

mentioned above. Whatever the units of flow may be, the summation of the flow processes must, of course, add up to the gross composition of the liquid.

The formulation of the entropy of activation of flow in these complex liquids is generally impossible so that the best that can be done is to assume that it is the same at different temperatures and pressures for the same liquid, or that it is the same at different compositions of a liquid mixture, such as a series of $\text{Na}_2\text{O}-\text{SiO}_2$ glasses. For instance, in the calculation of the change of viscosity of a lubricating oil with pressure it was assumed that the entropy of activation was the same at different pressures. These are only approximations, but often give useful results. In any case the entropy factor is not as important as the energy factor, and a high energy of activation will always mean a high viscosity, and *vice versa*.

The degree of structure in the liquids of Group II changes with the temperature. The higher the temperature the fewer bonds are present in the liquid and the weaker these bonds are. As a result of one or both these factors the energy of activation of flow for such liquids becomes less and less with increasing temperature. Fig. 8 shows plots of $\log \eta$ vs. $1/T$ for some liquids representing Groups I(b), II(a) and II(b). The curves are all practically straight at viscosities greater than 10^9 poises, and this means that in this range the bond structure of these liquids has become constant and probably that the maximum possible number of bonds have been formed, e.g., four Si-O bonds per SiO_2 in silica glass.

Glasses and Resins

Glasses and resins are grouped together because they are in reality identical in the basis of their properties and in their *raison d'être*. Glasses and resins are both found in Groups I(b) (e.g., selenium and polyisobutylene), II(a) (e.g., glucose and cresol-formaldehyde resin), and II(b) (e.g., silica and glyptal), and for the same reasons. The liquids of Group II readily supercool and vitrify since the energy of orienting a molecule preparatory to crystallization involves the breaking of structural bonds. Hence the energy of activation for the crystallization

process is very high, and the rate of crystallization is extremely slow.^c Since hydrogen bonds are relatively weak (about 6000 cal.), the tendency to vitrify is not as strong in Group II(a) as in II(b).

The Group I(b) liquids usually vitrify, and the reason for this is usually stated to be that the tangled "brush heap" structure of the long chains prevents crystallization. More precisely stated, the orientation required for crystallization involves a large decrease in entropy for these long chains so that the entropy of activation for the crystallization process is a large

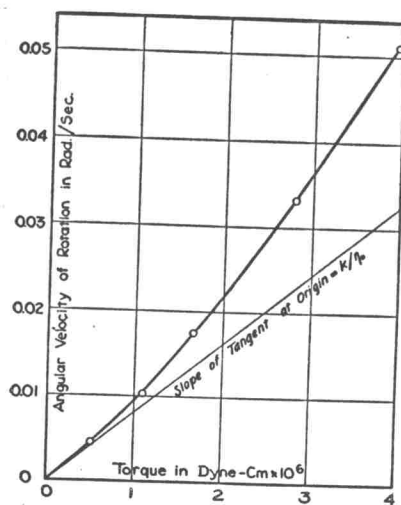


Fig. 10. "Consistency" curve for polyisobutylene at 275.8°K. ||

negative number and $-T\Delta S$ is a large positive number, and the rate of crystallization is very slow, even though the energy of activation may not be very large. In addition, these long chain glass-forming liquids are composed of chains of varying lengths, possibly several hundred different molecular species, as in the polystyrene resins, and it may be that there is never a stable crystalline phase, until temperatures corresponding to extremely high viscosities are reached. The same may be true for mixtures of hydrocarbons such as lubricating oils.

^c The rate of crystallization has, of course, no relation to the magnitude of the thermodynamic free energy change on crystallization.

|| After J. D. Ferry and G. S. Parks, *Physics*, 6, 359 (1935).

The structure has been studied by workers. Silica with each silicon tetrahedrally that whatever four Si-O bonds of flow. The energy to be about 1 so ΔE_{vis} shows energy, or 20 which this for complete. The slope by 2.303R gives

The addition reduces the viscosity a structure in bridges are bound ONa_2O Fig. 9, taken The sodium and the inter the following and $\text{O}_1-\text{O}_1=$ repulsions, all bridge, and a bridge breaks indicated by this requires flow may be, If three of the ONa_2O bridge 185,000 cal.; if ONa_2O bridge 170,000 cal., the lower will lower the viscosity composition is accounted for Similar consistency glasses, such as replacement of $-\text{O}-\text{Si}$ bridge this bridge is viscosity measurements of glasses show that