Viscosity, Plasticity, and Diffusion as Examples of Absolute Reaction Rates

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Since to form a hole the size of a molecule in a liquid requires almost the same increase in free energy as to vaporize a molecule, the concentration of vapor above the liquid is a measure of such "molecular" holes in the liquid. This provides an explanation of the law of rectilinear diameters of Cailletet and Mathias. The theory of reaction rates yields an equation for absolute viscosity applicable to cases involving activation energies where the usual theory of energy transfer does not apply. This equation reduces to a number of the successful empirical equations under the appropriate limiting conditions. The increase of viscosity with shearing stress is explained. The same theory yields an equation for the diffusion coefficient which when combined with the viscosity and applied to the results of Orr and Butler for the diffusion of heavy into light water gives a satisfactory and suggestive interpretation. The usual theories for diffusion coefficients and absolute electrical conductance should be replaced by those developed here when ion and solvent molecule are of about the same size.

INTRODUCTION

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]

$$k' = \mathcal{K}(F_a/F_n)(\bar{p}/m^*). \tag{1}$$

Here F_a is the partition function for the activated complex per unit of length along the coordinate normal to the top of the potential barrier. The average velocity $\bar{p}/m^*$ along this coordinate must of course be expressed in these same units of length, $\bar{p}$ and m^* being the corresponding average momentum and reduced mass, respectively. F_n is the partition function for the normal state and $\mathcal{K}$, the transmission coefficient, is the chance that a system having once crossed the potential barrier will react and not recross in the reverse direction. In (1) both partition functions are to be measured from the same zero of energy.

If the curvature normal to the barrier is sufficiently small we may treat motion in this direction as a pure translation, in which case (1) becomes:

$$k' = \mathcal{K}\frac{F_a^*}{F_n}\frac{kT}{h}e^{-E_0/kT}. \tag{2}$$

Here F_a^* differs from F_a in two ways. First it is calculated by using a zero of energy higher by E_0 than for F_n and secondly the partition function for the degree of freedom normal to the

barrier is omitted from F_a^* and included in the frequency factor kT/h. Here k, T and h are the Boltzmann constant, the absolute temperature, and the Planck constant, respectively.

The potential surface along the degree of freedom normal to the barrier is really curved and we can take account of "tunneling" up to terms involving the second power of h by multiplying (2) by the factor $(1+(1/24)(h\nu/kT)^2)$ to give

$$k' = \mathcal{K}\frac{F_a^*}{F_n}\frac{kT}{h}\exp\left(-\frac{E_0}{kT}\right)\left(1+\frac{1}{24}\left(\frac{h\nu_n}{kT}\right)^2\right), \tag{3}$$

where $i\nu_n = (1/2\pi)(f_n/m^*)^{\frac{1}{2}}$ and f_n and m^* are the force constant and reduced mass normal to the top of the potential barrier.[2] f_n is negative. The ratio of partition functions in (2) and (3) can be written as the equilibrium constants $K = F_a/F_n$ and $K^* = F_a^* e^{-E_0/kT}/F_r$ and all the thermodynamic and statistical mechanical methods for treating or discussing any equilibrium constant are available for reaction rates.

Now if we actually calculate our potential energy surfaces and particularly if we are discussing isotope effects we may prefer to write (3) in the entirely equivalent form:

$$k' = \mathcal{K}\left(\frac{F_a^*}{F_n}\right)_c\frac{kT}{h}\left(1+\frac{1}{24}\left(\frac{h\nu_n}{kT}\right)^2\right)$$
$$\exp\left(-E_c/kT\right). \tag{4}$$

Here instead of using E_0 the actual activation energy at the absolute zero we use E_c the "classi-

[1] (a) Eyring, J. Chem. Phys. **3**, 107 (1935); (b) Evans and Polanyi, Trans. Faraday Soc. **21**, 875 (1935); (c) Wynne-Jones and Eyring, J. Chem. Phys. **3**, 492 (1935).

[2] Wigner, Zeits. f. physik. Chemie **B19**, 203 (1932).

cal activation energy at the absolute zero." This simply involves absorbing the corresponding zero point energies in the partition functions. Thus in the ratio F_a*/F_n in (2) and (3) the partition function corresponding to the normal vibration ν_i is written as $(1-\exp (h\nu_i/kT))^{-1}$. In $(F_a*/F_n)_c$ in (4) this same partition function is written as:

$$\left[\exp\left(-\frac{h\nu_i}{2kT}\right)\left(1-\exp\left(-\frac{h\nu_i}{kT}\right)\right)^{-1}\right]$$
$$= (2 \sinh h\nu_i/2kT)^{-1}.$$

There is of course no real difference between (3) and (4) and they can be used interchangeably.

Now in certain reactions such as associations of atoms and of some types of radicals there is no activation energy and, therefore, no activated state. However, when we treat the energy of rotation as a potential energy there is an activation energy and the procedure described above becomes immediately applicable.[3]

The Theory of Holes and the "Law of Rectilinear Diameters" of Cailletet and Mathias

Suppose we have N molecules forming a liquid. Then each of them is bound to the others by bonds adding up to the total energy $E = \sum_i n_i E_i$ where n_i is the number of bonds of a particular kind each of which has the bond strength E_i. To vaporize the N molecules requires an energy of exactly $NE/2$, since each bond belongs to two molecules. Therefore to vaporize a single molecule requires the energy $E/2$ providing no hole is left in the liquid. However, if we vaporize one molecule leaving the hole we must supply exactly the energy E. If we then return this gas molecule to the liquid we get back the energy $E/2$; so that it requires rigorously the same energy $E/2$ to make a hole in a liquid of a size which will just accommodate a single molecule, as it does to vaporize one molecule without leaving a hole. Stated differently it takes just the same energy for a hole the size of a molecule to detach itself from the empty space above a liquid and pass into the liquid as it does for a molecule to detach

itself from the liquid and pass into the empty space. Now a molecule in empty space because it can move around freely has a considerably higher entropy than in the liquid state. That is to say it has accessible to it a large number of different states which it can assume without increasing its energy. Exactly the same is true of the hole dissolved in the liquid. A hole can take up a great many different positions in the liquid each of which has exactly the same energy. If we imagine ourselves watching these holes we would see them darting in a random fashion through the solution with a velocity characteristic of the liquid molecules at this temperature. A liquid is much like a crystal in having a more or less definite lattice arrangement. Wherever there is a hole a neighboring molecule can jump into the empty lattice point leaving a hole behind and as this process goes on continuously each hole contributes in effect a new degree of translation to the liquid. Below the critical temperature this translation in the liquid is not quite as free as in the vapor phase so that the apparent partition function to be used for the holes is somewhat smaller than for vapor molecules. At the critical temperature, however, the mobilities and therefore the two partition functions become equal. Thus for holes dissolved in liquids as for molecules dissolved in empty space we have the theorem of equal (or very nearly equal) entropies as well as energies. Now how much energy is required for the association or dissociation of holes of about molecular size depends of course upon the solvent. However, since these processes take place both in the gas and the liquid phase we assume as a first approximation that association or dissociation will not affect the distribution ratio of holes between the phases. In that case at the critical temperature we should have exactly as much matter in a cc of otherwise empty space as we have holes in a cc of matter. As we lower the temperature a plot of this average density against temperature would almost parallel the temperature axis, the density increasing slightly as the temperature decreases. Thus the average density of the vapor and liquid phase should to this approximation be nearly independent of the vapor pressure (or the temperature). Now the law of rectilinear diameters states that for actual cases such a plot of average

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[3] Eyring, Gershinowitz and Sun, J. Chem. Phys. **3**, 786 (1935).

density is a straight line but that it may and in general is somewhat inclined with respect to the temperature axis. Thus the law of Cailletet and Mathias follows from the statistical mechanical consideration of holes.

The theorem of equal energy, and approximately equal entropy for holes in matter as for molecules in empty space frequently applies in the same way to solids as to liquids, and the concentration of the vapor is then a rough measure of the number of holes in the condensed phase. Polarization forces necessitate modification of this idea of equal energy in some solids as Schottky has pointed out.[4]

The theory of holes is important for all phenomena in which a part of the matter in a condensed phase moves with respect to other parts, since at the borders of holes such motions can be set up with a minimum of disturbance to molecules not participating in the motion. In certain phenomena it may be simpler to fix attention on the few holes than the much more numerous molecules. Thus in the melting of crystals the disorder which must set in by one group of molecules first moving with respect to a second group and so releasing the latter from a part of their restraining potential (this in turn releasing a third group, etc.) may begin at a hole. More probably, however, it will begin at a crystal boundary since the heat is ordinarily supplied there. If the melting involves expansion then small holes will not permit the melting to go far just as reactions involving expansions cannot take place except at an interface. Sharp melting points only occur in well ordered crystals, not for example in glasses. This is as we would expect since only in very precisely ordered arrangements can the attainment of a critical motion by a few molecules profoundly affect the stability of neighbors and these in turn release still others from their restraining potential. The problem of order-disorder has been discussed at length by Bragg and Williams,[5] by Fowler and others.[6]

Some support for the general point of view with respect to holes as developed here may be obtained from discussions of the Wilson theory of semiconductors. In this theory electrical conductance is assumed to arise from thermal fluctuations which raise an electron of low energy up to the conduction levels leaving a positive hole behind. The theory seems to account satisfactorily for the observed facts.[7] We now proceed to develop a theory of viscosity in condensed phases from the point of view of absolute reaction rates.

VISCOSITY

The perpendicular distance between two neighboring layers of molecules sliding past each other is taken as λ_1. The motion is assumed to take place by an individual molecule in a plane (or layer) occasionally acquiring the activation energy necessary to slip over the potential barrier (arising from squeezing against its neighbors) to the next equilibrium position in this same plane. The average distance between these 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. The molecule to molecule distance in the plane normal to the direction of motion is written as λ_3. 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 a distance λ_1 apart. Now the number of times that a molecule moves in the forward direction in a second may be written as the corresponding specific reaction rate

$$k_f = 3C\frac{F_a^*}{F_n}\frac{kT}{h}\left(1 + \frac{1}{24}\left(\frac{h\nu_i}{kT}\right)^2\right)$$
$$\exp\left(-\frac{(E_0 - \frac{1}{2}f\lambda_2\lambda_3\lambda)}{kT}\right) = k_1\exp\frac{f\lambda_2\lambda_3\lambda}{2kT}, \quad (5)$$

Here k_1 is the absolute rate for the transition (see Eq. (3)) when no force is applied. The significance of the term $\exp f\lambda_2\lambda_3\lambda/2kT$ may be seen as follows. The force acting on a single molecule is clearly $f\lambda_2\lambda_3$ and it acts to lessen the work of passing over the barrier through a distance $\lambda/2$;

[4] Schottky, Zeits. f. physik. Chemie B29, 335 (1935).
[5] Bragg and Williams, Proc. Roy. Soc. A145, 699 (1934).
[6] Fowler, Proc. Roy. Soc. A151, 1 (1935); Mott, Proc. Roy. Soc. A146, 465 (1934).

[7] Fowler, Proc. Roy. Soc. A140, 505 (1933); Frenkel, Todes and Ismailow, Acta Physicochimica U.S.S.R. 1, 97 (1934).

so that in this 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. Thus for the backward direction we have $k_b = k_1 \exp(-f\lambda_2\lambda_3\lambda/2)$. Now ΔV for each molecule in the fast layer and therefore for the layer as a whole is then just:

$$\Delta V = \lambda k_1 \left(\exp \frac{f\lambda_2\lambda_3\lambda}{2kT} - \exp \left(-\frac{f\lambda_2\lambda_3\lambda}{2kT} \right) \right) \quad (6)$$

or $\Delta V = \lambda k_1 2 \sinh (f\lambda_2\lambda_3\lambda/2kT)$.   (7)

So that

$$\eta = f\lambda_1 \left(\lambda k_1 \exp \left(\frac{f\lambda_2\lambda_3\lambda}{2kT} \right) - \exp \left(\frac{-f\lambda_2\lambda_3\lambda}{2kT} \right) \right)^{-1}$$

$$= \lambda_1 f(\lambda k_1 2 \sinh (f\lambda_2\lambda_3\lambda/2kT))^{-1}. \quad (8)$$

Now for ordinary viscous flow $f\lambda_2\lambda_3\lambda/2 \ll kT$ so that expanding the exponentials and keeping terms only up to the first power we have after cancelation

$$\eta = \lambda_1 kT (\lambda^2\lambda_2\lambda_3 k_1)^{-1}. \quad (9)$$

Now if we substitute our explicit expression for this frequency k_1 we obtain:

$$\eta = (\lambda_1 h F_n / \lambda^2\lambda_2\lambda_3 F_a^* \mathfrak{X}) \exp (E_0/kT). \quad (10)$$

Since viscous flow is a rate process we know it will proceed by all possible mechanisms but chiefly by the fastest ones. Thus those orientations of the molecules are favored which lessen the viscosity. First in importance: a molecule in the activated state will be oriented in such a way as to make the activation energy E_0 as small as possible in spite of the fact that such a requirement of nearly exact orientation tends to make F_a^* smaller and therefore F_n/F_a^* larger. Other things being equal then E_0 will tend to be small and $\lambda^2\lambda_2\lambda_3/\lambda_1$ large. $\mathfrak{X}$, the chance that after a system has once reached the activated configuration it will pass over the barrier and not immediately return to the initial configuration, is probably very nearly unity. Thus from (10) we see that a molecule like benzene will tend to have its plane in the plane of the layer as it passes through the activated configuration as this will make λ_1 and E_0 smaller and $\lambda^2\lambda_2\lambda_3$ larger. Now a molecule is oriented in this way $(k_f + k_b)$ times per second so that if τ_R is its relaxation time

through rotation after orientation the fraction of the time it is thus oriented will be approximately

$$a = (k_f + k_b)\tau_R \quad (11)$$

as long as a is considerably less than 1. Since $(k_f + k_b)$ can be determined from the measured viscosity either τ_R or a follows from a knowledge of the other. Since relaxation by rotation will in general involve the passage over a potential energy barrier we can write $\tau_R = 1/k_2$ where k_2 is the k' of Eq. (3) after an appropriate assignment of values for the quantities therein. A good approximation for such rotations in most cases will be

$$1/\tau_R = k_2 = (kT/h) \exp (-E_0/kT) \quad (12)$$

where the activation energy is the only unknown. If E_0 is negligibly small $\tau_R \approx h/kT \approx 2 \times 10^{-13}$ sec. around room temperature. However, there are cases such as the orientation of the dipoles of water in an alternating field near the melting point where these dipoles seem unable to follow the field for frequencies in excess of 60,000 cycles.[8] Substituting this number for k_2' in (12) we find that this relaxation must involve passage over a barrier of about 10 kcal. Hysteresis effects and relaxation processes are in general simply reaction processes to be treated by Eqs. (3) or in the simpler cases by (12).[8a] One can of course regard k_1, k_f, k_b in our viscosity equations as the reciprocals of the various relaxation times required for vibration to change into translation.

COMPARISON OF THE THEORY OF VISCOSITY FOR LIQUIDS AND GASES

For the viscosity theory to apply as we have developed it the following condition must be fulfilled. A molecule after making the jump from one minimum to the next must remain in the new minimum long enough to dissipate the energy it possessed while passing over the last barrier. Thus at each minimum it must acquire anew the activation energy as a purely random process. When these conditions are not fulfilled we can

[8] Smyth and Hitchcock, J. Am. Chem. Soc. **54**, 4631 (1932).
[8a] In this sense even very large relaxation times have physical significance and may be employed serviceably in the interpretation of liquid-vitreous and vitreous-crystal transitions as Professor W. T. Richards points out in a paper soon to be published.

more appropriately assume the usual mechanism of transfer of momentum from one layer to the next by the molecules themselves passing back and forth between fast and slow layers. In this case the momentum transferred per square centimeter per second is readily seen to be $\eta dv/dz = \frac{1}{3}\nu \bar{c}ml dv/dz$; so that

$$\eta = \frac{1}{3}\nu \bar{c}ml. \tag{13}$$

Here dv/dz, ν, $\bar{c}$, m and l are the velocity gradient, molecules per cc, mean velocity of the molecules $(\bar{c}=2(2kT/\pi m)^{\frac{1}{2}})$, mass and mean free path, respectively. Clearly (10) will apply if the activation energy for the forward direction $(E_0-f\lambda_2\lambda_3\lambda/2)$ is equal to or greater than about twice kT since then the molecule will have a sufficient number of collisions with neighbors in between passages over successive barriers so that equilibrium statistics will apply. The equation should still apply approximately even for cases where the activation energy drops to kT. It is of some interest to see how (10) compares formally with (13) if we apply the former arbitrarily to liquids or gases not showing an activation energy. In that case η takes the form

$$\eta = \frac{\lambda_1 h}{\mathfrak{X}\lambda^2\lambda_2\lambda_3} \frac{F_n}{F_a{}^*} \approx \frac{\lambda_1 h}{\mathfrak{X}\lambda^2\lambda_2\lambda_3} \frac{(2\pi mkT)^{\frac{1}{2}}\lambda}{h}$$

$$\approx (2\pi mkT)^{\frac{1}{2}}/\lambda^2. \tag{14}$$

Here we have assumed that the λ's become equal to each other, $E_0=0$, and

$$F_n/F_a{}^* = (2\pi mkT)^{\frac{1}{2}}\lambda/h \tag{15}$$

and of course $\mathfrak{X}=1$. Comparing this with Eq. (13) after substituting the value for $\bar{c}$ we find that the two mechanisms lead to the same result only if we make the identification

$$l\lambda^2 = (1/\nu)(3\pi/2). \tag{16}$$

In the case of liquids without activation energy we might very well take (16) as a defining equation for l or λ^2. In any case any reasonable way of arriving at λ^2 will lead to satisfactory values for λ in this critical region of activation energies where neither the reaction theory of viscosities (Eq. (10)) nor the momentum transfer theory (Eq. (13)) strictly applies. An exactly parallel situation arises in "unimolecular" reactions where at high pressure the slow (rate determining) process is passage over the potential barrier (inside a molecule) while at very low pressures the rate determining process becomes the rate at which energy is supplied by collisions. In the theory of viscosity it may be possible to bridge the intermediate region by the same type of treatment used for reaction rates. We shall not, however, develop this part of the theory further here.

Andrade[9] has proposed applying the momentum transfer theory to liquids as well as gases. He modifies the gas treatment by taking account of the fact that energy transfer in liquids is due to vibrations instead of translations. For the metals he secures excellent numerical agreement with experiment by a reasonable choice of the quantities entering into his equation. It is just these cases for which gas-like transfer is to be expected since $(E-f\lambda_2\lambda_3\lambda^2/2)(kT)^{-1}$ is very small. On the other hand where this exponential factor is not very small we must adopt the reaction rate picture for viscosity which leads us to Eq. (10).

COMPARISON OF THE VISCOSITY EQUATION WITH EXPERIMENT

In the second paper Andrade has proposed an equation $\eta = (A/v^{\frac{1}{3}}) \exp (c/vT)$ where A and c are parameters left undetermined; v is the specific volume and T the temperature. He has then determined A and c for a wide variety of substances using the available experimental values for η over a temperature range and assembled the results in his Table IV which we need not reproduce. The present theory supplies these parameters only if we can calculate the difference in energy for the initial and the activated configurations as well as the corresponding vibrational frequencies and moments of inertia. To do this exactly we would have to treat the whole liquid mechanically as though it were a single molecule. Fortunately in the ratio of partition functions $F_n/F_a{}^*$ of (10) all degrees of freedom which are unchanged in the initial and final states disappear and the same is of course true with regard to the energy term E_0. Further, any process involving a large E_0 will be of negligible importance compared with those having smaller

⁹ Andrade, Phil. Mag. 17, 497, 698 (1934).

energies. The result of this is that for the important rate processes only a very few degrees of freedom will be modified—more profound changes being excluded by the Boltzmann factor. In chemical reactions this is exemplified by the existence of type reactions which remain almost unchanged by profound changes in the molecule at distances two or three atoms away from the seat of reaction. This fact is of fundamental importance for the general mechanical approach to rate processes. Here it means that for ordinary viscous flow we shall expect the layers to slip over each other by one molecule at a time slipping past the surrounding molecules into a small hole. It would be unnaturally extravagant of energy to provide a hole the size of a molecule.

The partition function F_n for the normal state contains one more degree of freedom than F_a^* for the activated state. The simplest assumption then is that all but this one degree of freedom cancels out in the ratio of partition functions and that

$$F_n/F_a^* = (1 - \exp - h\nu_i/kT)^{-1}, \qquad (17)$$

where ν_i is a vibration which can be estimated from the specific heat of the liquid. The existence of an activation energy for flow is the best possible justification for treating this additional degree of freedom in F_n as a vibration rather than a translation. In some cases ν_i may be fairly large in which case $F_n/F_a^* \approx 1$. By trying this latter approximation for this ratio and taking the transmission coefficient $\mathcal{K} = 1$ (which must in general be a very good approximation) (10) becomes:

$$\eta = (\lambda_1 h/\lambda^2 \lambda_2 \lambda_3) \exp (E_0/kT). \qquad (18)$$

If the distance λ between minima for the moving molecule is taken equal to λ_1, the distance between layers, we get finally that

$$\eta = (Nh/V) \exp (E_0/kT), \qquad (19)$$

where N is Avogadro's number and V is the molal volume. Now if for the molal volume we take as a rough average value $V = 39.6$ cc in order to get (19) in round numbers we obtain

$$\eta = 10^{-4} \exp E_0/kT). \qquad (19)$$

The constant factor 10^{-4} is about one-quarter to one-fifth of Andrade's values for about seventy of his hundred odd examples. Now the factor

(17) which has been neglected is necessarily greater than 1 and at $T = 300°$ absolute it becomes equal to 4 and 5 for the respective values 1.8×10^{12} and 1.4×10^{12} for ν_i. This is about the values for the frequencies which Lindemann's theory for melting leads to. These frequencies can also be estimated from the vapor pressures of the liquids and from the specific heat c_v if we assume the expression $(1 - \exp - h\nu_i/kT)^{-3}$ for the three "translational" degrees of freedom. The values obtained in this way are also of about the right size to account for these properties.

Thus for nonassociated liquids the formula

$$\eta = \frac{Nh \exp (E_0/kT)}{V\left(1 - \exp\left(-\dfrac{h\nu_i}{kT}\right)\right)} \qquad (20)$$

seems satisfactory where ν_i can be chosen to fit the viscosity at a particular temperature or estimated from some other property as mentioned above. Instead of treating this partition function as a vibration we can, of course, treat the liquid molecule as though it were moving in a box of length d where we can think of d^3 as the "free space" per molecule. In this way we get

$$F_n/F_a^* = (2\pi mkT)^{\frac{1}{2}}d/h \qquad (21)$$

and

$$\eta = (Nd/V)(2\pi mkT)^{\frac{1}{2}} \exp (E_0/kT). \qquad (22)$$

Again reasonable values for d give agreement with experiment. The cases which do not agree with (20) and (22) fall into two categories. First those in which the activation energy is very small so that the condition that the molecule remains in a minimum long enough to dissipate and then reacquire the activation energy before continuing the journey is not fulfilled. These, however, are the cases to which the momentum transfer theory as developed by Andrade apply. The other examples are those which Andrade classifies as associated. Here he gets lower values for this constant. That this should be so follows immediately from (10) since F_n the partition function for the normal state is decreased by association more than F_a^*, and the activation process will now involve dissociation with a correspondingly high activation energy. This is another example of the general phenomenon in reaction rates that with an abnormally high E_0 there is in general

associated an abnormally high F_a*/F_n. The reason is that the large E_0 arises from loosening an abnormally large number of bonds (or from loosening very strong bonds) and this automatically means a large value for the ratio F_a*/F_n. This same situation is familiar in equilibrium processes.

COMPARISON WITH OTHER EQUATIONS

We now consider the value of E_0. The energy required to provide a hole in the liquid has already been related to the vapor pressure and this as well as the energy for an atom to pass over the energy barrier is, of course, related to the internal energy plus the energy required to overcome the external pressure. Following Andrade and Bridgman[10] we assume it is at least approximately of the form $E_0 = (p+a/v^2)s$ where we write van der Waals equation as $(p+a/v^2) \times (v-b) = RT$, s is of course a volume, and the other quantities have their usual meaning. Substituting in (19) we have

$$\eta = \frac{Nh \exp \dfrac{(p+a/v^2)\, s}{RT}}{V\left(1-\exp\left(-\dfrac{h\nu_i}{kT}\right)\right)}$$

$$= \frac{Nh \exp \dfrac{s}{V-b}}{V\left(1-\exp\left(-\dfrac{h\nu_i}{kT}\right)\right)}. \quad (23)$$

Now not too far below the critical temperature where $s/(V-b)$ is small we can write

$$\exp \frac{s}{V-b} = 1 + \frac{s}{V-b} = \frac{V-b+s}{V-b}$$

and

$$\eta = \frac{Nh(V-b-s)}{V(1-\exp -(h\nu_i/kT))} \frac{1}{V-b} \approx \frac{c'}{V-b}. \quad (24)$$

Batschinski[11] proposed an equation of just the form of (24) where c' is a constant. As a matter of fact he used the specific volume as we can do

[10] Bridgman, *The Physics of High Pressure* (Macmillan), p. 356.
[11] Batschinski, Zeits. f. physik. Chemie **84**, 643 (1913). See also Hatschek, *The Viscosity of Liquids* (G. Bell & Sons), Chapter V.

also by simply dividing numerator and denominator by the molecular weight. He obtained very good agreement with experiment for all non-associated compounds. Inspection of Andrade's Table IV indicates that the ratio $s/(V-b)$ in Eq. (23) should be in the neighborhood of two or three for most of the substances provided they are nonassociated and are not too near the critical temperature. Now from experiment as well as from the theory of holes $V-b$ is about half the critical volume, V_c, at temperatures corresponding to low vapor pressures and $b = V_c/3$; so that if s is taken equal to b we have $s/(V-b) = b/(V-b) \approx 2$. In other words for nonassociated liquids E_0/kT is approximately the volume, b, occupied by the molecules themselves divided by the volume occupied by the holes, $V-b$. This last interpretation in spite of its attractiveness should not be taken too seriously, however, since b of van der Waals' equation has no very precise meaning in terms of molecular structure and is much smaller than we would deduce for example by equating $V-b$, the volume occupied by holes in the liquid, to the volume occupied by the molecules themselves in the vapor phase. This last comparison is suggested by the theory of holes.

It is interesting to compare (9) with Maxwell's equation[12] for viscosity $\eta = \epsilon \tau$ where ϵ is the elasticity and τ is the relaxation time. Doing this gives the equalities $\tau = 1/k_1$ and $\epsilon = \lambda_1 kT/\lambda^2\lambda_2\lambda_3 \approx kT/\lambda^3$. Thus we see that Maxwell's elasticity can be thought of as the pressure exerted by a molecule restricted to its actual volume in the liquid if it obeyed the perfect gas law.

PLASTICITY AND THE BEHAVIOR OF VISCOSITY FOR LARGE SHEARING FORCES

From Eq. (8) we see that viscosity is independent of the shear only when the work done by the applied force in carrying a molecule over the barrier is small compared with kT. In cases where a fairly rigid structure is being disrupted as for example in certain gels[13] and in glasses or crystals (8) must be used instead of (10). Expanding $\sinh (f\lambda_2\lambda_3\lambda/2kT)$ in (8) and dividing the f out we obtain

[12] J. C. Maxwell, Phil. Mag. **35**, 133 (1868).
[13] Hatschek, *The Viscosity of Liquids*, Chapter XII.

$$\eta = \frac{\lambda_1 kT}{\lambda^2 k_1 \lambda_2 \lambda_3}\left(1 + \frac{1}{6}\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right)^2\right.$$
$$\left. + \frac{1}{120}\left(\frac{f\lambda_2\lambda_3\lambda}{2kT}\right)^4 + \cdots\right)^{-1}, \quad (24)$$

which is the limiting viscosity for zero force divided by a sum of even powers of $f\lambda_2\lambda_3\lambda/2kT$. (24) explains the generally observed fact that the viscosity decreases with the shearing force. This decrease might be expected to manifest itself particularly strongly in colloidal solutions which are inhomogeneous since then the stress concentrates on the resisting structure and the work $f\lambda\lambda_2\lambda_3/2$ done in surmounting a potential barrier may approach or even exceed kT in magnitude.

In cases where $f\lambda\lambda_2\lambda_3/2 \gg kT$ we may even neglect k_b in comparison with k_f in which case we can write (8) in the form:

$$\eta = f\lambda_1(\lambda k_f)^{-1}. \quad (25)$$

Let us now consider the rate of release of the strain f in a glass at a temperature below the softening point. If to release the strain each molecule must on the average surmount m barriers and if the average time, t, to surmount a barrier is the relaxation time $\tau = 1/k_f$ then:

$$\frac{df}{dt} = \frac{f}{m\tau} = \frac{fk_f}{m} = \frac{f^2\lambda_1}{m\lambda\eta}. \quad (26)$$

This dependence of the time derivative on the square of the stress for glass has been observed by Adams and Williamson.[14] Hampton[15] has determined experimentally that the constant which we have written as $\lambda_1/m\lambda$ in (26) has the value 1000 for glass if the measured viscosity η for flow is used. This factor might arise in several ways. First, for example, the release of stress may proceed by some other relaxation than flow so that a different relaxation time (or viscosity) say that for rotation should be used. This still would give the same dependence on force squared but in that case a different η should be used. A second possibility is that the strain in the glass is such that the gth layer (each of thickness λ_1) normal to the planes of flow is strained

a distance λ with respect to the first layer along the direction of flow. This strain can then be released by a displacement of an amount λ of any one of the g molecules lying in the direction in which λ_1 is measured or by an average displacement of $m = 1/g$ of all of them. If g equals a thousand or more precisely if $\lambda_1/m\lambda = 1000$ we obtain Hampton's result. Thirdly this same average relaxation time of $\tau/1000$ would be obtained if in the cooled glass a thousand molecules jump together with the same relaxation time that one jumped under the circumstances for which η was measured. The fact that quite generally solids have only about $1/1000$ the tensile strength that might be expected theoretically has been explained as due to the fact that large groups of atoms move together with no more shearing force than would be expected for one. Polanyi[16] has pointed out that if due to strain the first and $(n+1)$st atom in one row coincides with the first and nth in a second row where in each row they are uniformly spaced then one group can be displaced with respect to the other with $1/n$th the energy required when the n atoms in one layer coincide with n in the other. In any case the law $df/dt = $ constant f^2/η is to be expected whenever the stress is large.

When the stress is small we expect

$$df/dt = f/\tau = fk_1 = \lambda_1 kTf/\lambda^2\lambda_2\lambda_3\eta. \quad (27)$$

Here we have used (9) to determine the relaxation time $\tau = 1/k_1$. Hence for small stresses $df/dt = $ constant f/η. Some cases will no doubt approximate the two extremes while others will be intermediate. The absolute reaction rate theory thus seems to give a very satisfactory account of viscosity and plasticity. For the latter it yields relations at least very similar to those of Prandtl, Becker, Orowan, G. I. Taylor and Polanyi as presented in their papers and which W. G. and J. M. Burgers[17] have summarized along with their own ideas in a recent report on elasticity and plasticity. Hysteresis and polymorphic transformations like any other reactions can be treated by the general theory but in each case we must secure the potential energy surface or the equivalent in other information.

[14] Adams and Williamson, J. Frank. Inst. **190**, 619 (1920); Adams, ibid. **216**, 39 (1933).
[15] Hampton, Trans. Opt. Soc. London **27**, 173 (1925–1926).

[16] Polanyi, Zeits. f. Physik **89**, 660 (1935).
[17] W. G. Burgers and J. M. Burgers. Verh. Akad. Amsterdam (1) **15**, Chapter V (1935).

DIFFUSION

We assume the concentration gradient is in the x direction and is equal to dc_1/dx and further that the distance between two successive minima for the diffusing molecules is λ. Then if the concentration at one minimum is c_1 that at the next minimum in the positive direction is $c_1 + \lambda dc_1/dx$. Now the number of molecules of type one passing through the y, z plane per square centimeter in the positive x direction is $N\lambda k_1 c_1$ and in the reverse direction $N\lambda k_1(c_1 + dc_1/dx)$. The excess proceeding in the negative x direction is $DN dc_1/dx = N\lambda^2 k_1 dc_1/dx$. Thus the diffusion coefficient is

$$D = \lambda^2 k_1 \qquad (28)$$

N is again Avogadro's number and the other quantities have also been defined. The net flow in one direction of molecules of one kind is of course compensated for by the corresponding flow in the reverse direction of other types of molecules. This treatment only applies when the molecules are of approximately the same size. If for example one type of molecule is very much larger than the other it is customary to assume that the large molecules behave like very large balls around which the smaller molecules stream. Then Stokes[18] equation $\dot{x} = X/6\pi r\eta$ applies to the large molecules where $\dot{x}$, r and X are the velocity, radius and force acting on one of them and η is the viscosity of the small ones. The osmotic force acting on the large molecule is $X = -V \times (dc/dx)NkT$; so that the excess of large molecules passing in the positive x direction per cm² per second is

$$\frac{\dot{x}}{V} = -\frac{kT}{6\pi r\eta}\frac{dc_1}{dx}N = -D\frac{dc_1}{dx}N, \qquad (29)$$

which gives the well-known relationship

$$D = kT/6\pi r\eta. \qquad (30)$$

The definition of all the quantities is the same used previously where c_1 is the concentration of the large molecules in moles per cc and V is the reciprocal of the number of these large molecules per cc.

On the other hand for molecules of the same size where (9) and (28) apply we obtain:

$$D = \lambda_1 kT/\lambda_2\lambda_3\eta. \qquad (31)$$

Thus (30) and (31) each have a well-defined region in which they do and do not apply. There is an intermediate region which requires closer consideration, and which we hope to consider further at another time. We now apply (31) to the diffusion of heavy into light water. Orr and Butler[19] give for this diffusion coefficient 1.46×10^{-5} at 0°C and 4.75×10^{-5} at 45°C. The viscosities at these two temperatures given by Landolt-Börnstein are 0.0179 and 0.00667, respectively. Substituting in (31) we obtain for $\lambda_2\lambda_3/\lambda_1$ at 0° the value 1.43×10^{-7} and at 45°C the value 1.38×10^{-7} cm. Now the geometrical mean of the λ's is $(\lambda_1\lambda_2\lambda_3)^{\frac{1}{3}} = (18/N)^{\frac{1}{3}} = 3.1 \times 10^{-8}$ cm. Combining these values we find that at 45°, $\lambda_1 = 1.47 \times 10^{-8}$ and $(\lambda_2\lambda_3)^{\frac{1}{2}} = 4.50 \times 10^{-8}$ cm, while the values for zero degrees give $\lambda_1 = 1.44 \times 10^{-8}$ and $(\lambda_2\lambda_3)^{\frac{1}{2}} = 4.54 \times 10^{-8}$ cm. This is precisely the kind of result that would be predicted since from general principles we expected that in viscous flow the plane of the H_2O molecule would tend to coincide with a plane of flow, i.e., that λ_1 would be the thin dimension of H_2O. In our calculation we have used the viscosity of H_2O whereas we should have used a value intermediate between that of H_2O and the value for pure D_2O which is about 30 percent higher than the former. Such a correction would decrease somewhat the ratio $(\lambda_2\lambda_3)^{\frac{1}{2}}\lambda_1^{-1}$ but would leave our general result unchanged. Thus we apparently have a very suggestive check of the theory. Eq. (30) on the other hand leads to the unreasonably small values for $2r$ of 1.46×10^{-8} cm at 45° and 1.56×10^{-8} cm at 0°C.

In electrical conductance the use of (30) for the diffusion coefficient certainly tends to give too low results for ionic mobility and is only justified if the ions are very much solvated or for other reasons very large as compared with the solvent. If the ions are of the same size as the solvent we should use (31) and in any case for large potential gradients we should use η in the form (8) or (24) where f is now the force acting on the ion due to the applied potential modified of course in the usual way by the other charges.

I want to thank Mr. R. H. Ewell for calling my attention to the interesting nature of the problem of viscosity.

[18] C.f. Herzfeld, *Kinetische Theory der Wärme* (Müller-Pouillets Lehrbuch der physik., 1925), Chapter VII.

[19] Orr and Butler, J. Chem. Soc. 1273 (1935).