

where  $f$  = force per sq. cm tending to displace one layer with respect to another  
 $\lambda$  = distance between equilibrium positions in the direction of flow  
 $\lambda_2$  = distance between adjacent molecules in the direction of flow  
 $\lambda_3$  = distance between molecules in the plane of flow and normal to the direction of flow.

The area of a molecule in the plane of flow will be  $\lambda_2\lambda_3$ , the force acting on the molecule will then be  $f\lambda_2\lambda_3$ , and if the force acts through a distance  $\lambda/2$ , the energy of activation will be raised or lowered by  $\frac{1}{2}f\lambda_2\lambda_3\lambda$ . Fig. 2 shows these energy relations diagrammatically.

The viscosity is given hydrodynamically by

$$\eta = \frac{f\lambda_1}{\Delta V} = \frac{f\lambda_1}{\lambda(k_f - k_b)}$$

where  $\lambda_1$  = perpendicular distance between adjacent layers of molecules,  
 $\Delta V$  = difference in velocity of two layers a distance  $\lambda_1$  apart  
 $= \lambda(k_f - k_b)$ ,

so that

$$\eta = \frac{f\lambda_1}{\lambda k_1 (e^{f\lambda_2\lambda_3\lambda/2kT} - e^{-f\lambda_2\lambda_3\lambda/2kT})}$$

$$= \frac{f\lambda_1}{\lambda k_1^2 \sinh f\lambda_2\lambda_3\lambda/2kT} \quad (2)$$

The expansion of  $\sinh x$  is  $\sinh x = x + 1/6x^3 + 1/120x^5 + \dots$ , so that for ordinary viscous flow, where  $f\lambda_2\lambda_3\lambda/2 \ll kT$ ,

$$\sinh f\lambda_2\lambda_3\lambda/2kT \cong f\lambda_2\lambda_3\lambda/2kT$$

and we have

$$\eta = \frac{\lambda_1 h}{\lambda^2 \lambda_2 \lambda_3} \frac{F_n}{F_a^*} e^{\Delta E_a/kT} \quad (3)$$

Eq. (2) may be considered the fundamental equation of flow, and also Eq. (3) with the limitation mentioned.

Now if we assume that a molecule flows one intermolecular distance in each elementary process, i.e., that  $\lambda = \lambda_2$ , and for an equant molecule  $\lambda_1 = \lambda_2 = \lambda_3$

$$\lambda_1/\lambda^2 \lambda_2 \lambda_3 = N/V,$$

where  $N$  = Avogadro's number  
 $V$  = molar volume.

If we assume that the degree of freedom corresponding to flow is a translational one, and that other degrees of freedom are the same for the initial and activated states:

$$\frac{F_n}{F_a^*} = \frac{((2\pi mkT)^{3/2}/h^3) V_f F_{rot} F_{vib}}{(2\pi mkT/h^2) V_f^3 F_{rot} F_{vib}} = \frac{(2\pi mkT)^{1/2}}{h} V_f^2$$

where  $V_f$  = the free volume per molecule. Eyring and Hirschfelder<sup>4</sup> have formulated the free volume

$$V_f^2 = \frac{bRT}{V^2 N^2 (p + a/V^2)} \text{ per molecule}$$

$$= \frac{bRTV^2}{N^2 \Delta E_{vap}} \text{ if } \frac{a}{V^2} = \frac{\Delta E_{vap}}{V} \gg p,$$

where  $\Delta E_{vap}$  = energy of vaporization per mole  
 $= \Delta H_{vap} - \Delta(pv)$ ,

$b = 2$  for simple cubic packing and has not very different values for other types of packing.

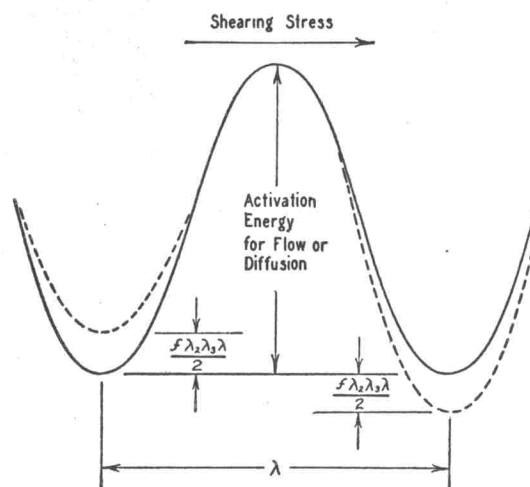


FIG. 2. Energy profile of the path of a flowing molecule.

As stated before the activation energy takes the form of providing a hole for the molecule to flow into, but this may not necessarily have to be a hole the full size of a molecule. A consideration of the attractive and repulsive forces involved in vaporization shows that for any liquid the energy

required to leave a molecule (neglecting either making of transfer without leaving a hole) is discussed. Thus the activation energy will be something,  $\Delta E_a =$  Combinations of Eq.

$$\eta = \dots = 1$$

if we take  $b$  per mole.

On testing values of viscosity for the experiment of viscometers for liquids containing molecules of polar or electric character the closest agreement is for carbon tetrachloride. As an example for each liquid the coefficient of viscosity for carbon tetrachloride is of observed values.

The fact that two classes of molecules (C<sub>2</sub>H<sub>4</sub>Br<sub>2</sub>) were significant. The molecules are approximately spherical. This is and is very

$n = 3$	CCl <sub>4</sub>
$n = 3\frac{1}{2}$	C <sub>2</sub> H <sub>4</sub>
$n = 4$	pentane, ether, CH <sub>3</sub>

\* The anomaly is due to its paramagnetism for the ethylene halides.