

We now review⁴⁻⁶ briefly the application of this general theory of reaction rates to liquids and treat certain aspects more explicitly. The most probable mechanism of liquid flow is the rolling past each other to new equilibrium positions of pairs of molecules in adjoining layers; the frequent occurrence of this basic process shifts the layers of molecules and constitutes flow. This process is illustrated in Fig. 4 of Hirschfelder, Stevenson and Eyring.⁷ The configuration in which the molecules are halfway by each other, having broken part of their bonds and having also accumulated the necessary extra space, constitutes the activated complex. The activation energy required for the passing of the molecules is the energy of activation of viscous flow, $\Delta E_{vis} (\equiv \Delta E_0)$.

The distance measured along the velocity gradient between two neighboring pairs of molecules sliding past each other is taken as λ_1 . The average distance between equilibrium positions in the direction of motion is taken as λ while the distance between neighboring molecules in this same direction is λ_2 , which may or may not equal λ . λ_3 indicates the molecule-to-molecule distance normal to the direction of motion and to λ_2 and λ_1 . By definition we have for the viscosity $\eta = f\lambda_1/\Delta v$. Here f is the force per square centimeter tending to displace one layer with respect to the other, and Δv is the difference in velocity of these two layers which are at a distance λ_1 apart. The force acting on a single molecule is $f\lambda_2\lambda_3$, and it acts to lessen the work of passing over the barrier through a distance $\lambda/2$, so that in the forward direction the height of the barrier is in effect lowered by the amount $f\lambda_2\lambda_3\lambda/2$, while in the backward direction it is raised by the same amount. The number of times that a molecule moves in the forward direction in a second may be written as the corresponding specific reaction rate:

$$k_f = (F^\ddagger/F_n)kT/h \times \exp [-(2\Delta E_0 - f\lambda_2\lambda_3\lambda)/2kT]. \quad (4)$$

For the backward direction:

$$k_b = (F^\ddagger/F_n)kT/h \times \exp [-(2\Delta E_0 + \lambda_2\lambda_3\lambda)/2kT]. \quad (5)$$

⁴ H. Eyring, *J. Chem. Phys.* **4**, 283 (1936).

⁵ R. H. Ewell and H. Eyring, *J. Chem. Phys.* **5**, 726 (1937).

⁶ H. M. Smallwood, *J. App. Phys.* **8**, 505 (1937).

⁷ Hirschfelder, Stevenson and Eyring, *J. Chem. Phys.* **5**, 896 (1937).

Hence:

$$\begin{aligned} \Delta v &= \lambda(k_f - k_b) \\ &= \lambda(F^\ddagger/F_n)kT/h \\ &\quad \times \exp(-\Delta E_0/kT) \{ \exp f\lambda_2\lambda_3/2kT \\ &\quad \quad \quad - \exp(-f\lambda_2\lambda_3\lambda/2kT) \} \\ &= \lambda(F^\ddagger/F_n)kT/h \\ &\quad \times \exp(-\Delta E_0/kT) 2 \sinh(f\lambda_2\lambda_3\lambda/2kT) \end{aligned} \quad (6)$$

and

$$\eta = f\lambda_1/\Delta v = f\lambda_1[\lambda(F^\ddagger/F_n)kT/h \times \exp(-\Delta E_0/kT) 2 \sinh(f\lambda_2\lambda_3\lambda/2kT)]^{-1}. \quad (7)$$

Now for ordinary viscous flow $f\lambda_2\lambda_3\lambda \ll kT$, so that expanding the exponential and keeping the first power terms only we have after cancellation:

$$\begin{aligned} \eta &= \lambda_1 kT [\lambda^2 \lambda_2 \lambda_3 (F^\ddagger/F_n) kT/h \\ &\quad \times \exp(-\Delta E_0/kT)]^{-1} \\ &= (\lambda_1 h / \lambda^2 \lambda_2 \lambda_3) (F_n / F^\ddagger) \exp(\Delta E_0/kT). \end{aligned} \quad (8)$$

It is interesting to check the assumption $f\lambda_2\lambda_3\lambda \ll kT$. While Bridgman⁸ does not give the exact data necessary to compute f , we can determine its order of magnitude. The annular space between the falling weight and the cylinder wall in his experiment was of the order of 10^{-2} cm. The weight fell at a velocity roughly of the order of 1 cm/sec. Viscosity is defined by the equation: $\eta = fd/\Delta v$ where d is the distance between the layers across which the velocity gradient Δv is measured.

$$f = \eta \Delta v / d \approx 10^{-2} / 10^{-2} = 1 \text{ dyne/cm.}^2$$

Since

$$\begin{aligned} \lambda_2 \lambda_3 \lambda &\approx V/N \\ f \lambda_2 \lambda_3 \lambda &\approx 10^2 / 10^{23} = 10^{-21} \\ T &\approx 300^\circ K \\ k &\approx 10^{-16} \text{ erg/deg./mole} \\ kT &\approx 10^{-14}. \end{aligned}$$

So we are justified by a factor 10^{-7} in assuming $f\lambda_2\lambda_3\lambda \ll kT$. We develop somewhat more fully than has been done previously the form of the general expression

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

for the particular case of a bimolecular process. By bimolecular we mean that molecules one and two in two contiguous layers move simultane-

⁸ P. M. Bridgman, *The Physics of High Pressure* (Macmillan Co., 1931).

ously in such coordinates of x_1, y_2, z_2 , it is co three coordina pair

$$\begin{aligned} X &= \\ Y &= \\ Z &= \end{aligned}$$

$$(F^\ddagger/F_n)(kT/h)$$

The arbitrary path normal to is seen to carry we have assumed all degrees of ordinate. The is $\mu^* = m_1 m_2 / (x = x_1 - x_2$ in the fact that configuration which $x_1 > x_2$,

This then gives

$$F_n$$

where V_f is the integral over which is due center of grav

Combining

$$\eta = \lambda_1 / \lambda^2 \lambda_2 \lambda_3 (2$$

If λ is equal

and we have

$$\tau = (\pi R M T)^{1/2} /$$

in which all un assumed the pr $N\mu^* = (N(m_1 m$

Kincaid and $V_f^1 = (u_0/u_1) V$ in the gas and liquid. Substit

⁹ Kincaid and

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