

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

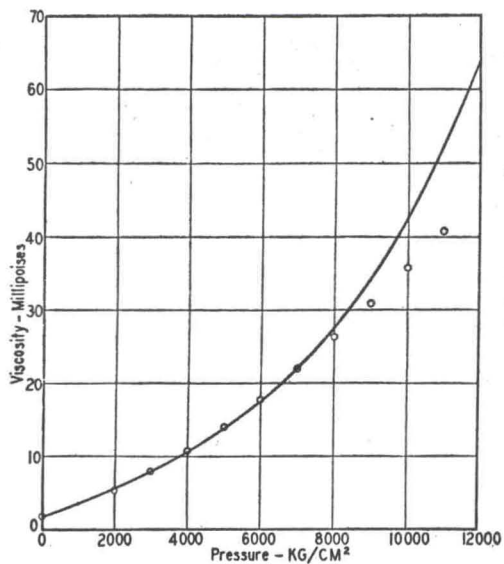


FIG. 6. Calculated and observed viscosities of ether as a function of the external pressure.

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

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

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

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.

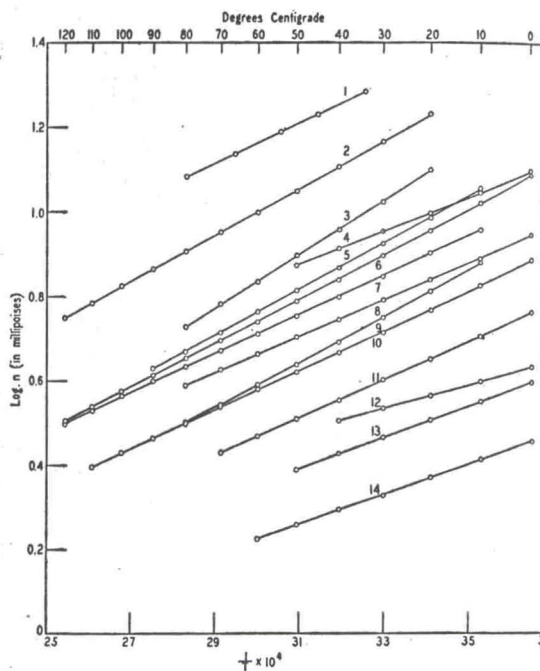


FIG. 7. Plots of $\log \eta$ vs. $1/T$ for some normal liquids.†

† 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 Empiric

If Eq. (4) i
we get

$$\Delta E_{vis}^b = Rd \ln$$

where $\alpha = \text{coe}$

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