# Contributed Original Research

## Pressure and Temperature Effects on the Viscosity of Liquids*

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The free energy of activation for viscous flow is related to an entropy and energy of activation by the same equations as any equilibrium. This, for the theory of viscosity is perfectly general and independent of the mechanism. The rolling over each other of pairs of molecules lying in adjoining layers is the mechanism which appears to be the most probable, and the equations for this bimolecular flow process are developed here. At low pressures the heat of activation for viscous flow is about one-third the energy of vaporization, but as the pressure is raised, it increases rapidly because of the work term, $PV/n'$. Here $P$ is the external pressure, $V$ is molal volume and $V/n'$ is the extra volume required before the flow process can take place. Calculations made for *n*-pentane, ether, benzene, iso-pentane, water, and mercury over as extended a temperature and pressure range as the data permit are found to agree satisfactorily with the experimental viscosity. The results are interpreted in terms of the liquid structure and the mechanism of viscous flow. The results of applying our theory to the liquids for which the necessary data is available show that the effect of pressure on viscosity can be calculated *a priori*, with thermodynamic data only, with reasonable success.

THE general equation for the rate of any process in which matter rearranges by surmounting a potential energy barrier has been proposed in the following form:[1-3]

$$k' = \kappa(F^*/F_n)(\bar{p}/m^*), \tag{1}$$

where $F^*$ is the partition function for the activated complex per unit length normal to the potential barrier, $\bar{p}$ is the corresponding average momentum, and $m^*$ is the reduced mass. $F_n$ is the partition function for the normal state; $\kappa$ is the transmission coefficient, the chance that a system having once crossed the potential barrier will react and not recross in the reverse direction. Eq. (1) states that the absolute rate of a reaction is the product of the number of molecules per unit length in phase space at the top of the barrier by the velocity at the top of the barrier, multiplied by an efficiency factor.

We assume that there is no "tunneling" under the barrier, and that the activated complex has nearly all the properties of an ordinary molecule except that instead of having only the three regular translational degrees of freedom, it has a fourth, along which it approaches the barrier, crosses it, and flies to pieces. We can now write $(F^*/F_n)$ as $(F^\ddagger/F_n)(2\pi\mu^* kT)^{\frac{1}{2}}/h \exp(-\Delta E_0/kT)$ where $F^\ddagger$ is the partition function of the activated complex without the fourth degree of translational freedom per unit length represented by $(2\pi\mu^* kT)^{\frac{1}{2}}1/h$, and $\Delta E_0$ is the energy of activation. The usual expression for the average velocity in the forward direction across the barrier is:

$$(\bar{p}/\mu^*) = (kT/2\pi m^*)^{\frac{1}{2}} \tag{2}$$

and Eq. (1) becomes

$$\begin{aligned} k' &= \kappa(F^\ddagger/F_n)(2\pi m^* kT)^{\frac{1}{2}}/h \\ &\quad \times \exp(-\Delta E_0/kT)(kT/2\pi m^*)^{\frac{1}{2}} \\ &= \kappa(F^\ddagger/F_n)kT/h \exp(-\Delta E_0/kT). \end{aligned} \tag{3}$$

Assuming $\kappa = 1$, this becomes

$$k' = (F^\ddagger/F_n)(kT/h) \exp(-\Delta E_0/kT).$$

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[1] H. Eyring, J. Chem. Phys. **3**, 107 (1935).
[2] Evans and Polanyi, Trans. Faraday Soc. **21**, 875 (1935).
[3] W. Wynne-Jones and H. Eyring, J. Chem. Phys. **3**, 492 (1935).