

ously in such a way as to pass each other. If the coordinates of molecule one are  $x_1, y_1, z_1$  and of two  $x_2, y_2, z_2$ , it is convenient to replace these with the three coordinates of the center of gravity of the pair

$$\begin{aligned} X &= (m_1x_1 + m_2x_2)/(m_1 + m_2), \\ Y &= (m_1y_1 + m_2y_2)/(m_1 + m_2), \\ Z &= (m_1z_1 + m_2z_2)/(m_1 + m_2), \end{aligned}$$

and the three components of the distance between the pair  $x = x_2 - x_1$ ,  $y = y_2 - y_1$ ,  $z = z_2 - z_1$ . Now if the direction of flow is in the  $x$  direction, the activated state will correspond to  $x = 0$ , and we can speak of  $x$  as the reaction coordinate. Using classical mechanics which is adequate for viscous flow in the cases with which we are here concerned, we obtain:

$$\begin{aligned} (F^\ddagger/F_n)(kT/h) &= \delta q \int_0^\infty \exp(-p^2/2\mu^*kT) (p/\mu^*\delta q) dp \left[ \int_{-\infty}^{+\infty} \exp(-p^2/2\mu^*kT) \int_0^{V_f^\ddagger} dx \right]^{-1} \\ &= (kT/2\pi\mu^*)^{1/2} \cdot V_f^{-1} = (kT(m_1+m_2)/2\pi m_1 m_2)^{1/2} V_f^{-1}. \quad (9) \end{aligned}$$

The arbitrary length,  $\delta q$ , along the reaction path normal to the top of the potential barrier is seen to cancel out of the final result. Here we have assumed that  $F^\ddagger$  and  $F_n$  cancel for all degrees of freedom except the reaction coordinate. The reduced mass in the  $x$  direction is  $\mu^* = m_1 m_2 / (m_1 + m_2)$ . The limits 0 to  $V_f^\ddagger$  for  $x = x_1 - x_2$  in the above integral follow from the fact that configurations of the normal state for which  $x_1 > x_2$ , only, are to be considered.

This then gives us

$$F_n/F^\ddagger = (2\pi\mu^*kT)^{1/2} V_f^\ddagger/h, \quad (10)$$

where  $V_f$  is the free volume, defined as the total integral over that part of the potential energy which is due to thermal displacements of the center of gravity from its equilibrium position.

Combining Eqs. (8) and (10) we have

$$\eta = \lambda_1/\lambda^2 \lambda_2 \lambda_3 (2\pi\mu^*kT)^{1/2} V_f^\ddagger \exp(\Delta E_{\text{visc}}/kT). \quad (11)$$

If  $\lambda$  is equal to  $\lambda_1$ ,

$$\lambda_1/\lambda^2 \lambda_2 \lambda_3 = N/V \quad (12)$$

and we have

$$\eta = (\pi RMT)^{1/2} / V (V_f^\ddagger/N^{1/2}) \exp(\Delta E_{\text{visc}}/RT), \quad (13)$$

in which all units are now molar. Since we have assumed the process bimolecular, we have written  $N\mu^* = (N(m_1 m_2 / m_1 + m_2)) = M/2$ .

Kincaid and Eyring<sup>9</sup> develop the equation  $V_f^\ddagger = (u_g/u_l) V_l^\ddagger$  where  $u_g$  is the velocity of sound in the gas and  $u_l$  the velocity of sound in the liquid. Substituting we get

<sup>9</sup> Kincaid and Eyring, J. Chem. Phys. 6, 620 (1938).

$$\eta = (\pi RMT)^{1/2} N^{-1/2} (u_g/u_l V_l^\ddagger) \times \exp(\Delta E_{\text{visc}}/RT). \quad (14)$$

Both velocities may be evaluated by the hydrodynamic formula  $u = (v/\beta_s)^{1/2}$  where  $v$  is the specific volume and  $\beta_s$  the adiabatic compressibility. This becomes  $u_g = (\gamma RT/M)^{1/2}$  for an ideal gas, where  $\gamma$  is the ratio of specific heat at constant pressure to that at constant volume.

We must now evaluate  $\Delta E_{\text{visc}}$ , the energy of activation for viscous flow. This energy is required to adjust the surroundings of a pair of molecules so that they can pass each other. At comparatively low pressures all that is needed is that some fraction of the bonds between two adjacent molecules and their neighbors be broken or stretched enough so that this pair can pass by each other. The energy of activation for viscous flow at low pressures turns out to be about  $\frac{1}{4}$  the energy of vaporization. Our equation now becomes

$$\eta = (\pi RMT)^{1/2} N^{-1/2} (u_g/u_l V_l^\ddagger) \times \exp(\Delta E_{\text{vap}}/nRT), \quad (15)$$

where  $n$  is a constant lying between 3 and 5 for normal liquids. The fraction of bonds broken is a function of the type of molecule and the structure of the liquid. For any normal liquid the fraction of bonds broken will not vary with the temperature, i.e.,  $n$  is a constant. Hence the empirical rule,  $\eta = A \exp(B/T)$ .

This evaluation of the activation energy for viscous flow holds at comparatively low pressures only, for only then can we neglect the work of expansion against the external pressure necessary