[CONTRIBUTION FROM CHEMISTRY DEPARTMENT, UNIVERSITY OF ABERDEEN]

The Diffusion of Gases Through Polyvinyl Acetate[1]

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The diffusion of helium, neon, argon, oxygen and hydrogen through high molecular weight polyvinyl acetate has been studied in the temperature range 4–44°. The polymer samples were thin disc membranes cut from mercury cast films and showed no orientation discernible by optical means. The very low permeabilities encountered were measured using a micro-Pirani gage to minimize the volume of the outgoing side of the diffusion system. Diffusion coefficients were determined using the time-lag method and permeabilities from steady state measurements. Solubilities were obtained from the ratios of these coefficients. Fick's and Henry's laws were accurately obeyed for all the gases over the temperature and pressure range investigated. Logarithmic plots of diffusion, permeability and solubility coefficients against reciprocal temperature show two transition temperatures. The upper one, 26°, is the same for all the gases and corresponds with the usually quoted second-order transition of polyvinyl acetate. The lower one decreases from 18–15° as the molecular size of the diffusing gas increases. The heats of solution of the gases usually reverse sign from negative to positive on entering the transition region from below. The activation energy for diffusion is small over the transition region, and is larger above the region than below it. The results are interpreted in terms of a molecular-kinetic picture of the change in bulk structure of the polymer in passing through the transition region.

Several investigations have shown that the solution and diffusion of simple gases in rubbers[2] and plastics[3] obey Henry's law and Fick's laws, with a diffusion coefficient independent of concentration. This contrasts with the behavior of organic vapors which have strongly concentration dependent diffusion coefficients and non-linear sorption isotherms. The ideality of the process with gases is due to their relative insolubility so that at ordinarily accessible temperatures and pressures the quantity of gas dissolved in the polymer is insufficient to alter its properties to any observable extent and encounters between gas molecules within the polymer are rare. It was found[2] that the diffusion coefficients D had the exponential temperature dependence of an activated process. Thus

$$D = D^0 e^{-E/RT} \qquad (1)$$

where D^0 and the activation energy E were almost independent of temperature. The energies of activation for diffusion in rubbers were close to the energies of activation for viscous flow indicating that movement of polymer segments was required. The factor D^0 was related to an entropy or zone of activation within the rubber which was found to be much larger than the corresponding zone of activation accompanying diffusion in simple liquids. With this established basis a study of diffusion in polymers can be used to solve detailed structural and dynamic problems.

Most polymers show a second-order transition temperature externally characterized by a change from hard glass-like to rubber-like properties. It has been suggested[4] that it is only an apparent transition the appearance of which depends upon the rate at which observations are made. An alternative view, summarized by Buchdahl and Nielsen,[5] is that the transition is accompanied by the freeing of hindered rotations about –C–C– bonds in the polymer chain. This view, supported by the evidence of recent investigations,[6–8] requires a change in the internal molecular state of the polymer at the transition from an amorphous solid to a quasi-liquid. There is no freedom, as in a true liquid, for place interchange of whole molecules.

The physical implications of such a transition can be visualized in terms of the "hole" theory of liquids. The Gibbs free energy G of a polymer sample at a given temperature and pressure is dependent upon its volume V through two variables. These are the average internuclear separation between segments of neighboring chains in close packed regions, and the number and size of the "holes" present. The former factor is concerned mainly with the heat content and the latter with the entropy of the sample. At temperatures above the transition both variables are continuously adjusted in such a way that the actual volume of the sample represents a minimum on a $V \times G$ plot and hence a true thermodynamic equilibrium state. At temperatures below the transition the freezing of the segmental rotations immobilizes the "holes." Hence, as the temperature is further decreased, only the internuclear separation can adjust itself to minimize G, the number of "holes" remaining fixed at the number which prevailed at equilibrium at the transition temperature. Thus the actual physically realized volume of the sample represents the lowest practically attainable free energy but not a minimum on a $V \times G$ plot. This therefore is not a thermodynamic equilibrium state. However the rate at which true equilibrium is established is so slow that, in so far as the segmental rotations become frozen, over a narrow temperature range, the normal state of the polymer sample below the transition can be uniquely defined in terms of temperature and pressure, provided the sample is cooled from above the transition at such a rate that there is time for true equilibrium to be established at the transition temperature.

Such a change in the internal mobility of the polymer should be reflected in its diffusion properties. The present study was undertaken with the object of relating the values of D^0 and E to the ex-

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(1) Presented at the 124th meeting of the American Chemical Society, Chicago, 14th September, 1953.

(2) R. M. Barrer, *Trans. Faraday Soc.*, **35**, 628, 644 (1939); G. J. van Amerongen, *J. Applied Phys.*, **17**, 972 (1946); *J. Polymer Sci.*, **5**, 307 (1950).

(3) S. A. Reitlinger, *J. Gen. Chem. (U.S.S.R.)*, **14**, 420 (1944).

(4) R. F. Boyer and R. S. Spencer, *J. Applied Phys.*, **17**, 398 (1946).

(5) R. Buchdahl and L. E. Nielsen, *ibid.*, **21**, 482 (1950).

(6) T. G. Fox and P. J. Flory, *ibid.*, **21**, 581 (1950).

(7) L. V. Holroyd, R. S. Codrington, B. A. Mrowca and E. Guth, *ibid.*, **22**, 696 (1951).

(8) R. S. Witte and R. L. Anthony, *ibid.*, **22**, 689 (1951).

tent of internal mobility. Recent evidence has shown that the diffusion of organic vapors into polyvinyl acetate[9] and polystyrene[10] is markedly different above and below the second-order transition temperature. The diffusion of vapors into polymers below the transition temperature does not obey Fick's laws and so presents in itself an interesting and incompletely solved problem. These data do not therefore provide a clear indication as to the nature of the transition process.

In this investigation polyvinyl acetate has been studied as its second-order transition lies in a convenient temperature range. The gases helium, neon, argon, hydrogen and oxygen were used ensuring ideal behavior in the gas phase. The well established method of diffusion through disc membranes was employed[2,11] so that the diffusion coefficient D was obtained from the time lag in establishing a steady state and the permeability coefficient P from the steady state permeation rate. The solubility coefficient s is then given by

$$s = P/D \tag{2}$$

This method requires that equilibrium shall always exist between the gas phase and the membrane surface with which it is in contact, a condition which is almost certainly satisfied when the permeation rates within the membrane are as low as were encountered here.

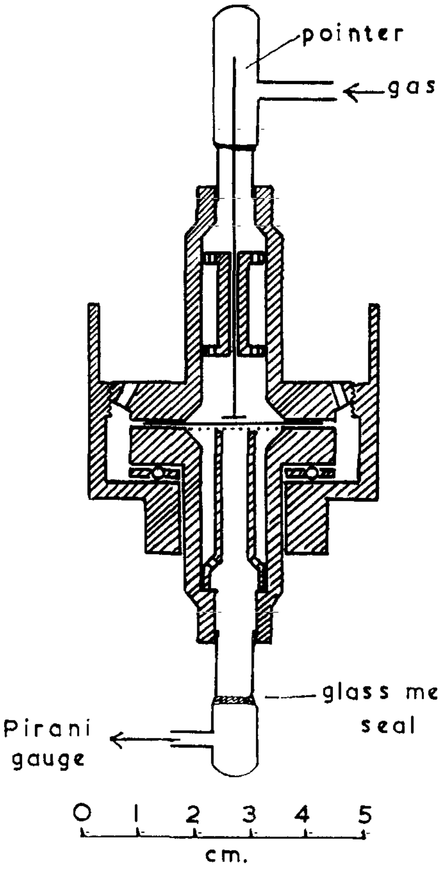

Fig. 1.—The diffusion cell.

Experimental

The gases were British Oxygen Co. spectrally pure samples. Purity is very important as, for example, the permeability to helium is 100 times that to argon, hence 1% helium in the argon would double the apparent permeability.

The polyvinyl acetate, Shawinigan Gelva 145, was of very high molecular weight and probably branched but completely soluble. A high molecular weight was desirable to eliminate the molecular weight dependence of the transition temperature[6] and also to reduce the risk of viscous deformation of the membranes at the higher temperatures. Any low molecular weight material was removed by a rough fractional precipitation from acetone with a mixture of equal volumes of water and methyl alcohol. The polymer was then cast into a thick sheet on mercury from acetone solution. Diffusion membranes were made from pieces cut from this sheet and so were of identical material.

Diffusion membranes of various thicknesses were cast by pouring 10% solutions in dry acetone into stainless steel rings sitting in mercury and allowing to evaporate at room temperature, with careful exclusion of dust. The rings were removed while the membranes were still pliable and discs for the diffusion cell cut from their centers. These were placed horizontally between linen sheets in a glass frame and outgassed under high vacuum for many weeks at temperatures increasing slowly to 70°. The membranes were transparent and showed no orientation in the polarizing microscope. Thicknesses were measured with a micrometer screw gage with a weak ratchet spring and were uniform over the whole membrane to ±1%. The permeability to neon at 22° was used to check the uniformity of properties and confirm all thickness measurements relative to the thickest membrane. Three membranes were used, thicknesses 1.332 mm., 0.286 mm. and 0.135 mm., the measurements on any one gas being completed with the same membrane.

The diffusion cell shown in Fig. 1 was developed from the design of Barrer.[2] It was constructed of stainless steel with copper to glass seals silver soldered into each half cell. The membrane was supported on the low pressure side by a copper gauze resting on an inset round the cell flange and a rigidly located central tube. The cell was warmed before inserting the membrane so that a vacuum seal between membrane and flanges was obtained without screwing tightly. The unchanged membrane thicknesses after use showed that this method avoided distortion. The seal was completed by filling the surrounding cup with mercury. The correct seating of the membrane could be checked from externally with the aid of a pointer. A light stainless steel tube with a small piece of soft iron at its upper end and a disc of platinum foil at its lower end slid in a centrally mounted tube in the upper half of the cell. With the platinum disc resting on the membrane the height of the soft iron tip in the glass tube above the cell was observed with a cathetometer. When not in use this pointer was held clear of the membrane by a magnet.

The cell was supported in a glass jacket closed at the top by a cork and immersed in a well lagged deep water thermostat controllable between 1 and 50° to ±0.005°. Connection of the outgoing side of the cell to the vacuum system was by 2 mm. capillary and of the ingoing side by 4 mm. bore glass tubing to minimize thermal conduction and convection. There was never a detectable temperature difference between the mercury surrounding the cell and the thermostat so that the whole of the membrane was assumed to be at the thermostat temperature.

Permeability Determinations.—The boundary conditions for the simplest solution of the diffusion equation require that the cell be initially evacuated on both sides of the membrane. At zero time a pressure of gas is applied to the ingoing side (the upper side in this apparatus) and the total amount of gas which permeates to the outgoing side observed as a function of time. The pressure on the outgoing side must always be negligible compared with the ingoing pressure.

Ingoing pressures from 2–30 cm. were used and recorded to 0.01 cm. by observing wide bore mercury manometers with a cathetometer. The ingoing pressure was kept constant by manipulating a Toepler pump connected to the gas reservoir, but adjustment was rarely necessary as the amount of gas permeating was very small and room temperature was controlled to ±1°.

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[9] R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1951).

[10] F. A. Long and R. J. Kokes, This Journal, **75**, 2232 (1953).

[11] H. A. Daynes, *Proc. Roy. Soc.* (*London*), **A97**, 286 (1920).

The outgoing side of the diffusion apparatus was a constant volume system consisting of the diffusion cell connecting through a liquid oxygen surrounded U-trap to a micro-Pirani gage. It was isolated by mercury cutoffs from the vacuum line and a McLeod gage. The "effective volume" of this outgoing system was about 70 cc. calculated on the basis that all the gas it contained was at room temperature. It was calibrated by pressure drop on expansion measurements against the standard volume of the McLeod gage. Variation of the "effective volume" with thermostat temperature was too small to be significant. The liquid oxygen surrounding the U-trap was brought to a constant level at a standard time before every observation. The lack of dependence of the "effective volume" on the pressure or gas with which it was determined showed that negligible gas sorption occurred in the U-trap.

The Pirani gage, which was of differential type one half being evacuated and sealed off, was contained in an oil filled earthed brass shield immersed in an oil thermostat at 25 ± 0.01°. It formed two arms of a d.c. resistance bridge the other arms being a 10^4 ohm standard resistance and a 10^4 ohm decade box. A constant P.D. of 1.7 ± 0.001 volts was maintained across the bridge which could be balanced to ±0.05 ohm. This gave a pressure sensitivity better than 1×10^{-5} mm. with all gases. Calibration curves of change in bridge balance against pressure were constructed for each gas using the McLeod as an absolute gage.

General Precautions.—The pressure on the outgoing side was never allowed to exceed 10^{-2} mm. This was always negligible compared with the ingoing pressure. Experiments were continued for six to ten times the time lag, the steady state was established after between two and three times the time lag. The apparatus was evacuated between runs for at least 20 times the time lag at the experimental temperature. Observations at different temperatures were made at random. The rate of change of temperature of the cell was less than 1° per hour and the temperature maintained constant for a day before making measurements. Under these conditions no hysteresis or time effects, so frequently associated with polymer transitions, were observed.

Results

Permeability measurements with each gas have been made at many temperatures in the range 4–44°. Each recorded value is the mean of at least two experiments at the same temperature and different ingoing pressures. Diffusion and permeability coefficients were independent of ingoing pressure, confirming the validity of Fick's and Henry's laws.

The diffusion coefficient was calculated from

$$D = L^2/6\theta \qquad (3)$$

where L is the membrane thickness in cm. at the temperature of the experiment, and θ the time lag in seconds obtained by extrapolating the linear part of the pressure *vs.* time graph to zero pressure. The permeability coefficient is given by

$$P = \frac{273}{T_{\text{room}}} \times \frac{VL}{76ap_{\text{in}}} \times \frac{dp}{dt} \qquad (4)$$

where V is the effective volume in cc. of the outgoing side, T_{room} the absolute room temperature, dp/dt the time rate of increase of pressure in the outgoing system during the steady state in cm. sec.$^{-1}$, a the membrane area in cm.^{2} available for permeation and p_{in} the ingoing pressure in cm. P gives the amount of gas, expressed as cc. at N.T.P., passing in 1 second through 1 cm.^{2} of polymer 1 cm. thick when the pressure difference across this sample is 1 cm. The Bunsen solubility coefficient expressed as cc. of gas, measured at N.T.P., dissolving in 1 cc. of polymer, at the temperature of the experiment, and at a partial pressure of 1 atm. is given by

$$s = 76P/D \qquad (5)$$

Observation of the diffusion cell pointer in contact with the membrane at different temperatures showed no measurable change in height. It was concluded that the membrane remained in contact with the supporting gauze. The thermal expansion of the steel cell being negligible, the area of the membrane remained constant, its thermal expansion being completely accounted for by an increase in thickness. The measured thicknesses at 20° have been corrected for temperature on this basis using the specific volume data of Kokes, Long and Hoard.[9] Though the change in thickness between 4 and 44° is only 1%, the use of this correction changes the observed activation energies for diffusion by almost 10%.

The experimental results are presented in Figs. 2–6 in which decadic logarithms of the coefficients P, D and s are plotted against reciprocal absolute temperature.

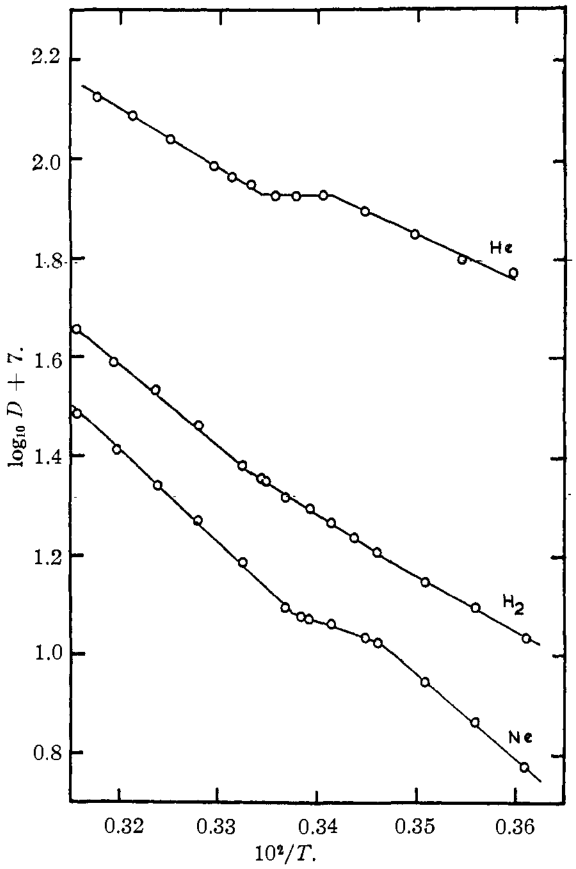

Fig. 2.—Diffusion coefficients D for helium, hydrogen and neon in polyvinyl acetate.

Discussion

For a simple activated diffusion process, within a medium where the only effect of temperature is thermal expansion due to increased molecular vibrations, $\log_{10} D \times T^{-1}$ would give an almost linear plot. When, as is usually the case, the heat of solution of gas in polymer is almost independent of temperature, $\log_{10} s \times T^{-1}$ and hence $\log_{10} P \times T^{-1}$ should also be linear. Examination of Figs. 2–6 shows that in no case can the data for any one gas be represented by a single straight line. In general

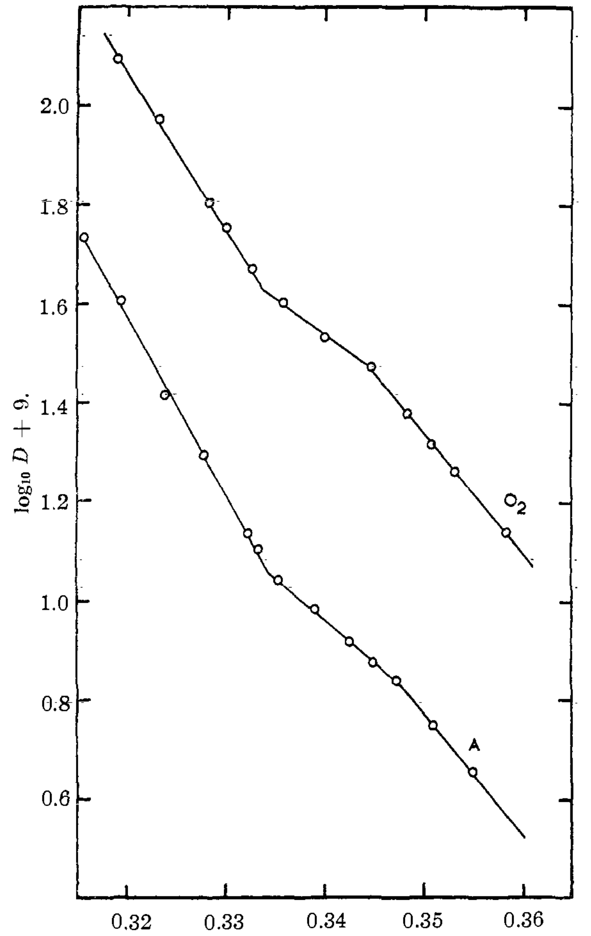

Fig. 3.—Diffusion coefficients D for oxygen and argon in polyvinyl acetate.

the experimental points lie on three distinct straight lines with two intersections. In one case, owing to the coincidental interplay of D and s, one intersection of the $\log_{10} P \times T^{-1}$ plot is difficult to locate. As there are no transitions in the gases, the temperatures of these intersections must reflect a change in the polymer medium. The intersection temperatures from the graphs are assembled in Table I. It may be fairest to conclude that P, D and s with all gases reveal the same two transition temperatures in polyvinyl acetate at 26° and 17°. The downward trend of the lower one from 18 to 15° with increasing molecular size may however be genuine. The upper temperature corresponds with the normally observed second-order transition for which values between 25 and 31° have been reported. It is of interest that the transitions are revealed not only by the kinetic process of diffusion but also by the equilibrium property of solubility.

TABLE I

TRANSITION TEMPERATURES IN POLYVINYL ACETATE

Gas	Method of observation P	 D	 s	Average
1. Upper transition temperature, °C.				
Helium	26.0	25.6	28.0	26.5
Hydrogen	25.3	26.7	26.2	26.1
Neon	Indefinite	23.9	24.2	24.1
Oxygen	25.0	26.1	27.8	26.3
Argon	28.7	26.0	25.2	26.3
2. Lower transition temperature, °C.				
Helium	16.7	19.8	17.6	18.0
Hydrogen	16.9	16.0	18.1	17.0
Neon	16.3	16.5	16.8	16.5
Oxygen	16.6	17.5	16.9	17.0
Argon	15.8	15.0	15.1	15.3

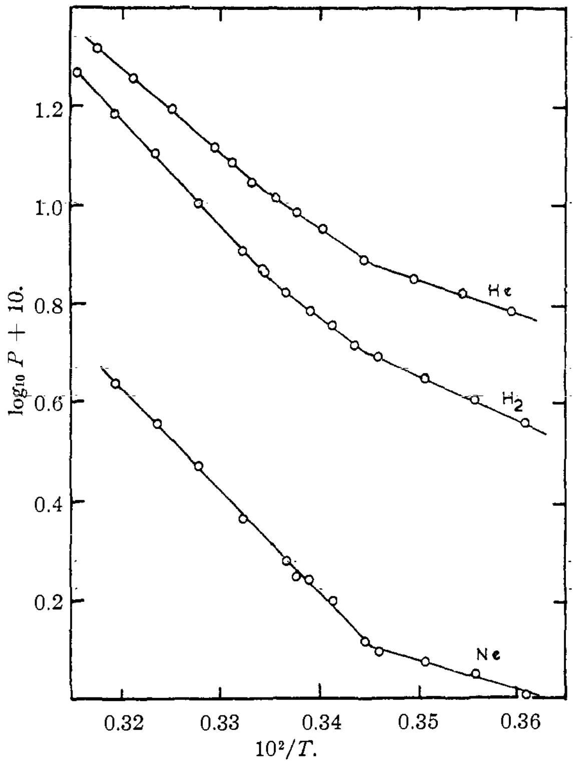

Fig. 4.—Permeability coefficients P for helium, hydrogen and neon in polyvinyl acetate.

The Solubility Data.—A knowledge of the equilibrium state of the dissolved molecules is important in understanding the diffusion processes. For a perfect gas solution obeying Henry's law, the change in partial molar heat content $\Delta\bar{H}$ for 1 mole transferred isothermally from the gas phase at any pressure to infinite bulk of solution at equilibrium is

$$\Delta\bar{H} = -R\left(\frac{\mathrm{d}\ln s}{\mathrm{d}1/T}\right) \qquad (6)$$

Values for the gases below the transition region $\Delta\bar{H}_1$, between the transition temperatures $\Delta\bar{H}_2$ and above the transition $\Delta\bar{H}_3$ are given in Table II.

The negative values (heat evolved) of $\Delta\bar{H}_1$ support the suggestion that a polymer below its transition contains more than the equilibrium number of holes for a liquid of similar cohesive energy density at the same temperature.[12] Dissolved gas molecules are accommodated in holes already present in the polymer bulk structure. The gas molecule in a hole is in a potential minimum of depth determined by the dispersion interaction between it and the surrounding polymer. This is determined by the number of electrons in the outer shell.[13] Thus

(12) P. Meares, *Trans. Faraday Soc.*, **49**, 1133 (1953).

(13) J. C. Slater and J. G. Kirkwood, *Phys. Rev.*, **37**, 682 (1931).

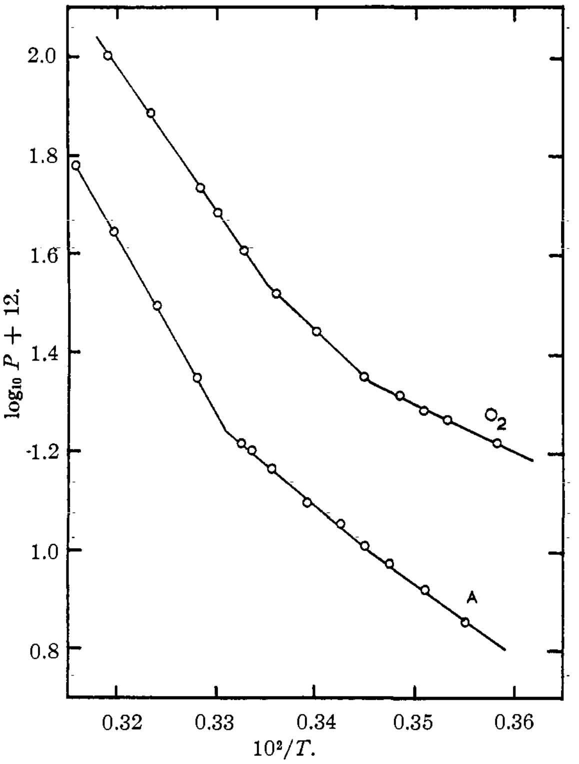

Fig. 5.—Permeability coefficients P for oxygen and argon in polyvinyl acetate.

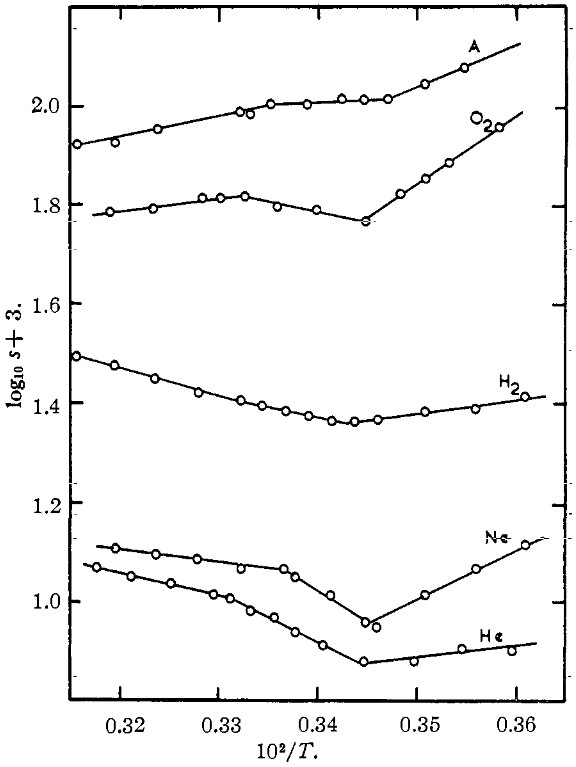

Fig. 6.—Bunsen solubility coefficients s for argon, oxygen, hydrogen, neon and helium in polyvinyl acetate.

helium and hydrogen with two have $\Delta\bar{H}_1 \simeq 1{,}000$ cal., neon and argon with eight about 4,000 cal. and oxygen with twelve about 6,000 cal.

Above the transition region the partial rotational freedom, which must exist to account for the elastic properties, allows a liquid-like equilibrium distribution of holes and matter in the bulk polymer. Gas molecules dissolving have to create their own space by separating interchain polymer contacts. The heat of solution is the sum of the work required to create a hole to accommodate the solute particle and the interaction energy between this particle and the surrounding polymer. As the difference in temperature is small, this interaction energy is given by the heat of solution below the transition. Thus $(\Delta\bar{H}_3 - \Delta\bar{H}_1)$ (Table II, col. V) is the work of hole formation. The cohesive energy density of polyvinyl acetate, from heats of solution,[14] is about 90 cal./ml. so that the work of hole formation corresponds to partial molar volumes from 35 ml. for helium to 60 ml. for oxygen, reasonable except for argon which is too small.

Excepting hydrogen, which also shows anomalous diffusion in the transition region, the heats of solution between the transition temperatures are larger than above them. The following speculative explanation conforms with the observations. Small molecules, usually plasticizer or solvent molecules, lower the transition temperature of a polymer. Hence at a temperature somewhat below 26° a gas molecule in the polyvinyl acetate will disturb the packing of the surrounding segments in the same way as a plasticizer molecule. This will create a small region in which the polymer segments acquire the freedom of motion they normally enjoy above 26°. Each mode of energy storage freed by the gas molecule will absorb $^1/_2\ RT$ appearing as a positive contribution to the heat of solution. This is given by $(\Delta\bar{H}_2 - \Delta\bar{H}_3)$ in the last column of Table II and corresponds to about 10 degrees of freedom. Below the lower transition temperature the gas molecules are unable to loosen the surrounding polymer. The larger the gas molecule the more it will disrupt the surrounding structure in agreement with the observation that the lower transition temperature decreases as the size of the gas molecule increases.

TABLE II

HEATS OF SOLUTION IN POLYVINYL ACETATE (CAL. MOLE^{-1})

Gas	Below 17° $\Delta\bar{H}_1$	17–26° $\Delta\bar{H}_2$	Above 26° $\Delta\bar{H}_3$	$\Delta\bar{H}_3 -$ $\Delta\bar{H}_1$	$\Delta\bar{H}_2 -$ $\Delta\bar{H}_3$
Helium	−1010	4701	2110	3120	2600
Hydrogen	−1420	1740	2470	3890	−730
Neon	−4620	5710	1050	5670	4660
Oxygen	−6260	1600	−1100	5160	2700
Argon	−3700	−550	−1880	1820	1330

The Diffusion Data.—The observed activation energies for diffusion, from eq. 1, are presented in Table III, and the values of D^0 in Table IV. The activation energies below the transition region E_1 and above the transition E_3 increase with the size of the diffusing molecule. This is also true over the transition region (E_2) if hydrogen is excluded. The same trends over a wider numerical range are apparent in D^0. For diffusion in rubbers the activation energy is close to the activation energy for viscous flow of the rubber.[15] For polyvinyl ace-

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[14] P. Meares, *Trans. Faraday Soc.*, **47**, 699 (1951).

[15] R. M. Barrer, *ibid.*, **38**, 322 (1942).

TABLE III

ENERGIES OF ACTIVATION FOR DIFFUSION IN POLYVINYL ACETATE (CAL. MOLE^{-1})

Gas	Below 17° E_1	17–26° E_2	Above 26° E_3	d^2, Å.^{2}
Helium	4,160	0	5,350	4.75
Hydrogen	5,170	5720	7,500	7.39
Neon	7,360	3160	8,460	6.75
Oxygen	11,090	6500	14,490	13.12
Argon	11,380	7960	16,500	13.41

TABLE IV

VALUES OF D^0 FOR DIFFUSION IN POLYVINYL ACETATE

Gas	Below 17° D^0_1	17–26° D^0_2	Above 26° D^0_3
Helium	1.10×10^{-2}	8.32×10^{-6}	6.92×10^{-2}
Hydrogen	1.32×10^{-2}	3.89×10^{-2}	6.61×10^{-1}
Neon	3.89×10^{-1}	2.63×10^{-4}	2.09
Oxygen	6.31	2.34×10^{-3}	1.59×10^{3}
Argon	2.69	7.41×10^{-3}	1.26×10^{4}

tate the activation energy for viscous flow is very large, 60–80 kcal. mole^{-1}.[16] The activation energy for diffusion never reaches a quarter of this value so that diffusion cannot involve the movement of polymer segments of the size contributing to viscous flow. If E_1 and E_3 are plotted against the squares of the diameters of the gas molecules, from gas viscosity data[17] (d^2 in Table III, col. V), fairly linear relations from the origin are obtained (Fig. 7). This is not so if E_1 and E_3 are plotted against d^3. The unit diffusion step appears to be governed by the energy required to separate the surrounding medium to give a space of sufficient cross section for the diffusing molecule to pass and not the energy required to produce a hole for the molecule to pass into.

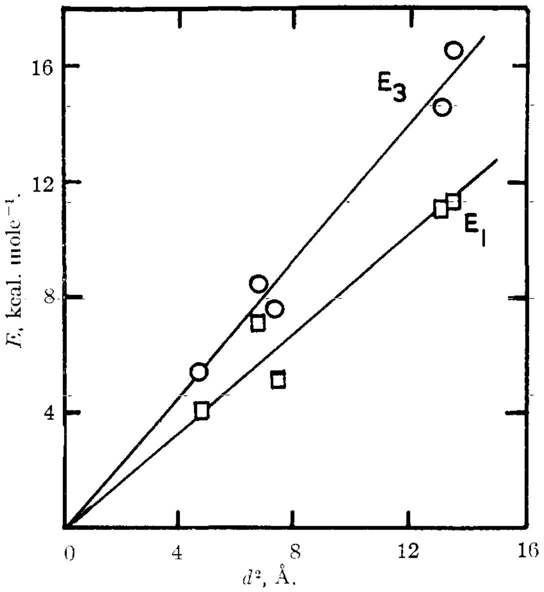

Fig. 7.—Activation energy for diffusion *vs.* (collision diameter)^2 below (□) and above (○) the transition region.

Above the transition temperature the activation process is the breaking of van der Waals bonds between polymer segments which separate by synchronized rotation or torsional oscillation about –C–C– bonds to produce a cylindrical void along which the diffusing molecule can travel. If the bulk polymer is regarded as randomly oriented regions of roughly parallel polymer segments, in analogy with the quasi-crystalline picture of a liquid, creation of a void involves breaking contacts between about four chains. Complete separation beyond the limit of van der Waals interaction would not be required for the small molecules, but for oxygen and argon this will be nearly the case. As a lateral displacement of the polymer segments of less than ~2 Å. is required and the structure possesses some internal mobility, the compression of the surrounding chains will be small and most of the activation energy used in breaking the physical bonds between the polymer segments. It has been estimated[18] that 3.2 kcal. mole^{-1} are required to separate a 5 Å. length of polyvinyl acetate from four neighboring chains. For oxygen and argon, E_3 corresponds to the complete separation of segments about 25 Å. in length. A similar value is obtained by a more direct treatment of the data. For each gas the activation energy is the energy required to produce a cavity of cross section $^1/_4\pi d^2$. If the cavity length is λ_3 its volume is $^1/_4\pi d^2\lambda_3$. The energy of a mole of such cavities in a liquid-like structure of cohesive energy density 90 cal./ml. may be equated to the activation energy and used to calculate λ_3

$$90 \times {}^1/_4\pi d^2 N\lambda_3 = E_3 \qquad (7)$$

The values, given in Table V, are about the same for all gases and average 27 Å. This is characteristic of polyvinyl acetate and represents the average length of the rotating chain segments above the transition temperature.

TABLE V

PATH LENGTHS AND ENTROPIES OF ACTIVATION FOR DIFFUSION IN POLYVINYL ACETATE

Gas	Below 17° λ_1 Å.	Below 17° ΔS^*_1, cal. mole^{-1} deg.$^{-1}$	Above 26° λ_3 Å.	Above 26° ΔS^*_3, cal. mole^{-1} deg.$^{-1}$
Helium	9.3	−5.0	26.5	−5.7
Hydrogen	7.5	−4.6	23.9	−1.2
Neon	11.6	2.1	29.5	1.1
Oxygen	8.9	7.6	25.9	14.2
Argon	9.1	5.9	28.9	18.4

The application of the theory of absolute reaction rates to diffusion[19] gives

$$D = e\lambda^2 \frac{kT}{h} e^{\Delta S^*/R} e^{-E/RT} \qquad (8)$$

where ΔS^* is the entropy of activation associated with a mole of unit diffusion acts and λ the unit distance travelled. Comparison with eq. 1 shows

$$D^0 = e\lambda^2 \frac{kT}{h} e^{\Delta S^*/R} \qquad (9)$$

For rubbers if λ is assumed to be 3–5 Å. ΔS^* is large indicating activation of a considerable zone of the medium accompanying diffusion. However, in polyvinyl acetate above 26° the activation energy

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[16] D. R. Morey, *J. Phys. Chem.*, **53**, 569 (1949).

[17] J. Jeans, "An Introduction to the Kinetic Theory of Gases," Cambridge University Press, London, 1940, p. 183.

[18] H. Mark, *Ind. Eng. Chem.*, **34**, 1345 (1942).

[19] S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 524.

is sufficient to open a path of 27 Å. The average time for a molecule at 300°K. possessing one degree of translational freedom to travel 27 Å. varies from 2.5×10^{-12} sec. for hydrogen to 10^{-11} sec. for argon. The frequency of rotation or torsional oscillation of segments 27 Å. long cannot be greater than 10^{10} sec.$^{-1}$ and is probably less than 10^{9} sec.$^{-1}$ so that the diffusing molecule could traverse the whole path many times during the activated state. Also it will spend most of its time at the ends of the cavity where the velocity passes through zero. Hence, using 27 Å. for λ, the values of ΔS^*_3 in Table V were calculated from D^0_3 at 300°K. Plotting ΔS^*_3 against E_3 gives a linear relation (Fig. 8) as predicted by Barrer[20] for a process in which the activation energy is shared between a number of degrees of freedom in a zone of activation. The fulfillment of this condition, which is valid for viscous flow in liquids and diffusion in rubbers, is evidence for the existence of internal mobility in polyvinyl acetate above 26°.

ΔS^* contains contributions from the diffusing gas molecule and from the medium. A sorbed gas molecule occupying an equilibrium site behaves as an isotropic three-dimensional harmonic oscillator. During diffusion one degree of vibration is exchanged for a degree of translational freedom. If diffusion takes place through a tunnel of cross section determined by the collision diameter of the molecule, then the other two vibrational degrees are restrained during the translation. For small gas molecules at 300°K. the partial molar volumes are such that rotational freedom is unrestricted in the sorbed state, and at these low sorbed gas concentrations the configurational entropy will be negligibly affected by the translational freedom during diffusion. Thus the entropy of activation of the diffusing molecule can be calculated if its vibrational frequency is known. Vibration frequencies of hydrogen and argon sorbed in various polymers at 300°K. have been shown[21] to be almost independent of the nature of the polymer and about 3×10^{12} and 0.7×10^{12} sec.$^{-1}$, respectively. The translational entropy for one degree of freedom is

$$S_{\text{tran}} = R \ln \left[\frac{(2\pi mkT)^{1/2}\lambda}{h}\right] + \frac{1}{2}R \qquad (10)$$

the vibrational entropy in three dimensions is

$$S_{\text{vib}} = 3\left[\frac{Nh\nu}{T(e^{h\nu/kT} - 1)} - R \ln (1 - e^{-h\nu/kT})\right] \qquad (11)$$

and the entropy of activation of the diffusion molecule is

$$\Delta S^*_{\text{gas}} = S_{\text{tran}} - S_{\text{vib}} \qquad (12)$$

Hence for hydrogen ΔS^*_{gas} is -2.19 cal. mole^{-1} deg.$^{-1}$ and for argon -7.79 cal. mole^{-1} deg.$^{-1}$. The entropy of activation of the medium is

$$\Delta S^*_{\text{med}} = \Delta S^*_{\text{s}} - \Delta S^*_{\text{gas}} \qquad (13)$$

This for hydrogen is 1.0 cal. mole^{-1} deg.$^{-1}$ and for argon 26.2 cal. mole^{-1} deg.$^{-1}$. It is clear that for the diffusion of very small molecules little disturbance of the medium is required but for the larger ones such as argon the production of a cavity for diffusion involves a large zone of activation. It seems that for the diffusion of small molecules cooperative oscillation of the polymer segments is sufficient but for larger ones complete rotation may be required.

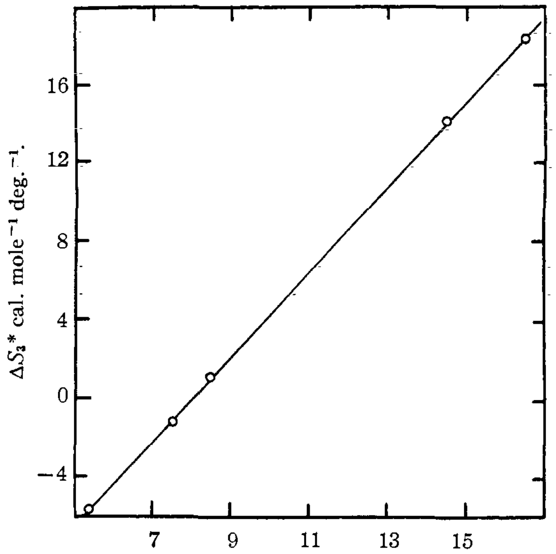

Fig. 8.—Linear relation between energy and entropy of activation for diffusion above the transition.

Below the transition the polymer consists of regions of densely packed and arranged chains, exerting the maximum van der Waals attractions and possessing no freedom of rotation, separated by less dense regions of disordered chains which are the "holes" into which exothermic sorption occurs. Molecules diffusing between "holes" must travel through the well ordered regions where the energy required to produce a cavity will be much larger. The van der Waals bonds between chains have to be loosened and the surrounding chains have to be compressed to provide space for the cavity. The internal energy change when a substance of compressibility β and thermal expansion coefficient α is compressed ΔV is $\Delta VT\alpha/\beta$. At ordinary pressures, $T\alpha/\beta$ is almost equal to the cohesive energy density. Hence the energy required to produce an internal cavity of volume ΔV at constant external volume is twice the energy of vaporization of ΔV of the substance. The cohesive energy density of these ordered regions will be greater than the observed cohesive energy density above the transition temperature, 90 cal./ml. An estimate of 100 cal./ml. is probably conservative. Taking the cavity cross section as equal to the collision area of the diffusing molecule and proceeding as for λ_3 the cavity lengths λ_1 in Table V were obtained from E_1. Clearly the unit diffusion step is much shorter in the hard state of the polymer. Using a mean value of 9 Å. for λ_1 the values of ΔS^*_1 in Table V were calculated from D^0_1 at 285°K. For the smaller molecules, where little disturbance of the polymer is required for diffusion, ΔS^* is about equal above and below the transition. For the larger molecules ΔS^* below the transition is much smaller than above it. This suggests that the diffusing molecule forces apart two or three monomer units of the im-

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(20) R. M. Barrer, *Trans. Faraday Soc.*, **39**, 237 (1943).

(21) R. M. Barrer, *ibid.*, **43**, 3 (1947).

mediately surrounding chains without involving a large zone of activation.

It remains to interpret the diffusion data over the transition region. The heat of solution evidence is that the sorbed gas molecules in this temperature range are surrounded by a region of polymer possessing some freedom for rotation and torsional oscillation while the main bulk of the polymer has not this freedom. The size of these zones will increase with temperature and with the size of the sorbed molecule. The kinetic movements within these zones and their lack of precise boundaries will make them wander in a random manner with low energy of activation through the medium carrying the gas molecule along. This is in qualitative agreement with the data except for hydrogen where the activation energy lies between the values above and below the two transition temperatures. A possible explanation of this and the anomaly in its heats of solution is that the hydrogen molecule is too light to create a zone of disturbance, but it is then difficult to understand why it shows a lower transition temperature.

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OLD ABERDEEN, SCOTLAND

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Polyvinylacetate. A Light Scattering and Viscosity Study[1,2]

BY A. R. SHULTZ

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Light scattering measurements on polyvinylacetate fractions in dilute solution confirm the prediction that the extent to which a linear polymer molecule is expanded beyond its random-flight dimensions is a function of its molecular weight. Thus the ratio of the mean-square radius of a linear polymer chain to its molecular weight, R^2/M, increases with increasing molecular weight for a polymer in a thermodynamically good solvent. The Flory–Fox limiting viscosity number theory is found to be valid for high molecular weight polyvinylacetate fractions in methyl ethyl ketone. The value $\Phi = 2.2 \times 10^{21}$ is observed for the universal viscosity constant. The osmotic second virial coefficients, A_2, are empirically correlated with $\overline{M}_w$, $\overline{R^2}_w$ and $[\eta]$ in accord with the qualitative predictions of recent thermodynamic theories.

The effect of solvent media upon the dimensions of polymer molecules in dilute solutions has received considerable attention in recent years. Statistical theories attempting the description of average or most probable polymer coil configurations and the resultant physical dimensions and solution properties have yielded interesting, and upon occasion divergent, predictions. Some discussion of work in this field and further extension of theory has appeared very recently.[3,4]

The dependence of polymer coil dimensions and osmotic second virial coefficients of polymer molecules in dilute solution upon similar contributory factors presents the possibility of correlating these two properties.[3,5,6] Measurements of the concentration dependence and angular dependence of light scattered from dilute polymer solutions permit evaluation of both these quantities for comparison.

Theoretical treatments of limiting viscosity numbers[7,8] have suggested to Flory and Fox[9] the possibility of applying an equivalent hydrodynamic sphere approximation to relate the limiting viscosity numbers of flexible polymer coils to their average dimensions and molecular weights. Subsequent studies[10–14] have shown that this approach possesses considerable merit in describing and predicting viscosities.

The present investigation was conducted to determine experimentally the relationships among the molecular weights, coil dimensions, osmotic second virial coefficients and limiting viscosity numbers of carefully prepared high molecular weight polyvinylacetate fractions in dilute solutions. The data are discussed briefly in terms of recent theories. An attempt has been made to minimize the uncertainty inherent in correlating the various physical observables which depend upon different moments of the molecular weight distributions of the polymer samples.

Experimental

Materials. **Solvents.**—Reagent grade methyl ethyl ketone, methyl isopropyl ketone and *n*-heptane were dried over $CaSO_4$ and distilled before use. They were stored in the dark at 0°.

Preparation of Polymer.—"Niacet" vinyl acetate was freed of hydroquinone and trace inhibitors by distillation under one atmosphere of nitrogen through a Podbielniak column of 160 theoretical plates. The distilled monomer was stored in the dark at 0°.

The vinyl acetate was bulk polymerized in two sets of two Pyrex glass tubes (A, B and C, D). Azo-bis-isobutyronitrile in the presence of illumination from a medium-pressure mercury lamp was the initiator. Each tube containing monomer and initiator was thoroughly outgassed before

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[2] Presented at the 124th National Meeting of the American Chemical Society in Chicago, Ill., Sept., 1953.

[3] B. H. Zimm, W. H. Stockmayer and M. Fixman, *J. Chem. Phys.*, **21**, 1716 (1953).

[4] H. M. James, *ibid.*, **21**, 1628 (1953).

[5] B. H. Zimm, *ibid.*, **14**, 164 (1946).

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[7] P. Debye and A. M. Bueche, *ibid.*, **16**, 573 (1948).

[8] J. G. Kirkwood and J. Riseman, *ibid.*, **16**, 565 (1948).

[9] P. J. Flory, *ibid.*, **17**, 303 (1949); T. G. Fox, Jr., and P. J. Flory, *J. Phys. Colloid Chem.*, **53**, 197 (1949); P. J. Flory and T. G. Fox, Jr., THIS JOURNAL, **73**, 1904 (1951).

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[13] L. Mandelkern and P. J. Flory, *ibid.*, **74**, 2517 (1952).

[14] P. J. Flory, L. Mandelkern, J. B. Kinsinger and W. B. Shultz, *ibid.*, **74**, 3364 (1952).