

Guzman noticed that in a few cases ΔE_{vis} was nearly equal to the heat of fusion, but that this was not true in many more cases. Later writers

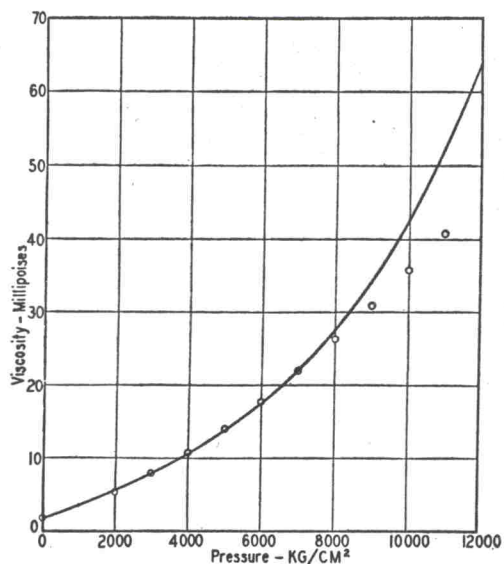


FIG. 6. Calculated and observed viscosities of ether as a function of the external pressure.

have persisted in continuing this heat of fusion relationship, although its empirical basis is a meager coincidence and its theoretical basis is nonexistent. Various terms have been applied to ΔE_{vis} , such as "heat of disorientation," "heat of de-aggregation," "energy required to overcome the attraction of its neighbors," *et al.* These terms are all quite vague, but it is difficult to see how they could have led their authors so uniformly to the erroneous relationship with the heat of fusion. The adoption of the heat of fusion must have been intuitional in any case since until November 1937⁵ there had been no adequate theory of the heat of fusion and the melting process.

Equation (4) can be put in the form

$$\eta = Nh / V e^{-\Delta S_a / R} e^{-\Delta E_a / RT},$$

$$\eta V = N h e^{-\Delta F_a / RT}, \quad (10)$$

where $\Delta F_a = \Delta E_a - T\Delta S_a$

$$= \Delta E_{vap/n} - T\Delta S_a,$$

ΔS_a is a small negative number for most liquids ranging from -1 to -5 cal./deg., so that

$-T\Delta S_a$ is a positive quantity of the order of 1000 cal. ΔE_a decreases and $-T\Delta S_a$ increases with increasing temperature so that ΔF_a is more independent of temperature than either ΔE_a or $T\Delta S_a$.

The form of Eq. (10) is that of the variants of Cragoe and of Souders, where these latter have the specific volume and Eq. (10) has the molar volume. Evidently ΔE_{vis} is to be identified with the free energy of activation of flow, and the constant A should be equal to Nh . Nh has the value $1/250$, while the experimentally determined constant A is about $1/100$ for most liquids. This simply means that the free energy is not entirely independent of temperature, but is of the form $\Delta E_{vis} + bT$, where b would have a value of about 2 to give agreement between the theory and experiment. The experimental constant ΔE_{vis} is in fact then the constant part of the free energy of activation for flow.

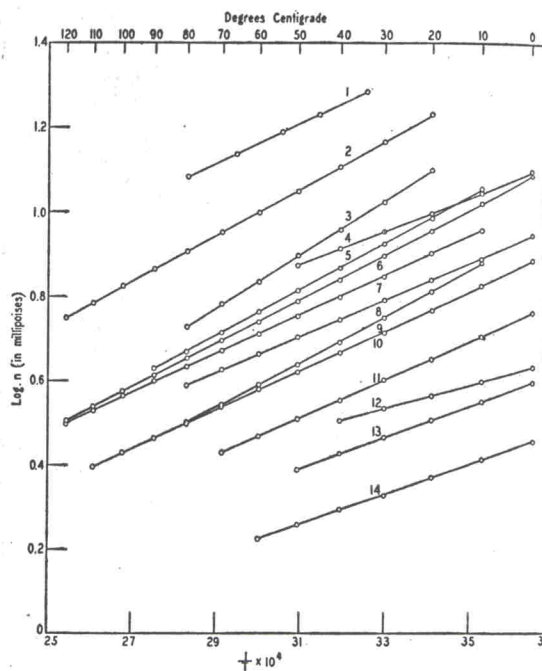


FIG. 7. Plots of $\log \eta$ vs. $1/T$ for some normal liquids.†

† The data were taken from Landolt-Börnstein Tabellen, and are largely those of Thorpe and Rodger. The liquids represented are:

- | | |
|-------------------------|----------------------|
| 1. Phosphorus | 8. Isopropyl iodide |
| 2. Ethylene dibromide | 9. Benzene |
| 3. Dioxane | 10. Toluene |
| 4. Bromine | 11. Ethyl acetate |
| 5. Carbon tetrachloride | 12. Carbon disulfide |
| 6. Acetic anhydride | 13. Acetone |
| 7. Chlorobenzene | 14. Diethyl ether |

The Empirical

If Eq. (4) is used, we get

$$\Delta E_{vis}^b = R d \ln \eta$$

where $\alpha = \text{coefficient}$

$$\Delta C_V = \text{change in specific heat}$$

The first two terms increase with temperature, the third remains constant, and so ΔE_{vis} increases with temperature. Table V gives values for ΔE_{vis} and $\Delta E_{vap/n}$. Table I with values for ΔE_{vis} and $\Delta E_{vap/n}$ point for all liquids.

It is seen that ΔE_{vis} ranges from 1000 to 2000 cal. for liquids from which are shown in Table I. It has been made at 100°C., e.g., about 1000 cal. for all the values of ΔE_{vis} (since $\Delta E_{vap/n}$ is about 1000 cal. for the $n=3$ liquids (except for the liquids which show that even at 100°C. the temperature ΔE_{vis} at any temperature is a rough index of the value of ΔE_{vis} or more precisely of ΔE_{vis} is much greater than the unit of vaporization, the single unit of vaporization $\Delta E_{vap/n}$ reverse is indicated in Table I. It will be discussed in the next section.

^b ΔE_{vis} is the energy of activation of flow, which will be called the free energy of activation of flow, independent of temperature, increasing temperature.