where f = force per sq. cm tending to displace one layer with respect to another

λ = distance between equilibrium positions in the direction of flow

λ_2 = distance between adjacent molecules in the direction of flow

λ_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 λ_1 = perpendicular distance between adjacent layers of molecules,

ΔV = difference in velocity of two layers a distance λ_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 $\sinh x = x + 1/6x^3 + 1/120x^5 + \cdots$, 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:

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

where V_f = the free volume per molecule. Eyring and Hirschfelder[4] have formulated the free volume

$$V_f^{\frac{1}{3}} = \frac{bRT}{V^{\frac{1}{3}}N^{\frac{1}{3}}(p+a/V^2)} \text{ per molecule}$$

$$= \frac{bRTV^{\frac{1}{3}}}{N^{\frac{1}{3}}\Delta E_{vap}} \quad \text{if} \quad \frac{a}{V^2} = \frac{\Delta E_{vap}}{V} \gg p,$$

where ΔE_{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.
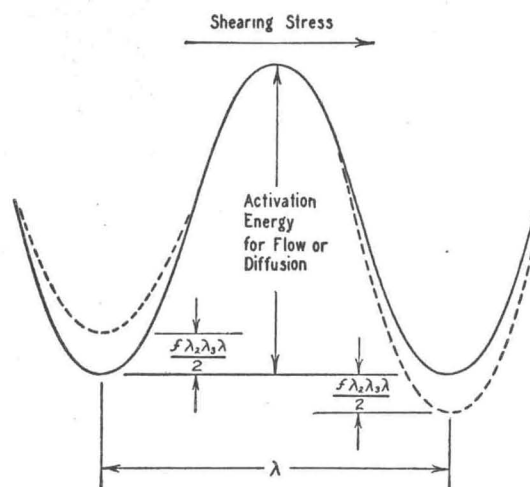

FIG. 2. Energy profile of the path of a flowing molecule.

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 m (neglecting either maki of transferr without lea discussion of Thus the a will be som tion, $\Delta E_a =$

Combinir ties of Eq.

$$\eta = \frac{N}{}$$

$$= 1$$

if we take b per mole.

On testir values of v density for the experim cient of vis liquids con molecules a polar or el the closest As an exam for each liqu for carbon te of observed

The fact two classes $C_2H_4Br_2$) w significant. mately sphe cules. This i and is very

$n=3$	CCl₄
$n=3\frac{1}{2}$	C_2H
$n=4$	pent
	ethe
	CH_3

* The anomaly to its paramagnet for the ethylene h

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