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SORPTION AND DIFFUSION IN POLYMERS*

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Abstract—Sorption and diffusion of gases and vapours in polymers are frequently the subjects of a single investigation. The rate at which a substance is absorbed by or permeates through a polymer is a function of the solubility and diffusion coefficients of the substance in the polymer.

Gases in polymers closely obey the ideal laws of Henry and Fick. The mechanism of their diffusion in homogeneous polymers is well understood and information about the motions and distribution of the polymer chains has been obtained from studies of diffusion as a function of temperature.

Organic vapours diffuse in polymers by a place-exchange mechanism. At high temperatures and concentrations of diffusate Fick's law is obeyed but with a diffusion coefficient which increases with concentration. The concentration dependence of the diffusion coefficient is a function of free volume in a way related to a number of other properties of polymers + organic diluents. Sorption cannot be described satisfactorily by Henry's law but obeys the Flory–Huggins theory quite well.

At lower temperatures and concentrations Fick's law is not obeyed and the apparent diffusion coefficient varies with time as a result of the slow relaxation processes which accompany the swelling of the polymer by diffusate. Because the characteristics of these relaxation processes are a function of the local concentration of diffusate, complex phenomena are observed in systems undergoing transient diffusion.

The range of phenomena which may be observed are illustrated by discussing the rates of sorption of vapours by polymers and their interpretation. The examples chosen are restricted to amorphous polymers.

THE SORPTION and diffusion of substances of relatively low molecular weights in polymers are phenomena of practical importance because polymers in use are normally in contact with such substances. Sorption equilibrium is a thermodynamic phenomenon and diffusion is a kinetic phenomenon nevertheless they are frequently studied and discussed together. One reason for combining these studies is that the effect of any penetrant on the properties of a polymer is a function of the total amount taken up at any time as well as of the distribution of the penetrant in the polymer.

Penetration takes place from the surface of the polymer sample into the interior. Because transport inside the polymer is always relatively slow the concentration of the penetrant at the surface quickly reaches a value which is close to, though not always identical with, that corresponding to equilibrium with the surrounding gas or liquid phase. The overall rate at which the penetrant is subsequently absorbed by the sample is a function of this surface concentration and of the rate of diffusion from the surface into the interior of the polymer.

Many experimental methods of studying diffusion depend upon measuring the total amount of diffusate taken up by or transferred through the polymer as a function of time. The data obtained from these experiments are influenced by the solubility and by the diffusion coefficients. Hence both must be determined and a properly designed single experiment will frequently give the values of both.

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Simple gases in polymers

Once the principles of sorption and diffusion are well understood measurements of these phenomena give valuable fundamental information about the molecular motions and packing in polymers. The study of simple gases in polymers has been particularly useful in this connection because the data can be given a straighforward molecular interpretation.

In a homogeneous polymer the sorption of a gas normally obeys Henry's law up to moderate pressures and can be characterized by a constant solubility coefficient s defined by

$$s = 22{,}400 \times 76\, c_{\infty}/P \tag{1}$$

where c_{∞} mole cm^{-3} is the equilibrium concentration of the gas in the polymer when the external pressure is P cm Hg. Diffusion of the gas in such a polymer obeys Fick's laws with a diffusion coefficient D which is independent of the concentration of gas in the polymer.

The behaviour of gases follows these simple laws because the molecules interact only weakly with polymers and so are relatively insoluble in them. The molecules of a gas are comparable in size with the elements of free volume which are widely distributed in a tangled mass of polymer chains. Consequently the gas molecules can be accommodated with relatively little disturbance of the chain conformations and only a minute fraction of the free-volume cavities are occupied by gas molecules at any reasonable pressure.

Diffusion is the result of the random molecular Brownian motion. In a binary mixture in which one component is a polymer the frequency of the motions of its segments is very low compared with that of the small molecules present. Rates of diffusion are therefore controlled very largely by the motions of the polymer chains. When the diffusate molecules are very small their movements within the polymer require only slight co-operation between the motions of the adjacent polymer chain segments.

Although s and D are independent of the diffusate concentration they vary with temperature and from data on this variation the heat and entropy of sorption and the energy and entropy of activation for diffusion may be determined. By measuring these quantities for a range of gases and polymers a great deal has already been deduced about the motions, flexibility and distribution of the chain segments in elastomers⁽¹⁾ and harder polymers⁽²⁾ and also about the mechanism of the glass transition.⁽³⁾

Recently Frisch and Rogers⁽⁴⁾ have pointed out that, because the energy of activation for diffusion is a measure of the difference between the energy of a gas molecule in a cavity in the polymer and its energy when penetrating the denser material between cavities, it should be a function of the isotopic mass of the penetrant in some circumstances. This effect arises because the translational motions of a light particle in a small volume element are quantized. The heat of sorption from the ideal gas state should also be a function of the energy levels in the dissolved state.

Frisch and Rogers found that in rubber and polyethylene the heat of sorption of H_2 was larger than that of D_2 whereas the energy of activation for diffusion of H_2 was smaller than that of D_2.

A fuller study of this interesting new effect may give valuable information on the states of gas molecules in polymers and on the distribution and motions of the polymer segments. Some experiments along these lines are to be reported here by Eirich.⁽⁵⁾

Vapours in polymers

Small polar molecules such as H_2O are also comparable in size with the free-volume cavities in many polymers, especially in their glassy states. Such molecules however interact strongly with one another and with any polar groups in the polymer. They may become attached to these by the formation of hydrogen bonds. This has a number of effects on the diffusion behaviour which varies greatly from polymer to polymer in a way which is too complex to discuss here.(6)

Where hydrogen bonds are formed between a polymeric sorbent and a polar sorbate such as water vapour the phenomenon often bears more similarity to adsorption than to dissolution. In such circumstances Henry's law is not obeyed and some of the sorption isotherms which are obtained will be described by Ramsden.(7)

The molecules of many simple organic substances are comparable with or larger than the monomer residues composing the polymer chains. Such molecules cannot be accommodated in the statistical voids in the polymer. They diffuse by exchanging places with the chain segments and chain conformations have to alter in each diffusion step. This requires co-operation between the motions of a number of particles and gives rise to a large negative entropy of activation for diffusion.

Polymers are often brought into contact with organic penetrants in the form of vapours, although the penetrants may also be in the liquid or dissolved state. It has become a habit to speak of "the diffusion of vapours in polymers" but it should not be imagined that the penetrant exists in the polymer as a separate vapour phase permeating through a series of channels in a porous polymer matrix.

These organic substances are frequently similar to the polymers in their main chemical groupings. The van der Waals interactions between the molecules of the organic diffusate and the polymer are not very different therefore from those between diffusate and diffusate or between polymer and polymer. In such circumstances the diffusate exists as a molecularly-dispersed solute in the polymer which acts as the solvent. The mixing of polymer and diffusate is accompanied by an increase in the entropies of both components. Because of their general chemical similarity the molar and volume concentrations of the penetrant in the polymer at equilibrium are high even at relatively low external pressures of penetrant vapour. Thus the polymer becomes swollen and this has a number of important consequences.

The swelling of the polymer means that there is a flow of mass of both components during sorption. The mechanical constraints to which the system is inevitably subjected modify these flows from the values which would be expected from the laws of free interdiffusion. This raises problems regarding the units of length and frame of reference which have to be defined before a diffusion coefficient can be calculated from the experimental results. Although several different useful diffusion coefficients may be defined they are interrelated algebraically.(8) It is not universally agreed which is the most suitable form to use in a theoretical discussion of the molecular behaviour accompanying diffusion.

The heat motion of the polymer is considerably altered by the presence in it of the penetrant which acts as a plasticizer. Each penetrant molecule adds to the total free volume and, particularly in its own locality, it loosens the chain segments and increases their Brownian jumping frequency. Thus the diffusion coefficient increases, usually exponentially, with the concentration of the diffusate.(9)

A variable diffusion coefficient can be accommodated in Fick's law of diffusion by expressing it as:

$$\mathrm{d}c/\mathrm{d}t = \mathrm{div}(D\,\mathrm{grad}\,c), \tag{2}$$

or, for flow in one dimension x, as:

$$\mathrm{d}c/\mathrm{d}t = (\mathrm{d}/\mathrm{d}x)(D\,\mathrm{d}c/\mathrm{d}x) \tag{3}$$

A non-constant D complicates the form of the concentration profile in an interdiffusing system and so makes the solution of the diffusion equation more complex. It follows also that sufficient experimental work must be carried out to determine the relation between D and c if it is intended to draw basic conclusions from the results. Each of the foregoing consequences of the swelling accompanying diffusion is understood in principle and may be taken into account by appropriate modification of the simple laws of diffusion,

Although the sorption of vapours in polymers above the glass transition does not obey Henry's law it can usually be satisfactorily interpreted in terms of the Flory–Huggins theory of polymer solutions.(10) This is often at its most successful at the low concentrations of diluent with which one is concerned here.

Below the glass transition and especially at very low concentrations of penetrant the behaviour is more complex and may sometimes be likened to adsorption.

A third consequence of swelling cannot be dealt with so straighforwardly. During the process of penetration of the polymer by the diffusate the swelling is non-uniform and a complex pattern of stresses is set up in the polymer. This phenomenon is most marked when the polymer is initially in the glassy state and the glass transition occurs locally within it along an advancing front as a result of the increasing concentration of penetrant during a diffusion experiment. Swelling stresses may also have important effects on diffusion in polymers which are above their glass temperatures and which are discussed later.

Stresses may affect the uptake of vapour by a polymer in two main ways. The equilibrium concentration in a stressed system is different from that in an unstressed system.(11) Consequently the concentration of penetrant at the surface of the polymer may change with time as the stresses build up and then relax even though the phases in contact at the surface are always in instantaneous thermodynamic equilibrium. Secondly the diffusion coefficient may be a function not only of the concentration but also of the stress and strain history of the polymer because this affects its density and molecular orientation. The size, direction and time-course of the swelling stresses are influenced by the size and shape of the sample as well as by its nature. The variation of the diffusion coefficient with time and position in the polymer is therefore highly complex and cannot be dealt with within the framework of Fick's law of diffusion.

No general treatment of this type of diffusion has yet been devised although mathematical formulation has been given to specific examples of diffusion and simultaneous relaxation.(12)

The kinetics of the sorption of vapours

All the complications which have been mentioned can be illustrated by discussing the study of sorption kinetics. This is probably the most popular method of combining measurements of sorption and diffusion because it is experimentally quite simple. A polymer sample of known dimensions is suspended from a quartz spiral or other sensitive balance in the vapour maintained at constant temperature and pressure and the change in weight of the sample is recorded as a function of time. With modifications the method can also be adapted to study a liquid diffusate.

If the sample is a thin sheet of area large enough for penetration at its edges to be ignored then diffusion is one dimensional and the appropriate solution of the diffusion equation, if D is independent of c, is an infinite series.(13) For small values of time t the series reduces to

$$M_t/M_\infty = \frac{4}{l}\left(\frac{Dt}{\pi}\right)^{\frac{1}{2}} \tag{4}$$

Here M_t is the mass of vapour taken up at time t, M_∞ the mass taken up at equilibrium and l is the thickness of the unswollen sheet whose area is assumed to remain constant.

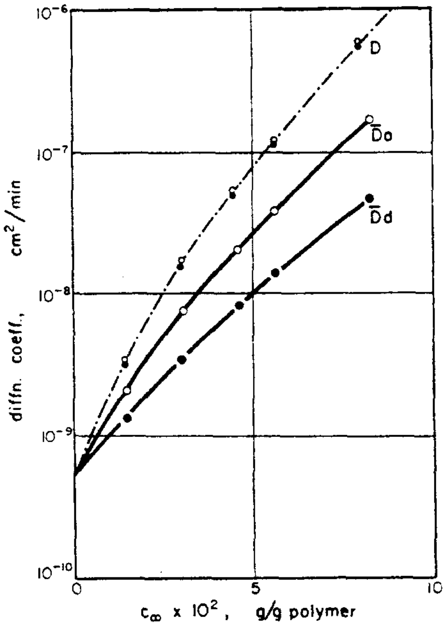

FIG. 1. Integral absorption and desorption diffusion coefficients $\bar{D}_a$ and $\bar{D}_d$, differential diffusion coefficient D of allyl chloride in polyvinyl acetate at 40°. The open circles on the broken curve were calculated from $\bar{D}_a$ and the solid circles from $\bar{D}_d$ (see Ref. 13), the broken curve itself was calculated from the steady state permeation data in Fig. 2. (Reproduced from Ref. 19 by courtesy of Interscience Publishers Inc.)

A plot of the experimental data in the form of M_t vs. $t^{\frac{1}{2}}$ starts as a straight line, later it becomes concave and finally parallel to the $t^{\frac{1}{2}}$ axis. The limiting value of M_t is M_∞ and the slope of the initial linear region is $4M_\infty D^{\frac{1}{2}}/\pi^{\frac{1}{2}} l$ so that the coefficients of sorption and diffusion may both be obtained from the graph provided the sample thickness is known.

When, as is often the case, D varies with c Eqn. (3) has to be used in place of the simplest form of Fick's law. Its solution is more complicated than that discussed above but M_t/M_∞ is often found to be an initially linear function of $t^{\frac{1}{2}}$. The slope of this line may therefore be used to define through Eqn. (4) an integral diffusion coefficient of absorption $\bar{D}_a$.

After the establishment of sorption equilibrium the vapour phase can be suddenly removed and desorption followed by observing the loss in weight of the sample as a function of time. If M'_t and M'_∞ are the masses lost at times t and ∞ respectively then a plot of M'_t/M'_∞ vs. $t^{\frac{1}{2}}$ looks rather similar to the absorption plot. Its initial slope can be measured and used to define the integral diffusion coefficient of desorption $\bar{D}_d$.

When D is a constant then $\bar{D}_a = \bar{D}_d$ and the absorption and desorption curves are identical. When D increases with c then $\bar{D}_a > \bar{D}_d$ and a typical pair of curves is shown in Fig. 1.

If D is the differential diffusion coefficient, i.e. the true value at a particular concentration of vapour in the polymer, the integral coefficient $\bar{D}$ is given by:

$$\bar{D} = \frac{1}{c_\infty}\int_0^{c_\infty} D\,\mathrm{d}c \tag{5}$$

when sorption starts from "dry" polymer ($c=0$). To a fair approximation

$$\bar{D} \simeq \tfrac{1}{2}(\bar{D}_a + \bar{D}_d) \tag{6}$$

holds but more precise relations are discussed by Crank.(13) D may therefore be obtained as a function of c from a series of absorption and desorption curves determined at different values of c_∞ i.e. at different pressures of vapour.

When calculated in this way D is the diffusion coefficient expressed relative to the centre of mass of the polymer as a fixed reference. The differences between the values of diffusion coefficients defined in different ways may be quite large in systems which swell appreciably during sorption. In theoretical discussions the intrinsic diffusion coefficient $\mathscr{D}$ is often preferred. It is defined relative to a plane across which the net flow of mass is zero. $\mathscr{D}$ may be obtained from D by using the relation:

$$\mathscr{D} = D v_p^{-3} \tag{7}$$

where v_p is the volume fraction of polymer at the concentration of diffusate to which the value of D refers. $\bar{D}$, D and $\mathscr{D}$ are compared for one typical system in Fig. 2.

The so-called "thermodynamic diffusion coefficient" $\mathscr{D}_T$ is also important. It is obtained by replacing the gradient of logarithmic concentration, which is equivalent to the driving force used in defining $\mathscr{D}$, by the gradient of logarithmic activity. Thus $\mathscr{D}$ and $\mathscr{D}_T$ are related by

$$\mathscr{D}_T = \mathscr{D}(\partial \ln v_v / \partial \ln a_v) \tag{8}$$

Here v_v and a_v are the volume fraction and the activity of the penetrating vapour in the polymer. The differential coefficient in Eqn. (8) is obtained from the equilibrium sorption isotherm so that $\mathscr{D}_T$ may be obtained as a function of concentration from a set of kinetic sorption and desorption experiments.

The relation between $\mathscr{D}$ and the penetrant concentration has been explained through the concept of free volume(9) and $\mathscr{D}_T$ has been related quantitatively to the variation of other quantities, such as bulk viscosity and relaxation-time spectra, with diluent concentration by using the Williams, Landel and Ferry principle.(14,15)

The methods of study which have been described are satisfactory when D is a function of c but is not a function of t. To test whether this condition holds the criterion usually adopted is that a plot of M_t/M_∞ vs. $t^{\frac{1}{2}}$ should be initially linear and later concave to the $t^{\frac{1}{2}}$ axis and nowhere convex to this axis. It was found long ago that many glassy polymers deviated from this criterion(16,17) while above the glass transition the criterion was obeyed and diffusion was said to be "Fickian". Examples of non-Fickian sorption and desorption curves are shown in Fig. 3.

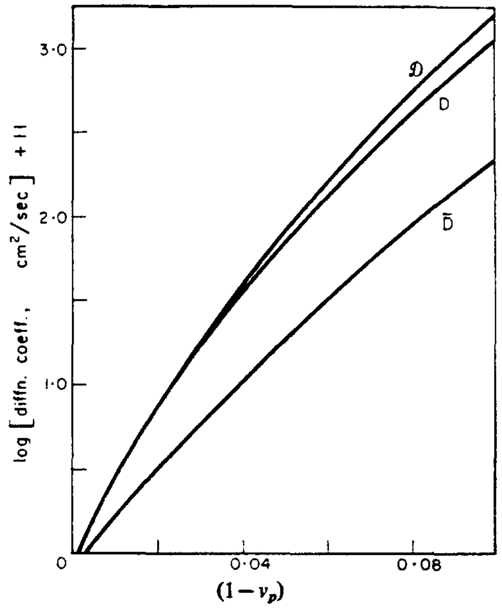

Fig. 2. Integral *D*, differential D and intrinsic $\mathscr{D}$ diffusion coefficients of allyl chloride in polyvinyl acetate at 40°. (Reproduced from Ref. 9 by courtesy of Interscience Publishers Inc.)

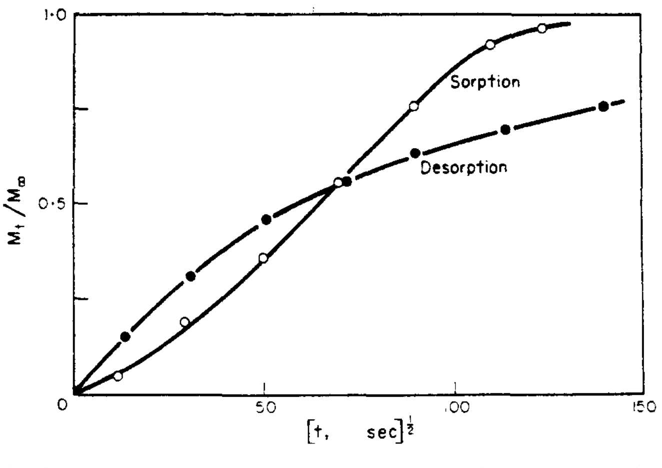

Fig. 3. A pair of non-Fickian sorption and desorption curves for methylene chloride in polystyrene at 25°. (Reproduced from Ref. 18 by courtesy of the University of Kyoto)

A polymer may be above its glass transition either because the temperature is above the glass temperature T_g of the pure polymer or because the concentration of diluent in it is greater than c_g, the concentration required to lower the glass temperature to the experimental temperature.

A number of studies have been carried out on this non-Fickian behaviour. In the most informative investigations sorption kinetic experiments were made by starting from pure polymer and proceeding in a series of steps over small intervals of increasing pressure of vapour. Sorption equilibrium was established in each step, and the final concentration reached was greater than c_g. Thus in each step sorption started from some uniform concentration c_0 and proceeded to some higher concentration c_∞. The total uptake M_t was plotted against $t^{\frac{1}{2}}$ and this gave a series of curves covering a range of concentration intervals.

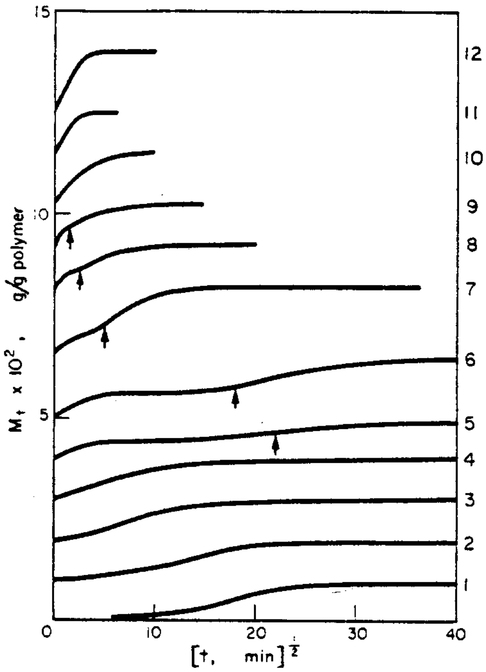

FIG. 4. Interval sorption curves of methyl acetate in polymethyl methacrylate at 30°. The arrows indicate the inflections in the two-stage curves. The curves numbered 1–12 were obtained in order over the pressure intervals: 0→25→50→66→80→90→100→110→115→124→130→134→140 mm Hg. (Reproduced from Ref. 18 by courtesy of the University of Kyoto)

The wide variety of curves which have been obtained is illustrated in Fig. 4. They may be classified as; sigmoid (curves 1–3), two-stage (curves 5–9), pseudo-Fickian (curves 4 and 10) and Fickian (curves 11 and 12). It is possible here to give only a very brief explanation of these curves; a full discussion has been given by Fujita, Kishimoto and Odani.(18)

At the lowest concentrations the hard polymer will not extend and allow the diffusate to penetrate the surface freely until a little has entered very slowly and plasticized the outer layers. Sorption then accelerates as the retardation times of the chain motions are lowered. This causes the sigmoid curves. As the concentration is increased the time which has to elapse before the acceleration of sorption becomes shorter and the inflexion moves progressively closer to the ordinate (*cf.* curves 1–3). When the inflexion cuts the ordinate it produces the pseudo-Fickian curve 4. The straight portion of this curve is so short and the curved approach to equilibrium is so long that it can be recognized as not representing a truly Fickian penetration.

The two-stage curves arise when there is initially a Fickian sorption which leads to a stressed swollen state. This corresponds with the plateau in curves 5–9. On the plateau the concentration of penetrant in the sample has been found to be uniform but it is lower than in the final relaxed equilibrium. The second stage of sorption is controlled entirely by the rate of stress relaxation and swelling of the polymer and not by concentration-gradient controlled diffusion.

At the highest concentrations the mixture of polymer and penetrant is above the glass transition and the sorption curves (11 and 12 in Fig. 4) appear to satisfy the criteria of Fickian diffusion. It has been found however that when M_t/M_∞ was plotted against $t^{\frac{1}{2}}/l$ for a series of samples which differed only in thickness l then, although the polymer was above the glass transition and the curves appeared to be Fickian, they had different

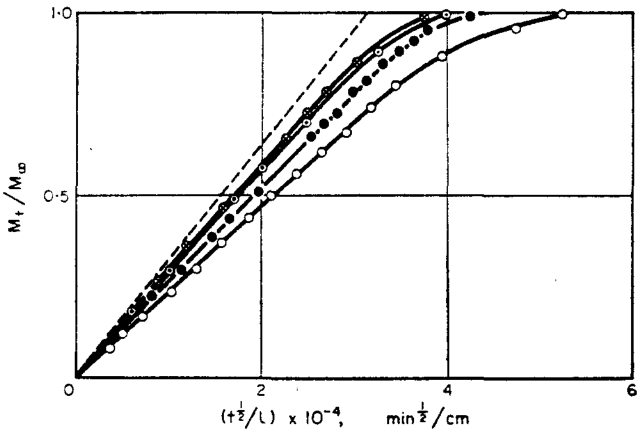

FIG. 5. Sorption curves of allyl chloride in polyvinyl acetate at 40° and 130 mm Hg. The curves appear to be Fickian but should all have the same initial slopes independent of the film thickness l which was:— ○ 19·0, ● 30·5, ⊙ 40·3, ⊗ 63·0μ. (Reproduced from Ref. 19 by courtesy of Interscience Publishers Inc.)

initial slopes. This slope in true Fickian diffusion is $(16\,\bar{D}/\pi)^{\frac{1}{2}}$; thus $\bar{D}$ appeared to vary with the sample thickness. This effect has been noted in polyvinyl acetate at 40° (at least 10° above T_g) and Fig. 5 shows that the slope increased as the thickness increased.(19)

Such behaviour was predicted several years ago by Crank(20) in the case when diffusion was accompanied by a slow relaxation process which affected D. He showed that the true diffusion coefficient could be obtained by plotting the initial slopes against $1/l^2$ and extrapolating to infinite sample thickness i.e. $1/l^2=0$.

The equilibrium concentration of penetrant in the experiments shown in Fig. 5 was [~ 6% by v/v.] At lower concentrations [~2% (v/v)] more complex and obviously non-Fickian curves were obtained (Fig. 6). They include S-shaped ones as predicted by Crank and also some two-stage curves with very steep initial sections. Similarly complicated phemomena have been observed also with sorption in polymethyl acrylate at 15°($T_g \simeq 3°$).

At temperatures more than 20° above T_g the "thickness effect" is absent and D is a function only of c. It has been concluded from this observation that when vapour is admitted to the polymer the surface concentration immediately rises to a value very close indeed to the final equilibrium concentration.

Even in elastomers some small stress effects may still be detectable during swelling. Their presence has been suspected by Barrer and Fergusson(21) who studied the uptake of benzene by rubber. These effects are especially marked when there is a large swelling during sorption since the stresses created in a lightly vulcanized material may partly relax as physical entanglements of chain segments become resolved. Some experiments which conclusively demonstrate the importance of considering stress and relaxation in the study of the uptake of liquids by rubber will be described by Thomas.(22)

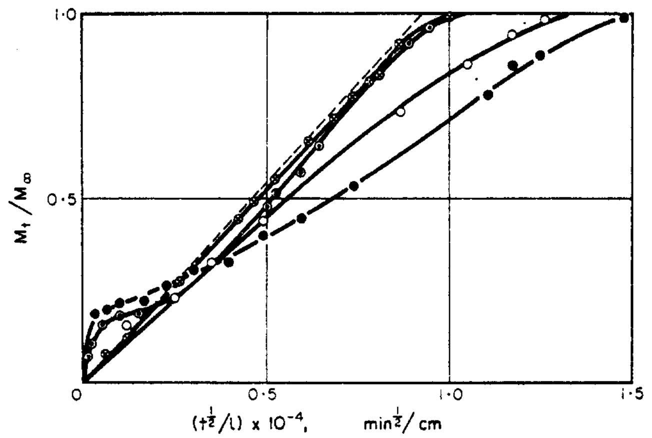

FIG. 6. Sorption curves of allyl chloride in polyvinyl acetate at 40° and 43·4 mm Hg. The curves are obviously non-Fickian especially for the thinnest films. Thicknesses l were: ○ 16·2, ● 30·4, ⊙ 67·5, ⊗ 89·2μ. (Reproduced from Ref. 19 by courtesy of Interscience Publishers Inc.)

In conclusion it must be stated that the foregoing survey of the phenomena which accompany the sorption and diffusion of gases refers only to polymers which are initially homogeneous and relaxed. A partly crystalline polymer, or a polymer far below its glass temperature, may contain micro-pores. Pores can also exist transiently in the interior of a thin sample as a result of the stresses set up by mechanical strains or by the swelling of the surface layers in the initial period of sorption. True gas or vapour flow may take place in these micro-pores and they may form an interconnecting network in the polymer. This gives rise to an additional means of transport which operates in parallel with the homogeneous mechanism which has been discussed. Such flow has been noted by Schultz and Gerrens in polystyrene far below T_g.(2) It may also account for the initial steep regions in the anomalous sorption curves of Fig. 6. It can however be more directly observed by studying the permeation of gases and vapours through thin films(23, 24) rather than by the method of sorption kinetics.

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Résumé—L'absorption et la diffusion de gaz et de vapeurs dans les polymères sont fréquemment les objets d'une seule investigation. La quantité proportionnelle suivant laquelle une substance est absorbée par ou filtrée à travers un polymère est une fonction des coefficients de solubilité et de diffusion de la substance dans le polymère.

Les gaz dans les polymères obéissent de très près aux lois de Henry et Fick. Le mécanisme de leur diffusion dans des polymères homogènes est bien compris et des informations concernant la motion et la distribution de chaînes de polymères ont été obtenues par des études de la diffusion en tant que fonction de température.

Des vapeurs organiques se diffusent dans les polymères par un mécanisme d'échange de place. A des températures et concentrations élevées du produit de la diffusion la loi de Fick est obéie mais avec un coefficient de diffusion qui augmente avec la concentration. La dépendance de la concentration du coefficient de diffusion est une fonction de volume libre reliée d'une certaine façon à un nombre d'autres propriétés des polymères + des diluants organiques. L'absorption ne peut pas être décrite d'une façon satisfaisante par la loi d'Henry mais obéit assez bien à la théorie Flory-Huggins.

A des températures et concentrations plus basses la loi de Fick n'est pas obéie et le coefficient de diffusion apparent varie avec le temps ayant pour cause le processus de lente relaxation qui accompagne l'enflement du polymère par le produit de diffusion. Etant donné que les caractéristiques de ces processus de relaxation sont une fonction de la concentration locale du produit de la diffusion, des phénomènes complexes sont observés dans des systèmes subissant une diffusion transitoire.

La gamme de phénomènes qui peuvent être observés et illustrés en discutant la quantité proportionnelle d'adsorption de vapeur par les polymères et leurs interprétations. Les exemples choisis sont restreints aux polymères amorphes.

Sommario—L'assorbimento estratto e la diffusione dei vapori e dei gas nei polimeri, sono spesso i soggetti di una investigazione unica. Il ritmo a cui una sostanza viene assorbita o permeata attraverso un polimero è una funzione dei coefficienti di solubilità e diffusione della sostanza del polimero.

I gas nei polimeri obbediscono le ideali leggi di Henry e di Fick. Il meccanismo della loro diffusione nei polimeri omogenei è comunemente bene accettata e informazioni circa i movimenti e distribuzione delle catene polimere è stata ottenuta da studi sulla diffusione come funzione della temperatura. I vapori organici si diffondono nei polimeri tramite un meccanismo cambio-posto.

Ad alte temperature e concentrazioni dei prodotti diffusi, viene obbedita la legge di Fick, ma con un coefficiente di diffusione che aumenta con la concentrazione. La concentrazione dipendendo dal coefficiente di diffusione, è una funzione di volume libero in un certo modo relativo al numero delle altre proprietà del polimero + diluenti organici. L'assorbimento non può essere descritto dalla legge di Henry ma segue discretamente la teoria Flory-Huggins.

A temperature e concentrazioni più basse, la legge di Fick non viene seguita e l'apparente coefficiente di diffusione, varia col tempo come risultato dei lenti processi di rilassamento che accompagnano il gonfiamento del polimero per mezzo dei prodotti diffusi. Siccome le caratteristiche di questi processi di rilassamento sono funzione della concentrazione locale dei prodotti diffusi, vengono osservati dei complessi fenomeni in sistemi sottoposti a diffusione transitoria.

La quantita di fenomeni che possono essere osservati, sono illustrati dalla discussione dei ritmi di assorbimento dei vapori da polimeri e la loro interpretazione. Gli esempi scelti concernono soltanto polimeri amorfi.

Zusammenfassung—Sorption und Diffusion von Gasen und Dämpfen in Polymeren werden häufig zum Gegenstand von Einzeluntersuchungen gemacht. Die Geschwindigkeit der Absorption oder Wanderung einer Substanz in einem Polymeren ist abhängig von der Löslichkeit und dem Diffusionskoeffizienten.

Gase gehorchen in Polymeren weitgehend den Gesetzen von Henry und Fick. Der Mechanismus ihrer Diffusion in homogenen Polymeren ist wohlbekannt und Aussagen über die Bewegung und Verteilung von Polymerketten waren durch die Untersuchung der Diffusion in Abhängigkeit von der Temperatur möglich.

Organische Dämpfe diffundieren in Polymeren durch Platzwechselvorgänge. Bei hohen Temperaturen und hohen Konzentrationen an diffundierender Substanz ist das Ficksche Gesetz erfüllt, jedoch mit einem Diffusionskoeffizienten der mit steigender Konzentration größer wird. Die Konzentrationsabhängigkeit des Diffusionskoeffizienten ist eine Funktion des freien Volumens und in gewisser Hinsicht mit einer Anzahl anderer Eigenschaften des Systems Polymeres—organisches Verdünnungsmittel verknüpft. Die Sorption kann mit dem Henryschen Gesetz nicht befriedigend beschrieben werden, jedoch wird die Flory-Huggins Theorie recht gut erfüllt.

Bei niedrigen Temperaturen und Konzentrationen wird das Ficksche Gesetz nicht mehr befolgt, und der scheinbare Diffusionskoeffizient ändert sich über die Zeit, verursacht durch die langsamen Relexationsprozesse, die mit der Quellung des Polymeren verbunden sind. Da die Charakteristika dieser Relaxationsprozesse von der örtlichen Konzentration der diffundierenden Substanzen abhängig sind, werden in Systemen mit veränderlicher Diffusion komplexe Erscheinungen beobachtet.

Die Breite der Erscheinungen, die beobachtet werden können, sollen durch die Diskussion der Sorptionsgeschwindigkeit von Dämpfen in Polymeren und deren Interpretation erörtert werden. Die gewählten Beispiele beschränken sich auf amorphe Polymere.