The viscosity of liquids

I wish very briefly to supplement the remarks made in a previous communication on this subject in which I have suggested that the viscosity of liquids and its variation with temperature may be explained on the hypothesis that the liquid state of aggregation is composite in character; that is, is composed in part of molecules "rigidly" attached to each other as in a solid, and in part of molecules which are relatively mobile as in the gaseous state (*Nature*, April 21, p. 532).

That the supposition made regarding the constitution of liquids is *prima facie* a reasonable one is, I think, clear from thermodynamical considerations. The liquid stands midway between the solid and the gas and has affinities to both. The volume of a liquid at temperatures slightly higher than the melting point is only moderately different from that of the solid, and hence the probability that many of the molecules are at any instant at the same distance from each other as in a solid is considerable. This probability may indeed be found from the latent heat of fusion of the substance. If W be the heat of fusion in ergs per mol, the number of molecules in the "rigid" and "mobile" states should be approximately, in the ratio $e^{W/RT}$.

The mechanism of viscous flow of a liquid is perhaps clearest if we consider the case of a thin layer enclosed between two parallel plates, one of which slides over the other. When a steady state is reached, the "rigid" parts of the liquid move practically as complete wholes, and hence the effect of their existence is to diminish the thickness of the layer through which momentum has to be transported by the "mobile" molecules, and thus to increase the viscosity. As a rough approximation, this increase is in the proportion of the numbers of the two types of molecules. A more exact theory should take into account also the volumes occupied by the two types of aggregation and their changes with temperature.

The effect of pressure on viscosity of liquids would arise in two distinct ways. In the first place, we have a change of volume on fusion, and hence, by the Le Chatelier–Braun principle, the assumed dissociation from the "solid" to the "mobile" aggregation would be retarded by pressure, so that the viscosity should be increased. With substances such as ice which contract on melting, we have the opposite effect. In the second place, pressure diminishes the volume occupied by the "mobile" molecules, and therefore also the distance through which they have to transport momentum. This would increase the viscosity. At temperatures not much higher than the melting point, the first effect would preponderate. This is

strikingly illustrated in the case of water, the pressure-coefficient of viscosity of which is negative up to 32° C, that is, even at temperatures much higher than that of maximum density.

C V RAMAN

210 Bowbazaar Street Calcutta
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