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On the Diffusion of Vapors through Polymers

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The rate of permeation of a gas through a polymer as a function of temperature may be represented as $P = P_0 e^{-E/RT}$. All available data on the permeability of gases through polymers show that for a given gas there is a linear relation between log P_0 and E (the energy of activation for permeation). An explanation is offered for this apparent relationship. The effect of plasticization on permeation of water vapor is studied experimentally and it is shown that the lowering of the heat of solution is the predominant effect. From the data the entropy of solution may be calculated and interpreted as showing that water molecules dissolved in the unplasticized polymer exhibit much less freedom than when they are dissolved in plasticized polymer. Other calculations show (in agreement with Barrer) that a large number of degrees of freedom are simultaneously operative in the process of the diffusion of a gas molecule through a polymer.

INTRODUCTION

THE studies of Barrer[1] together with his compilation and analysis of existing data[2] have contributed most significantly to our fundamental understanding of the transmission of gases and vapors through polymeric substances. These investigations demonstrated that transmission results from activated diffusion and that the molecular diameter of the diffusing gas is of only secondary importance. The process of permeation is visualized as follows when a film of polymeric substance separates two quantities of gas or vapor at different pressures. The gas molecules dissolve in the polymer and move about by jumping into holes which form and disappear in their immediate neighborhood. These holes are the result of fluctuations in the thermal motion of segments of the polymer molecules. The concentration gradient in the film causes a drift of the diffusing gas toward the lower concentration region.

The rate of transfer of vapor across a film of unit thickness per unit area per unit pressure difference is known as the permeability constant and characterizes the effectiveness of the film as a barrier. It has been shown that the permeability constant, P, may be resolved into the product of the diffusion constant, D, and the solubility coefficient, S. The dimensions of D are area per unit time; S has dimensions of volume of gas (at stated conditions) per volume of polymer. With a proper choice of units we may write: $P = DS$. This relation has been verified for permanent gases[1,2] and water vapor[3] in a number of polymeric substances.

It is important to note that it has likewise been verified that P, D, and S vary exponentially with reciprocal absolute temperature for permanent gases. Thus:

$$P = P_0 \exp(-E/RT), \qquad (1)$$

$$D = D_0 \exp(-E_D/RT), \qquad (2)$$

$$S = S_0 \exp(-\Delta H/RT). \qquad (3)$$

Since P and D are essentially rate constants, E and E_D may be interpreted as energy of activation for permeation and diffusion, respectively. The solubility coefficient is an equilibrium constant, hence ΔH may be identified as the heat of solution. Moreover, P_0 and D_0 correspond to frequency factors in the Arrhenius equation of chemical kinetics. Barrer[1,2] has interpreted his measurements of these quantities in terms of the transition state theory to show that the activated state for diffusion involves many degrees of freedom indicative of the formation of a "hole" for the diffusion molecule to move into.

In this paper it is desired to present some further interpretations of this problem based upon investigations of water vapor-polymer systems, some of which have been previously

[1] R. M. Barrer, Trans. Faraday Soc. **34**, 849 (1938); **35**, 628 (1939); **35**, 644 (1939); **36**, 1235 (1940).
[2] R. M. Barrer, *Diffusion in and through Solids* (Cambridge University Press, New York, 1941).
[3] P. M. Doty, W. H. Aiken, and H. Mark, Ind. Eng. Chem. (in press).

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published.[3] Specifically, we should like to point out an apparent relation between P_0 and E in Eq. (1) and report some measurements on the water vapor-polyvinyl chloride system with and without plasticizer from which some significant conclusions may be drawn. Finally, it may be shown that our data confirm Barrer's views summarized in the preceding paragraph.

THE APPARENT RELATION BETWEEN P_0 AND E

The temperature dependence of the permeability constant has been determined for a number of polymers with water vapor.[3] From these data P_0 and E in Eq. (1) can be evaluated. In Table I these constants are listed for all the materials measured.

In Fig. 1, $\log P_0$ is plotted *versus* E. Two other measurements of polyvinyl chloride-acetate, which are mentioned later, are included in the graph. The diameters of the circles are rough indications of the probable experimental error involved. The closeness of fit of the experimental data to a straight line, the large range of variables covered (ten decades in P_0 and 18,000 calories in E), and the complete randomness with which the materials tested were selected clearly indicate that in a very general sense $\log P_0$ has been demonstrated to be a linear function of the energy of activation. Such a conclusion recalls the controversies that have occurred in chemical kinetics over apparent relations between A and E in the Arrhenius equation ($k = Ae^{-E/RT}$) for reaction rates.[4] A number of these claims were shown to be illusory because the rate constant, k, was nearly constant in the series of reactions considered, thus forcing a change in E to be reflected in $\log A$. This situation hardly exists here because the permeability constant (corre-
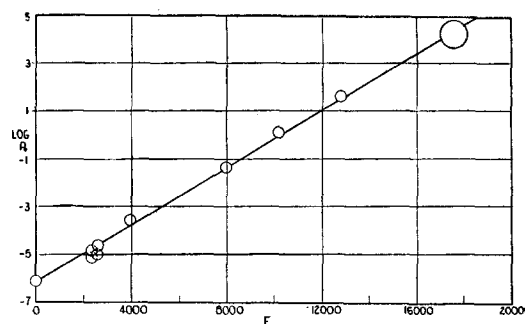

FIG. 1. The correlation of $\log P_0$ and E (cal./mole) for the permeation of water vapor through various polymeric materials.

sponding to k) for the films measured varied one thousand-fold.

If we accept the relation as real, it is necessary to attempt an interpretation, consider its range of application, and test it on other data if any exist. In the few cases in chemical kinetics where a *bona fide* relation between $\log A$ and E has been found, an explanation involving the frequency of vibration in the activated state has been postulated.[4] Evidence described in the next section indicates that there is no direct relation between heat of solution and E. It seems therefore unwise to seek an analogy with this case in chemical kinetics. However, it is relevant to note that Hammett *et al.*[5] have demonstrated that in a number of cases $\log A$ varies only with that portion of the energy of activation which is kinetic energy. In view of the picture of the permeation process described in the Introduction, it would seem that, since no bonds are broken in the diffusion process, the energy of activation is largely kinetic energy, and we may reason as follows. Imagine that in some particular reference system the permeation was characterized by a certain P_0 and E. On passing then to a system with a lower energy of activation E', it seems reasonable, in view of the picture of permeation described above, that the lowering of E has been due to the simultaneous cooperation of a number of factors. That is, in this latter case, more degrees of freedom are activated in hole formation. A hole is considered to form when several segments simultaneously move outward from a given region. The translational motion of each

TABLE I. Energies of activation for permeation and $\log P_0$ for water vapor.

Polymer	E(cal./mole)	$\log P_0$
Polystyrene	0	-6.08
Polyvinyl chloride-acetate	2350	$-5.10, -4.80$
Polyvinyl chloride	4000	-3.51
Polyethylene (calendered)	8000	-1.34
Polyethylene (cast)	10200	$+0.13$
Rubber hydrochloride	12800	$+1.63$
Polyvinylidene chloride	17500	$+4.20$

[4] C. N. Hinshelwood, *The Kinetics of Chemical Change* (Oxford University Press, New York, 1940).

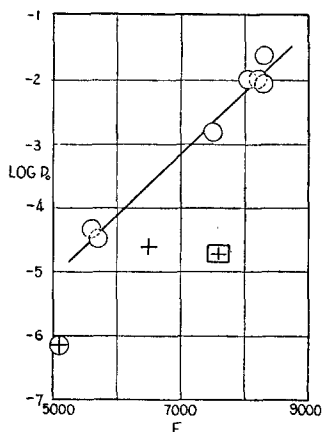[5] L. P. Hammett, *Physical Organic Chemistry* (McGraw-Hill Book Company, Inc., New York, 1940).

FIG. 2. The correlation of log P_0 and E (cal./mole) for the permeation of hydrogen through various polymeric materials. $\oplus$ = Bakelite; $+$ = ebonite; $\boxed{+}$ = Cellophane.

segment would involve at least three degrees of freedom. Each additional degree of freedom operative in the latter case can be thought of as reducing E by a given amount e, and if n degrees of freedom are involved the change is given by $E - E' = \Delta E = ne$. However, the chance that each of these degrees of freedom is favorably activated at the moment of activation is considerably less than unity. Thus for n of them to be favorable at once the probability of reaction will be reduced in the ratio $P'/P = a^n$, where a is less than unity and is the average probability of one degree of freedom being favorably activated at the time of the activation. If we take logarithms and eliminate n there is obtained

$$\log P - \log P' = (\Delta E/e) \log 1/a$$
$$\Delta \log P = \Delta E[(1/e) \log 1/a] = k\Delta E. \quad (4)$$

Thus it is found that $\log P$ will be a linear function of E. The validity of the relation just derived requires that $\log (1/a)$ is directly proportional to e. That is, the more the energy of activation is lowered by the proper activation of a certain degree of freedom, the less likely (logarithmically) is this activation to occur. This concept is statistical in nature: it cannot be expected to hold for every degree of freedom concerned with permeation in all polymers. However, it is expected that the average behavior of the various degrees of freedom would conform; consequently, the essential point in this logarithmic relation is the assumption that the pri-

mary act of permeation* depends upon a number of rarely fulfilled conditions corresponding to a large number of degrees of freedom. The conformance of experimental data to the derived logarithmic relation lends credence to the assumption on which the derivation was based.

It is necessary to note the probable limitations of this general behavior. All of the materials investigated were pure, unplasticized, linear polymers. On the basis of the present information nothing can be stated regarding plasticized polymers, cross-linked polymers, or polymers with which the diffusing gas has a specific interaction, such as the water-cellulose system.

The only other data available for testing this apparent relation between P_0 and E are those of Barrer[1] and deBoer and Fast[6] on the permeation of hydrogen and of Barrer on helium and nitrogen through several organic membranes. In Table II values of log P_0 calculated from these data are listed together with the energy of activation for all films studied. These values are plotted in Figs. 2–4. Unfortunately these data do not

TABLE II. Energies of activation for permeation and log P_0 for some permanent gases.

Material	E(cal./mole)	log P_0
—Hydrogen—		
Bakelite	5100	−6.14
Celluloid	5600	−4.35
Nitrocellulose	5700	−4.49
Ebonite	6500	−4.64
Cellulose triacetate	7500	−2.85
Cellophane	7600	−5.23
Polyethylene	8050	−2.00
Butadiene-acrylonitrile copolymer	8200	−1.99
Polychloroprene	8300	−2.08
Neoprene (vulcanized)	8300	−1.65
—Helium—		
Ebonite	5900	−4.52
Rubber (vulcanized)	6300	−3.59
Polyethylene	7700	−2.44
Neoprene (vulcanized)	8800	−1.55
Cellophane	10100	−3.13
—Nitrogen—		
Butadiene-styrene copolymer	7900	−2.67
Butadiene-methyl methacrylate copolymer	9500	−1.68
Butadiene-acrylonitrile copolymer	9800	−1.89
Neoprene	10500	−1.27
Bakelite	10500	−3.01

* This argument could be presented equally well in terms of diffusion. See Discussion.

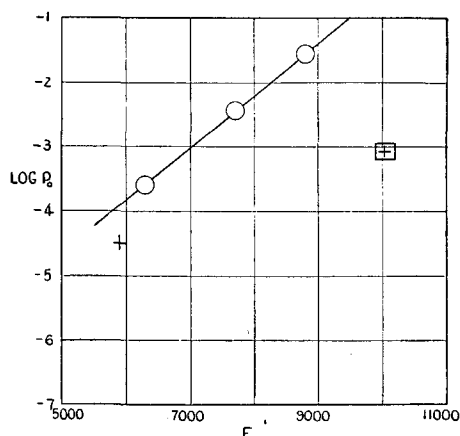[6] J. H. deBoer and J. Fast, Rec. Trav. chim. Pays-Bas. **57**, 317 (1938).

FIG. 3. The correlation of log P_0 and E (cal./mole) for the permeation of helium through various polymeric materials. + = ebonite; ⊞ = Cellophane.

extend over a large range of the variables and hence they cannot be considered decisive. However, it is encouraging to note that a linear relation is exhibited by all systems measured except those of Cellophane, ebonite, and Bakelite. Since none of these materials are pure linear polymers, the relation is confirmed with the restrictions originally pointed out. Vulcanized rubbers also fall in the linear relationship. It thus appears as though moderate cross-linking does not cause deviations from linear behavior, but excessive cross-linking such as is found in Bakelite and ebonite does cause deviations. Consequently, we may conclude that all available data on the temperature dependence of permeability of gases in pure polymeric substances conform to the equation $P = P_0 e^{-E/RT}$ and exhibit a linear relationship between log P_0 and E, except for very highly cross-linked materials.

THE EFFECT OF PLASTICIZATION ON PERMEATION

In order to determine in detail the effect of plasticization and composition on the permeability constant, the diffusion constant, and the solubility coefficient, some experiments have been performed on pure polyvinyl chloride, a polyvinyl chloride-acetate copolymer (Vinylite VYNW), and the latter polymer with the two different plasticizers added. The permeability constants and diffusion constants were measured in the manner described in a previous publica-

tion.[7] The data for polyvinyl chloride are taken from a previous publication.[3]

Polyvinyl chloride was chosen as the pure polymer with which comparisons could be made. The chloride-acetate copolymer differs from the polyvinyl chloride in that five percent of the chlorine is replaced by acetate groups. For plasticization, two plasticizers were chosen which represent rather extreme degrees of interaction with water. Tricresyl phosphate is typical of plasticizers which are immiscible with water, whereas the other plasticizer chosen was a mixed glycol ester of 6, 8, and 10 carbon fatty acids (SC plasticizer), which is fairly miscible with water but is also quite miscible with the polymer.

The results of our measurements with these four films at various temperatures are summarized in Table III. In Figs. 5–8 the logarithms of P, D, and S are plotted against reciprocal absolute temperature. From the slopes of these graphs the energies of activation for permeation and diffusion and the heat of solution have been calculated and are recorded in Table IV.

There are several interesting conclusions to be obtained from the data as summarized in Table IV. First of all, the resolution of P into the product of D and S appears to be verified under the rather diverse conditions existing in the films measured. Moreover, the variation of these quantities with temperatures is in all cases of the
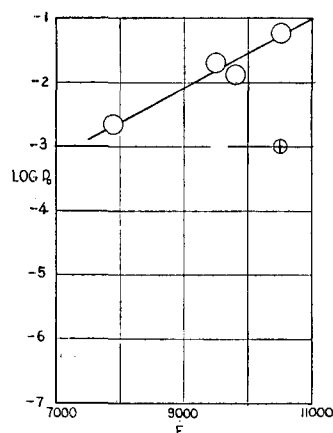

FIG. 4. The correlation of log P_0 and E (cal./mole) for the permeation of helium through various polymeric materials. ⊕ = Bakelite.

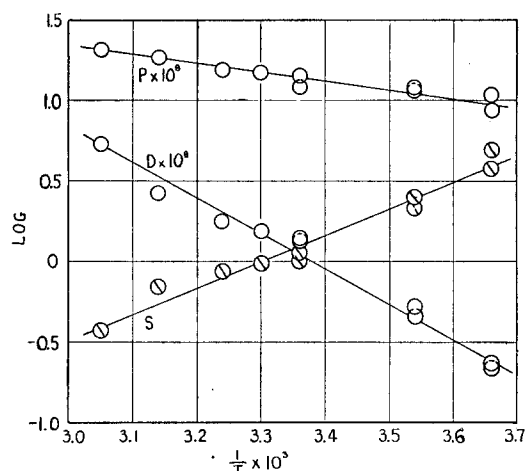[7] P. M. Doty, W. H. Aiken, and H. Mark, Ind. Eng. Chem. 16, 686 (1944).

FIG. 5. A plot of logarithm of P, D, and S versus reciprocal absolute temperature for the permeation of water vapor through polyvinyl chloride.
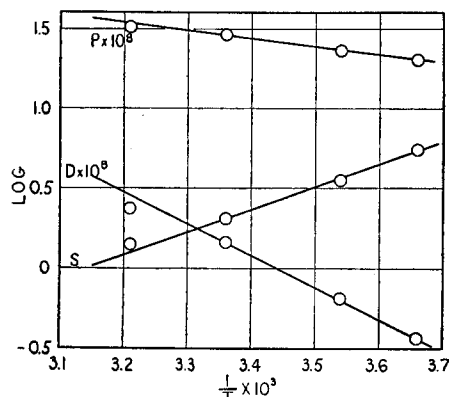

FIG. 6. A plot of logarithm of P, D, and S versus reciprocal absolute temperature for the permeation of water vapor through polyvinyl chloride-acetate.

form previously found for the transmission of permanent gases through polymer membranes. In other words, the inclusion of a rather large amount of solvent into the polymeric system does not alter the fundamental nature of the permeation.

Examination of Table IV indicates that E has the same value for the two pure polymers, but the value is considerably increased by the addition of either of the plasticizers. Moreover, this increase due to plasticization results almost entirely from the change in the heat of solution that has taken place. That is, the energy of activation for diffusion is relatively constant in all four films, but the heat of solution is quite sensitive to composition both of the polymer

itself and that of the added solvent. Similarly, P_0 is greatly increased by the addition of plasticizer, but D_0 is not significantly changed.

The heat of solution of water vapor in polyvinyl chloride is very large. This probably results from the strong interaction of the C—Cl dipoles with the OH groups. When some of the chlorine is replaced by acetate in the copolymer, the heat of mixing is somewhat lowered; the addition of 25 percent trioctyl phosphate or SC plasticizer reduces the heat of mixing very considerably. Either the plasticizer molecules solvate the C—Cl dipoles to a great extent, thus preventing their
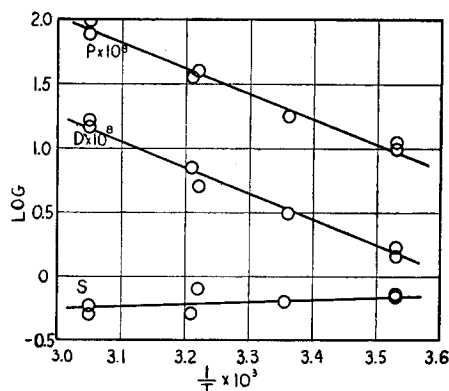

FIG. 7. A plot of logarithm of P, D, and S versus reciprocal absolute temperature for the permeation of water vapor through chloride-acetate plus 25 percent tricresyl phosphate.

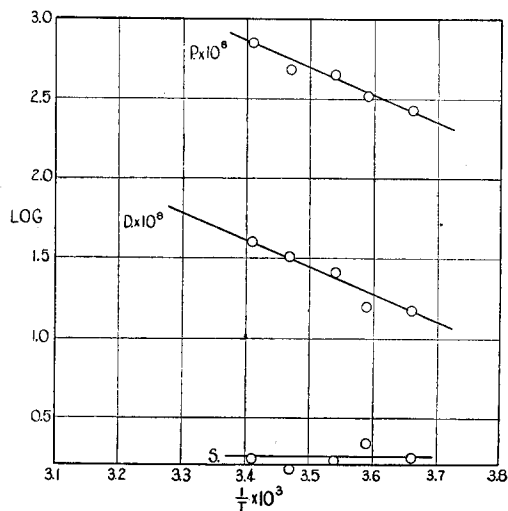

FIG. 8. A plot of logarithm of P, D, and S versus reciprocal absolute temperature for the permeation of water vapor through chloride-acetate plus 25 percent mixed glycol esters of 6, 8, and 10 carbon fatty acids (SC plasticizer).

TABLE III. P, D, and S (calc.) at different temperatures for the permeation of water vapor through polyvinyl chloride.

Temperature	$P \times 10^8$	$D \times 10^8$	S
Polyvinyl chloride			
0°	8.58	.232	3.7
0	10.95	.218	5.02
10	11.5	.525	2.19
10	12.2	.476	2.56
25	14.1	1.63	.863
25	11.9	1.35	.882
30	14.9	1.55	.96
35	15.5	1.76	.88
45	18.7	2.61	.716
55	20.3	5.41	.375
Polyvinyl chloride-acetate-copolymer			
0°	16.0	.309	5.18
10	22.9	.65	3.52
25	29.2	1.45	2.01
38	32.4	2.31	1.40
Polyvinyl chloride acetate and 25 percent tricresyl phosphate			
10°	11.1	1.58	.70
10	9.9	1.4	.706
25	19.7	3.1	.635
38	42.0	5.14	.82
38	35.2	6.98	.504
55	103.0	16.6	.621
55	76.0	15.0	.506
Polyvinyl chloride acetate and 25 percent mixed glycol ester			
0°	26.6	15.1	1.76
5	32.7	15.3	2.20
10	44.2	26.2	1.69
15	47.1	31.9	1.48
20	70.0	39.7	1.76

interaction with water, or the plasticizer may be so hydrophobic as to almost neutralize the hydrophilic nature of the polymer. The former assumption seems more probable since both hydrophobic and hydrophilic plasticizers increase ΔH by about the same amount.

The above data may also be used to calculate the entropy change which occurs when a mole of water vapor dissolves in the polymeric material. Thus one can estimate the amount of freedom which the dissolved water molecules possess. The free energy change for the transfer of one mole of water from the vapor (at 1-cm Hg pressure) to the polymer, is $\Delta F = -RT \ln S$. ΔH for the same process is listed in Table IV. ΔS, the change in entropy, is then found from the relation, $\Delta F = \Delta H - T\Delta S$. The entropy changes at 20° and 50° are recorded in Table V.

It can be seen from Table V that there is a considerable entropy decrease involved in the process of solution of water in polyvinyl chloride. Its magnitude indicates that the water molecules have lost almost as much entropy as that involved when the vapor condenses to ice. They must, therefore, be rather tightly held in the film, possessing little freedom except when moving from one point of attraction to another. In the copolymer almost the same conditions prevail. However, when plasticizer is introduced, the entropy change is lowered to that corresponding to the ordinary solution of a gas in a liquid. Thus water molecules in the plasticized film are about as free to move as they would be in an ordinary liquid solvent. It appears then that the effect of the plasticizer has been twofold. First, it has greatly lowered the heat of solution of water in the film and this in turn has increased $\log P_0$ and E. Second, the freedom of movement of the water molecules is enormously increased when plasticizer is present.

DISCUSSION

If the values of $\log P_0$ and E for the plasticized samples of polyvinyl chloride-acetate (Table IV) were plotted on the graph in Fig. 1, it is seen that these two points would fall above the straight line joining the points for pure polymeric substances. In considering Barrer's data for permanent gases it was noted that the points for Bakelite and ebonite were considerably lower than the straight line determined by the other materials. The data for Cellophane must be excluded from consideration because it is a composite film. Since it is a coated regenerated cellulose material the actual thickness which is

TABLE IV. Energies of activation and heats of solution.

Film material	E	$\log P_0$	E_D	$\log D_0$	ΔH
Polyvinyl chloride	2600	−4.96	10,000	−1.17	−7400
Polyvinyl chloride-acetate	2600	−4.62	9,100	−0.60	−6500
Polyvinyl chloride-acetate +25% tricresyl phosphate	8700	−0.30	9,300	−0.72	− 600
Polyvinyl chloride-acetate +25% SC plasticizer	7800	+0.30	7,800	−0.61	0

used in evaluating the permeability constant is meaningless.

An obvious suggestion may be advanced to explain the deviations just summarized, if we interpret the behavior as the increase or decrease of the energy of activation at constant value of

log P_0, that is, at a constant value of the entropy of activation, $\Delta S\ddagger$. Viewed in this manner the addition of small molecules (liquid) merely lowers the energy of activation for permeation by acting essentially as a lubricant for the matrix of polymer chains through which the gas molecules diffuse. Conversely, excessive cross-linking produces such rigidity even on a sub-microscopic scale that the attainment of the activated state requires a greater energy.

The explanation offered here for the observed relations between log P_0 and E are admittedly not compelling and have clearly been motivated by the data and not by *a priori* reasoning. At least two objections could arise. First, a linear relation between log P_0 and E may seem unreal since it has been demonstrated that P_0 is a composite quantity equal to the product of D_0 and S_0 and that E is equal to E_D plus ΔH. If D_0, S_0, E_D, and ΔH were all independent quantities, it would be practically impossible to believe that a simple linear relation had been found between log $D_0 S_0$ and $(E_D + \Delta H)$. This situation could be resolved if it could be shown that S_0 and ΔH change very little from system to system in comparison to D_0 and E_D and hence it is only the relation between log D_0 and E_D that is actually being considered. Since data on these quantities are not available for the measurements with water vapor, we can only examine the data on the permanent gases. Here the ΔH for the various systems vary up to 500 cal./mole and log S_0 up to 0.4 from the average. Since the points in Figs. 2–4 seem to follow a linear relation with just about these tolerances, we can conclude that in view of the available experimental data the apparent linear relation between log P_0 and E may be a reflection of a real linear relation between log D_0 and E_D.

Secondly, in the argument used to obtain a relation between log P_0 and E it may appear that the energy of activation of a particular degree of freedom will surely differ as the polymer is changed, and hence the argument would be useful only in explaining a trend—not a relationship. As previously pointed out this objection becomes less and less valid the larger the number of degrees of freedom involved, for the deviation of the quantity from the average is less significant the larger the number of degrees of freedom.

TABLE V. Entropies of solution of water in various polymers.

Polymer	20°	50°
Polyvinyl chloride	−24.4	−24.2
Polyvinyl chloride-acetate	−20.8	−20.1
Polyvinyl chloride-acetate+25% tricresyl phosphate	−3.6	−3.6
Polyvinyl chloride-acetate+25% SC plasticizer	−2.7	−2.7

It is just this condition of a large number of degrees of freedom operating in the activated state that Barrer[1,2] has postulated on the basis of both kinetic and statistical considerations. Using the following equation due to Wheeler,[8] the number of degrees of freedom used in acquiring energy of activation for diffusion may be calculated on the basis of a reasonable model assuming the vibration frequency of the diffusing particle to be approximated by 2.5×10^2.

$$d^2 = D_0 e^{(n-1)} \frac{6(n-1)!}{2} \left(\frac{RT}{E_D + (n-1)RT} \right)^{(n-1)}. \quad (5)$$

d is the mean free path and n is the number of degrees of freedom involved. Using data contained in Table IV this equation can be solved for d by assigning various values to n. Thus for $n = 6$, $d = 4.5$A, and for $n = 11$, $d = 1.6$A, it is to be expected that the mean free path of a water molecule would certainly be somewhat less than the distance between the carbon-chlorine dipoles along the polyvinyl chloride chain. Thus a value of 1.6A is a good estimate and it thus appears that Wheeler's treatment of diffusion may be interpreted as postulating a large number of degrees of freedom for activation.

Wynne-Jones and Eyring[9] have derived an expression for the rate constant which may be transformed into the following expression for D_0 with only moderate approximations.

$$D_0 = \exp(\Delta S\ddagger/R)(kT/h)(d^2/2.72). \quad (6)$$

If we assume that the mean free path of the water molecule in polyvinyl chloride systems is 1.6A, Eq. (6) can be solved to obtain $\Delta S\ddagger = 13.9$ e.u. Slightly larger values were obtained by

[8] T. S. Wheeler, Trans. Nat. Inst. Sci. India 1, 333 (1938).
[9] W. F. Wynne-Jones and H. Eyring, J. Chem. Phys. 3, 492 (1935).

Barrer using 5.0A for the mean free path in the case of the permanent gases. Even if these estimated values of d are doubled, $\Delta S\ddagger$ is only reduced by about 3 e.u. This large value of $\Delta S\ddagger$, if it were all due to the diffusing molecule, would correspond to more than its entropy of solution. Since this is not possible, the medium must share in the entropy change. Thus the data on the diffusion of water vapor corroborate the conclusions reached by Barrer for permanent gases: that activation energy is shared in part or wholly in various degrees of freedom of the polymeric system.

The Electrical Potential at the Interface between Vitreous Silica and Solutions of Barium Chloride

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(Received February 18, 1946)

The zeta-potential of vitreous silica in contact with several solutions of barium chloride has been determined by the measurement of streaming potentials. Solutions of seven concentrations between $10^{-6} M$ and $10^{-2} M$, inclusive, were studied, and the zeta-potential was found to decrease in a regular manner with increasing concentration. It is evident that there is no maximum in the curve of the zeta-potential *vs.* concentration, as most experimenters have reported.

IT is the purpose here to report measurements of the zeta-potential of vitreous silica in contact with solutions of barium chloride. The zeta-potential is not directly measurable, but is obtained conveniently from measurement of streaming potentials arising from the flow of the solutions through vitreous silica capillaries. The physical significance of the streaming potential measurements and their relation through Helmholtz's equation to the zeta-potential have been critically examined elsewhere.[1] The apparatus and technique for obtaining the necessary reliable streaming potential data for the computation of zeta-potentials have been described previously,[2] together with measurements of the zeta-potential of silica in contact with dilute potassium chloride solutions. Added interest is lent to this investigation by the fact that the data obtained make possible a test of Langmuir's interpretation[3] of the Jones-Ray effect[4] observed with barium chloride.

EXPERIMENTAL

The apparatus and experimental technique employed in this investigation have been described previously[2] and no important changes have been made. Duplicate sets of streaming potential apparatus with capillaries of different diameters were operated concurrently so that observations with one could be corroborated with the other. Previous work has demonstrated that initial measurements of the zeta-potential are not usually reliable, because the surfaces of the capillaries sometimes require many days to attain equilibrium with the solution. It has not

[1] L. A. Wood, J. Am. Chem. Soc. **68**, 432 (1946).
[2] Grinnell Jones and L. A. Wood, J. Chem. Phys. **13**, 106 (1945).
[3] I. Langmuir, Science **88**, 430 (1938); J. Chem. Phys. **6**, 894 (1938).
[4] Grinnell Jones and W. A. Ray, J. Am. Chem. Soc. **59**, 187 (1937); **63**, 288 (1941); **63**, 3262 (1941); **64**, 2744 (1942).