

THE THEORY OF ABSOLUTE REACTION RATES AND ITS
APPLICATION TO VISCOSITY AND DIFFUSION IN THE
LIQUID STATE

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A summary of the formulas of statistical mechanics is given, followed by a discussion of potential-energy surfaces. This is used as a background for a discussion of the theory of absolute reaction rates. The formal equations for viscous flow in liquids are then developed, followed by a discussion of the evaluation of the quantities entering into the equations. Applications of the theory to viscous flow in normal liquids, associated liquids, and μ - and λ -sulfur are then described, as well as the effect of high hydrostatic pressure on viscosity. Diffusion in liquids is then treated as a rate process, and conclusions as to the nature of the process are drawn from inspection of the available data.

With the aid of the theory and generalizations discussed here it is possible from thermodynamic data to calculate the viscosity of any normal liquid to within a small factor at any temperature from its freezing point to its boiling point, and at any pressure from 1 to 10,000 atmospheres.

The treatment of the viscosity of liquids described here is based on the theory of absolute reaction rates developed to treat ordinary chemical reactions (13, 17, 18, 71). Since this theory is based on the concepts and equations of elementary statistical mechanics, a brief survey of the subject will be given at this point, followed by the development of the theory of absolute reaction rates. The applications which have been made to problems of viscous flow and diffusion will then be described.¹

¹ The symbols used in this paper are as follows:

a = activity

A = Helmholtz free energy

A, B, C = moments of inertia for a non-linear molecule

c = kinetic theory velocity

I. A BRIEF SURVEY OF STATISTICAL MECHANICS

Suppose that we have a system, two of whose energy levels are ϵ' and ϵ . The ratio of the probabilities, p'/p , of the system being in these two states is given by the Boltzmann equation (24):

$$p'/p = \exp(-(\epsilon' - \epsilon)/kT) \quad (1)$$

where k and T are, as usual, the gas constant (Boltzmann) and the absolute temperature, respectively. Subject to the restriction imposed by the energy difference, all states are taken to be equally probable. In quantum statistics, different states of the system are distinguished not by different energies but by different solutions of ψ in the wave equation

$$\frac{\hbar^2}{8\pi^2 m_i} (\partial^2 \psi / \partial x_i^2 + \partial^2 \psi / \partial y_i^2 + \partial^2 \psi / \partial z_i^2) + (E - V)\psi = 0 \quad (2)$$

Thus, two *different* states may have the *same* energy and, according to our postulate, should therefore be equally probable. The number of states having a certain energy is called the *a priori* probability or statistical weight and is designated by the symbol ω .

With the aid of the Boltzmann factor, one may readily obtain expressions for the thermodynamic properties of the system. Let a be the probability

- C = concentration
- C_p = specific heat at constant pressure
- C_v = specific heat at constant volume
- D = diffusion constant
- d = diameter
- E = energy
- F = partition function with the volume divided out; Gibbs free energy
- f = partition function per system; force
- H = Hamiltonian; heat content
- h = Planck's constant
- I = moment of inertia for a linear molecule
- j = quantum number for rigid rotator
- K = equilibrium constant; thermal conductivity
- k = Boltzmann's constant
- k = rate constant
- l = length
- M = molecular weight
- m = mass of a molecule
- N = Avogadro's number; mole fraction
- n = quantum number for particle in a box and harmonic oscillator; number of molecules per cubic centimeter
- P = pressure
- p = probability; momentum
- q = generalized coördinate; \dot{q} = generalized velocity
- R = gas constant

that the system will be in the state of lowest energy. Then the ratio of the probability of the system being in any other state to the probability that it will be in the lowest state is given by equation 1. Since the sum of the probabilities that the system will be in some one of the states is unity, we have

$$\begin{aligned} 1 &= a\omega_0 + a\omega_1 \exp(-\epsilon_1/kT) + a\omega_2 \exp(-\epsilon_2/kT) + \dots \\ &= a \sum_i \omega_i \exp(-\epsilon_i/kT) \end{aligned} \quad (3)$$

or

$$1/a = \sum_i \omega_i \exp(-\epsilon_i/kT) \quad (4)$$

where ϵ_i is the energy of the system in the i^{th} state, referred to its energy in the lowest state. The average energy, $\bar{\epsilon}$, in excess of that in the lowest state, is seen to be

$$\bar{\epsilon} = a\omega_0\epsilon_0 + a\omega_1\epsilon_1 \exp(-\epsilon_1/kT) + a\omega_2\epsilon_2 \exp(-\epsilon_2/kT) + \dots \quad (5)$$

$$\bar{\epsilon} = a \sum_i \omega_i \epsilon_i \exp(-\epsilon_i/kT) = \frac{\sum_i \omega_i \epsilon_i \exp(-\epsilon_i/kT)}{\sum_i \omega_i \exp(-\epsilon_i/kT)} \quad (6)$$

r = radius
 S = entropy
 T = absolute temperature; kinetic energy
 t = Centigrade temperature
 u = velocity of sound
 V = molal volume; potential energy
 v = volume per molecule; velocity
 V_f = free volume per mole
 v_f = free volume per molecule
 x, y, z = Cartesian coördinates

α = accommodation coefficient
 β = compressibility ($\equiv -(1/V)(\partial V/\partial P)_T$)
 γ = ratio of C_p to C_v ; activity coefficient
 ϵ = energy level
 η = viscosity
 Θ = Einstein characteristic temperature
 κ = partition function for a crystal; force constant; transmission coefficient
 λ = dimension of a molecule
 μ = reduced mass
 ν = frequency
 σ = symmetry number; collision diameter
 φ = fluidity ($\equiv 1/\eta$)
 ψ = wave function
 ω = statistical weight

The summation giving $1/a$ (equation 4) is called the partition function of the system and is designated by the symbol f . Using this notation, equation 6 becomes

$$\epsilon = kT^2 d(\ln f)/dT \quad (7)$$

If we are concerned with a large number, N , of systems,² the energy is N times that for a single one. Thus, if we wish to know the total energy of a mole of dilute benzene vapor, and f is the partition function of a single molecule, the required value is given by

$$\bar{E} = NkT^2 d(\ln f)/dT = kT^2 d(\ln f^N)/dT \quad (8)$$

This expression for the energy, \bar{E} , in terms of the partition function, can be related to the Helmholtz free energy, A , by the thermodynamic relation,

$$\bar{E} = E = -T^2 d(A/T)/dT \quad (9)$$

where E is the usual thermodynamic energy.

For these two expressions to be consistent we must have

$$A/T = -k \ln f^N + \text{constant} \quad (10)$$

The value of the constant is found by the third law of thermodynamics or by quantum mechanics to be equal to the logarithm of factorial N ($\ln N!$), where N is the number of identical systems in the assembly. If the systems are identical, and if one uses quantum mechanics to solve for the allowed energy levels of the ensemble, one would then find directly for the partition function, $\ln (f^N/N!)$. In this case the $N!$ enters because the Pauli exclusion principle allows only eigenfunctions which are anti-symmetric in the N identical systems (9, 50). This treatment then gives

$$A/T = -k \ln f^N + \ln N! \quad (11)$$

In order to simplify this formula, Stirling's approximation (8) may be used.

$$\ln N! = N \ln N - N \quad (12)$$

Substitution of equation 12 into equation 11 gives

$$A = -RT[\ln (f/N) + 1] \quad (13)$$

a formula which, from the nature of its origin, must be valid for gases.

² The word "system" is used here in the same sense as Fowler (24) employs it, to mean something which possesses a set of energy levels. This may be a single oscillator, a molecule, an entire crystal, or a liquid. "Assembly" is the term employed to denote a large number of systems whose energy levels are coupled by an amount sufficient to permit exchange of energy but insufficient to cause these levels to be different from those for the isolated system.

The procedure for crystals is to calculate the partition function κ for the N atoms or molecules as a single system so that, in this case, one has for the Helmholtz free energy

$$A = -kT \ln \kappa \quad (14)$$

Having expressions for the free energy and the energy, the entropy in terms of the partition function follows directly from the thermodynamic equation,

$$A = E - TS \quad (15)$$

Substituting equation 13 or 14 and equation 8 into equation 15, we obtain

$$S = R[\ln (f/N) + 1] + \bar{E}/T \text{ (gas)} \quad (16)$$

and

$$S = k \ln \kappa + \bar{E}/T \text{ (crystal)} \quad (17)$$

The equation of state also follows from the partition function by means of the equation,

$$P = -(\partial A/\partial V)_T \quad (18)$$

A. *Explicit expressions for the partition functions*

Thus far, the partition function has been defined in a perfectly general way in terms of the energy levels. However, the energy levels vary in a simple fashion for many systems met with in physical problems, so that the sums can be put into more convenient forms.

The energy levels obtained by the aid of equation 2 for a particle moving in a cubical box of edge l and possessing kinetic but not potential energy are

$$\epsilon_n = \frac{\hbar^2(n_x^2 + n_y^2 + n_z^2)}{8ml^2} \quad (19)$$

where the n 's are integers. The partition function defined by equation 4 is found to be

$$f = (2\pi mkT/\hbar^2)^{3/2} l^3 \quad (20)$$

when the summation is approximated by an integration. The error introduced by this approximation is inappreciable, except at very low temperatures or high pressures. Even for the extreme case of hydrogen molecules at 1°K. enclosed in a box of 10^{-2} cm. (neglecting molecular interaction as we have done), the error made is only 1 in 10^5 in f (32).

The energy levels for the harmonic oscillator are $\epsilon_n = (n + 1/2)h\nu$, and the partition function for a single oscillator of this type is

$$f_\nu = [1 - \exp(-h\nu/kT)]^{-1} \quad (21)$$

The rigid linear rotator has energy levels,

$$\epsilon_j = \frac{h^2(j)(j+1)}{8\pi^2 I} \quad j = 0, 1, 2, \dots \quad (22)$$

each energy level being $(2j + 1)$ -fold degenerate, and the corresponding partition function is closely approximated by

$$f_R = 8\pi^2 I kT / \sigma h^2 \quad (23)$$

Here I is the moment of inertia, and σ is the symmetry number. For a diatomic molecule composed of two like atoms, σ is equal to 2. The quantum mechanics of the three-dimensional rotator with three unequal moments of inertia has not been completely solved, but the classical integration over phase space (a procedure exactly analogous to taking the sum (4), except that the energy levels are considered to be continuous rather than discrete) yields

$$f_R = 8\pi^2 (8\pi^3 k^3 T^3 ABC)^{1/2} / \sigma h^3 \quad (24)$$

where A , B , and C are the three principal moments of inertia.

The division of the complete partition function into factors corresponding to translational, rotational, and vibrational terms is valid only in case there is no interaction between these various degrees of freedom. In that case the energy levels can be expressed as sums of terms, and the partition function corresponding to each degree of freedom can be factored out. In making computations of the thermodynamic properties of gases from spectroscopic data, interaction terms between rotational and vibrational energy levels are often included.

B. Classical integration over phase space

It will be useful at this point to inquire into the relationship of the above formulae to those obtained by the use of classical statistics.

The classical analog of the quantum-mechanical sum of states is defined by

$$f = (1/h^N) \iiint \dots \iiint \exp(-H/kT) dp_1 \dots dp_n, dq_1 \dots dq_n \quad (25)$$

where the integration is to be taken over the whole of momentum coordinate phase space and H is the classical Hamiltonian, defined by

$$H = T + V \quad (26)$$

where T is the kinetic energy, and V is the potential energy of the assembly. For a single particle, T is given by

$$T = (1/2)mv^2 \equiv (1/2m)(p_x^2 + p_y^2 + p_z^2) \quad (27)$$

p_x , p_y , and p_z being the momenta along the three axes.

For a free particle, V is equal to zero, and equation 25 becomes

$$f = (1/h^3) \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} \int_{-\infty}^{+\infty} [\exp(-1/2mkT) \cdot (p_x^2 + p_y^2 + p_z^2)] dp_x dp_y dp_z \\ \times \int_0^{l_x} \int_0^{l_y} \int_0^{l_z} dx dy dz \quad (28)$$

$$f_T = (2\pi mkT/h^2)^{3/2} V \quad (29)$$

since the volume V is given by the product $l_x l_y l_z$.

The classical partition function for the one-dimensional simple harmonic oscillator may be obtained from equation 25 by direct integration, recalling that

$$H = (1/2m)(p_x^2) + (1/2)\kappa x^2 \quad (30)$$

and that the frequency, ν , is related to the force constant, κ , by the equation,

$$\nu = (1/2\pi)(\kappa/m)^{1/2} \quad (31)$$

The expression obtained for the partition function,

$$f_\nu = kT/h\nu \quad (32)$$

may also be obtained from equation 21 by expanding the exponential in powers of $h\nu/kT$ and dropping all but the first two terms. Equation 32 is thus seen to be a good approximation only if $h\nu/kT$ is small.

The classical partition function for the two-dimensional rigid rotator is the same as that already obtained (equation 23) by replacing the summation over states by an integration.

II. THEORY OF ABSOLUTE REACTION RATES

A. Potential-energy surfaces (22, 24, 43, 44)

The statistical treatment of reaction rates involves the concept of a potential-energy surface giving the potential energy of the reacting molecules as a function of their position, orientation, and interatomic distances. Such surfaces giving the potential energy at every point in configuration space are generally drawn as contour graphs, each line on the graph being a line of equal potential energy, called an equipotential line. If a complete surface is considered, extending all the way from the stable reactants to

the stable products, it will be seen that there is an "easiest reaction path" between the two, i.e., a path drawn such that the potential energy at all points along the line increases in a direction at right angles to the line. The velocity with which the reaction proceeds depends on the temperature, on the difference in energy between the initial state and the point of highest energy on the easiest reaction path, and on other factors which are discussed below. Most of the thousands of compounds which are known are thermodynamically unstable; their apparent stability depends on the height of the easiest path that separates them from their more stable reaction products. On the basis of this picture, the existence of thermodynamically unstable compounds and their reaction to form more stable products is easy to understand. The compounds correspond to potential energy valleys separated from their possible reaction products by passes which have potential energy mountains on either side.

In general, $3n$ coordinates are required to describe the system of n atoms that are taking part in the reaction. But since the position of the center of gravity of the system is irrelevant, and since the potential energy of the system is practically independent of the rotation of the complex as a whole, the number of coordinates required to define the potential-energy function and the essential details of the relative motion reduces to $3n - 6$ or $3n - 5$, depending on whether the configuration is non-linear or linear.

Such a surface is illustrated in figure 1 for a simple three-atom reaction, the exchange of hydrogen for hydrogen in the para-hydrogen molecule to form an ortho-hydrogen molecule and a hydrogen atom. The surface is drawn for a linear triatomic molecule and should thus require $3 \times 3 - 5 = 4$ coordinates. However, this is reduced to two if the two degrees of freedom corresponding to bending vibrations are excluded. The axes are inclined at an angle of 60° to each other in order that the representation of the potential energies of various configurations of the system of three atoms will have exactly the same variation of its coordinates with time as a single point moving in the potential field with the inclined axes would have. Stated in another way, the particular manner of construction that is used eliminates cross terms from the potential function. The method of determining the effective mass of the single particle and the correct inclination of the axes to each other has been given by Wigner. The result³ is quoted by Eyring and Polanyi (22).

In terms of this surface the reaction is pictured as taking place as follows: As the hydrogen atom approaches the molecule of para-hydrogen, the bond between the hydrogen atoms weakens, and at the top of the easiest pass the configuration of lowest energy is one in which the three atoms

³ Because of an error in sign, the angle between the axes was originally given as 120° rather than 60° .

are arranged in a linear manner with the distances between neighboring atoms slightly greater than the distance in the normal hydrogen molecule. The potential energy is seen to become greater as the reactants approach each other, reaching a maximum value at two points where the configuration is intermediate between that of the reactants and products, and becoming less again as the products are formed. The point of highest energy on the easiest path from reactants to products is known as the activated state, and the configuration of the atoms at this point is called the activated complex. Owing to the symmetry of the reaction we are discussing here,

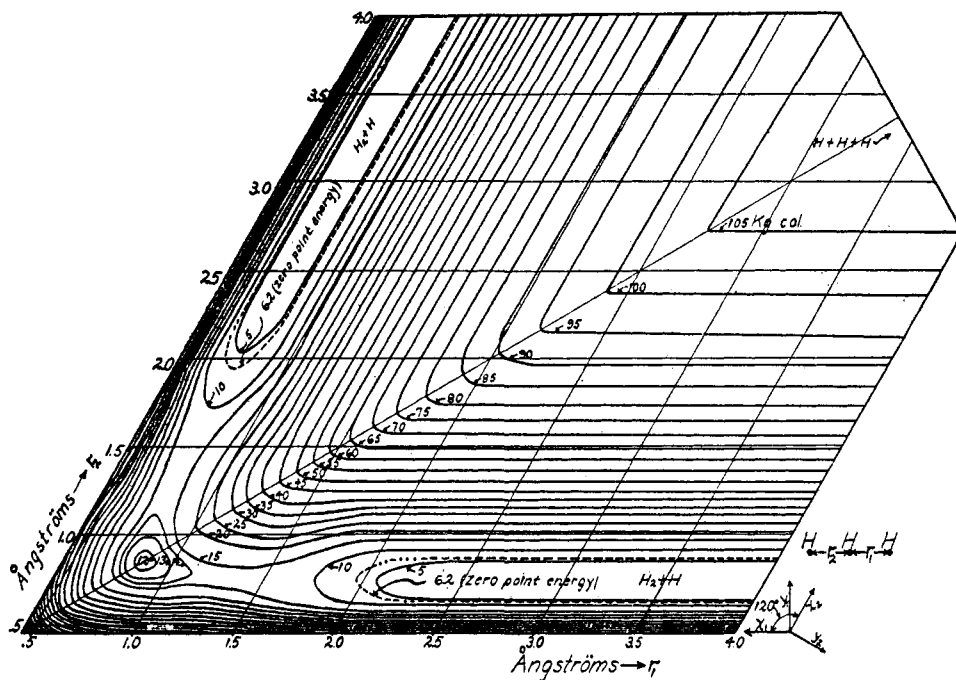


FIG. 1. Potential energy surface for three hydrogen atoms arranged in a line (20)

there are two symmetrical saddle points along the easiest path which are separated by a potential-energy basin. The presence of two saddle points along the easiest path is of importance in treating the transmission coefficient κ , which will be discussed in the next section.

The important point is that the properties of an activated complex are just those of an ordinary molecule except in the one degree of freedom along the easiest path, i.e., normal to the barrier. This becomes clear when it is recalled that by definition the activated complex is the configuration corresponding to the highest point (or points) along the easiest reaction path.

Thus the system is in stable equilibrium with respect to small displacements in every direction except the one normal to the barrier. The theory of small vibrations leads to a set of frequencies in exactly the same way as for an ordinary molecule, except that the square of the frequency for the degree of freedom normal to the barrier comes out with a negative instead of a positive sign, and hence from equation 31 it has a negative force constant. Figure 2 shows the normal modes of vibration for a symmetrical linear triatomic molecule. The one marked A has the negative force constant, the force constants for the normal modes B, C, and D being positive. The frequencies C and D are equal and correspond to a bending vibration in planes perpendicular to each other.

The mechanism described here for the reaction of $H + H_2(\text{para})$ has the same general features as that of any other chemical reaction having an activation energy. There is always an easiest reaction path between

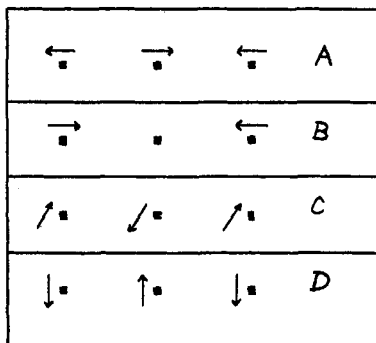


FIG. 2. Normal modes for a linear symmetrical triatomic molecule

reactants and products, and one or more saddle points along that path. The configuration at the highest saddle point is called the activated complex, which has the characteristics discussed above. Of course, the *actual* reaction paths will have a Boltzmann distribution about the *easiest* reaction path, and all these paths are included with their proper weight in the treatment of reaction rates by the ordinary statistical mechanical methods. Further, any rate process can be treated by the same general method. We now go on to develop the general equations which are applicable to any rate process.

B. Statistical formulation of reaction rate equations⁴

Equations giving the absolute rate of any rate process taking place on a single potential-energy surface may now be formulated in a perfectly

⁴ The formulation that we shall use is essentially the same as that given by Eyring (18). See, also, Pelzer and Wigner (51) for a treatment of reactions involving

general way as follows: The rate of reaction is given by the concentration of activated complexes, multiplied by the rate at which they decompose to form the reaction products. In general, the rate of reaction will be less than the rate of formation of activated complexes, since some of the activated complexes will return to the initial configuration without reacting. This can be expected to be the case in those very common instances where the easiest reaction path has two saddle points with a high-level basin lying between them. When there is no such high-level basin, the rate of reaction is simply the rate at which activated complexes reach the pass in such a direction that (regarded as classical particles) they can pass over and through it. When there is such a basin, the reaction rate is the rate

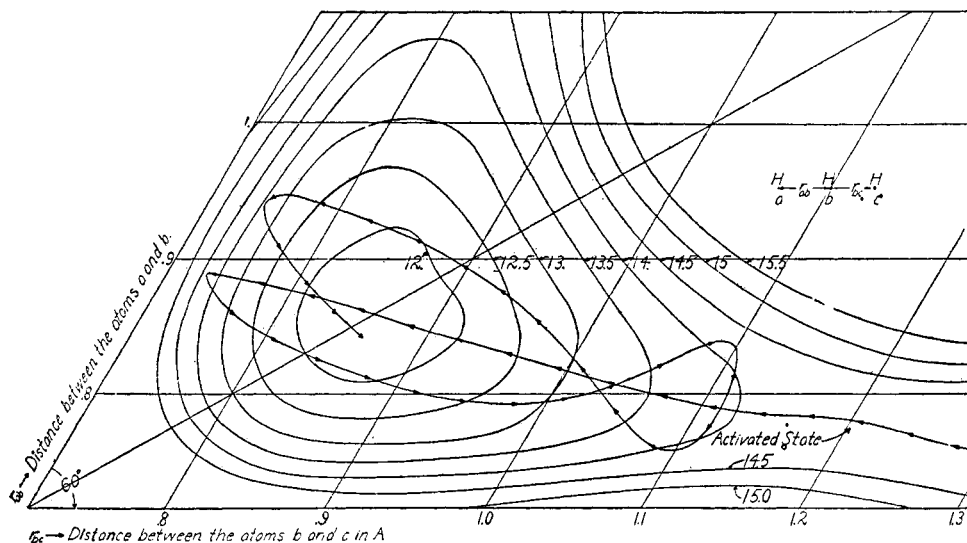


FIG. 3. The vibrational trajectory for linear H_3 , indicated by the line with arrows, was computed by employing the classical equations of motion (29).

at which activated particles pass into it, multiplied by the probability that the exit will be in a direction corresponding to reaction. This proba-

three atoms and Wigner (68) for a treatment of leakage and a quantum-mechanical extension of the earlier treatment. For the treatment from the quasi-thermodynamic point of view, see the papers of Evans and Polanyi (13) and Wynne-Jones and Eyring (71). A much earlier and interesting formulation of reaction rates by Marcelen (46) necessarily lacked the concept of the crossing of a potential barrier in configuration space which the London formulation suggested (44) and which led Eyring and Polanyi (22) to formulate explicitly the problem as the motion of a particle on a suitably constructed potential-energy surface. Further quantum-mechanical corrections are carefully considered in a recent article by Hirschfelder and Wigner (31) and are found to be, in general, small.

bility, called the transmission coefficient, is given the symbol κ . Figure 3 shows a trajectory of a particle following a linear vibrational distortion given it after it has passed the activated point into the high-level basin. The randomness of the path, combined with the fact that in this case the entry and exit are symmetrical, leads us to the conclusion that in this case κ must be very nearly equal to one-half. In other more complex cases the value of κ cannot be predicted exactly, but there is reason to believe that its value will generally not depart greatly from unity for the adiabatic reactions considered here.⁵ Another effect that may contribute to the rate is that of tunneling through the barrier, i.e., the reaction of molecules which do not possess the requisite energy. This effect has been considered by Wigner (31, 51, 68) and by Eckart (10). The correction term thus introduced is small for barriers of small curvature, but may become of importance for very thin barriers.

Then to the approximation that tunneling may be neglected, we may write for the specific reaction rate constant:

$$k = \kappa K^* \bar{p}/m^* \quad (33)$$

where m^* is the reduced mass of the activated complex, \bar{p}/m^* is its average velocity in the forward direction along the reaction path, and K^* is the equilibrium constant between activated complexes and reactants expressed in concentration units, per unit of length along the reaction path and per unit of volume, respectively. K^* may be written in terms of the partition functions of the activated complex and of the reactants. The expression for k then becomes:

$$k = \kappa (F^*/F_n) (\bar{p}/m^*) \quad (34)$$

or

$$k = \kappa (F^*/F_n) (\bar{p}/m^*) \exp(-E_0/RT) \quad (35)$$

where F^* is the partition function of the activated complex, and F_n represents that of the reactant molecules.

In equations 34 and 35 the F 's represent partition functions with the volumes divided out. Equation 34 differs from equation 35 only in that in the former the energy levels for both F^* and F_n must be referred to a common zero, while the latter refers the energy levels to the lowest state of the molecule to which the partition function applies. These equations are applicable to reactions in any phase. However, the partition func-

⁵ The term "adiabatic" is used here in Ehrenfest's sense to mean a reaction that takes place on a single potential surface in configuration space. Cases of reactions involving the transition of the system from one surface to another can also be treated by special methods. See Stearn and Eyring (62) and Evans, Eyring, and Kincaid (12).

tions vary with the phase in question. The equilibrium constant between reactants and the activated complex and therefore the rates in the liquid phase may be readily obtained from the corresponding expressions in the gas if vapor pressures are known. This is, of course, true of all equilibrium constants, and the calculations of the change of reaction rates and of equilibrium constants on taking systems from the gaseous to the liquid phase should ultimately be the most important chemical application of theories of liquids and solutions.

The average velocity, \bar{p}/m^* , with which the activated configuration travels over the barrier may be regarded as a pure translation for sufficiently flat surfaces, and its value is given in the usual way by the expression:

$$\begin{aligned} \frac{\bar{p}}{m^*} &= \left[\int_0^\infty \frac{p}{m^*} \exp\left(-\frac{p^2}{2m^*kT}\right) dp \right] \left[\int_{-\infty}^{+\infty} \exp\left(-\frac{p^2}{2m^*kT}\right) dp \right]^{-1} \quad (36) \\ &= \frac{kT}{(2\pi m^*kT)^{1/2}} \end{aligned}$$

However, the partition function for the activated complex per unit length along the reaction path contains the term $(2\pi m^*kT/h^2)^{1/2}$, so that the product of this term and \bar{p}/m^* equals kT/h . We then write as our final equation for k :

$$k = \kappa(kT/h)(F^\ddagger/F_n) \exp(-E_0/RT) \quad (37)$$

where E_0 is the energy of activation at the absolute zero and F^\ddagger is the partition function for the activated complex, taking the partition function for the degree of freedom in which the molecule is decomposing as equal to unity instead of $(2\pi mkT/h^2)^{1/2}$. It may be noted that F^\ddagger is formally the same as the partition function of a molecule exactly like the activated complex, with the degree of freedom normal to the barrier being a vibration sufficiently stiff for its partition function to reduce to unity. This idealized activated complex is a convenient concept for defining the free energy and entropy of activation in the usual way in terms of equilibrium constants. Thus,

$$\Delta F^\ddagger = -RT \ln K^\ddagger \quad (38)$$

and

$$\Delta F^\ddagger = \Delta H^\ddagger - T\Delta S^\ddagger \quad (39)$$

Using relations 38 and 39, the equation for k may be written in the equivalent forms,

$$k = (\kappa kT/h) \exp(-\Delta F^\ddagger/RT) \quad (40)$$

$$k = (\kappa kT/h) \exp(-\Delta H^\ddagger/RT) \exp(\Delta S^\ddagger/R) \quad (41)$$

These equations are not limited to the gaseous phase and may be applied to any rate process if the free energy of activation is known from any source.

A point of view which is less useful than that employed above, but which may aid in giving one an intuitive feeling for the significance of the factor kT/h in equations 37 to 41, is the following: The degree of freedom in which the decomposition is occurring has been regarded as a translation, but it may equally well be considered as a vibration. In this case the classical partition function is $kT/h\nu^*$. But the rate at which the decomposition is taking place must be equal to ν^* , the frequency of vibration along the coordinate normal to the barrier, since the force constant for this vibration is negative. That is, every vibration leads to decomposition. The product of $kT/h\nu^*$ and ν^* then gives kT/h as before.

In the use of equation 37 it should be emphasized that the partition functions contain all the energy levels which contribute at the temperature involved, i.e., excited electronic states should be included if they are not sufficiently high to be neglected.

C. Kinetic theory equations

Some of the simplest applications of the theory of absolute reaction rates are to be found in the derivation of ordinary kinetic theory formulae. The equations which are derived are, of course, identical with those secured by the ordinary methods, but the derivations are often simpler and clearly bring out the approximations which are made.

The rate at which molecules at a pressure P and temperature T strike a square centimeter of surface is found as follows: The activation energy for this process is equal to zero, and the activated complex is a molecule just breaking away from the wall with two degrees of translational freedom besides the one in which decomposition is occurring. κ is unity for such a process, and there is no possibility of leakage through a barrier, so that equation 37 reduces to

$$k = \frac{(kT/h)(2\pi m^* kT/h^2) F_R^\ddagger F_v^\ddagger}{(2\pi m kT/h^2)^{3/2} F_R F_v} \quad (42)$$

where F_R and F_v are rotational and vibrational partition functions, respectively. Since m^* , F_R^\ddagger , and F_v^\ddagger are the same for the activated complex as for the normal molecule, equation 42 may be simplified by cancellation to give

$$k = (kT/2\pi m)^{1/2} \quad (43)$$

The rate is given by the product, nk , where n is the number of molecules per cubic centimeter, so that equation 43 reduces to

$$\text{Rate} = nk = nkT/(2\pi m kT)^{1/2} = P/(2\pi m kT)^{1/2} \quad (44)$$

Another illustration which may be given is the calculation of the number of collisions between molecules in the gas phase. Consider first the case of the rate of collision between unlike molecules. In order to arrive at the conventional formula it is necessary to assume either that the colliding molecules are monatomic and hence have no rotational terms in their partition functions or that the rotations in the normal state are the same as those in the activated complex. The activated complex can be taken as the system of two molecules just breaking away from each other. We have thus:

$$F^\ddagger = (2\pi(m_1 + m_2)kT/h^2)^{3/2} 8\pi^2 I kT/h^2 \quad (45)$$

and

$$F_n = (2\pi m_1 kT/h^2)^{3/2} (2\pi m_2 kT/h^2)^{3/2} \quad (46)$$

and for the rate of collision, $Z_{1,2}$,

$$Z_{1,2} = n_1 n_2 k = n_1 n_2 \frac{k T F^\ddagger}{h F_n} \quad (47)$$

On substituting equations 45 and 46 into equation 47 and simplifying we arrive at

$$Z_{1,2} = \frac{2n_1 n_2 (2\pi kT)^{1/2} \sigma_{1,2}^2}{\mu^{1/2}} \quad (48)$$

where μ is the reduced mass defined by $\mu = m_1 m_2 / (m_1 + m_2)$, and $\sigma_{1,2}$ is the usual collision diameter. The collision diameter enters into the expression from the definition, $I = \mu \sigma_{1,2}^2$.

As a final illustration we give a derivation of the formula giving the number of collisions between unlike molecules having a relative velocity greater than a certain value. Consider the motion of two molecules of masses m_1 and m_2 having velocities along their line of centers \dot{q}_1 and \dot{q}_2 , respectively. Then the relative velocity, \dot{Q} , is defined by

$$\dot{Q} = \dot{q}_1 - \dot{q}_2 \quad (49)$$

The kinetic energy and momentum are given by

$$T = (1/2)m_1 \dot{q}_1^2 + (1/2)m_2 \dot{q}_2^2 \quad (50)$$

and

$$P = m_1 \dot{q}_1 + m_2 \dot{q}_2 \quad (51)$$

Since the motion of the center of gravity of the system may be taken equal to zero, we have

$$\dot{q}_1 = -m_2 \dot{q}_2 / m_1 \quad (52)$$

a relation which may be combined with equations 49 and 50 to give an expression for T in terms of \dot{Q} :

$$T = (1/2)\mu\dot{Q}^2 \quad (53)$$

Since this is the general expression for the kinetic energy relative to the line of centers, it must also be true at the point of collision. The rate expression may now be written

$$Z_{1,2} = \frac{n_1 n_2 (2\pi(m_1 + m_2)kT/h^2)^{3/2} (8\pi^2 I kT/h^2) (2\pi m^* kT/h^2)^{1/2} (\bar{p}'/m^*)}{(2\pi m_1 kT/h^2)^{3/2} (2\pi m_2 kT/h^2)^{3/2}} \quad (54)$$

where \bar{p}'/m^* is now not the over-all average velocity normal to the barrier, but the average velocity in the range of velocities we are considering. This value may be obtained by a procedure exactly analogous to that used in equation 36, except that the lower limit of integration is taken to be the minimum momentum P_0 instead of zero. This procedure gives

$$\bar{p}'/m^* = kT / (2\pi m^* kT)^{1/2} \exp(-P_0^2 / 2m^* kT) \quad (55)$$

Combining these last two expressions, we have

$$Z_{1,2} = 2n_1 n_2 (2\pi kT/\mu)^{1/2} \exp(-\mu\dot{Q}^2 / 2kT) \quad (56)$$

if we remember that in this case $m^* = \mu$.

It is interesting to note that if the term $\exp(-\mu\dot{Q}^2 / 2kT)$ had been regarded as an activation energy, we would have written down the expression 56 directly from the theory of absolute reaction rates. While the usual kinetic theory derivations of rate processes and those obtained by using the activated complex theory are interchangeable for simple atoms, only the latter theory is adequate for treating complicated molecules.

III. EQUATIONS FOR VISCOSITY AND DIFFUSION (19)

In this section we shall develop the formal equations for viscosity and diffusion, based on the following mechanism: Viscous flow is assumed to take place by the activated jumping of an aggregate composed of one or more molecules from an initial normal configuration to a second normal configuration. In common with chemical reactions, normal configurations are assumed to be separated by an intermediate, activated state corresponding to the activated complex. It is thus possible to use all the machinery developed in the preceding sections for the treatment of viscosity and diffusion. The magnitude of the free energy of activation and the exact mechanism for flow will be treated in section IV. In this section we shall only assume that the mechanism is such that the theory of absolute reaction rates is applicable.

The perpendicular distance between two neighboring aggregates 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 aggregates in this same direction is λ_2 , which may or may not be equal to λ . The distance between aggregates in the plane normal to the direction of motion is written as λ_3 . By definition we have for the viscosity,

$$\eta = f\lambda_1/\Delta v \quad (57)$$

where 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 process of diffusion is continually taking place, with or without an applied force tending to cause viscous flow. The application of such a force simply tends to make a preferred direction in which the molecules move. On the basis of this picture, the velocity Δv between two successive flow layers is simply the difference between the reaction rate in the direction of flow and in the opposite direction multiplied by the average distance it moves at each reaction. The general equation giving the rate of any reaction which has been modified by some external agency may be written:

$$k' = (kT/h) \exp(-\Delta F^\ddagger/RT - \Delta F^{t'}/RT) \quad (58)$$

Here $\Delta F^{t'}$ is the contribution made by external agency to the free energy of activation, and κ has been set equal to unity. The magnitude of $\Delta F^{t'}$ caused by the applied force may be evaluated in this case as follows: The force acting on a single aggregate is $f\lambda_2\lambda_3$, and it acts to lessen the work of passing over the barrier through the distance $\lambda/2$. That this distance is just $\lambda/2$ follows from the reasonable assumption that the activated complex is a configuration just half way between the initial and final states. Thus the applied force tends to lessen the free energy of activation in the forward direction by an amount $f\lambda_2\lambda_3\lambda/2$, while in the backward direction it is *raised* by the same amount. If the reaction rate constant in the forward direction be denoted by k_f and that in the backward direction by k_b , we have

$$k_f = (kT/h) \exp(-\Delta F^\ddagger/RT + Nf\lambda_2\lambda_3\lambda/2RT) = k \exp(f\lambda_2\lambda_3\lambda/2kT) \quad (59)$$

and

$$k_b = (kT/h) \exp(-\Delta F^\ddagger/RT - Nf\lambda_2\lambda_3\lambda/2RT) = k \exp(f\lambda_2\lambda_3\lambda/2kT) \quad (60)$$

Here k is the specific reaction rate constant giving the number of times per second that an aggregate will jump in the direction of flow when no force is applied, and ΔF^\ddagger is the corresponding free energy of activation.

Now Δv for each aggregate is also Δv for the layer as a whole. Thus the relative rate of displacement of neighboring layers is

$$\Delta v = \lambda k [\exp(f\lambda_2\lambda_3\lambda/2kT) - \exp(-f\lambda_2\lambda_3\lambda/2kT)] \quad (61)$$

or

$$\Delta v = 2\lambda k \sinh (f\lambda_2\lambda_3\lambda/2kT)$$

The viscosity then is given by

$$\eta = f\lambda_1/2\lambda k \sinh (f\lambda_2\lambda_3\lambda/2kT) \quad (62)$$

Since for the forces ordinarily employed in the measurement of viscosity, $f\lambda_2\lambda_3\lambda/2kT \ll 1$, the exponentials in equation 62 may be expanded and higher powers dropped, leaving

$$\eta = kT\lambda_1/\lambda^2\lambda_2\lambda_3k \quad (63)$$

or

$$\eta = (h\lambda_1/\lambda^2\lambda_2\lambda_3) \exp (\Delta F^\ddagger/RT) \quad (64)$$

The formula for the diffusion of one liquid into another when they form perfect solutions is very simply derived as follows: Assume that the concentration gradient is in the X direction and is equal to dC_1/dX and, further, that the distance between two successive potential-energy minima for the diffusing aggregate 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 passing through the Y, Z plane per square centimeter in the positive X direction is $N\lambda kC_1$ and in the reverse direction is $Nk\lambda(C_1 + \lambda dC_1/dX)$. The excess proceeding in the negative X direction is $N\lambda^2k dC_1/dX$, which must be equal to $DN dC_1/dX$ from the definition of the diffusion coefficient, D . Thus D is

$$D = \lambda^2k \quad (65)$$

In the case of self-diffusion, k and λ^2 may be eliminated from equations 63 and 65 to give

$$\eta D = kT\lambda_1/\lambda_2\lambda_3 \quad (66)$$

Equation 66 holds for perfect solutions whenever the mechanisms for viscous flow and diffusion are the same. In securing a similar relation for the diffusion of one liquid into another it must be remembered that neither k nor λ^2 is necessarily the same for the diffusing molecule as for the solvent. Designating the molecular species which is acting as the medium by the subscript m and the diffusing species by D , we have

$$\eta D = kT\lambda_1\lambda_D^2k_D/\lambda^2\lambda_2\lambda_3k_m \quad (67)$$

$$\eta D = kT(\lambda_1/\lambda_2\lambda_3)(\lambda_D^2/\lambda_m^2) \exp (\Delta F_m^\ddagger - \Delta F_D^\ddagger) \quad (68)$$

This equation, which applies when the solvent and solute molecules are of very nearly the same size, is to be compared to the well-known Stokes-Einstein diffusion equation,

$$D = kT/6\pi r \quad (69)$$

which is applicable when the diffusing molecule is so large compared to the molecules of the medium in which it is diffusing that by comparison the medium may be thought of as a continuum. Here r is the radius of the diffusing molecule, considered to be spherical. Appropriate variants have been obtained by Stearn and Eyring (61) and by Powell, Roseveare, and Eyring (52) for treating imperfect solutions. If we picture a solute, partitioned at equilibrium between two different solvents, it is clear that

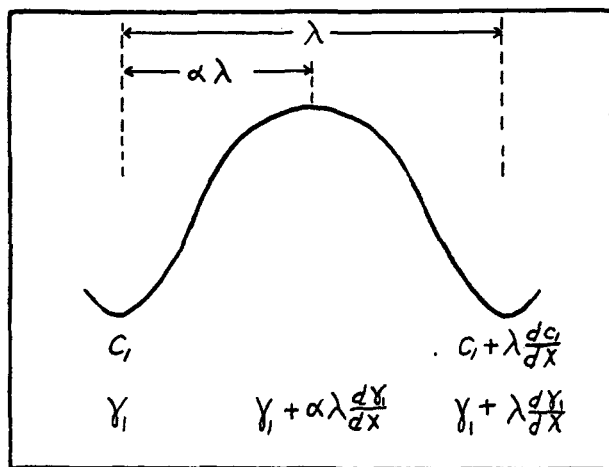


FIG. 4. Potential barrier for diffusion process in non-ideal solution

there is no net diffusion across the interface. Hence it is the activity, and not the concentration, which is the driving force in diffusion.

Consider a unimolecular mechanism by which a diffusing molecule passes over a potential barrier as shown in figure 4, with concentrations and activities as illustrated. The general rate equation (40) will be modified to

$$k = (kT/h) \exp(-\Delta F^\ddagger/RT)(\gamma_n/\gamma^\ddagger) = k^0(\gamma_n/\gamma^\ddagger) \quad (70)$$

where the γ 's are activity coefficients.

The net diffusion rate will then be the difference between the forward and backward rates of transport,

$$\text{Rate}_{\text{net}} = C_1 \lambda k^0 \frac{1}{1 + \frac{\alpha \lambda}{\gamma_1} \frac{d\gamma_1}{dx}} - \left(C_1 + \lambda \frac{dC_1}{dx} \right) \lambda k^0 \frac{1 + \frac{\lambda}{\gamma_1} \frac{d\gamma_1}{dx}}{1 + \frac{\alpha \lambda}{\gamma_1} \frac{d\gamma_1}{dx}} \quad (71)$$

which, upon simplifying, becomes

$$\text{Rate}_{\text{net}} = -\frac{dC_1}{dx} \lambda^2 k^0 \left[1 + \frac{d \ln \gamma_1}{d \ln C_1} \right] \quad (72)$$

Since the diffusion constant is defined by

$$\text{Rate}_{\text{net}} = -D \frac{dC_1}{dx}$$

we have

$$D = \lambda^2 k^0 \left[1 + \frac{d \ln \gamma_1}{d \ln C_1} \right] \quad (73)$$

If the molal volumes of the solute and solvent molecules, V_1 and V_2 , are not too different, equation 73 may be put in the form

$$D = \lambda^2 k^0 \frac{d \ln a_1}{d \ln N_1} \quad (74)$$

In writing equation 74 for equation 73, a small correction factor,

$$1 - N_1 \left(1 - \frac{V_1}{V_2} \right)$$

due to changing from concentration units to mole fraction, is neglected. This factor reduces to unity for $V_1 = V_2$, and even, in general, since it is a linear function of mole fraction, it will simply be absorbed into the corresponding values of λ^2 . For systems such that ΔF^\ddagger for viscous flow is the same as ΔF^\ddagger for diffusion, we would have

$$\eta D = \frac{\lambda_1}{\lambda_2 \lambda_3} kT \frac{d \ln a_1}{d \ln N_1} \quad (75)$$

IV. THE FREE ENERGY OF ACTIVATION FOR VISCOUS FLOW

In this section an attempt will be made to identify the quantities occurring in equation 64 with properties characteristic of the liquid to which it is being applied. To do this we shall employ the theorem, "The amount of energy required to make a hole in the liquid the size of a molecule is equal to the energy of vaporization" (19). This theorem is easily derived as follows: 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 $NE/2$, 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. Clearly a large hole will require more energy for its formation than a small one, but the energy of formation of a hole need not, and in general will not, be strictly proportional to the size of the hole. This is illustrated by the effect of pressure on viscosity discussed in a later section.

In relating the quantities occurring in equation 64 with properties of the liquid, the first thing to decide is whether the flow aggregate is a single molecule or a group of molecules. In making the decision as to which is the more probable mechanism, a guiding principle that applies to all rate processes must be kept in mind: *viz.*, any rate process proceeds by all possible mechanisms and therefore chiefly by the fastest ones. If different possible mechanisms do not involve greatly varying values of the contribution of the entropy of activation to the free energy of activation, then the fastest process will be the one with the smallest energy of activation. Now a molecule can flow only if there is a hole in the liquid for it to flow into, and thus the difference in energy between the activated and normal states is chiefly due to the extra volume required by the activated state. Hence the most probable mechanism is one that requires the smallest amount of extra volume for the process to take place. Clearly, this condition will be most nearly satisfied by a mechanism involving only one or two molecules. Figure 5 illustrates one suggested mechanism by means of which one molecule could move past another. The figure illustrates the instantaneous formation of a double molecule which then rotates through an arc of about 90° . The initial position of the molecules is illustrated by the dotted lines, and after rotation they occupy the position indicated by the heavy black circles.

This mechanism identifies the λ 's of the flow aggregate with the dimensions of a single molecule. If, further, the distance between successive minima, λ , is identified with λ_1 , the perpendicular distance between adjacent layers of molecules, then the product $\lambda_1\lambda_2\lambda_3$, in the denominator of equation 64, is just equal to V/N , where V is the molal volume of the liquid.

Equation 64 may then be written,

$$\eta = (hN/V) \exp(\Delta F^\ddagger/RT) \quad (76)$$

There remains the problem of deciding the method for determining the free energy of activation for viscous flow. This may be estimated as some fraction of the free-energy change of an analogous reaction. Powell, Roseveare, and Eyring (52) base their choice of the analogous reaction on the following model of the unit flow process: An individual molecule occasionally acquires the activation energy necessary to squeeze past its

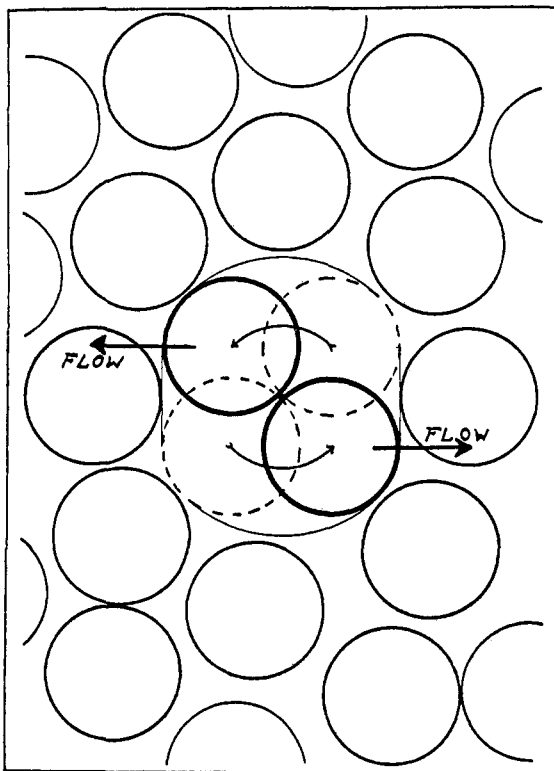


FIG. 5. Viscous flow by means of double molecules as illustrated by Hirschfelder, Stevenson, and Eyring (30). Two molecules collide to form a double molecule. If there is sufficient space available, this double molecule can rotate and then dissociate. One layer of liquid can flow past another by a succession of these processes.

neighbors into the next equilibrium position. The bonds which must be broken are the same bonds that would be broken in the process of vaporization. However, the work of expansion to the vapor state will not be needed, and the entropy of this expansion will not be available. Thus we may expect ΔF^\ddagger to be correlated with

$$\Delta F_{\text{vap}} + T\Delta S_{\text{vap}} - RT = \Delta H_{\text{vap}} - RT = \Delta E_{\text{vap}}$$

In figure 6, ΔF^\ddagger for viscous flow has been plotted against ΔE_{vap} for ninety-three inorganic and organic liquids at their boiling points. The points fall along a straight line which passes through the origin, and has a slope 1/2.45. Equation 76 can then be written

$$\eta = Nh/V \exp(\Delta E_{\text{vap}}/2.45RT) \quad (77)$$

When ΔH^\ddagger is plotted against ΔE_{vap} , the results for normal liquids are about as good as for ΔF^\ddagger , but hydrogen-bonded liquids involve large deviations in the direction of high activation energies. These abnormal activation energies are in large measure compensated by abnormal entropies of

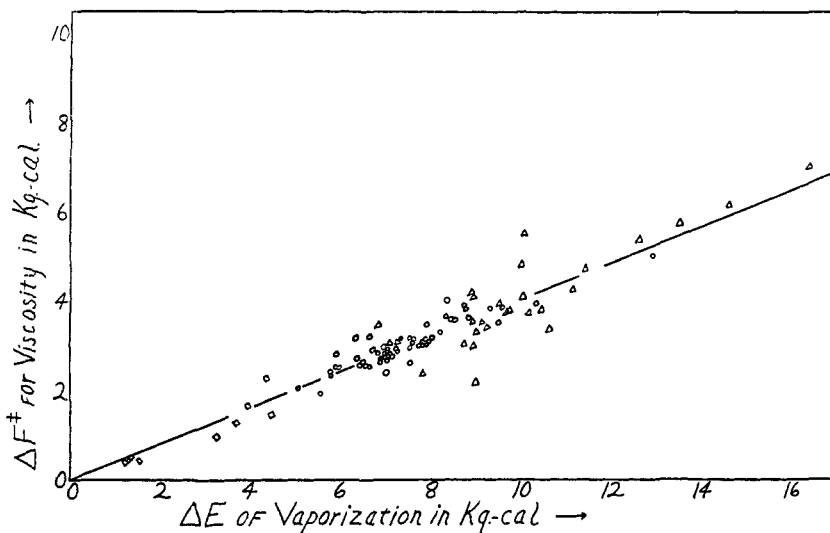


FIG. 6. The squares represent "permanent gases," the triangles represent hydrogen-bonded liquids, and the circles represent the other liquids.

activation. This compensation is a common phenomenon for both rate and equilibrium processes.

It is of interest to examine other proposed equations which, in general, permit prediction of viscosity to within a factor of 2 to 3. We first recall that ΔF^\ddagger includes one more degree of freedom for the normal than for the activated state. The degree of freedom corresponding to decomposition of the activated complex is omitted from ΔF^\ddagger , being included in the frequency kT/h . If classical statistics is applicable, there is no difference in the parts of the partition functions depending on kinetic energy for the normal and for the activated state. This may be seen by inspection of equations 25 and 26 if it is recalled that in classical mechanics the kinetic

energy, T , is independent of the potential field to which the system is confined. If we then make the approximation that the partition function for the liquid as a whole is obtainable from the partition function for an average molecule moving in the field of its neighbors, we have:

$$f = (2\pi mkT/h^2)^{3/2} \iiint \exp(-V/RT) dx dy dz \quad (78)$$

$$= (2\pi mkT/h^2)^{3/2} v_f$$

where V is the potential due to the presence of neighbors and

$$v_f \left(\equiv \iiint \exp(-V/RT) dx dy dz \right)$$

is the free volume. Only translational degrees of freedom are considered in equation 78. Since the extra degree of freedom in the normal molecules is a translation, we have, from equations 76 and 78,

$$\eta = (hN_A/V)(2\pi m^*kT/h^2)^{1/2} v_f^{1/3} \exp(\Delta F'/RT) \quad (79)$$

Here $\Delta F'$ includes all contributions to the free energy of activation for viscous flow other than those involving the degree of freedom in which decomposition is occurring.

Equation 79 contains two unknown quantities, v_f and $\Delta F'$. The free volume plays an important rôle in many properties of liquids other than the viscosity, and a discussion of its evaluation is given below. $\Delta F'$ may be divided into the energy of activation for viscous flow, ΔE_{vis} , and an entropy of activation. Since a molecule cannot flow unless there exists a cavity for it to flow into, ΔE_{vis} is due chiefly to the energy of forming a hole in the liquid. It is thus closely related to the energy of vaporization, a relationship which has already been discussed. By comparison with experiment it is found that the entropy term in $\Delta F'$ is small and may to a good approximation be set equal to zero.

V. FREE VOLUMES OF MOLECULES IN LIQUIDS

A. Free volumes from the energy-volume coefficient

In order to obtain values of the free volume, v_f , to use in equation 79, it is necessary to consider certain simple models for liquids. One simple model that has been used is that employed by Eyring and Hirschfelder (21). It is assumed that the potential energy does not change as the molecule moves from its equilibrium position until it collides with its neighbors. At this point the potential energy goes to infinity. The molecule thus moves in a potential box with a flat bottom and straight sides, the size of the box being governed by the total volume and the size and packing of

the molecules. If, further, the rotational motion of the molecules is not changed on changing the volume of the liquid or on vaporization, a term for it need not be included in the partition function for the liquid in considering the vapor pressure or the equation of state. The same thing may be said for the degrees of freedom corresponding to internal vibrations.

The mathematical statement of this picture is as follows: If f^N is the partition function for the liquid, it may be written

$$f^N = [(2\pi mkt/h^2)^{3/2}(v_f)]^N \exp(\Delta S_c/R) \exp(-\Delta E_{\text{vap}}/RT) \quad (80)$$

where ΔS_c would be equal to zero if the function f^N were like that for a solid and would equal R if it were like that for a gas. Hirschfelder, Stevenson, and Eyring (30) considered that ΔS_c should approach the limiting value R and called it communal entropy. Lennard-Jones and Devenshire (40) and Monroe and Kirkwood (47) have more recently estimated this extra randomness of liquids over that for solids. Lennard-Jones and Devenshire assumed that it arose from a random distribution between lattice positions present in the solid and new lattice positions which accompanied the increase in volume during melting and subsequently. Later in this paper we shall have more to say about the nature of ΔS_c . To the approximation employed here, the energy of vaporization, ΔE_{vap} , is just the difference in potential energy between the liquid and gas. This follows because the kinetic-energy terms are the same for both phases, and it is assumed that no potential-energy terms are associated with either the rotation of the molecules or with their oscillation about their equilibrium positions. v_f is the size of the box in which the geometrical center of the molecule can move without change in potential energy.

In order to determine v_f , suppose that the molecules in the liquid are arranged in a simple cubic lattice and that each molecule, on the average, can move until it touches its neighbors when they are in their mean positions. Then if d is the incompressible diameter of each molecule, we have from figure 7 that $2(V/N)^{1/3} - 2d$ is the distance that the central molecule is free to move along each axis. v_f is then this quantity cubed,⁶ i.e.,

$$v_f = 8[(V/N)^{1/3} - d]^3 \quad (81)$$

The equation of state is obtained by differentiation of $\ln f^N$ with respect to the volume and multiplication by kT .

We have from equations 13, 18, and 80,

$$P = -kT(\partial \ln f^N/\partial V)_T = RT(\partial \ln v_f/\partial V)_T - (\partial \Delta E_{\text{vap}}/\partial V)_T \quad (82)$$

⁶ It will sometimes be convenient to use the quantity $Nv_f \equiv V_f$. Similarly, we shall use $v = V/N$ to indicate the volume per molecule.

From equation 81

$$(\partial \ln v_f / \partial V)_T = (V - N^{1/3} d V^{2/3})^{-1} = 2/V^{2/3} V_f^{1/3} \quad (83)$$

On combining equations 82 and 83 we arrive at

$$[P + (\partial \Delta E_{\text{vap}} / \partial V)_T] V^{2/3} V_f^{1/3} = 2RT \quad (84)$$

an equation which relates the free volume to known properties of the liquid. In employing equation 84 it must be remembered that the quantity $(\partial \Delta E_{\text{vap}} / \partial V)_T$ is, in general, not known and must be estimated. A closely related quantity is $(\partial E / \partial V)_T$, but this is also frequently unknown. The difficulty is resolved with the aid of the generalization, pointed out by Hildebrand (28), that $(\partial E / \partial V)_T$ is very nearly equal to $\Delta E_{\text{vap}} / V$ at low pressures for a large number of cases. Water and other hydrogen-bonded liquids, liquid metals, and all liquids at high pressures have values of $(\partial E / \partial V)_T$ which are less than $\Delta E_{\text{vap}} / V$. Free volumes computed from

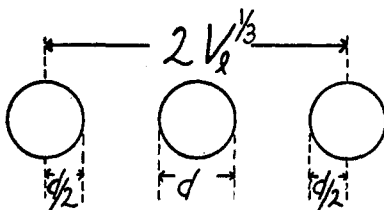


FIG. 7. The relationship between the free and the total volume

$$v_f^{1/3} = 2v^{1/3} - 2d$$

equation 84 agree well with those obtained by other methods, which are discussed below. Further considerations similar to those discussed above lead to reasonable agreement with experiment for expansion coefficients and compressibilities of liquids, as well as to a derivation of Trouton's and Hildebrand's rules (21).

B. Free volumes from velocity of sound

It has been found possible to modify certain kinetic theory formulae for gases in such a way as to make them applicable to liquids (37). The point of view employed is to treat the molecule moving in its free volume in the liquid as equivalent to the molecule moving in the total volume in the gas phase.

The velocity of sound, u , in any homogeneous medium is given by the general hydrodynamic formula:

$$u = (V/\beta_s)^{1/2} \quad (85)$$

where v is the specific volume and β_s is the adiabatic compressibility defined by

$$\beta_s \equiv -(1/V)(\partial V/\partial P)_s$$

For the special case of an ideal gas, equation 85 becomes

$$u = (RT\gamma/M)^{1/2} \quad (86)$$

where γ is the ratio of the specific heat at constant pressure to that at constant volume, and M is the molecular weight of the gas.

Equation 86 may be compared to that for \bar{c} , the average kinetic theory velocity of the molecules.

$$\bar{c} = (8RT/\pi M)^{1/2} \quad (87)$$

It is seen that u is proportional to \bar{c} but is slightly smaller, since the factor $(8/\pi)^{1/2}$ is always greater than $\gamma^{1/2}$. This is what one might suppose, since a wave propagated by matter would hardly be expected to travel

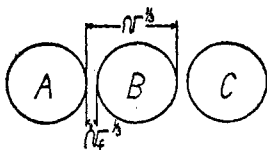


FIG. 8. Illustration of the mechanism which explains the observation that the velocity of sound in liquids is greater than the kinetic theory velocity of the molecules.

faster than the molecules which carry it. However, when the velocity of sound in liquids is compared to the kinetic theory velocity of the molecules, it is found that u for most liquids is greater than \bar{c} by factors ranging from 5 to 10. For example, for benzene at 25°C., \bar{c} is 2.83×10^4 , u (gas) is 1.88×10^4 , while u (liquid) is 13.0×10^4 cm. per second. Figure 8 illustrates the mechanism responsible for the fact that the velocity of sound in liquids can be so much greater than the kinetic theory velocity of the molecules. The wave front is assumed to travel from the edge of molecule A to the adjacent edge of molecule B with the velocity given by equation 86. As A collides with B, however, the signal is transmitted almost instantaneously to the opposite edge of molecule B.

This follows from the fact that sound waves are longitudinal, or compression, waves. Since the ratio of the total distance to the free space between two points in the liquid is given by the ratio $(V/V_f)^{1/3}$, this leads at once to the equation,

$$u \text{ (liquid)} = u \text{ (gas)} (V/V_f)^{1/3} = (RT\gamma/M)^{1/2} (V/V_f)^{1/3} \quad (88)$$

Equation 88 may be employed either to find the velocity of sound in liquids if V_f is known from some other source, or to determine free volumes if sound velocity measurements have been made.

C. The relation between free volume and thermal conductivity in liquids

A test of the general point of view outlined above is desirable, and is provided by considering the thermal conductivity of liquids (37).

A straightforward application of the kinetic theory of gases gives the relation for the thermal conductivity K ,

$$K \text{ (gas)} = (1/3)(N/V)\bar{c}Lc_v \quad (89)$$

where N/V is the number of molecules per cubic centimeter, L is the mean free path, and c_v is the specific heat per molecule. It is found, however, that equation 89 gives values which are too low for the thermal conductivity of gases, and Eucken (11) gives the correction factor $1/4(9\gamma' - 5)$, where γ' is the ratio of c_p to c_v . Equation 89 may now be rewritten,

$$K \text{ (gas)} = (1/3)[1/4(9\gamma' - 5)](N/V)\bar{c}Lc_v \quad (90)$$

a relation which may be tested in the form,

$$K \text{ (gas)} = \eta(c_v/m)(1/4)(9\gamma' - 5) \quad (91)$$

since the viscosity, η , is given by $(1/3)(N/V)m\bar{c}L$. Equation 91 has been observed to give excellent agreement with experiment (42).

In order to convert equation 90 into a form applicable to liquids the following identifications may be made: (N/V) becomes the number of molecules per cubic centimeter of liquid rather than per cubic centimeter of gas. The average velocity \bar{c} must be multiplied by the ratio $(V/V_f)^{1/3}$, for the same reasons as are given above for justifying equation 88. The distance that the energy is carried is now $(v)^{1/3}$ rather than L , the mean free path for the gas. c_v for the gas is replaced by αc_v , where α is the accommodation coefficient which takes account of the number of degrees of freedom which come into equilibrium in the thermal conduction process. Making all these substitutions we have:

$$K \text{ (liquid)} = (1/12)(9\gamma' - 5)(1/v)(8RT/\pi M)^{1/2}(V/V_f)^{1/3}(v)^{1/3}(\alpha c_v) \quad (92)$$

On substituting equation 88 and simplifying, we have

$$K \text{ (liquid)} = (1/12)(9\gamma' - 5)(8/\pi\gamma)^{1/2}(N/V)^{2/3}u(\alpha c_v) \quad (93)$$

Here u is the velocity of sound in the liquid, γ' is the effective value of the ratio of c_p to c_v for thermal conduction in the gas, and γ is the same quantity for the transmission of sound.

Equation 93 is very similar to one given by Bridgman for the thermal

conductivity of liquids (5, 6). In order to have equation 93 reduce to the one successfully employed by Bridgman, αc_v must be assigned the value $3k$ per molecule. For the liquids composed of polyatomic molecules, which Bridgman studied, this is understandable if only the kinetic energy of translation and rotation transfer appreciable energy in the process of thermal conduction. Using a value of αc_v equal to $3k$, γ' becomes $4/3$ and equation 93 reduces to

$$K(\text{liquid}) = (0.931/\gamma^{1/2}) 3k (N/V)^{2/3} u \quad (94)$$

This formula has the same form as that employed by Bridgman, but the numerical coefficient is about 12 per cent smaller, as a result of the factor $0.931/\gamma^{1/2}$ replacing unity in his expression.

TABLE 1

Comparison of the observed thermal conductivities of liquids at 30°C. with those computed from equation 94

SUBSTANCE	K (OBSERVED (5))	K (CALCULATED)	$\frac{K(\text{OBSERVED})}{K(\text{CALCULATED})}$
	$\times 10^3$ C.G.S. units	$\times 10^3$ C.G.S. units	
Methyl alcohol.....	21.1	22.3	0.95
Ethyl alcohol.....	18.0	19.2	0.94
Propyl alcohol.....	15.4	17.3	0.89
Butyl alcohol.....	16.7	13.3	1.26
Isoamyl alcohol.....	14.8	14.1	1.05
Ether.....	13.7	10.9	1.26
Acetone.....	17.9	16.3	1.10
Carbon disulfide.....	15.9	16.1	0.99
Ethyl bromide.....	12.0	12.8	0.94
Ethyl iodide.....	11.1	10.6	1.05
Water.....	60.1	51.7	1.16

Table 1 shows values for K at 30°C. for a number of liquids computed by equation 94 for comparison with Bridgman's experimental values. The agreement, somewhat better than Bridgman's earlier computations, suggests that the general point of view cannot be far wrong. Equation 94 not only works remarkably well for the variation of K from liquid to liquid at atmospheric pressure, but, as Bridgman has pointed out, it also gives approximately the temperature variation of K . It is, therefore, quite surprising that it does not predict the pressure effect correctly. Whereas most liquids increase their thermal conductivity by approximately a factor of 2 on going from atmospheric pressure to 12,000 atmospheres, the formula predicts an increase by about a factor of 4. It has been suggested that such a decrease in the value of α might be due to quantization of the

mass motions of the molecules at high pressures (37). The effective heat capacity, ac_v , would have to become $1.5k$ in order to explain the observations at the highest pressures to which the experiments extend.

D. A comparison of values of free volumes of liquids computed by different methods

Table 2 gives a comparison of free volumes for a number of liquids calculated from equations 84 and 88. The agreement indicates that, for the type of liquid considered in table 2 at atmospheric pressure, it is immaterial whether equation 84 or equation 88 is employed in the viscosity equation. Since equation 84 fails badly when applied to liquid mercury (21), it provides no check of the sound velocity equation 88 for this case. Consequently it is of interest to compare equation 88 with an equa-

TABLE 2
Values of the free volume for various liquids (30)

Sub- stance..	Acetone		Ether		Chloroform		Toluene		Carbon tetrachloride		Carbon disulfide	
	V_f FROM EQUATION 88	V_f FROM EQUATION 84	V_f FROM EQUATION 88	V_f FROM EQUATION 84	V_f FROM EQUATION 88	V_f FROM EQUATION 84	V_f FROM EQUATION 88	V_f FROM EQUATION 84	V_f FROM EQUATION 88	V_f FROM EQUATION 84	V_f FROM EQUATION 88	V_f FROM EQUATION 84
°C.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.	cc.
0			0.48	0.47	0.21	0.25	0.16	0.16	0.16	0.21	0.23	0.45
10			0.57	0.55	0.24	0.29	0.19	0.19	0.24	0.26	0.26	0.52
20	0.45	0.54	0.70	0.65	0.29	0.34	0.22	0.22	0.28	0.31	0.30	0.58
30			0.90	0.79	0.34	0.40	0.26	0.26	0.33	0.37	0.36	0.66
40	0.64	0.63			0.40	0.47	0.31	0.31	0.38	0.43	0.39	0.75
50					0.48		0.36	0.36	0.45	0.50	0.47	0.84

tion for the free volume of mercury which is known to be consistent with its thermodynamic properties. The simplest model which might be employed is to assume that the Einstein characteristic temperature is the same for the liquid as for the solid phase. Application of equation 78 should then lead to approximate values for v_f . A better value of the characteristic temperature of the liquid may be obtained by choosing it so as to fit the observed entropy of fusion (36). Further, since the observed values for the specific heat at constant volume for mercury fall below the classical value for a harmonic oscillator as the temperature is raised, the expression for the free volume must be modified to take account of this effect. An expression for V_f consistent with these requirements is

$$V_f = N \left[\frac{T/\Theta}{(2\pi mkT/h^2)^{1/2}} + 2(V/N)^{1/3} - (2V_0/N)^{1/3} \right]^3 \quad (95)$$

Here Θ is the characteristic temperature of the liquid and V_0 is identified as the volume of the liquid at the melting point. The form of the potential function corresponding to equation 95 is shown in figure 9, and values for V_f computed from equation 95 are compared with those obtained from the sound velocity equation in table 3. The general agreement is of particular

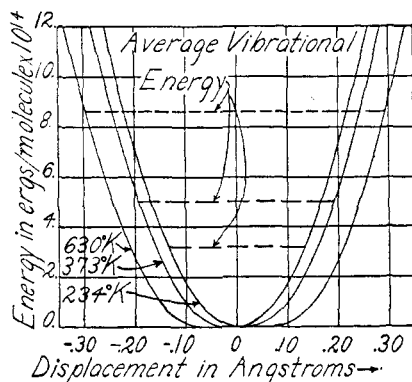


FIG. 9. Potential-energy function for displacements of a mercury atom from its equilibrium position (37).

TABLE 3

Free volumes for liquid mercury at different temperatures and pressures

t °C.	P atmospheres	V_f FROM EQUATION 88	V_f FROM EQUATION 95
		cc.	cc.
-39	1		0.0081
0	1	0.0120	0.0120
100	1	0.0220	0.0256
200	1		0.0434
300	1		0.0718
357	1		0.0904
0	1	0.0120	0.0120
0	1000	0.0117	0.0116
0	2000	0.0114	0.0114
0	3000	0.0111	0.0111
0	4000	0.0107	0.0109
0	5000	0.0104	0.0107
0	6000	0.0101	0.0105
0	7000	0.0098	0.0103

interest, since the free volumes are of a different order of magnitude than those of the non-metallic liquids discussed above.

VI. THE VISCOSITY OF LIQUIDS

Since means are now available for estimating the free volume, it is possible to apply equation 79 to the problem of the viscosity of liquids.

The equation may be rewritten in the form,

$$\eta = (hN/V)(2\pi m^*kT/h^2)^{1/2}v_f^{1/3} \exp(\Delta E_{\text{vis}}/RT) \exp(-\Delta S'/R) \quad (96)$$

where $\Delta E'$ will be some fraction of the energy of vaporization. This follows from the assumption that the energy of activation for viscous flow is due chiefly to the extra volume required by the activated complex, since the energy of formation of a hole of molecular size is equal to the energy of vaporization. The hole required for the flow process to take place will not, in general, be as large as a cavity of molecular dimensions, since this would be unnaturally extravagant of free energy. The bimolecular mechanism illustrated in figure 5, for example, would require a cavity of about one-third the size of a molecule. The situation is somewhat different when each molecule forms directed bonds (e.g., hydrogen bonds) with its neighbors, and these cases will be discussed later.

For those cases where $(\partial\Delta E_{\text{vap}}/\partial V)_T$ may be taken equal to $\Delta E_{\text{vap}}/V$, and where the external pressure may be neglected in comparison to $\Delta E_{\text{vap}}/V$, equation 84 reduces to

$$V_f^{1/3} = 2RTV^{1/3}/\Delta E_{\text{vap}} \quad (97)$$

If, further, ΔE_{vis} is written as $\Delta E_{\text{vap}}/n$, then equation 96 may be written

$$\eta = 7.71 \times 10^{-4} (M^{1/2}T^{2/3}/V^{2/3}\Delta E_{\text{vap}}) \exp(\Delta E_{\text{vap}}/nRT) \exp(-\Delta S'/R) \quad (98)$$

where ΔE_{vap} is in calories per mole.⁷ Equation 98 has been tested by Ewell and Eyring (16) in the following manner: The n appearing in the exponential of equation 98 was chosen to give the correct temperature coefficient of viscosity by computing values for η neglecting the entropy of activation. The computed values of the viscosity are then plotted as $\ln \eta$ against $1/T$. The value of n which gives a plot parallel to the straight line of the observed viscosities is taken as the value of n which gives the correct temperature coefficient. The calculations were carried out for most of the liquids for which reliable values of the viscosities and the heats of vaporization are known over a temperature range. The results to the nearest half integer are given in table 4. As examples, table 5 shows the calculations for carbon tetrachloride, and figure 10 shows the plots for carbon tetrachloride, nitrogen, hexane, and chloroform. Computations similar to those

⁷ The coefficient 7.71×10^{-4} given in equation 98 is smaller by a factor equal to $\sqrt{2}$ than the coefficient given by Ewell and Eyring (16). This is because Ewell and Eyring assumed a unimolecular mechanism, while a bimolecular mechanism is assumed in equation 98. It is difficult to choose between the unimolecular and bimolecular mechanism from the viscosity data alone, but when this is taken in conjunction with diffusion data, the unimolecular mechanism seems the more likely, as we shall see.

given in table 5 and plots similar to those in figure 10 were made for all the liquids listed in table 4.

Inspection of table 5 reveals the fact that there seems to be some correlation between the symmetry and polarity of the molecule and the value of n required to give the correct temperature coefficient of viscosity. Thus, all the liquids with a value of n equal to 3 are non-polar,⁸ and many of them are spherically symmetrical. This is certainly true of carbon tetrachloride, methane, and argon and is approximately true of nitrogen and carbon monoxide when the kinetic theory shell is considered. The liquids

TABLE 4
Values of n for different substances

$n = 3$	Carbon tetrachloride, benzene, cyclohexane, methane, nitrogen, carbon monoxide, argon
$n = 3.5$	Dichloroethane, dibromoethane, oxygen
$n = 4$	Pentane, hexane, heptane, carbon disulfide, chloroform, toluene, ether, ethyl acetate, acetone, ethyl iodide, ethyl bromide, methyl iodide, ethylene

TABLE 5
Computation of viscosity of carbon tetrachloride

t	V	ΔE_{vap}	$\eta(\text{OBSERVED})$	$\eta(\text{CALCULATED}) + \eta(\text{OBSERVED})$		
				$n = 2$	$n = 3$	$n = 4$
$^{\circ}\text{C.}$	<i>cc. per mole</i>	<i>kg.-cal. per mole</i>	<i>millipoises</i>			
0	94.3	7.56	13.47	30.7	2.12	0.95
20	96.6	7.30	9.69	24.0	2.11	1.04
40	99.0	7.06	7.38	19.7	2.07	1.13
60	101.6	6.81	5.84	16.4	2.06	1.24
80	104.4	6.56	4.68	14.2	2.08	1.36

with values of n greater than 3 are not spherically symmetrical and most of them are polar. If the molecule is not symmetrical and makes a better bond with one neighbor than with the others, it will be able to preserve this bond in the activated state, so that the energy of activation will tend to fall *below* the normal value for symmetrical molecules. On the other hand, if a molecule forms strong directional bonds with a number of nearest neighbors, the energy of activation will tend to be *above* the normal value. Molecules with a single large dipole, such as ethyl iodide, ethyl

⁸ Carbon monoxide has a small dipole moment of the order of 0.15 Debye unit.

bromide, and acetone, are examples falling in the first category, while water (to be discussed later) exemplifies the second.

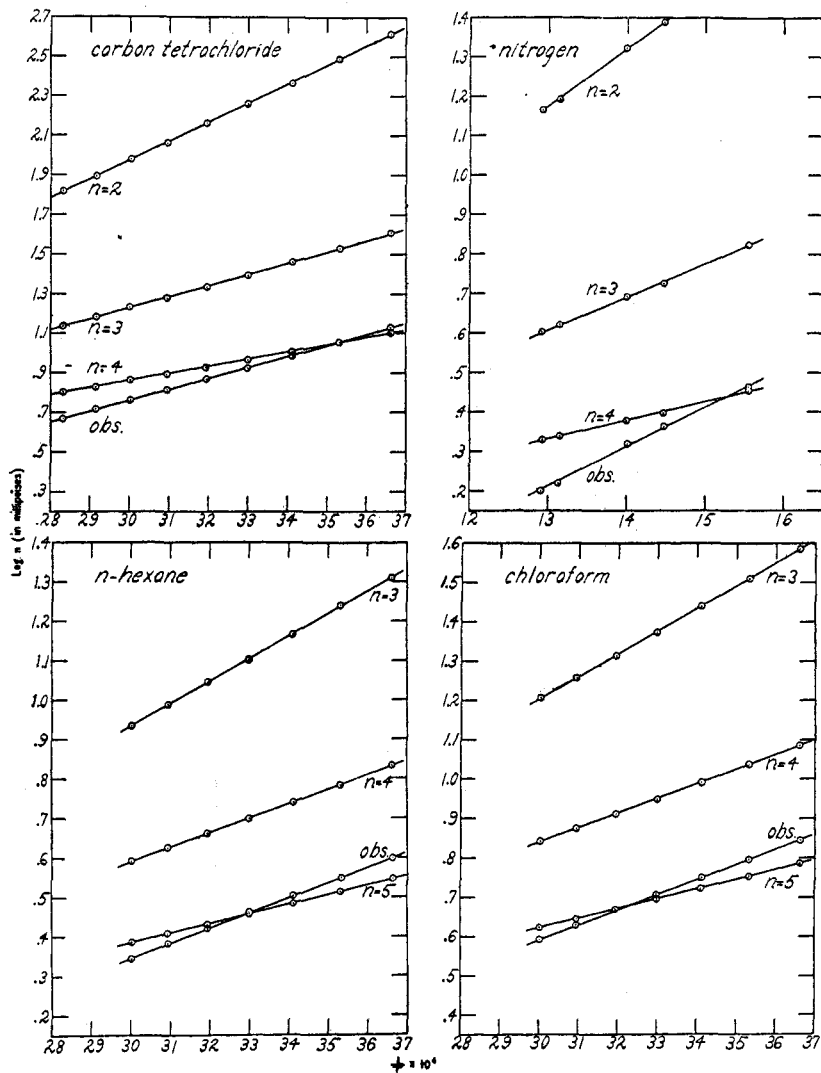


FIG. 10. Plots of $\log \eta$ versus $1/T$ for observed and calculated viscosities, using integral values of n in equation 98 (from Ewell and Eyring (16)). Ordinates are $\log \eta$ in millipoises; abscissas are $\frac{1}{T} \times 10^4$.

For the rolling mechanism indicated in figure 5, the ratio of the size of the hole required to the molecular volume will vary with the liquid struc-

ture, which in turn will depend on the shape of the molecules. Experiments seem to indicate that for the long cylinders, such as the paraffins, this ratio is smaller (about 1:4) than for spherical molecules, where the ratio is about 1:3. A different value for n is to be anticipated for molecules with shapes which preclude the above mechanism. Large flat molecules of the anthracene type will presumably provide such examples.

TABLE 6
Comparison of values of n with $\Delta E_{\text{vap}}/B$

LIQUID	B	ΔE_{vap} AT BOILING POINT	$\frac{\Delta E_{\text{vap}}}{B}$	n
	kg.-cal. per mole	kg.-cal. per mole		
CCl ₄	2.50	6.60	2.7	3
C ₆ H ₆	2.54	6.66	2.6	3
C ₆ H ₁₂ (cyclohexane).....	2.89	6.70	2.3	3
CH ₄	0.72	1.82	2.5	3
A.....	0.52	1.42	2.8	3
N ₂	0.45	1.21	2.7	3
CO.....	0.47	1.31	2.8	3
O ₂	0.40	1.47	3.7	3.5
C ₂ H ₄ Cl ₂	2.27	6.93	3.1	3.5
C ₂ H ₄ Br ₂	2.59	7.89	3.0	3.5
C ₅ H ₁₂ (pentane).....	1.58	5.51	3.5	4
C ₆ H ₁₄ (hexane).....	1.72	6.22	3.6	4
CHCl ₃	1.76	6.63	3.8	4
C ₂ H ₅ I.....	1.72	6.40	3.7	4
C ₂ H ₅ Br.....	1.59	6.08	3.8	4
CS ₂	1.28	5.92	4.6	4
C ₆ H ₅ CH ₃	2.12	7.24	3.4	4
(C ₂ H ₅) ₂ O.....	1.61	5.70	3.5	4
CH ₃ COCH ₃	1.66	6.40	3.9	4
C ₂ H ₄	0.79	3.50	4.4	4

Inspection of figure 10 shows that the plots of the logarithms of the viscosity against the reciprocal of the temperature are straight lines for both the calculated and the observed curves. This means that they can be fitted with an equation of the form

$$\eta = A \exp (B/RT) \quad (99)$$

Here A is an entropy-dependent factor, and B is an energy factor.

Then B will be the experimentally determined quantity, $R \, d \ln \eta / d(1/T)$. Because this can be taken as a constant for most liquids throughout their

normal liquid range, it can be considered to be an average activation energy for viscous flow. Since ΔE_{vap} varies only slowly with temperature, the ratio $\Delta E_{\text{vap}}/B$ should be approximately equal to 3 or 4 anywhere in the temperature range where B is a constant. Table 6 gives a comparison of values of n , as determined by the method given above, with $\Delta E_{\text{vap}}/B$, where ΔE_{vap} is taken at the normal boiling point for all the liquids in the table. Inspection of table 6 shows that there is a correlation between the values of n and the ratio $\Delta E_{\text{vap}}/B$, so that this ratio may be taken as a rough measure of n .

A correlation between B and ΔE_{vis} having been established, it is of interest to examine further approximate values of n for quite unsymmetrical molecules, cases for which complete data for applying equation 98 are not available. Table 7 shows values of $\Delta E_{\text{vap}}/B$ for the normal paraffin hydro-

TABLE 7
Values of $\Delta E_{\text{vap}}/B$ for normal paraffin hydrocarbons

HYDROCARBON	RANGE	B	ΔE_{vap}	$\Delta E_{\text{vap}}/B$
	°C.	kg. cal per mole	kg. cal per mole	
$n\text{-C}_5\text{H}_{12}$	0-b.p.	1.58	5.71	3.6
$n\text{-C}_6\text{H}_{14}$	0-b.p.	1.73	6.96	4.0
$n\text{-C}_7\text{H}_{16}$	0-b.p.	1.91	8.11	4.3
$n\text{-C}_8\text{H}_{18}$	0-b.p.	2.14	9.21	4.3
$n\text{-C}_9\text{H}_{20}$	0-40	2.44	10.21	4.2
$n\text{-C}_{10}\text{H}_{22}$	0-30	2.60	11.11	4.3
$n\text{-C}_{11}\text{H}_{24}$	0-30	3.06	11.96	3.9
$n\text{-C}_{14}\text{H}_{30}$	20-40	3.60	14.21	4.0
$n\text{-C}_{16}\text{H}_{34}$	20-40	4.01	15.51	3.9
$n\text{-C}_{18}\text{H}_{38}$	40-60	4.15	16.76	4.0

carbons (16). This ratio is seen to be about 4 for all these molecules. Part of the increase in the ratio with increasing molecular weight is due to the fact that the comparison is made at 25°C. rather than at corresponding temperatures, such as their boiling points. Here, again, the energy of activation for viscous flow is seen to be about one-fourth the energy of vaporization. This result for long-chain molecules is consistent with the mechanism illustrated in figure 5, if the circles in figure 5 illustrate cylinders rolling over each other as viewed along their axes. A pile of logs might be expected to roll over each other by an analogous mechanism.

A. The entropy of activation for viscous flow

Inspection of figure 10 will reveal that the plots of the observed viscosity and the parallel ones which were calculated neglecting $\Delta S'$ do not coincide. The calculated values are greater by an average factor of about 2, when

the value of n giving the right temperature coefficient is used and the entropy of activation is neglected. The following are the factors by which the viscosities calculated, neglecting the factor $(-\Delta S'/R)$, are too high: carbon tetrachloride, 2.5; benzene, 2.5; cyclohexane, 1.5; methane, 2.5; argon, 1.6; nitrogen, 1.7; carbon monoxide, 1.8; pentane, 1.2; hexane, 1.2; heptane, 1.4; carbon disulfide, 1.3; ether, 1.4; ethyl acetate, 1.5; toluene, 2.5; acetone, 1.6.

If all the other terms in the equation are correctly evaluated, these factors indicate a value of $\Delta S'$ of the order of one entropy unit. That the activated configuration should have a greater entropy than the normal one is a reasonable result. Indeed, it would be surprising if $\Delta S'$ were exactly zero, and it is an interesting fact that it is almost equal for such a wide variety of substances.

A number of the approximations that have been made in order to apply equation 98 may be responsible for part of this factor which is interpreted as $\Delta S'$. The expression 97 for $V_f^{1/3}$ may not be just equal to what one would obtain by an exact integration over potential energy if such an integration could be carried out. κ may not be unity for the flow process, and a value smaller than unity would lead to greater calculated entropies of activation. The identification of λ and λ_1 may not be justified in all cases.

We now consider in greater detail the methods available for estimating the energy of activation. Various thermodynamic processes may be used to estimate the energy of forming a hole. How exact an estimate they provide of the energy of activation for viscous flow depends on how nearly the thermodynamic process approximates the formation of the hole in the flow process. The energy of vaporization measures exactly the cost in energy of a hole into which a molecule fitted if *all the other molecules remained exactly as they were before the molecule was removed*. However, the molecules surrounding such a hole will tend to decrease this free energy somewhat by reorienting. This effect has been considered in detail by Kirkwood (39).

The thermodynamic quantity $(\partial E/\partial V)_T$ measures the energy required for a uniform expansion of the liquid. This function, multiplied by the extra volume required by the activated complex, gives the energy of activation for viscous flow *if the uniform volume expansion takes place in just the same way as the process of forming a hole required for viscous flow*. For the liquids considered in the previous section the two methods of estimating ΔE_{vis} give the same results, and as $V(\partial E/\partial V)_T$ and ΔE_{vap} have essentially the same magnitude and temperature dependence at atmospheric pressure. However, at the high pressures considered in the next section, the two quantities are quite different. Figure 11 illustrates the fact that

the pressure at which $-\Delta E_{\text{vap}}$ is a *maximum* is the point at which $(\partial E/\partial V)_T$ equals zero. Hence, if ΔV is the extra volume required for the flow process, the heat of activation in the two cases will be

$$\Delta H_{\text{vis}} = \Delta E_{\text{vap}}/n + P\Delta V \quad (100)$$

and

$$\Delta H_{\text{vis}} = (\partial E/\partial V)_T \Delta V + P\Delta V \quad (101)$$

depending on which process most nearly approximates the process of forming the cavity for flow. Both equation 100 and equation 101 have been applied to data at high pressures.

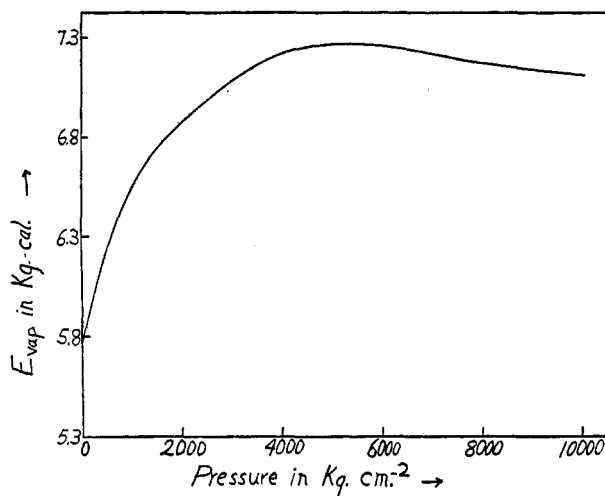


FIG. 11. The energy of vaporization of *n*-pentane at 30°C. as a function of the external pressure.

B. The effect of pressure on viscosity

The application of external pressure has the greatest effect on the rate of those reactions in condensed phases which have the greatest increase in volume resulting from the formation of the activated complex from the reactants. Since the free-energy difference between the normal and activated states for viscous flow in normal liquids results almost entirely from this increase in volume, it is not surprising that viscosity has a greater variation with pressure than any other property of pure liquids which has been studied.

In order to test equation 101, ΔV is identified with V/n , where n is the value required to give the correct temperature coefficient of viscosity.

This is equivalent to assuming that there is a linear relation between the size of the hole and the energy required to form it, and thus an n equal to 3 means that a cavity just one-third the size of the molecule is required.

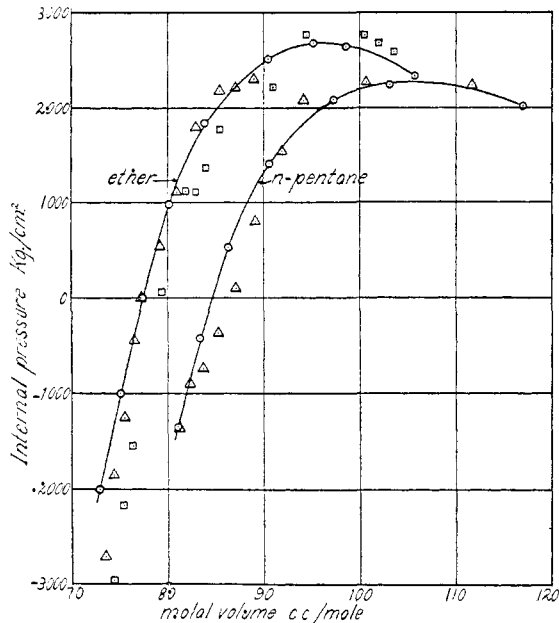


FIG. 12. Plots of internal pressure versus molal volume for ether and *n*-pentane (16). The circles are values computed from equation 102, using Bridgman's data for viscosity under pressure (6). The triangles and squares are values computed from the thermodynamic equation $P_i = (\partial E/\partial V)_T = T(\partial P/\partial T)_V - P$, using Bridgman's newer (1931) and older (1914) compression data, respectively (6).

If, following Hildebrand (28), we designate $(\partial E/\partial V)_T$ as P_i (the internal pressure), we have from equations 79, 84, and 101

$$\eta = 7.71 \times 10^{-4} [M^{1/2} T^{2/3} / V^{5/3} (P_i + P)] \exp[(P_i + P)V/nRT] \exp(-\Delta S'/R) \quad (102)$$

Equation 102 may be most readily tested by making P_i the unknown and using observed values of viscosity to compute internal pressures for comparison with those obtained directly from P - V - T data. Figure 12 illustrates the application of this method, using Bridgman's data (6).

Equation 102 fails when applied to certain other liquids, notably mercury, and a viscosity-pressure equation based on equation 100 has proven to be more generally useful. This equation, giving the heat of activation

for viscous flow in terms of the energy of vaporization and the work against the external pressure, has been tested by Frisch, Eyring, and Kincaid (25). The expression employed for ΔH_{vis} is

$$\Delta H_{\text{vis}} = \Delta E_{\text{vap}}/n + PV/n' \quad (103)$$

Here ΔE_{vap} is the energy of vaporization at the particular pressure considered, and V/n' is the extra volume required for viscous flow. It is found that n' does not have the same value as n , being somewhat greater.

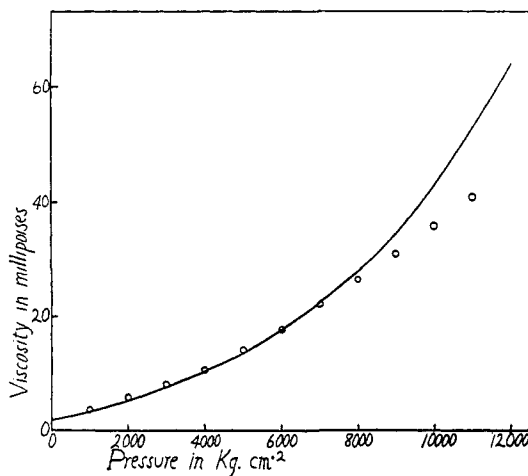


FIG. 13. Observed viscosities of ether (solid curve) as a function of pressure compared with calculated values (circles) computed on the internal pressure hypothesis (equation 102).

If the sound velocity method of getting the free volume is used, the equation giving the viscosity incorporating equation 103 may be written

$$\eta = (\pi RMT)^{1/2} (u_g/u_l) N^{-1/3} V^{-2/3} \exp(\Delta E_{\text{vap}}/nRT + PV/n'RT) \quad (104)$$

Here u_g is the velocity of sound in the gas, u_l is the same quantity for the liquid, and the other quantities have been defined. The procedure employed in testing equation 104 was to use the experimental viscosity, the energy of vaporization, the sound velocity in both the liquid and the gas, and the other terms on the right-hand side of equation 104 to determine the n giving the proper temperature variation of viscosity at atmospheric pressure. The values of n obtained in this way, given in table 8, are then employed in equation 104 in order to obtain values of n' at a given temperature and different pressures. A summary of the results for n' is given in table 9.

The values of n given in column three of table 7 are slightly different from those of Ewell and Eyring, because a different evaluation of the free volume has been used. Column six of table 8 shows that the value of n which gives the right temperature coefficient of viscosity also gives the absolute value to within an average value of 2 for liquids other than those classed as "hydrogen-bonded."

The individual computations of n' are shown in table 9. The treatments possible for benzene and for isopentane warrant giving only one value for

TABLE 8

Values of n which give the proper temperature variation of viscosity at atmospheric pressure (25)

SUBSTANCE	n (Ewell and Eyring (16))	n (Frisch, Eyring, and Kincaid (25))	n' MEAN VALUE	n'/n (Frisch, Eyring, and Kincaid (25))	$\frac{\eta \text{ (OBSERVED)}}{\eta \text{ (COMPUTED)}}$
<i>n</i> -Pentane.....	4	4.4	7.8	1.8	1.1
Ethyl ether.....	4	4.5	7.8	1.6	1.9
Benzene.....	3	3.3	5.5	1.7	0.6
Isopentane.....		4.4	8	1.8	1.9
Mercury.....	20	11	23	2.1	2.8

TABLE 9

Values of n' as computed from the data at various pressures

PRESSURE	<i>n</i> -PENTANE AT 30°C.	DIETHYL ETHER AT 52.5°C.	BENZENE AT 25°C.	ISOPENTANE AT 50°C.	MERCURY AT 0°C.	WATER AT 0°C.
<i>kg. per cm.</i> ²						
1,000	6.0		5.5	8		124
2,000	6.9	4.7			25.0	14
4,000	8.5	6.0			23.0	8.0
6,000	9.7	6.8			21.2	(5000)7.2
8,000	10.4	7.2				
10,000	10.8	7.6				
12,000		7.9				

n' . It will be noted that n' for *n*-pentane, ether, and mercury does not vary greatly over the entire experimental pressure range, but that n' for water ranges from 124 at 1000 *kg. per cm.*² to 7.2 at 5000 *kg. per cm.*² This variation is interpreted as follows: At low pressures water has an open, 4-coördinated structure (3), and no extra volume is required for the activated complex for flow to form. As the pressure is increased, the open structure collapses, and at high pressures the activated complex needs as much extra space to form as is required by any other non-spherical

molecule. It is probably incorrect to assume that n is constant for these liquids at one temperature and varying pressures, but the value of n' is not greatly affected by a considerable change in n . Table 10 illustrates that the n' values computed for water using different n 's converge to about the same limit at high pressures.

The fifth column of table 8 gives the ratio of the mean value of n' over the pressure range to the value of n . The fact that this ratio is nearly constant and equal to 1.6 to 1.8 for the four non-metallic liquids in table 8 is of some significance. It has been previously shown that the energy required to form a hole in a liquid the size of a molecule is equal to the energy of vaporization. Although it might be reasonable to assume a linear relationship between the size of the hole formed and the energy required to form it, the fact that the ratio n'/n is not unity but 1.75 indicates that this may not be the case. Taking the data for ether as an example,

TABLE 10
Values of n' for water for different values of n at 0°C . (25)

P <i>kg. per cm.²</i>	VALUES OF n'		
	$n = 2$	$n = 4$	$n = 5.4$
1000		16.1	124
2000	32	16	14
3000	19	11	9.7
4000	14	8.8	8.0
5000	10.6	7.7	7.2

we find an n' of 7, indicating that a hole approximately one-seventh the size of the molecule is required for viscous flow. However, the activation energy is two-ninths of the energy of vaporization. We accordingly have the interesting physical result that there is an energy of dissociation of large holes into smaller ones, i.e., two holes, each one-seventh the size of a molecule, cost considerably more energy than one hole two-sevenths molecular size. In the case of ether, seven holes, each one-seventh the size of a molecule, would liberate energy equal to fourteen-ninths of the energy of vaporization, on being combined into a single cavity of molecular dimensions.

The ratio n'/n for mercury does not differ greatly from that for the non-metallic liquids in table 8, but n and n' are themselves much greater. That the ratio of n' to n is again approximately 2 for a hole as small as one twenty-third the size of the atom is an interesting fact.

Figure 14 shows plots of observed and computed viscosities as a function

of pressure for ether, mercury, and *n*-pentane, with constant values of n and n' in equation 104. The agreement, while perhaps not as satisfactory as might be hoped for, is probably as good as can be expected.

It is clear that additional evidence is desirable before choosing between the two methods outlined above for treating the pressure variation of viscosity. The essential requirement is a simple, accurate method for securing the free energy of formation of a cavity in the liquid at any given temperature and pressure, and an entirely adequate treatment of viscosity

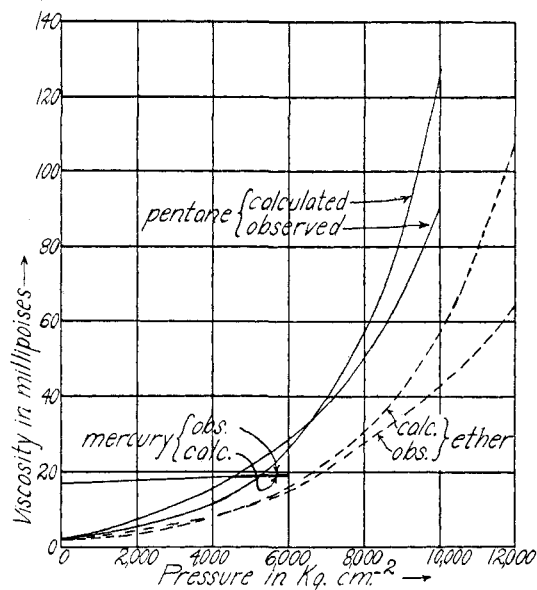


FIG. 14. Comparison of observed viscosities and those computed from equation 104. The values of n are 4.5, 12, and 4.4, and those of n' are 8, 23, and 10 for ether, mercury, and pentane, respectively.

under pressure cannot be given until this is available. The recent work of Kirkwood (39) may prove of value in this connection.

VII. APPLICATION TO VARIOUS CLASSES OF LIQUIDS

A. A classification of types of liquids

From the point of view of viscous behavior and of many other properties as well, Ewell (14) has given a classification of liquids which is essentially the same as that given below.

I. Those in which the forces between molecules are almost exclusively undirected:—(a) Relatively small molecules: e.g., carbon tetrachloride,

chlorine, argon, benzene. (b) Very long chain molecules: e.g., linear polymeric resins, such as polystyrene, polyisobutylene; very long chain hydrocarbons, such as some lubricating oils; selenium and μ -sulfur; raw rubber.

II. Those in which the cohesive forces are directed in part:—(a) Molecules containing dipoles: e.g., those with a single strong dipole making possible a weak association into pairs, e.g., ethyl chloride, ethyl bromide, acetone; those with two or more strong dipoles making possible a two- or three-dimensional network of dipole bonds, e.g., 1,5-dichloropentane, *p*-dinitrobenzene. (b) Molecules capable of forming hydrogen bonds,—e.g., water, phenol; in general, any liquid whose molecules have OH or NH groups. (c) Molecules capable of forming intermolecular covalent bonds, e.g., silicon dioxide, germanium dioxide, boron trioxide, beryllium fluoride, and all silicate, borate, and phosphate liquids which are not too basic.

III. Metallic liquids: molten metals.⁹

IV. Ionic liquids: molten salts.⁹

The applications of the theory thus far have been confined to examples chosen from types I(a), I(b), and II(a),—the so-called normal liquids. Although these are the ones to which the theory may be most easily applied, liquids of more complex structure may also be treated qualitatively, and a discussion of the applications to μ -sulfur and water will comprise the next two sections.

B. The viscosity of sulfur

As is well known, liquid sulfur is a fluid yellow liquid between the melting point and about 160°C. and also in the supercooled liquid region below the melting point. Above 160°C. the viscosity increases rapidly, increasing several thousandfold between 160° and 190°C., and thereafter the viscosity decreases in a normal way. Figure 15 shows the data of Rotinjanz (54) plotted as $\ln \eta$ against $1/T$. Rotinjanz's data show that between 160° and 250°C. the viscosity of sulfur is a function of the time as well as the temperature, and the values given in that range are only rough averages and probably not equilibrium values.

It is seen that the plot has two linear portions, below 160° and 250°C., for which B is 7.04 and 18.35 kg.-cal. per mole, respectively. In the region below 160°C., x-ray evidence (66) indicates that the molecule is a puckered S_8 ring, and by comparing this structure with cyclohexane, it seems likely that n would be 3 for this type of molecule. The heats of vaporization of sulfur have been accurately measured by West and Menzies (67). Their value of ΔE_{vap} at 120°C. (the middle of this linear part of the plot) is 2.59 kg.-cal. per gram-atom or 20.7 kg.-cal. per mole of S_8 . This is very nearly

⁹ Groups III and IV are really subdivisions of Group I, but are classified separately for obvious reasons.

three times 7.04, the value of B in this range, and this may be considered as further evidence toward confirming the S_8 molecule in the liquid in this range.

In the range above 250°C . the much larger slope of the curve indicates that the molecule is much larger than it is below 160°C . This larger sulfur molecule might be either a large ring, a branched chain, or a long straight chain, of which the latter seems most likely to be the correct structure. By analogy with the straight-chain hydrocarbons, n should be 4 for this type of molecule, and this would indicate a value of ΔE_{vap} of $4 \times 18.35 = 73.4$ kg.-cal. per mole on our hypothesis. West and Menzies give 2.05 kg.-cal. per gram-atom for ΔE_{vap} at 350°C . (the middle of this linear part

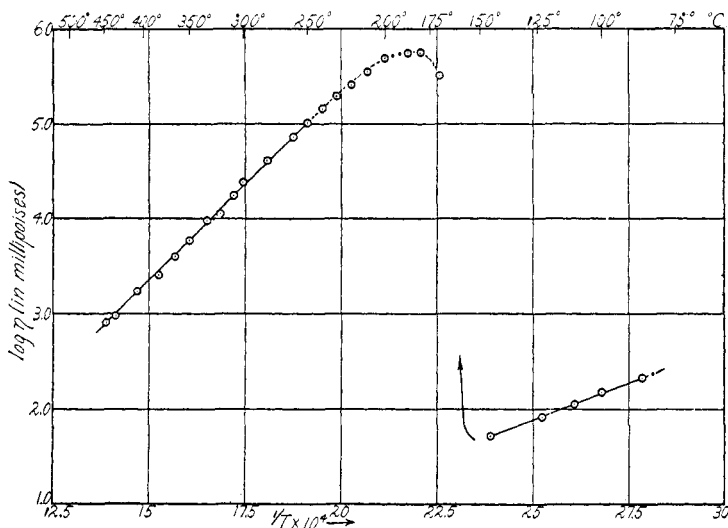


FIG. 15. Plot of $\log \eta$ versus $1/T$ for liquid sulfur from the data of Rotinjanz (16, 54)

of the curve) and, comparing this with the value deduced above, the molecular weight of the unit of flow is calculated to be S_{36} . In contrast to such a molecular weight of the unit of flow, the unit of vaporization is still S_8 , as shown by vapor density data (16).

This figure of 36 can be interpreted as an average chain length averaged over all the molecules in the liquid and averaged over the whole temperature range from 250° to 450°C . The alternative is that, although the chains may be longer, they flow in segments, the approximate number of atoms in the units of flow being 36. These segments, although tied together, jump as units. At any temperature there is probably an equilibrium mixture of chains of varying length, and, as the temperature is

raised, the average chain length will become smaller as the equilibrium constant changes. The linear relation between $\ln \eta$ and $1/T$ is not a sufficient condition for an unchanging molecular state in a liquid. Normal liquids composed of a single molecular species almost without exception give linear $\ln \eta$ versus $1/T$ plots. However, a liquid composed of an equilibrium mixture of several molecular species might also give a linear plot, since the equilibrium constant changes according to van't Hoff's equation, which is of the same form of temperature dependence as is the viscosity of a liquid.

The hypothesis had been advanced by Warren and Burwell (66) that the increase in viscosity above 160°C . is "probably due to the S_8 ring breaking open and forming irregular chains which tangle with one another and give rise to the marked increase in viscosity". These results give a more concrete form to this idea of long chains and obviate the necessity of postulating the indefinite concept of tangling of chains, since any liquid composed of chains averaging 36 atoms in length or more, e.g., a hydrocarbon, will be a very viscous liquid. The fact that liquid sulfur is not a normal close-packed liquid is shown by the work of Gingrich (26), who found that the liquid had about two nearest neighbors at the normal covalent bond distance, whereas liquid sodium or mercury has about eight nearest neighbors. This fact indicates that the molecule in the liquid sulfur is either a chain or a ring.

C. The viscosity of water and other associated liquids

Liquids belonging to Group II(b) of the above classification are ordinarily called abnormal or associated liquids. Among other anomalies these liquids, composed of molecules containing OH or NH groups, have much higher viscosities than would be expected from the size and structure of the molecules. For instance, water is much more viscous than hydrogen sulfide or methane; ethyl alcohol and ethylamine are much more viscous than propane; aniline and phenol are more viscous than toluene; etc. This abnormally large viscosity is due to the hydrogen-bond structure of these liquids. According to present concepts,³ for instance, each oxygen atom in the water molecule in ice is surrounded by four hydrogen atoms at approximately tetrahedral angles. Two of these four hydrogen atoms are bound to the central oxygen atom by primary valence forces and are a distance of 1.0 \AA . away. The other two are "hydrogen bonded" at a distance of 1.8 \AA . Ice at low temperatures has its maximum coördination of 4, i.e., there are four hydrogen bonds binding the water molecule to its neighbors, two through the oxygen and one for each hydrogen atom in the water molecule. Water at the melting point at 1 atmosphere pressure is still coördinated to some extent, but the degree of coördination is probably

somewhat below the maximum value of 4. Further, the degree of coördination¹⁰ will probably change with the temperature and pressure. Other liquids containing OH and NH groups are likewise thought to possess hydrogen-bonded structures to some extent. When viscous flow takes place in these liquids, not only must van der Waals' cohesion be overcome, but hydrogen bonds must be broken as well. Table 11 shows that $\ln \eta$ versus $1/T$ is not a straight line for water but that B decreases rapidly as the temperature is raised and, further, that the ratio $\Delta E_{\text{vap}}/B$ increases with the temperature. Ewell and Eyring (16) have interpreted the rapid decrease of η and B with rising temperature as due to a decrease in the number of hydrogen bonds that have to be broken for the flow process to take place. This conclusion is consistent with the observation (41, 65) that D_2O is about 25 per cent more viscous than H_2O . Since it requires more energy to break the deuterium bond than the hydrogen bond, and

TABLE 11
The energy of activation for viscous flow of water

t	η	B	ΔE_{vap}	$\Delta E_{\text{vap}}/B$
°C.	millipoises	kg.-cal. per mole	kg.-cal. per mole	
0	17.95	5.06	10.18	2.0
50	5.49	3.42	9.62	2.8
100	2.84	2.80	8.98	3.2
150	1.84	2.11	8.28	3.9

since this term occurs as an exponential in the viscosity formula, it is not surprising to find so great a difference.

Similar considerations apply to other associated liquids. Since the maximum possible average coördination is equal to twice the number of OH or NH groups in the molecule, monohydric alcohols have a maximum coördination of 2, and the fact that ethyl alcohol and water have about the same viscosity indicates that ethyl alcohol probably possesses a large fraction of its maximum 2-coördination.

Ethylene glycol has a maximum average coördination of 4, the same as water, and the fact that glycol is about twenty times as viscous as water or as alcohol indicates that the degree of coördination is much higher in glycol than in water or alcohol. This is probably due to the fact that the two OH groups are separated in glycol, giving less interference between the hydrogen bonds attached to the two groups. Similarly, glycerol has a maximum coördination of 6, so that as little as half of the maximum

¹⁰ The degree of coördination is used here only in the sense of the average number of hydrogen bonds per molecule.

coördination will permit a three-dimensional network of hydrogen bonds, giving rise to the high viscosity of glycerol. Quantitative work along the lines suggested qualitatively in this section should throw light on the question of the contributions to the cohesive energy of liquids made by van der Waals, dipole, and hydrogen-bond forces.

D. The viscosity of liquid metals

Most metals give linear $\ln \eta$ versus $1/T$ plots, just as normal covalent liquids do. The most striking fact regarding the metals is the large value of the $\Delta E_{\text{vap}}/B$ ratio, which ranges from 8 to 25, as compared to 3 or 4 for normal liquids. This low activation energy for flow is consistent with the conclusion that the unit involved in flow is much smaller than the

TABLE 12
The energy of activation for viscous flow in liquid metals

METAL	MIDPOINT OF TEMPERATURE RANGE	ΔE_{vap}	B	$\frac{\Delta E_{\text{vap}}}{B}$	$\frac{\Delta E_{\text{vap}}}{B} \times \left(\frac{r_{\text{ion}}}{r_{\text{atom}}}\right)^3$
	°C.	kg.-cal. per mole	kg.-cal. per mole		
Na.....	500	23.4	1.45	16.1	2.5
K.....	480	19.0	1.13	16.7	3.4
Ag.....	1400	60.7	4.82	12.5	3.8
Zn.....	850	26.5	3.09	8.6	2.1
Cd.....	750	22.5	1.65	13.5	4.0
Hg.....	250	13.6	0.65	20.8	2.4
	600	12.3	0.55	22.2	2.5
Ga.....	800	34.1	1.13	30.3	2.5
Sn.....	600	15.3	1.44	10.6	4.1
	1000	14.5	1.70	8.6	3.3
Pb.....	700	42.6	2.80	15.9	5.0

unit of vaporization. The unit of vaporization being the atom, the unit involved in flow is presumably the much smaller metal ion, i.e., the atom partially or completely stripped of its valence electron or electrons.

On this assumption an approximate value for the energy of activation is given by

$$B = \frac{\Delta E_{\text{vap}}}{n} \times \frac{\text{volume of ion}}{\text{volume of atom}} \quad (105)$$

where n has its usual value for normal liquids.

Table 12 shows the experimental values of the quantity

$$\frac{\Delta E_{\text{vap}}}{B} \times \frac{\text{volume of ion}}{\text{volume of atom}}$$

using the ionic atomic radii given by Wyckoff (70) to determine the volumes of the ion and atom, respectively. When the temperature variation of the energy of vaporization was known, a value was taken arbitrarily in the middle of the range over which the viscosities were measured. For the polyvalent metals the following were assumed to be the flowing ions: Hg^+ , Sn^{++} , Pb^{++} .

It is seen that the values of n given in column 6 cluster around the average value of about 3. While this result is interesting and suggestive, the situation is complicated by the nature of the bonding in metals. The theorem that the energy of forming a hole the size of a molecule equals the energy of vaporizing a molecule is only proved in the case where a bond between pairs is independent of the position of other atoms. It is by no means clear that such a theorem holds for a substance containing conducting electrons.

As we have already seen, ordinary liquids at high pressures obey the inequality $V(\partial E/\partial V)_T < \Delta E_{\text{vap}}$. This same inequality holds for metals even at atmospheric pressure, so that B should perhaps be compared to $V(\partial E/\partial V)_T$, rather than to ΔE_{vap} . Because of the above inequality, such a comparison would reduce the value of n required to reproduce the temperature coefficient of viscosity. The data are, in general, not available for such a comparison, but for mercury $V(\partial E/\partial V)_T/B$ equals 4.5. The qualitative concept of the metal ions moving short distances without their valence electrons is the counterpart of the theory of conducting electrons moving short distances without disturbing the ions.

E. Mixture law for viscosity

We give here the discussion of Powell, Roseveare, and Eyring (52). The viscosity of a mixture of liquids is not related to the viscosities of the pure components by any simple additive relation. Several equations have been tested in the search for an additive function for viscosity, among them being the following (*cf.* references 1, 4, 34, 35):

$$\varphi = N_1\varphi_1 + N_2\varphi_2 \quad (106)$$

$$\varphi^{1/2} = N_1\varphi_1^{1/2} + N_2\varphi_2^{1/2} \quad (107)$$

$$\varphi^n = N_1\varphi_1^n + N_2\varphi_2^n \quad (108)$$

$$\log \varphi = N_1 \log \varphi_1 + N_2 \log \varphi_2 \quad (109)$$

the weighting being done according to weight fraction, volume fraction, and mole fraction. There is also a wide variety of equations containing one or more adjustable constants. For example, an equation of the type of equation 108 has been used by petroleum engineers to estimate the viscosity of mixtures of lubricating oils: for high-viscosity paraffin base

plus low-viscosity naphthene base, the exponent is 1/30; for the opposite case, the exponent is 1/3.1; for two oils of the same base, the exponent is 1/6.5 (69). Such equations are convenient for interpolation purposes, but that they fit the experimental data is more a matter of arithmetical inevitability than of merit. Of the equations not containing an adjustable constant, equation 109 fits the experimental data rather better than the others.

If the flow process were strictly determined by the properties of one molecule flowing, equation 106 would be expected to hold. If it were determined by the properties of two molecules flowing past each other, equation 107 would be expected to hold. However, it is probable that the cheapest way for a hole to be made is for the flowing molecule to squeeze against its neighbors, which in turn squeeze against their neighbors, until the over-all result is the expansion of the entire liquid. Thus the average thermodynamic properties of the entire liquid may be involved when any individual molecule flows.

As a simple approximation, equation 76 may be used for mixtures if for V is inserted the actual value of the average molal volume, and for ΔF^\ddagger is inserted the weighted arithmetical mean of the values for the pure components. Thus

$$\varphi = \frac{V}{N\hbar} \exp \frac{-(N_1\Delta F_1^\ddagger + N_2\Delta F_2^\ddagger)}{RT} \quad (110)$$

When V_1 and V_2 are not too different, equation 110 reduces to equation 109.

As a test of equation 110, ΔF^\ddagger has been plotted against mole fraction for a number of pairs of liquids. Three types of curves are obtained: (a) Closely similar liquids, e.g., benzene and anisole, give a straight line. (b) Liquids which definitely form a compound, e.g., chloroform and ether, give a convex curve. (c) Liquids which are slightly dissimilar give a slightly concave curve; liquids which are markedly dissimilar, e.g., benzene and alcohol, give a markedly concave curve.

It has been pointed out (15) that the deviations from a linear fluidity law are roughly parabolic and are symmetric about the 50 mole per cent line. The same behavior is noted in the deviations of ΔF^\ddagger from a linear law. ΔH^\ddagger , on the contrary, always shows larger deviations, which are usually not symmetrical and may even change sign. These large deviations shown by ΔH^\ddagger tend to be counterbalanced by entropy changes.

It was early remarked that non-aqueous liquid pairs showing a minimum in the viscosity curve also showed a negative deviation from Raoult's law, and those showing a maximum in the viscosity curve showed a positive deviation from Raoult's law (72). In order to formulate this quantitatively, the deviations of ΔF^\ddagger from a linear law (calories at 50 mole per cent)

were plotted against the deviations from Raoult's law (calories at 50 mole per cent) for systems for which partial pressure data are available or can be estimated. The curve resembles closely that in figure 6, in that the points tend to fall along a line drawn through the origin with a slope of $1/2.45$. The mixture law of equation 110 is therefore to be modified to read

$$\varphi = \frac{\bar{V}}{N\bar{h}} \exp \left(- \left[(N_1 \Delta F_1^\ddagger + N_2 \Delta F_2^\ddagger) - \frac{\Delta F^E}{2.45} \right] / RT \right) \quad (111)$$

where ΔF^E is the excess free energy of mixing (55, 56).

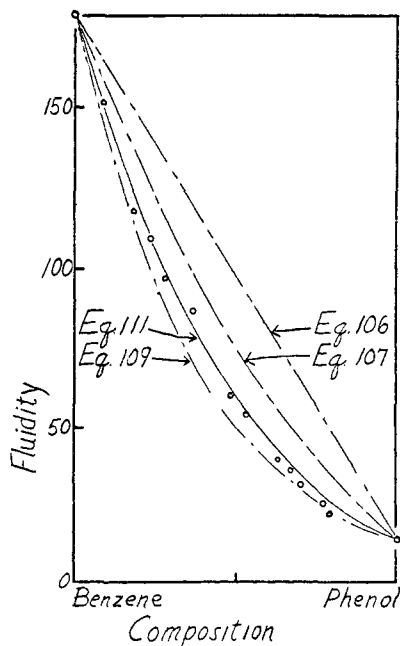


FIG. 16. Plots of various fluidity-composition equations for binary liquid mixtures applied to the system benzene-phenol, compared with observed fluidity values shown by circles.

The application of this mixture law is illustrated in figure 16, where the experimental values for the fluidity of the system benzene-phenol are plotted, together with curves calculated according to several different mixture laws.

F. Relation of fluidity to volume

Batschinski (2) has shown that, for a large number of liquids, there is a linear relationship between volume and fluidity. The data of Bridgman at high pressures (6), which show that, for non-associated liquids, the

temperature coefficient of fluidity at constant volume is insignificant compared to the temperature coefficient at constant pressure, indicate also that the fluidity of normal liquids under ordinary conditions is nearly a function of volume alone. Such linearity indicates that the theory of fluidity is fundamentally linked to the theory of liquid volume, and has led Powell, Roseveare, and Eyring (52) to the idea of a number of holes in the liquid which shows a variation approximately proportional to the volume change.

Cernuchi and Eyring (7) have considered liquids as being made up of a binary mixture of molecules and holes having the same volume as molecules. Kirkwood (39) pointed out that the theory of holes leads to results incompatible with critical data when the holes are the same size as the molecules. The temperature and pressure coefficients of viscosity indicate that the volume of a hole necessary for flow is a small fraction of the size of a molecule (25).

Powell, Roseveare, and Eyring (52) assumed that a liquid is a solution of holes and molecules and that the size of the holes is a characteristic of the material. The fusion of n molecules of a substance is the dissolving of n_h holes such that the entropy of solution is two units, or

$$\Delta S = 2 = -nk \ln \left(\frac{n}{n + n_h} \right) - n_h k \ln \left(\frac{n_h}{n + n_h} \right) \quad (112)$$

since the observed entropy of fusion is about two entropy units for a large number of monatomic substances (30). For one mole of substance $n = N$ and then, from equation 112, $n_h = 0.54N$. The solution of 0.54 mole of holes in 1 mole of a substance gives the required disorder entropy to change a solid into a liquid.

If the volume of a hole be taken as $1/h$ of the volume of a molecule, and v_s and v_l are the respective molecular volumes of the solid and liquid at the freezing point, then we have

$$r \frac{v_l - v_s}{v_s} = 0.54 \quad (113)$$

For a number of substances $\Delta V/V$ for fusion is approximately 0.1, making r about 5 or 6. Most metals have a value of r between 20 and 25. The result that a new equilibrium position has a volume about one-sixth that of the non-metal molecule and about one twenty-third the metal molecules is exactly the result found by Frisch, Kincaid, and Eyring (25) from the effect of pressure on viscosity. Thus this model relates quantitatively two otherwise apparently phenomena, i.e., melting and viscous flow. The experimental value of the volume of the solid in equation 113 has significance only if the short-range order of structure of the liquid is the same

as that of the solid. Water has a negative value of $\Delta V/V$ on melting, owing to a change in coördination number on melting.

For substances to which equation 113 may be applied, Powell, Roseveare, and Eyring find that, at the melting point, their fluidity behavior is better described by the partition function for the solid state for the extra degree of freedom possessed by the normal molecule, than by the liquid partition function, obtained from the gas function modified by the introduction of free volume.¹¹

For temperature ranges extending not too far above the normal boiling points, they would write, in place of equation 96,

$$\varphi = \frac{V_s}{Nh} \frac{\Theta Z r}{T} \frac{v_l - v_s}{v_s} \exp(-\Delta E'/RT) \quad (114)$$

In equation 114, Z is a numerical constant related to the coördination number; $\Delta E'$ is the energy of activation at constant volume¹² (in place of that at constant pressure in equation 96); Θ , the Debye characteristic temperature, while not often known, can be estimated by the relation (40)

$$\Theta = A \left[\frac{T_m}{MV^{2/3}} \right]^{1/2} \quad (115)$$

where A is a numerical constant, T_m is the melting temperature, and M is the molecular weight.

For many liquids the energy of activation for constant volume is very small, and when this is the case, there will be a temperature range in which the variation of the exponential term will compensate the $1/T$ factor, and there will result the frequently observed linear relation between φ and V_1 .

When $\Delta E'$ is large, as in the case of the higher alcohols, this is no longer the case. In figure 17 is shown a plot of fluidity against volume for isopropyl alcohol for which $\Delta E'$ is large. Data of Bridgman at intermediate pressures permit the estimation of the heat of activation at constant volume, yielding a value of 3900 calories. The result of plotting $\varphi T \exp(3900/T)$ against volume should be a straight line, which is shown to be the case in figure 17.

As another test of equation 114, $\log \varphi$ is plotted against $1/T$ in figure 18 for benzene. A number of such graphs may be found in the paper of Sheppard and Houck (58). The resulting curved line for benzene in

¹¹ Actually a combination of solid and gas partition functions is being investigated. This should approximate the function for the solid at the melting point for normal substances, and should approach the function for the gas at the critical temperature.

¹² The energy of activation at constant pressure may be thought of as principally that energy required to form the hole necessary for flow, while that at constant volume is merely the (usually) small energy required to activate the molecule for flow into a hole already present.

figure 18 is to be compared with the straight line which results from plotting $\log [\phi T / (V_i - V_s)]$ against $1/T$. In the case of many substances the data available are in a temperature range where both plots are straight lines.

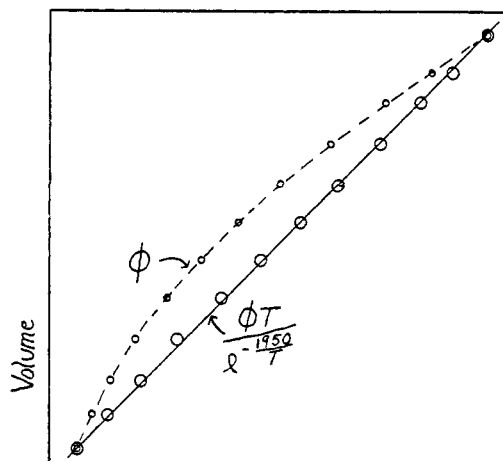


FIG. 17. Plots of volume *versus* fluidity (small circles) and $\phi T \exp(1950/T)$ (large circles) for isopropyl alcohol.

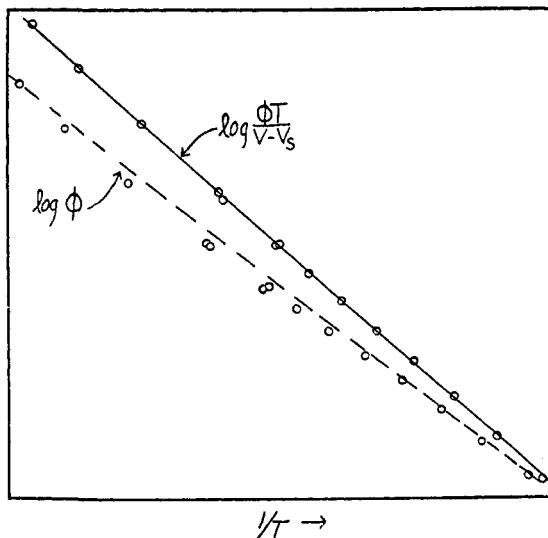


FIG. 18. Comparison of linearity of plots of $1/T$ against $\log \phi$ (broken line) and against $\log \phi T / (V_i - V_s)$ (solid line) for benzene. The temperature range involved is from about 280° to 460°A .

The linear relation between ϕ and V_i found for substances with small values of $\Delta E'$ holds not only for volume change due to temperature varia-

tion but also for that due to pressure variation through fairly wide pressure ranges. So long as the pressure has very little effect on the liquid structure other than to squeeze out holes, the linear relation holds. For very high pressures, fluidity decreases less rapidly with increased pressure than the linear law predicts. Figure 19 shows plots of fluidity against volume at constant temperature for pressures up to 12,000 kg. per cm.² for ether and for ethyl alcohol.

G. The flow of large molecules

For the viscous flow of hydrocarbons, Ewell and Eyring (16) have found that the heat of activation is usually very close to one-fourth the heat of

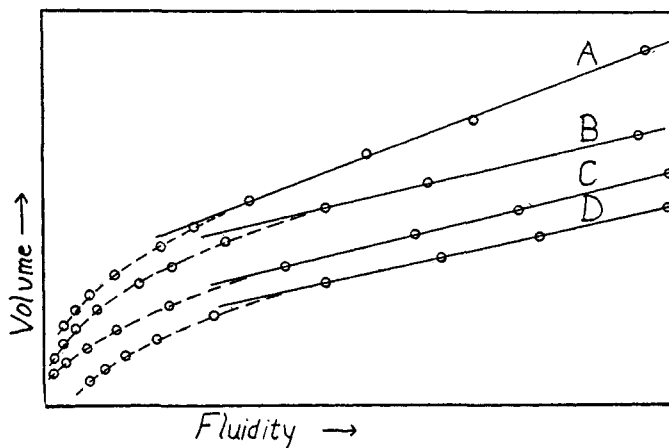


FIG. 19. Showing the relation of fluidity to volume at high pressures. Curve A is for ether at 75°C., curve B for ether at 30°C. Curve C is for ethyl alcohol at 75°C., and curve D for ethyl alcohol at 30°C. Abscissae are arbitrary. The break from linearity seems to occur at pressures between 2000 and 3000 atmospheres. The fourth point from the right in each curve is for 2000 atmospheres.

vaporization of a molecule the size of the unit of flow. Kauzmann and Eyring (33), on plotting ΔH^\ddagger of viscous flow for normal hydrocarbons against chain length, found that, for chains above about twelve atoms in length, there is a significant and increasing deviation from the relationship

$$\Delta H^\ddagger = (1/4)\Delta H_{\text{vap}}$$

for the molecule. This is taken to mean that chains longer than about twelve atoms do not move as a unit, but move in segments. Furthermore, there is an indication that, as the chain length increases beyond about fifty atoms, ΔH^\ddagger is independent of the total chain length, showing that, for molecules of this length, the size of the segments which move is independent of the length of the molecule. From the limiting values of ΔH^\ddagger thus

found, it is estimated that the segments involved in the flow of long hydrocarbon molecules are, on the average, twenty atoms in length.

An analogous treatment of results recently reported by Flory (23) for the behavior of polymers reveals that segments averaging about thirty atoms in length are involved. In rubber the segments are about forty atoms long, while in plastic sulfur they are about twenty atoms long.

Although the temperature variation of the viscosities of long-chain polymers is determined solely by the nature and size of the segments of which they are composed, there is definite evidence that a further factor, depending on chain length but not on temperature, operates to make long chains more viscous than short chains. Thus, in connection with the viscosities of the normal paraffins, long chains are definitely less fluid than would be expected from the recent extension of the hole theory of liquids. Flory's work indicates that the viscosities of long-chain molecules are proportional to $\exp(a\sqrt{Z})$, where Z is the chain length of the entire molecule and a is a temperature-independent constant.

This behavior is readily understood when it is realized that, although the segments in a large molecule are moving about just as rapidly as those in a small molecule, the movements of the segments of the large molecule must be coordinated to a far greater extent than those of a smaller molecule, in order for the molecule to move forward a given distance.

According to Kauzmann and Eyring (33), the exponential form found by Flory follows if we say that, on each jump by a segment, there is a chance of failure of $aZ^{1/2}/n$, where n is the number of segments in the molecule. The chance of success in a single jump by one segment is then $1 - \frac{aZ^{1/2}}{n}$, and the chance of successful jumps by n segments is

$$\left[1 - \frac{aZ^{1/2}}{n}\right]^n$$

But the fluidity is proportional to the fraction of successful jumps, so that

$$\varphi = K \left[1 - \frac{aZ^{1/2}}{n}\right]^n \quad (116)$$

Since

$$\left(1 - \frac{x}{n}\right)^n = \exp(-x)$$

when $n \gg x$, we have

$$\eta = 1/\varphi = K' \exp(a\sqrt{Z}) \quad (117)$$

VIII. DIFFUSION PROCESSES IN LIQUIDS

Although the viscosity of liquids has been extensively studied, data for diffusion in liquids are very meager. Thus the measurements of Orr and Butler (48) are the only ones available for testing the applicability of equation 66 for self-diffusion. Taking their values for the diffusion of heavy into light water at 0°C. and 45°C. and utilizing the data for the viscosity of ordinary water at the same temperatures, Eyring (19) has employed equation 66 to obtain values of the ratio $\lambda_1/\lambda_2\lambda_3$ of the dimensions of the diffusing molecule. This result may be combined with the product $\lambda_1\lambda_2\lambda_3 (= V/N)$ to yield a value of λ_1 equal to 1.44 Å. at 0°C. and 1.47 Å. at 45°C. At these same temperatures $(\lambda_2\lambda_3)^{1/2}$ equals 4.54 and 4.50 Å., respectively. This result is seen to be in accord with the principle that reactions will proceed by all possible mechanisms and therefore chiefly by the fastest ones when it is recalled that λ_1 is the dimension of the flowing molecule perpendicular to the plane of shear. It appears probable that in diffusion, as in viscous flow, the fastest process will be one in which the plane of the water molecule tends to coincide with the plane of flow, i.e., that λ_1 will be the thin dimension of the molecule. In the calculation, the viscosity of water has been used, whereas a value intermediate between that of H₂O and that of pure D₂O should have been used. This, however, would be a small correction, having no effect on the general conclusion. That the Stokes-Einstein diffusion equation is not applicable to this case is seen by the unreasonably small value of 1.46 Å. ($(V/N)^{1/3} = 3.1$ Å.) that it yields for the diameter of the diffusing molecule when the data at 45°C. are applied in equation 39. The dimensions of the water molecule, as determined from Fischer-Hirschfelder models, are $2.3 \times 4.0 \times 3.0$ Å., thus being in rough agreement with the dimensions derived from diffusion. There is no reason for expecting the Stokes-Einstein equation to be applicable here, since it is derived with the condition that the diffusing particle be so large in comparison to the solvent molecules that the solvent may be considered to be continuous.

Equation 65 may be rewritten in the form (61)

$$D = \lambda^2 \frac{kT}{h} \exp \left[\frac{-\Delta F^\ddagger}{RT} \right] \quad (118)$$

If we assume that the degree of freedom corresponding to flow is a translational one, and that the partition functions for other degrees of freedom are the same for the initial and activated states, then equation 118 may be transformed to

$$D = \lambda^2 \frac{kT}{h} \frac{h}{(2\pi mkT)^{1/2} v_f^{1/3}} \exp(\Delta H^\ddagger/RT) \quad (119)$$

$$= \frac{\lambda^2}{v_f^{1/3}} \left(\frac{kT}{2\pi m} \right)^{1/2} \exp(-\Delta E_{\text{vap}}/nRT) \quad (120)$$

where v_f is the free volume. For diffusion processes, just as for viscous flow, a hole must be provided to diffuse into. The energy necessary will involve some fraction of the energy of vaporization so that, in equation 120, we write $\Delta E_{\text{vap}}/n$ for ΔH^\ddagger . Although diffusion is a rate process and should thus show an exponential variation with temperature, the data have normally been represented as a linear function of temperature. However, the precision measurements of Cohen and Bruins (8) on the diffusion of tetrabromoethane in tetrachloroethane extending over the temperature range 0° to 51°C . could not be fitted with a linear interpolation formula, and these authors employed a quadratic formula to represent their measurements. Taylor (63), using the results of Cohen and Bruins, plotted $\log D$ against $1/T$ and obtained an excellent linear plot, from which an activation energy of diffusion equal to 3500 calories was obtained. This value lies

TABLE 13
Diffusion of tetrabromoethane in tetrachloroethane

TEMPERATURE	$\lambda^2 \times 10^{18}$	$v_f^{1/3} \times 10^6$	ΔE_{vap}	$D \times 10^6$ (OBSERVED)	$D \times 10^6$ (CALCULATED)	$D_{\text{obsd.}}/D_{\text{calcd.}}$
$^\circ\text{A.}$			<i>kg.-cal. per mole</i>			
273.4	3.124	6.45	9.852	0.351	0.64	0.55
280.7	3.140	6.69	9.784	0.419	0.77	0.54
288	3.155	6.92	9.719	0.497	0.92	0.54
298	3.174	7.25	9.624	0.611	1.14	0.54
308.6	3.195	7.59	9.525	0.741	1.42	0.52
324.1	3.230	8.13	9.383	0.954	1.89	0.51

between that for viscous flow in tetrachloroethane, 3000 calories, and that for viscous flow in tetrabromoethane, 3750 calories.¹³

Stearn and Eyring (61) have used the results of Cohen and Bruins as a test of equation 120, employing average values for the quantities occurring in equation 120, based on a liquid mixture containing 7.83 mole per cent of tetrabromoethane studied by Cohen and Bruins. For λ and $v_f^{1/3}$ they took the weighted arithmetical mean, and for ΔE_{vap} the weighted geometric mean. Their results are given in table 13. The constancy of the ratio $D_{\text{obsd.}}/D_{\text{calcd.}}$ shows that the calculated values of D reproduce the experimental temperature coefficient very closely. In agreement with Taylor (63) they took $n = 3$. (The value $n = 2.65$ would have reproduced the experimental results almost exactly.)

The data of Scheffer and Scheffer (57) on the diffusion of mannitol in

¹³ Value estimated from the boiling point, using the same Trouton's constant and value of $\Delta E_{\text{vap}}/B$ as for tetrachloroethane.

aqueous solutions in the temperature range 0° to 70°C. give activation energies varying slightly with temperature. The variations are of the same nature already noted for the viscous flow of water, probably owing to the hydrogen-bonded structure of the solution. However, when $\log D$ is plotted against $1/T$, the only point far off from the straight line giving an average slope is that for 0°C. The average slope gave $\Delta E_{\text{act}} = 4047$ calories, and this, with the average value of ΔE_{vap} for water between 0° and 70°C., gives a value of $n = 2.4$. In table 14 are given the results of Stearn and Eyring, using equation 120 to calculate D . They took ΔE_{vap} for water as 9700 calories and n equal to 2.4. The constancy of the ratio $D_{\text{obsd.}}/D_{\text{calcd.}}$ is again noted.

Although data for the temperature variation of diffusion are scanty except for measurements at two temperatures rather close together, nevertheless, on the basis of these data, Öholm (47) pointed out that substances showing a high value for the diffusion coefficient always showed a small

TABLE 14
Diffusion of mannitol in aqueous solutions

TEMPERATURE	$D_{\text{obsd.}} \times 10^5$	$D_{\text{calcd.}} \times 10^5$	$D_{\text{obsd.}}/D_{\text{calcd.}}$
273.0	0.26	0.26	1.0
296.2	0.61	0.43	1.4
305.9	0.75	0.52	1.4
316.4	0.97	0.63	1.5
325.3	1.14	0.74	1.5
335.0	1.35	0.89	1.5
343.2	1.56	1.05	1.5

temperature coefficient. This generalization is exemplified in the data in table 16, where values of the temperature coefficient α , defined by $D_2/D_1 = 1 + \alpha(T_2 - T_1)$, are to be compared with those of D . Such a relation is to be expected on a reaction rate theory of diffusion. If a series of reactions do not have greatly varying entropies of activation, then the slowest ones, as well as those with the largest temperature coefficients, will be those having the largest energy of activation. The generalization of Öholm on the diffusion process is analogous to the observation of Kohlrausch on ionic mobilities. These ions with the greatest ionic mobility have the smallest temperature coefficients of mobility. This is also the reason that the transport numbers of ions tend to approach 0.5 as the temperature is raised. The more slowly moving ions with transport numbers less than 0.5 at a given temperature will have greater temperature coefficients of mobility than the rapidly moving ones with transport numbers greater than 0.5.

A further test of equation 120 is given in tables 15 and 16, taken largely from Stearn, Irish, and Eyring (61). The results are grouped into three classes: aqueous diffusion, diffusion of different solutes in the same non-aqueous solvent, and diffusion of the same solute in different non-aqueous solvents. In table 16, values of $D\eta$ are given in order to test the validity of the Stokes-Einstein relation (equation 69), according to which $D\eta$ should be constant at constant temperature. The variation in $D\eta$ is much less than in D , but, applying equation 69 to values of $D\eta$, variation from two- to

TABLE 15
Diffusion data for different solutes in the same solvent

SOLUTE	$D_{\text{obsd.}} \times 10^6$	$D_{\text{calcd.}} \times 10^6$	$D_{\text{obsd.}}/D_{\text{calcd.}}$	$D \left(\frac{V_{\text{solute}}}{N} \right)^{1/3}$
Diffusion in aqueous solutions at 18-20°C.				
Methyl alcohol.....	1.37	0.39	3.5	555
Ethyl alcohol.....	1.10	0.38	2.9	504
<i>n</i> -Propyl alcohol.....	0.98	0.35	2.8	488
<i>n</i> -Butyl alcohol.....	0.88	0.34	2.8	468
<i>n</i> -Amyl alcohol.....	0.88	0.34	2.6	495
Allyl alcohol.....	0.99	0.35	2.8	477
Diffusion in benzene solutions at 7.5°C.				
Methyl iodide.....	2.06	3.46	0.59	964
Ethyl iodide.....	1.77	3.39	0.53	903
<i>n</i> -Propyl bromide.....	1.71	3.55	0.48	908
<i>n</i> -Propyl iodide.....	1.67	3.36	0.50	908
<i>n</i> -Butyl bromide.....	1.68	3.48	0.48	948
<i>n</i> -Butyl iodide.....	1.53	3.31	0.45	875
<i>n</i> -Amyl bromide.....	1.42	3.42	0.42	836
<i>n</i> -Amyl iodide.....	1.41	3.28	0.43	846
Octyl bromide.....	1.17	3.29	0.36	770
Ethylene dichloride.....	1.77	3.71	0.48	896
Carbon tetrachloride.....	1.51	3.40	0.43	818
Phenyl bromide.....	1.45	3.39	0.43	808
Phenyl iodide.....	1.35	3.27	0.42	768

three-fold in the radius of the diffusing molecule is noted. The constancy of $D\eta$, if equation 68 be applied, depends, however, on the equality of ΔF^\ddagger for viscous flow and for diffusion and on the equality of λ_η and λ_D , the distances between successive minima for the viscous flow process and the diffusion process, respectively. One might expect the quantity $D \frac{\lambda_2 \lambda_3}{\lambda_1}$ to be more nearly constant. It is impossible at present to evaluate $\frac{\lambda_2 \lambda_3}{\lambda_1}$

satisfactorily, but as a crude test we may, for similar molecules, identify this quantity with $(V/N)^{1/3}$, where V is the molecular volume and N is Avogadro's number. In table 15, values of $D(V/N)^{1/3}$ are given (η is

TABLE 16
Diffusion data for one solute in a number of solvents

SOLVENT	ΔE_{vap}	n	$D_{\text{obsd.}} \times 10^5$	$D_{\text{calcd.}} \times 10^5$	$D_{\text{obsd.}}/D_{\text{calcd.}}$	α	D
Diffusion of bromobenzene in various solvents at 7.5°C.							
Ether.....	6.16	4	3.50	16.5	0.21		962
Benzene.....	7.69	3	1.41	3.1	0.45		1113
Toluene.....	8.5	4	1.59	7.4	0.22		1097
Cyclohexane.....	7.59	3	1.16	3.3	0.35		1334
Hexane.....	7.0	4	2.59	13.3	0.20		932
<i>m</i> -Xylene.....	9.77	4	1.52	4.9	0.31		850
<i>m</i> -Cymene.....	10.3	4	1.18	4.1	0.29		
Diffusion of bromoform in various solvents at 20°C.							
Acetone.....	7.27	4	2.69	11.9	0.23	0.018	888
Ether.....	6.1	4	3.39	17.3	0.20	0.017	831
Benzene.....	7.45	3	1.69	3.7	0.45	0.024	1093
Methyl alcohol.....	8.44	3	1.93	2.6	0.74	0.022	1144
Ethyl alcohol.....	9.97	3	0.97	1.3	0.74	0.028	1154
Propyl alcohol.....	9.99	3	0.77	1.2	0.64	0.030	1740
Amyl alcohol.....	10.6	3	0.52	0.94	0.55	0.034	2340
Diffusion of iodine in various solvents at 20°C.							
Methylene bromide.....	8.25	3.5	0.83	3.82	0.22	0.020	1422
Benzene.....	7.45	3	1.93	2.79	0.50	0.018	1238
Carbon tetrachloride.....	8.0	3	1.37	2.39	0.59	0.019	1302
Toluene.....	7.99	4	1.96	9.26	0.21	0.016	1132
Chloroform.....	7.08	4	2.12	10.1	0.21	0.013	1226
Ethyl acetate.....	7.78	4	2.15	9.8	0.22	0.014	981
Heptane.....	7.59	4	2.77	11.4	0.24	0.016	1325
Carbon disulfide.....	6.60	4	3.12	12.4	0.25	0.012	1171
<i>m</i> -Xylene.....	8.80	4	1.68	7.2	0.23	0.017	1079
Isoamyl acetate.....	9.00	4	1.24	6.7	0.19	0.021	1077
Bromobenzene.....	8.80	3	1.20	1.7	0.71	0.017	1358
Carbon tetrabromide.....	11.2		.18			0.041	1782
Methyl alcohol.....	8.44		1.81			0.018	1108
Phenetole.....			0.97			0.023	1283
Anisole.....	8.8		1.13			0.024	1219

nearly constant for the dilute solutions in the same solvent). It is seen that these values are somewhat more constant than are those of D (or $D\eta$) for the series of alcohols diffusing in water and for the series of halogen-

substituted products diffusing in benzene. In calculating the values of D given in table 16, Stearn and Eyring use values of n found by Ewell and Eyring (16) to give the correct temperature variation of viscosity for the particular solvent. Those employed are shown in table 16.

It will be noted that the ratio $D_{\text{obsd.}}/D_{\text{calcd.}}$ is greater than 1 for aqueous solutions and less than 1 for non-aqueous solutions. Stearn and Eyring found this very generally true. They explain the variation of this ratio from unity as due at least partly to a factor in equation 120 which has not been considered. For the case of a liquid with structure, such as water, rotation in the normal state will be hindered more strongly than in the activated state. (Cf. Kincaid and Eyring (37)).

Thus in cancelling out all but one term in the partition functions corresponding to the two states, this factor is overlooked. This would lead to a calculated value too low. For liquids without such pronounced structure rotation may, on the other hand, be less hindered in the normal state, and neglect of this factor would then lead to results which are too high.

A. Diffusion in concentrated solutions

The results of Stearn, Irish, and Eyring (61) and of Powell, Roseveare, and Eyring (52) show three kinds of behavior, two of which are adequately described by equation 75. These classes of systems are:

(a) Liquid mixtures which form nearly perfect solutions, e.g., benzene-carbon tetrachloride. For this case ($d \ln a/d \ln N$) will be constant and $D\eta$ should be linear with composition, owing to change of $\lambda_1/\lambda_2\lambda_3$ with composition (cf. equation 66). This class is exemplified by curves A of figure 20.

(b) Liquid mixtures which do not form perfect solutions but which are such that ΔF^\ddagger for viscous flow is the same as ΔF^\ddagger for diffusion. For such cases $D\eta$ will not, in general, be linear with composition but $D\eta/(d \ln a_1/d \ln N_1)$ should be. This class is exemplified by curves B and C of figure 20, in which the changes of $D\eta$ and of $D\eta/(d \ln a_1/d \ln N_1)$ with composition are shown, respectively, for the systems chloroform-acetone and chloroform-ether.

(c) Liquid mixtures with well-defined structure such that ΔF^\ddagger for viscous flow may not cancel ΔF^\ddagger for diffusion. The behavior of two such systems, water-methyl alcohol and water-ethyl alcohol, is shown in curves D and E of figure 20. This behavior is typical of four such systems investigated, all four showing a maximum in the value of $D\eta/(d \ln a_1/d \ln N_1)$.

B. Relation of diffusion to volume

A further test of the idea that, for diffusion as well as for viscous flow, the energy of activation at constant pressure is in many cases predominantly the energy necessary to provide a hole to diffuse into would be

furnished by the relation between diffusion coefficient and volume. The only available data satisfactory for investigation are those of Cohen and Bruins (8). The same reasoning which explains the linear relationship

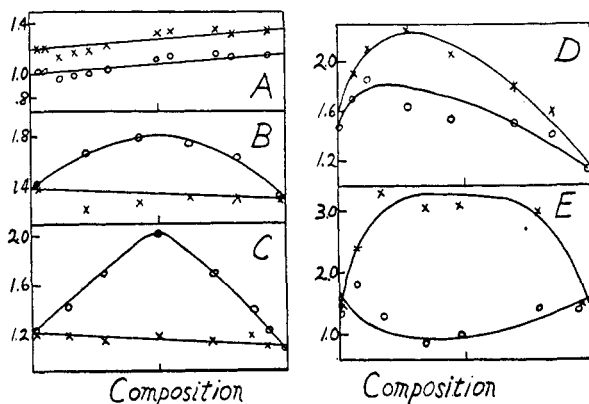


FIG. 20. Plots of composition in mole fraction *versus* $D\eta$ (circles) and *versus* $\frac{D\eta}{d \ln a_1/d \ln N_1}$ (crosses) for the complete composition range of several liquid pairs. Curves A are for benzene-carbon tetrachloride, curves B for chloroform-acetone, curves C for chloroform-ether, curves D for water-methyl alcohol, and curves E for water-ethyl alcohol. The ordinate scale for curves E is half that for the other curves.

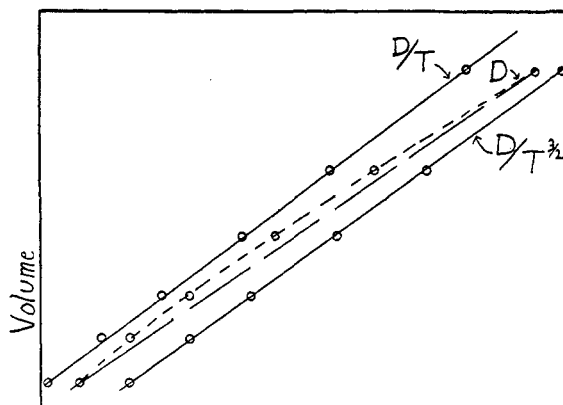


FIG. 21. Plots of volume *versus* D , D/T , and $D/T^{3/2}$, respectively, for the diffusion of tetrabromoethane in tetrachloroethane. The abscissa scales are arbitrary.

between fluidity and volume for certain values of temperature and activation energy leads to a prediction of a linear relationship between volume and either $D/T^{3/2}$ or D/T , depending on whether the partition function for the extra degree of freedom is taken as in equation 119 or that for the solid

(Θ/T) is used. Stearn (60) has used (figure 21) the data of Cohen and Bruins to plot volume against D , D/T , and $D/T^{3/2}$. While the plot of D versus V shows distinct curvature, both the other curves give straight lines.

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