

In conclusion the author wishes to express his thanks to Professor J. Oishi for helpful discussion in connection with the present work.

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5) F. Eirich and S. Simha, *J. Chem. Phys.*, **7**, 116 (1939) ; S. Kyropoulos, *ibid.*, **7**, 52 (1939).

6) A. Eucken, *Ber. Ak. Wiss. Berlin*, **22**, 682 (1914) ; A. Magnus, *Z. anorg. Chem.*, **171**, 73 (1928).