

The Empirical Criterion $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$

If Eq. (4) is differentiated with respect to $1/T$ we get

$$\Delta E_{\text{vis}}^b = R d \ln \eta / d(1/T) \\ = \frac{\Delta E_{\text{vap}}}{n} - \frac{3}{2}RT + \frac{2}{3}\alpha RT^2 + \frac{\Delta C_V}{\Delta E_{\text{vap}}}RT^2,$$

where α = coefficient of thermal expansion.

ΔC_V = change in molal heat capacity on vaporization.

The first two terms decrease and the last two increase with rising temperature such that ΔE_{vis} remains constant. The last two terms together are about equal in magnitude to the second term, and so ΔE_{vis} should be approximately equal to $\Delta E_{\text{vap}}/n$, or n should be equal to $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$. Table V gives a comparison of n taken from Table I with the ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ at the boiling point for all the liquids in the table.

It is seen that for all the $n=3$ liquids $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ ranges from 2.3 to 2.8, and for all the $n=4$ liquids from 3.4 to 3.9 (except CS_2 and C_2H_4 which are still higher). If the comparison had been made at a lower corresponding temperature, e.g., about four-fifths the absolute boiling point, all the values of the ratio would have been higher (since ΔE_{vap} would be larger), and the values of the ratio would have clustered around 3 for the $n=3$ liquids and around 4 for the $n=4$ liquids (except C_2H_4 and CS_2). These results show that even though ΔE_{vap} varies slowly with the temperature, the value of the ratio $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ at any temperature may be taken as a rough index of the size and shape of the molecule, or more precisely, of the unit of flow. If $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ is much larger than 3 or 4, it indicates that the unit of flow is much smaller than the unit of vaporization (which can be taken as the single molecule in most cases), and if $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ is much smaller than 3 or 4, the reverse is indicated. Examples of both these cases will be discussed below.

^b ΔE_{vis} is the experimental quantity $R d \ln \eta / d(1/T)$ and will be called the viscosity energy. This is a constant independent of temperature for most liquids, but decreases with rising temperature for liquids whose structure changes with temperature.

While theoretically ΔE_{vis} is to be identified with the constant part of the free energy of activation for flow, this discussion has shown that it is approximately equal to the energy of activation for flow. While this relation must be considered as empirical until the theory is developed further, it will be found to be a very useful one.

The empirical criterion $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ was applied by Ewell and Eyring² to several types of liquids with results as follows:

(a) *Liquid metals.* Most metals give a linear plot of $\log \eta$ vs. $1/T$ just as normal covalent liquids do. The most striking fact regarding the metals is the large value of the $\Delta E_{\text{vap}}/\Delta E_{\text{vis}}$ ratio, which ranges from 8 to 25 for different metals as compared to 3 or 4 for normal liquids. This means that the activation energy for flow is much less than a third the energy of vaporization and that the unit of flow is much smaller than the unit of vaporization. The unit of vaporization is the atom, of course, and the unit

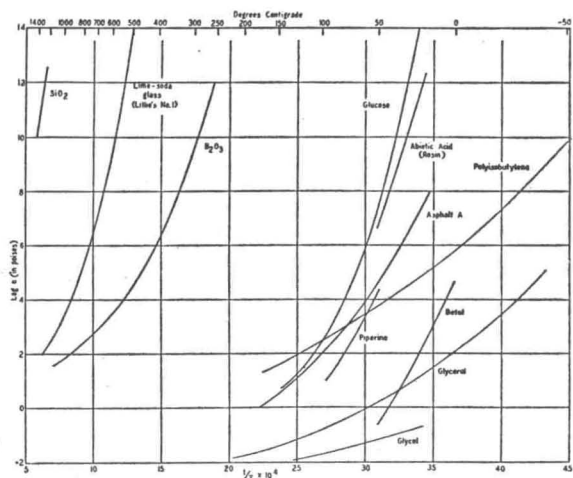


FIG. 8. Plots of $\log \eta$ vs. $1/T$ for some associated, very viscous and glass-forming liquids.†

† The data were from the following sources: SiO_2 , Volarovich and Leontievna, J. Soc. Glass Tech. 20, 139 (1936); soda lime glass, Lillie, J. Am. Cer. Soc. 16, 619 (1933); B_2O_3 , Parks and Spaght, Physics 6, 69 (1935); glucose, Parks, Barton, Spaght and Richardson, ibid. 5, 193 (1934); abietic acid, Bingham and Stephens, ibid. 5, 217 (1934); polyisobutylene, Ferry and Parks, ibid. 6, 356 (1935); asphalt, Pittman and Traxler, ibid. 5, 221 (1934); glycol, Bingham, and Fornwalt J. Rheol. 1, 373 (1930); piperine, betol and glycerol (below 0°C), Tammann and Hesse, Zeits. f. anorg. allgem. Chemie 156, 245 (1926); glycerol (above 0°C), unpublished data by the writer and R. F. Newton.