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Citation: *J. Chem. Phys.* **15**, 885 (1947); doi: 10.1063/1.1746417

View online: <http://dx.doi.org/10.1063/1.1746417>

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On the Frequency Factor in the Viscosity-Temperature Relationship of Liquids

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November 5, 1947

IN recent publications^{1,2} I clarified the term "activation energy" for viscous flow of liquids from the expression

$$\eta = Z \exp [\gamma(M/D-d)^{\frac{1}{3}} \cdot N^{\frac{1}{3}} / (\cos 30^\circ)^{\frac{1}{3}} / RT]. \quad (1)$$

Since it is possible to calculate E_{vis} directly according to (1), it is necessary to examine whether it is also possible to calculate the "frequency factor," Z , directly. Eyring *et al.*³ have derived the equation

$$\eta = (h/\lambda_2\lambda_3\lambda_1) \cdot (F/F_0) \cdot \exp [\epsilon_0/kT], \quad (2)$$

the symbols being the same as the original ones of Eyring *et al.* The product $\lambda_2\lambda_3\lambda_1$ has been assumed to be approximately the volume inhabited by a single molecule in the liquid state and, hence, it has been put equal to V/N , where V is the molar volume. Eyring *et al.*⁴ have further transformed Eq. (2) into

$$\eta = (hN/V) \cdot \exp \Delta E_{vap} / 2.45RT \quad (3)$$

Now, I find that the non-exponential term representing the "frequency factor" has to be also altered. The modified equation obtained by me is

$$\eta = (hN/V-b) \cdot \exp [\gamma(M/D-d)^{\frac{1}{3}} \cdot N^{\frac{1}{3}} / (\cos 30^\circ)^{\frac{1}{3}} / RT], \quad (4)$$

introducing a constant b , characteristic of each substance. The symbols in (4) are: η = viscosity, γ = surface tension, M = theoretical molecular weight, D = density of liquid, d = density of vapor, N = Avogadro number, R = gas constant (in ergs), T = absolute temperature, h = Planck's constant, and V = molar volume. The only unknown factor b in (4) can be easily evaluated by making appropriate substitutions for the experimental values of η , V , γ , D , d , and T , at one temperature. Calculating b from (4) in this manner, Table I shows that b/V_c is nearly the same for all the substances listed for illustration. The ratio of b to V_c , the molar critical volume, is very nearly $\frac{1}{3}$. It follows, therefore, that the factor b introduced in (4) is almost identical with van der Waals' constant b . This observation applies to other non-associated substances also and is valid at temperatures even far above the melting points.

The necessary data have been taken from the International Critical Tables and from Lange's Handbook of Chemistry.⁵

The correction factor b introduced indicates that $\lambda_2\lambda_3\lambda_1$ has to be interpreted as the free volume or a hole in the liquid and not as the total volume inhabited by a molecule. It is quite likely that $hN/(V-b)$ may be a mathematically simplified form of

$$\frac{hN}{V} \cdot \frac{V}{V-b} = \frac{hN}{V} \cdot \frac{(V-b)+b}{V-b} = \frac{hN}{V} \left(1 + \frac{b}{V-b} \right).$$

The complete equation would then be

$$\eta = \frac{hN}{V} \left(1 + \frac{b}{V-b} \right) \exp [\gamma(M/D-d)^{\frac{1}{3}} \cdot N^{\frac{1}{3}} / (\cos 30^\circ)^{\frac{1}{3}} / RT]. \quad (5)$$

TABLE I.

Substance	b/V_c
Acetone	0.313
Benzene	0.318
Carbon tetrachloride	0.338
Chloroform	0.338
Cyclohexane	0.346
Ethylene bromide	0.314*
Ethyl ether	0.344
n-Hexane	0.336
Mean.....	0.331

* V_c is calculated as thrice van der Waals' constant.

A somewhat similar idea has been incorporated by Eyring *et al.*⁶ in giving an alternative treatment of viscosity by the theory of absolute reaction rates. It is rather premature at this stage to arrive at any definite conclusion regarding the exact significance of the correction factor. However, a mathematical analysis of the factor may be briefly given here. The number of holes n_h per mole of liquid is equal to $V-b/v_h$, where v_h is the increase in volume required to form a single hole.⁷ If b/N is the volume of a single molecule, then $v_h = b/N$; since Eyring's interpretation of the "activation energy" as $\Delta E_{vap}/n = E_{vis}$ is no longer applicable, there seems to be no justification for assuming that v_h is not equal to b/N . Hence,

$$n_h = V - b/b \cdot N.$$

Thus,

$$\left(1 + \frac{b}{V-b} \right) = \frac{n_h + N}{n_h}.$$

¹ M. S. Telang, J. Chem. Phys. 15, 525 (1947).

² M. S. Telang, J. Chem. Phys. 15, 844 (1947).

³ S. Glasstone, K. J. Laidler, and H. Eyring, *The Theory of Rate Processes*, (McGraw-Hill Book Company, Inc., New York, 1941), p. 483.

⁴ See reference 3, p. 493.

⁵ N. A. Lange, *Handbook of Chemistry*, (Handbook Publishers, Inc., Ohio, 1944).

⁶ See reference 3, p. 488.

⁷ See reference 3, p. 510.

Prism Spectrometry from 24 to 37 Microns

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November 14, 1947

BY the use of a prism of KRS-5 (thallium bromide-iodide) with a refracting angle of 26° , it is possible to make measurements in the infra-red to 37 microns. With a thinner prism it may be possible to extend the observations to 40 microns. The prism was incorporated in a Perkin-Elmer spectrometer. The stray radiation is almost completely removed by the use of reflection filters of LiF and CaF₂. Greater deflections will be obtained by using a filter of NaF beyond 36 microns. The instrument was calibrated by the use of known absorption bands in this region. The dispersion of KRS-5 is very high from 0.546 to 1.00 micron, but from 2 to 15 microns it becomes extremely small. The dispersion is very good from 24 to 37 microns.

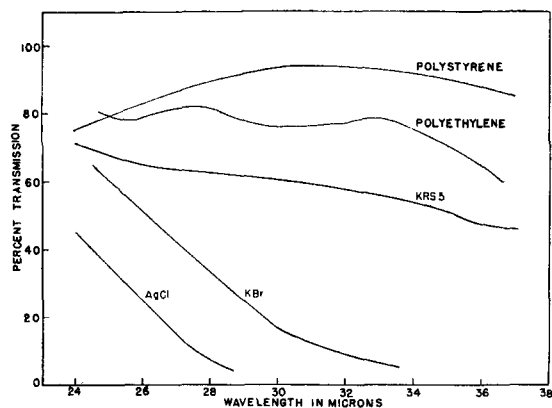


FIG. 1. Transmission of polystyrene 25 microns thick, polyethylene 240 microns, KRS-5 4 mm, KBr 6.4 mm, and AgCl 2.1 mm.

In Fig. 1 is shown the transmission of several materials. The sample of KRS-5 is 4 mm thick and transmits about 70 percent at 24.5 microns. This is about the amount transmitted at 20 microns, and most of the loss is due to reflection. As the wave-length is increased, the transmission decreases, and is 45 percent at 37 microns. Some samples

of KRS-5 have less transmission than the sample shown in Fig. 1. One sample examined is opaque beyond 32 microns. This difference between samples obtained from different sources may arise from impurities in the crystals. Polystyrene shows the highest transmission in this region of any substance measured. This is partly caused by the fact that the layer is only 25 microns thick. When a 1-mm thick layer is used only 25 percent of the incident radiation is transmitted at 33 microns. However, for coatings and windows thin films of polystyrene are useful. A layer of polyethylene 240 microns in thickness also shows high transmission in this region. Thinner layers show somewhat higher transmission. The irregular form of the transmission curve is probably caused by absorption bands in the material. Films of C_2F_4 , $C_2H_2F_2$, and $C_2H_2Cl_2$ were also measured but they have low transmission in this region. The KBr sample is 6.4 mm thick and transmits about 10 percent at 31.5 microns. Thus, in thicknesses of one mm or less KBr will be useful as a window to 30 microns. A sheet of AgCl, 2.1 mm thick, transmits 10 percent at 27.5 microns. However, the sample is slightly discolored and may not have as high transmission as would be found for a clear specimen. Now that the instrument has been calibrated, investigations are being carried out on a number of liquids and vapors.