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On the Mechanism of Viscosity of Liquids

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A new viscosity-temperature relationship for liquids has been derived, and its application has been studied. The derivation is based upon the theory of viscosity by Eyring *et al.*, rectifying the "activation energy" term. The "activation energy" term has been shown to be equivalent to the free energy of formation of a surface and the error committed by previous workers regarding the evaluation of "activation energy" has been discussed. The proposed equation is free from any arbitrary or empirical terms, and since, in particular, it does not involve any quantities derived from viscosity measurements, it makes a direct calculation of viscosity possible.

INTRODUCTION

REFERENCES to the literature on the viscosity of liquids have been cited in my earlier papers.^{1,2} Some preliminary aspects of this subject have been considered in my recent publications.³⁻⁵ The present paper is an attempt to deal with the mechanism of the viscosity of liquids as a whole. This paper incorporates generally the broad outlines of one of the two theories of viscosity of liquids proposed by Eyring *et al.* However, it has been found necessary to rectify the term "activation energy" employed by Eyring *et al.*, and this step is justified by the validity tests. Since the "activation energy" term has been altered, it has been possible to attribute a more precise meaning to the term "frequency factor." It will be observed that the "activation energy" term has been assumed to be equivalent to the free energy involved in the formation of a surface. Consequently, a discussion of the relation between surface tension and molecular volume, as outlined in the next section, has been rendered necessary.

RELATION BETWEEN SURFACE TENSION AND MOLECULAR VOLUME

Recent theories of the liquid state attribute to liquids a so-called "quasi-crystalline" or "pseudo-crystalline" structure.^{6,7} It is supposed that the average distribution of molecules about a particular molecule is the same at any instant; however, the structure is supposed to differ from that of a crystal because of thermal agitations in the liquid. As Bernal puts it, "around every molecule of the liquid, the arrangements of other molecules are statistically equivalent; or, put in another way, the probability of finding a molecule at a given distance from another molecule is independent of the position of either of them in the liquid." If

a number of instantaneous photographs could be taken, the molecular distribution about any molecule in the liquid state would appear to be random and homogeneous, but if the pictures were all put together, the statistical average would indicate a definite structure analogous to that of a solid. A molecule in a liquid is probably acted on all the time by about as many other molecules as it would be if in the solid state. The forces from these neighboring molecules imprison it in a cell from which it only rarely escapes. The main difference between a solid and a liquid is not that between captivity and freedom; it is only that the particle of a solid is held in fetters *all* the time, while that of a liquid is held in fetters *nearly all* the time, living a life of comparative freedom only in the very brief intervals between one term of imprisonment and the next.⁸ In the absence of any precise information, it would be reasonable to assume a uniform packing of molecules in liquids. We may now examine the consequences of such a uniform and close packing.

Consider a portion of a flat interface between liquid and vapor—the liquid being supposed to be made up of a number of molecules, the average distance between the centers of the closest neighbors being r . This assumption is justifiable over periods of time long compared with molecular vibrations. Further, the liquid will appear to consist of a number of layers of molecules parallel to the surface layer and lying in the bulk of the liquid phase below the surface layer. It follows from geometrical considerations that the distance of separation between two such consecutive layers will be $(\sqrt{2}/\sqrt{3}) \cdot r$. Each such layer will appear to be composed of a number of horizontal rows of molecules, the distance at right angles to and between two consecutive rows of molecules being obviously $(\sqrt{3}/2) \cdot r$. In a length of *one cm* in the row, the number of molecules will be $1/r$. In a distance of *one cm* at right angles to the row, the number of such parallel rows of molecules in the surface is

¹ M. S. Telang, *J. Phys. Chem.* **49**, 579 (1945).

² M. S. Telang, *J. Phys. Chem.* **50**, 373 (1946).

³ M. S. Telang, *J. Chem. Phys.* **15**, 525 (1947).

⁴ M. S. Telang, *J. Chem. Phys.* **15**, 844 (1947).

⁵ M. S. Telang, *J. Chem. Phys.* **15**, 885 (1947).

⁶ J. A. Prins, *Trans. Faraday Soc.* **33**, 110 (1937).

⁷ J. D. Bernal, *Trans. Faraday Soc.* **33**, 27 (1937).

⁸ J. Jeans, *Kinetic Theory of Gases* (Cambridge University Press, London, 1940), p. 7.

given by $(2/r\sqrt{3})$. Therefore, the number of molecules in *one sq. cm* of the interface will be $(2/r^2\sqrt{3})$. If we imagine the molecular volume V to be equivalent to the volume of a cube of a side $V^{1/3}$ taken in the bulk of the liquid phase, and if the top of the cube is made to coincide with the surface of the liquid, the surface area of the top will be $V^{2/3}$. Since $(2/r^2\sqrt{3})$ represents the number of molecules per sq. cm, the number of molecules in $V^{1/3}$ would be $(2V^{1/3}/r^2\sqrt{3})$. Since the distance of separation between two consecutive layers is $(\sqrt{2}/\sqrt{3}) \cdot r$, the number of layers in a length $V^{1/3}$ at right angles to the interface will be $(\sqrt{3} \cdot V^{1/3}/\sqrt{2} \cdot r)$. Therefore, the total number of molecules in all the layers in the cubical volume V will be given by

$$(2V^{1/3}/\sqrt{3} \cdot r^2) \times (\sqrt{3} \cdot V^{1/3}/\sqrt{2} \cdot r) = (\sqrt{2} \cdot V/r^3) = N \dots, \quad (1)$$

where N = Avogadro number.

$$\therefore r = (\sqrt{2}/N)^{1/3} \cdot (M/D)^{1/3} \dots, \quad (2)$$

where M = molecular weight and D = density of the liquid. Hence, the number of molecules per sq. cm in the surface will be

$$(2/\sqrt{3} \cdot r^2) = ((2N)^{1/3}/\sqrt{3}) \cdot (D/M)^{1/3} \dots \quad (3)$$

Surface tension γ is defined as the work done to bring $(2/\sqrt{3} \cdot r^2)$ molecules from the bulk of the liquid phase to the surface to form a fresh surface of *one sq. cm*. The free energy involved in the formation of one sq. cm of surface will be given by

$$\gamma = (2/r^3 \cdot \sqrt{3}) \times (\Delta\epsilon_s) \dots, \quad (4)$$

where $\Delta\epsilon_s$ = the free energy involved in the formation of a surface inhabited by an individual molecule. Combination of (3) and (4) gives

$$\Delta\epsilon_s = \gamma(M/D)^{1/3} \times (\sqrt{3}/(2N)^{1/3}) \dots \quad (5)$$

Multiplying (5) by N , we have

$$N\Delta\epsilon_s = 1.091 \cdot N^{1/3} \times \gamma(M/D)^{1/3} \dots \quad (6)$$

DERIVATION OF THE VISCOSITY-TEMPERATURE RELATIONSHIP FOR LIQUIDS

Eyring *et al.*⁹ have given an equation for fluidity, the reciprocal of which is

$$\eta = (\lambda_1/\lambda\lambda_2\lambda_3) \cdot (v_h/v - v_s) \cdot (2\pi mkT)^{1/2} \cdot e^{\Delta\epsilon_f/kT} \dots, \quad (7)$$

retaining the original symbols, *viz.*, η = the viscosity, λ_1 = the distance between two layers of molecules in a liquid sliding past each other under the influence of an applied force, λ = the distance between two equilibrium positions in the direction of motion, λ_3 = the distance between neighboring molecules in the same direction, λ_2 = the mean distance between two adjacent molecules in the moving

layer in the direction at right angles to the direction of motion, v_h = the volume of a single hole, or the increase in volume per equilibrium position, v = the volume inhabited by a single molecule, v_s = the contribution of a single molecule to the volume of the unexpanded solid, m = the mass of an individual molecule, k = the Boltzmann constant, T = the absolute temperature, and $\Delta\epsilon_f$ = the activation energy required for a single molecule to flow into a hole that is available, *in the absence of a shearing force*. The ratio of the partition functions, F^\ddagger and F , for unit volume, of the molecule in the activated and initial states, respectively, is written as¹⁰ (where v_f = the free volume per molecule and h = Planck's constant)

$$(F/F^\ddagger) = ((2\pi mkT)^{1/2}/h) \cdot v_f^{1/2} \dots \quad (8)$$

So,

$$(2\pi mkT)^{1/2} = (F/F^\ddagger) \cdot (h/v_f^{1/2}) \dots \quad (9)$$

Substituting (9) in (7), there results

$$\eta = (\lambda_1/\lambda\lambda_2\lambda_3) \cdot (v_h/v - v_s) \cdot (h/v_f^{1/2}) \cdot (F/F^\ddagger) \cdot e^{\Delta\epsilon_f/kT} \dots \quad (10)$$

The identity¹¹

$$(F/F^\ddagger) \exp(\epsilon_0/kT) = \exp(\Delta F^\ddagger/RT) \dots, \quad (11)$$

in which ϵ_0 = the energy of activation at 0°K, *i.e.*, the height of the energy barrier, when no force is acting on the liquid, ΔF^\ddagger = the standard free energy of activation per mole and R = the gas constant per mole, may now be utilized. If we assume ϵ_0 to be synonymous with $\Delta\epsilon_f$, substituting (11) in (10), we get

$$\eta = (\lambda_1/\lambda\lambda_2\lambda_3) \cdot (v_h/v - v_s) \cdot (h/v_f^{1/2}) \cdot \exp(\Delta F^\ddagger/RT) \dots \quad (12)$$

Further, $\lambda_1 \approx \lambda$, and $\lambda_2\lambda_3 = (V/N)^{2/3}$, where V = the molar volume and N = the Avogadro number. Using a new symbol $b = Nv_s = V_s$, we have $v - v_s = (V - b)/N = v_f$. Assuming that⁵ $v_h = (V_s/N) = (b/N)$, and making appropriate substitutions in (12), we obtain

$$\eta = (hN/V^{1/2}) \cdot (b/(V - b)^{4/3}) \cdot \exp(\Delta F^\ddagger/RT) \dots \quad (13)$$

For reasons to be explained a little later in this paper, we may put $N\Delta\epsilon_s = \Delta F^\ddagger = E_{vis.}$ per mole = $1.091N^{1/3} \cdot \gamma(M/D)^{1/3}$ according to (6). It is obvious, therefore, that (13) can be written as

$$\eta = (hN/V^{1/2}) \cdot (b/(V - b)^{4/3}) \cdot \exp(1.091N^{1/3}\gamma(M/D)^{1/3}/RT) \dots \quad (14)$$

We may express (14) in the form

$$\eta = Z \cdot \exp(E_{vis.}/RT) \dots, \quad (15)$$

where $Z = (hN/V^{1/2}) \cdot (b/(V - b)^{4/3})$ = the "frequency factor" and $E_{vis.}$ = the "activation energy" per mole for viscous flow.

⁹ S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes* (McGraw-Hill Book Company, Inc., New York, 1941), p. 488.

¹⁰ See reference 9, p. 485.

¹¹ See reference 9, p. 484.

TABLE I.

Substance	Temperature	b	b/V_0
Acetone	20°C	63.9	0.295
Carbon tetrachloride	20	89.3	0.324
Chloroform	10	76.5	0.331
Cyclohexane	20	106.6	0.342
<i>n</i> -hexane	20	117.5	0.319
Ethyl ether	20	91.8	0.325
Benzene	0	77.4	0.301
Benzene	70	88.73	0.345

INTERPRETATION OF THE TERM "ACTIVATION ENERGY"

In the foregoing derivation there are two points which need some clarification. The first one refers to the assumed equality of ϵ_0 and $\Delta\epsilon_f$, both of which imply quantities in the absence of a shearing force. Some confusion has arisen because of the interpretation of Eyring *et al.*⁹ that the total activation energy for viscous flow is to be regarded as consisting of two parts: (a) the energy required to form the hole, and (b) that required for the molecule to move into the hole. This conclusion of these authors was based on an erroneous assumption that $(\Delta E_{\text{vap.}}/\Delta F_{\text{vis.}})^{\ddagger} = 2.45$, as will be demonstrated in the following pages. Since there is no *a priori* reason for splitting the total activation energy into two parts in the manner of Eyring *et al.*, we may assume that the process of forming a site or a hole, and of moving a molecule into the prepared site, should be considered as the performance of one process on the whole. We may consequently put down ϵ_0 to be synonymous with $\Delta\epsilon_f$.

The relation $\Delta F_{\text{vis.}}^{\ddagger} = 1.091N^{\ddagger}\gamma(M/D)^{\ddagger}$ is the next point to be considered. Following Eyring *et al.*, in the treatment of viscous flow of liquids as a rate process, the jump of a moving molecule from one equilibrium position to the next is to be regarded as equivalent to the passage of the system over a potential energy barrier. By definition, surface energy per molecule corresponds to the work done in overcoming the difference in the potential energy of a molecule in the surface and that in the body of the liquid phase in order to bring an interior molecule to the surface to form a fresh surface inhabited by a single molecule. For this process, in order to accommodate the molecule to be brought up to the surface, a suitable site or hole will have to be made in the surface. Subsequently, one of the nearest neighbors from the bulk of the liquid phase will have to be moved into the prepared site. Therefore, the mechanisms of viscosity and surface tension, involving a transfer of molecules from one equilibrium position to another surmounting an energy barrier, appear to be identical so far as this part of the process is concerned. Consequently, it appears reasonable to assume that the activation energy for viscous flow

and the free energy of formation of a surface per molecule are equivalent. However, it is to be pointed out that we have no means of ascertaining this statement. The only justification for the assumption is to be sought for in its satisfactory application, as will be seen in the section on the application of the equation.

APPLICATION OF THE PROPOSED EQUATION

The validity of Eq. (14) can be studied in five ways, as shown below: (a) The Eötvös law¹² gives

$$\gamma(M/D)^{\ddagger} = k'(T_c - T) \dots, \quad (16)$$

where k' = the Eötvös constant and T_c the absolute critical temperature. Combination of (14)–(16) gives

$$\eta = Z \cdot \exp(1.091N^{\ddagger} \cdot k' \times (T_c - T)/RT) \dots \quad (17)$$

On taking logarithms and adding $\ln V^{\ddagger}$ to both sides of (17), we get

$$\ln \eta \cdot V^{\ddagger} = (\ln Z \cdot V^{\ddagger} - (1.091N^{\ddagger} \cdot k'/R)) + (1.091N^{\ddagger} \cdot k'/R) \cdot (T_c/T) \dots \quad (18)$$

Recently, Thomas¹³ has proposed and tested the following equation:

$$\ln \eta \cdot V^{\ddagger} = (c - k) + k(T_c/T) \dots \quad (19)$$

The close resemblance between (18) and (19) can be readily seen, and a comparison of the two gives

$$c = \ln Z \cdot V^{\ddagger} \quad \text{and} \quad k = (1.091N^{\ddagger} \cdot k'/R).$$

Expressing (18) in logarithms to the base 10,

$$\log_{10} \eta \cdot V^{\ddagger} = (\log_{10} Z \cdot V^{\ddagger} - (0.4343 \times 1.091N^{\ddagger} \cdot k'/R)) + (0.4343 \times 1.091N^{\ddagger} \cdot k'/R) \times (T_c/T) \dots \quad (20)$$

Taking the average value of the Eötvös constant $k' = 2$, we obtain

$$0.4343k = (0.4343 \times 1.091N^{\ddagger} \cdot k'/R) = 0.96,$$

expressing R in ergs, since γ is in ergs/cm². This value of $0.4343k = 0.96$ deduced from Eq. (20) is a fair intermediate between the two extreme values of 0.6 and 1.1 given by Thomas¹³ in his Table II.

(b) We are further led to a very significant conclusion that the usual method of determining the activation energy according to the relation $E_{\text{vis.}} = R(d \ln \eta / d(1/T))$ from the linear plot of $\ln \eta$ vs. $1/T$ is not justifiable. According to (18) (dropping the term $\ln V^{\ddagger}$), such a plot gives the slope as

$$(1.091N^{\ddagger} \cdot k'/R) \times T_c = 2.2T_c,$$

whereas the true slope ought to be in accordance with (17),

$$(1.091N^{\ddagger} \cdot k'/R) \times (T_c - T) = 2.2(T_c - T),$$

taking R in ergs. The activation energy is obtained by multiplying by R , and, for convenience, taking it in calories, we have the "true activation energy"

¹² R. Eötvös, Ann. d. Physik **27**, 448 (1886).

¹³ L. H. Thomas, J. Chem. Soc., 573 (1946).

as $4.4(T_c - T)$ calories. The "usual activation energy" is given by $4.4T_c$ calories. From the Guldberg-Guye law,¹⁴ $T_c = 1.5T_b$. At the absolute boiling point, T_b , the "true activation energy" will be $4.4(1.5T_b - T_b) = 2.2T_b$ calories, whereas the "usual activation energy" will be $4.4 \times 1.5T_b = 6.6T_b$ calories. So, the "usual activation energy" is three times greater than the "true activation energy."

Furthermore, Eyring *et al.*¹⁵ have obtained the ratio $(\Delta E_{\text{vap.}}/\text{usual } E_{\text{vis.}}) \approx 2.5$ to 3 for a number of substances. Hence, at the boiling point, $(\Delta E_{\text{vap.}}/\text{true } E_{\text{vis.}}) \approx 3 \times (2.5 \text{ to } 3) \approx 7.5$ to 9. This ratio can be alternatively obtained from Trouton's rule¹⁶ $(\Delta H_{\text{vap.}}/T_b) = 21$, or, $(\Delta E_{\text{vap.}}/T_b)$

$$= (\Delta H_{\text{vap.}} - RT_b)/T_b$$

$= 19$. Since, $2.2T_b$ calories is the "true activation energy" at the boiling point, $(\Delta E_{\text{vap.}}/\text{true } E_{\text{vis.}}) = (19T_b/2.2T_b) = 8.64$.

(c) Eyring *et al.*⁹ have shown that from Eq. (7) in the present paper, at *constant volume*, at the temperatures T_1 and T_2 , it is possible to obtain the relation

$$-\Delta E_f((1/T_1) - (1/T_2)) = R \ln(1/\eta_1/1/\eta_2) + \frac{1}{2} \ln(T_1/T_2) \dots \quad (21)$$

The values of ΔE_f derived from viscosity data at constant volume at two temperatures for a number of substances are of the order of 500 calories. It has been shown in (b) that the "true activation energy" is $2.2T_b$ calories. Carbon disulfide, for example, has a boiling point $T_b = 319^\circ\text{K}$ and so its $\Delta E_f = E_{\text{vis.}} = 2.2 \times 319 = 702$ calories. In view of the various approximations incorporated in obtaining $E_{\text{vis.}}$, the two values of ΔE_f for carbon disulfide may be said to be in good agreement. It is difficult to secure sufficient data to extend this method of testing the equation for a variety of substances. Even from the limited data available, one thing is clear—that the "true activation energy" discussed here is of the right order.

(d) Taking the values of η , γ , and D at two temperatures very close to each other, we can obtain from (14) the following relation:

$$M = 2.995 \{ \log_{10} \eta_1/\eta_2 / (\gamma_1/D_1^{\frac{1}{3}} \cdot T_1) - (\gamma_2/D_2^{\frac{1}{3}} \cdot T_2) \}^{\frac{1}{2}} \dots, \quad (22)$$

assuming that the change in V over a small temperature interval is negligible in comparison with the corresponding effect of temperature on η and γ . The values of M calculated from (22) are nearly equal to the theoretical molecular weights.⁴ This agreement establishes that the "activation energy" term deduced in the present paper is of the right form. Incidentally, it may be pointed out that the

numerical factor 2.995 is slightly different from the original value 3.176 previously used by me.⁴ This correction follows from the revision made in the activation energy term in Eq. (14).

(e) So far, our attention has been focused upon establishing that the activation energy term in Eq. (14) was of the right order. It is now necessary to show that the frequency factor in (14) is also of a correct form. Its absolute value independent of viscosity measurements can be calculated and compared with that derived from Eq. (14) by using experimental values of η , γ , and D at one temperature. Alternatively, Eq. (14) may be solved for b by substituting the experimental values of η , γ , etc., at any temperature. The ratio b/V_c , where V_c = the molar critical volume and b = the value obtained by solving (14), indicates that the term b in (14) corresponds to the b of van der Waals, justifying the significance attached to it in deriving (14) (see Table I). However, b is somewhat dependent on temperature, although its temperature coefficient is small, being approximately of the order of that of cubical expansion of the liquid. For example, the average temperature coefficient of b over the temperature interval given in Table I is 2.091×10^{-3} for benzene. Attempts have been made to show that the b of van der Waals is a function of pressure.¹⁷ It is not improbable that it might be a function of temperature also. As all the values in (14), excepting b , are available, if the value of b could be properly chosen, a direct calculation of η from (14) could be done with accuracy, which would be a great achievement of the theory of absolute reaction rates. The substances examined so far are normal unassociated organic liquids. Further work in connection with the behavior of associated or dissociated substances is in progress. It may be of interest to note that (14) can be reduced to the approximate form

$$\eta \approx (hN/V - b) \cdot \exp(1.091N^{\frac{1}{3}} \cdot \gamma(M/D)^{\frac{1}{3}}/RT) \dots \quad (23)$$

This equation is a slight modification of an equation given by me in an earlier paper.⁵ The term b is somewhat less than V , and $V^{\frac{1}{3}} \times (V - b)^{\frac{1}{3}}$ has the dimensions of a volume being not very different from b . Therefore, $(b/V^{\frac{1}{3}}(V - b)^{\frac{1}{3}})^{\frac{1}{2}} \approx 1$. Thus, (14) reduces to (23). Equation (23) is useful in obtaining the approximate value of b for solving Eq. (14) involving fractional exponents.

In conclusion, it may be stated that since Eq. (14) is amenable to a quantitative mathematical treatment, without using any arbitrary or empirical terms and particularly being not derived from viscosity measurements, a satisfactory interpretation of the mechanism of the viscosity of liquids appears to be within reach.

¹⁷ D. B. Macleod, *Trans. Faraday Soc.* **41**, 771 (1945).

¹⁴ C. M. Guldberg, *Zeits. f. physik. Chemie* **5**, 374 (1890); P. A. Guye, *Bull. Soc. Chim.* **4**, 262 (1890).

¹⁵ See reference 9, p. 492.

¹⁶ F. Trouton, *Phil. Mag.* [5] **18**, 54 (1884).