

A theory of the viscosity of liquids

As is well-known, the viscosity of gases and its variation with temperature has received a satisfactory explanation on the basis of molecular theory. Little progress has, however, been made towards explaining the phenomena of the viscosity of *condensed media*—that is, of liquids and solids from a molecular point of view. What is evidently required is a working hypothesis which will indicate why, when a substance passes from the state of vapour to that of liquid, its absolute viscosity is greatly increased but *diminishes* with rising temperature, while that of the vapour *increases* in the same circumstances. I propose in this note to put forward briefly the outline of a theory which appears to have claims to serious consideration, as it indicates a quantitative relation between the viscosity of a liquid and of the corresponding vapour which is supported by the experimental data.

The manner in which transverse stress is propagated through a material medium is known in the cases in which the substance is in the state of vapour and in that of a crystalline solid. In the former case, momentum is transferred through the diffusion of the molecules between parts of the medium in relative motion, and this is a relatively slow process. In the crystal, on the other hand, the stress is transmitted in the form of transverse elastic waves, and the latter process, at least for ordinary displacements, is extremely rapid. We may conceive that in a liquid, momentum is transported partly by the first process and partly by the second, and that the effective viscosity depends on their relative importance. The ratio in which the two modes of propagation are operative may be determined from thermodynamical considerations, combined with certain simple suppositions regarding the constitution of a liquid.

We shall assume that the state of aggregation of the molecules in a liquid is of a composite character; some of the molecules are quite free to move, and may be termed "vapour" molecules; the others are attached to each other somewhat as in a crystal, and may be termed "crystalline" molecules. In determining the proportion of the two types, we shall consider only binary encounters between molecules. Let E_1 be the work required to separate a pair of molecules of the first type, and E_2 those of the second type. Then applying Boltzmann's distribution law, we may, as a first approximation, take the relative proportion of the two types of aggregation in the dissociation equilibrium to be as $e^{E_1/RT}$ to $e^{E_2/RT}$, where R is the gas-constant and T the absolute temperature. The next step is to determine the rate of transport of momentum through the medium. In the "vapour" part of the aggregation, the transport occurs by bodily movements. In

the "crystalline" part, the rate of transport may be considered to be practically infinite. The effective rate of transport in the liquid is therefore greater than in the vapour at the same temperature and pressure in the ratio $e^{E_2/RT}/e^{E_1/RT}$. The viscosity of the liquid is therefore given by the formula $\eta_{\text{liquid}} = \eta_{\text{vapour}} e^{(E_2 - E_1)/RT}$. Since $E_2 > E_1$ it follows that the viscosity of the liquid will *diminish* with rising temperature.

The next step is to determine the absolute magnitudes of the energy constants E_1 and E_2 . As was first pointed out by Sutherland, in the cases of gases and vapours the attractive forces between the molecules tend to *increase* the frequency of collisions and thus *diminish* the viscosity. The matter has been further examined by Chapman, who has shown that Sutherland's constant is one-sixth of the mutual potential energy of the molecules when in contact. It is convenient to use an amended form of Sutherland's formula and write

$$\eta_{\text{vapour}} \propto T_2 e^{-E_3/RT},$$

where E_3 is another energy-constant. From Chapman's work it would appear that $E_2 = 6E_3$, and we may also take $E_1 = E_3$. Hence, finally, we have

$$\eta_{\text{liquid}} = \eta_{\text{vapour}} e^{5E_3/RT}.$$

E_3 may be found from the data for the viscosity of vapour at different temperatures, and the formula thus enables the viscosity of the liquid to be calculated *a priori*.

To illustrate the matter, it will suffice to take the case of benzene as an example. The table shows the viscosity of liquid benzene at different temperatures as

Viscosity of benzene liquid
A = 0.0000951 B = 1237

Temperature	Calculated viscosity	Observed viscosity	Difference
7.67°	0.00781	0.00789	+8
13.46	0.00714	0.00717	+3
19.39	0.00654	0.00654	0
25.96	0.00595	0.00595	0
32.07	0.00549	0.00547	-2
38.47	0.00504	0.00502	-2
45.35	0.00464	0.00461	-3
51.66	0.00429	0.00429	0
57.37	0.00403	0.00402	-1
63.29	0.00377	0.00377	0
69.41	0.00353	0.00354	+1
73.36	0.00332	0.00333	+1

Viscosity of benzene vapour at 100° C = 0.0000930.
 $5E_2$ calculated from the value at 212.5° C is 1300.

determined by Thorpe and Rodgers, and also as calculated from an empirical equation of the type $\eta = Ae^{B/T}$.

It will be seen that the formula represents the viscosity of the liquid within an average error of 2 parts in a thousand; and that the constants A and B are in fair agreement with the values calculated from the data for the viscosity of the vapour. An empirical formula of the type $Ae^{B/T}$ is found to represent closely the variation of the viscosity of many liquids, especially at the higher temperatures. As we have assumed that the "vapour" molecules are identical with those actually found in the gaseous state, we cannot expect the experimental constants A and B to agree exactly with those indicated by the theory outlined in this note in all cases. Considerable deviations actually occur in the case of "associated" liquids, in which presumably the effect of the molecular fields of force cannot be handled so simply.

The further discussion of this question and of the extension of the theory to the case of dense vapours on one hand, and to supercooled liquids and amorphous solids on the other hand, offers a most interesting field of research. The treatment suggested can obviously be improved in several directions, especially in the discussion of the dissociation equilibrium between the two types of molecules, and the effect of high pressures on the viscosity of liquids could probably be explained by a more exact investigation.

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March 1