factor of two, the quantitative agreement between the two procedures is quite satisfactory.

These comparisons indicate that the microradiographic technique is capable of following the process of diffusion of organic molecules in polymers and that the results obtained are in good agreement with those obtained by more standard methods of investigation. The method is experimentally fairly simple and has the virtue of giving direct information about the concentration gradients. In the present study the accuracy is not very high, probably lower than for the vapor sorption method. However, many of the details of the procedures could be improved with a consequent increase in accuracy. As one example, the conventional microtome is not a very good instrument for getting smooth, well-aligned slices of polymeric materials. An improvement here could both improve the accuracy and broaden the applicability of the method since at present the greatly softened polymer samples which result from extensive sorption are almost impossible to slice satisfactorily. It would also improve the procedure if reference slices of material of known thickness and absorption coefficient were included in all photographs. These could serve as internal standards and minimize errors due to variations in film, developing procedures, etc. In spite of these last comments the method in its present state is capable of following the diffusion process with an accuracy which is adequate for many purposes. It should be of particular use in situations where the diffusion is experimentally complex. The paper which follows illustrates this for the complicated case of sorption of vapors into glassy polymers.

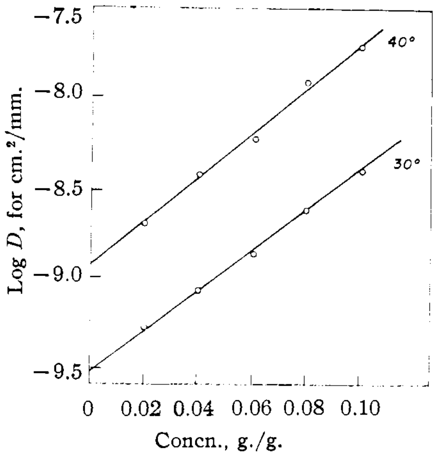

Fig. 5.—Diffusion coefficients calculated from concentration–distance curves for methyl iodide in PVA.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Concentration Gradients for Diffusion of Vapors in Glassy Polymers and their Relation to Time Dependent Diffusion Phenomena[1,2]

BY F. A. LONG AND DAVID RICHMAN

RECEIVED JULY 29, 1959

Conventional weight gain experiments have been made for the sorption of methyl iodide vapor into films of polyvinyl acetate at 20° and also into films of cellulose acetate at 40°. Both systems exhibit the characteristic "anomalous" behavior which normally accompanies diffusion of organic vapors into glassy polymers. The concentration gradients which result from this diffusion have been measured for these systems using the microradiographic procedure. The observed gradients are very different from those found for diffusion into non-glassy polymers. In particular the surface concentrations attain their equilibrium values only very slowly, varying with time according to the equation $C_s = C_0 + (C_{eq} - C_0)[1 - \exp(-\beta t)]$. The initial surface concentration C_0 is commonly only a small fraction of the final value C_{eq}. If one now assumes this dependence of surface concentration on time and also utilizes a constant value for the diffusion coefficient, it is possible to obtain explicit solutions for Fick's Law for diffusion both into an initially dry polymer and into a polymer preëquilibrated with a given amount of the vapor. The resulting equations can explain the anomalous behavior found for the former case and the two-stage behavior found for the latter.

Introduction

It is now well established that diffusion of vapors into polymers which are in the glassy state is frequently quite different than that for polymers which are at temperatures above that for their glass transition. For the latter situation the diffusion seems invariably to obey Fick's Law with the usual boundary condition that the concentration at the polymer surface is the equilibrium value for the particular pressure of vapor. If the concentration of vapor is very low, Fick's Law seems to be obeyed with glassy polymers also but the temperature coefficients are quite different from those found for non-glassy materials.[3-5] However, when the vapor concentrations are relatively high, diffusion into glassy polymers is often anomalous or non-Fickian in the sense that Fick's Law with the usual boundary conditions is not obeyed.[6-15] These differences are especially striking when the dif-

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[1] Work supported by a grant from the Office of Ordnance Research, U. S. Army.

[2] Presented in part at the 135th Meeting of the American Chemical Society, Boston, Mass., April, 1959.

[3] P. Meares, THIS JOURNAL, **76**, 3415 (1954).

[4] S. N. Zhurkov and G. Y. Ryskin, *Zhur. Tekh. Fiz.*, **24**, 797 (1954).

[5] G. Y. Ryskin, *ibid.*, **25**, 458 (1955).

[6] R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **20**, 1711 (1952).

[7] F. A. Long and R. J. Kokes, THIS JOURNAL, **75**, 2232 (1953).

[8] F. A. Long, E. Bagley and J. Wilkens, *J. Chem. Phys.*, **21**, 1412 (1953).

[9] E. Bagley and F. A. Long, THIS JOURNAL, **77**, 2172 (1955).

[10] J. Crank, *J. Polymer Sci.*, **11**, 151 (1953).

[11] G. S. Park, *ibid.*, **11**, 97 (1953).

[12] A. C. Newns, *Trans. Faraday Soc.*, **52**, 1533 (1956).

[13] L. Mandelkern and F. A. Long, *J. Polymer Sci.*, **6**, 457 (1951).

[14] A. R. di Pietro, Thesis, Cornell University, 1956.

[15] H. Fujita and A. Kishimoto, *J. Polymer Sci.*, **28**, 547, 569 (1958).

fusion process is followed by measuring the sorption or desorption of organic vapors.

In one type of vapor sorption experiment a film of dry polymer is exposed to vapor at a given pressure and the gain in weight is measured as a function of time. For constant boundary conditions and with a diffusion coefficient which is a function only of the concentration of sorbed vapor, Fick's Law predicts that the weight gain will be initially linear in the square root of time. This behavior is characteristically found for non-glassy polymers. In contrast, the vapor sorption of organic vapors into glassy polymers frequently is decidedly non-linear. The typical behavior is that the sorption is initially very slow but with a rate which increases with time leading to a sigmoid shaped sorption curve.[7,13] This result cannot in general be explained by Fick's Law with constant boundary conditions.[11]

A related type of procedure is that of interval sorption. This is a serial experiment in which the polymer is first exposed to vapor at a pressure p_1 until equilibrium is attained and then exposed to the vapor at a higher pressure p_2 until the new equilibrium is reached, etc. This process can be continued for as many steps as are of interest. It is evident that the first step of an interval sorption sequence is itself an integral sorption. For interval sorption of organic vapors into glassy polymers it is found that at a definite concentration of sorbed vapor, the sorption changes sharply from the low pressure sigmoid behavior to a remarkable two-stage behavior.[8,9,14] In the first stage of this the sorption is linear in root time, is easily reversible and shows other typical characteristics of Fickian diffusion to a quasi-equilibrium concentration. The subsequent second stage of sorption is very much slower, is typically sigmoid and in general indicates that Fick's Law with constant boundary conditions is not being obeyed.

There has been much speculation on the explanation of these anomalous results for glassy polymers. Crank and Park[10,11] considered the effects of such variables as surface skin, changing surface concentration, time dependent diffusion coefficient and internal stresses without arriving at a final explanation. The observation of two-stage behavior led Bagley and Long[9] to propose that the diffusion-controlled first stage involved elastic expansion of a polymer network and that the slow step for the second stage was not diffusion but was a macro rearrangement of the polymer chains. The implication was that the second stage mechanism was also concerned in the ordinary non-Fickian integral sorption. Newns[12] studying a different polymer-penetrant system, also suggested that a combination of diffusion and relaxation was involved.

A major deficiency of sorption measurements is that they give only the integrated vapor takeup. For systems which seem not to agree with Fick's Law it is clearly desirable to have detailed knowledge of surface concentrations and of concentration gradients. This sort of information can be obtained using the previously described microradiographic techniques[16] and the present paper reports on studies of this kind for two polymer-penetrant systems which show anomalous behavior. Initial experiments were with methyl iodide and polyvinyl acetate at temperatures below that for the glass transition. However, the large majority of the studies were with the similar but experimentally more accessible system of methyl iodide and cellulose acetate.

Experimental

The experimental procedures were essentially the same as in the previous study.[16] Both conventional weight gain measurements and microradiographic studies were made of the sorption of methyl iodide vapor by films of polyvinyl acetate at 20° and by films of cellulose acetate at 40°. The methyl iodide and the polyvinyl acetate were the same as previously used.[16] The cellulose acetate was type PH1, 37.9% acetyl, obtained from Hercules Powder Company. Films were prepared by casting on glass from an acetone solution. Thin films used to find equilibrium sorption values were cast on mercury from acetone solution.

Results

Initial studies were for sorption of methyl iodide at 96 mm. pressure into films of PVA at 20°, a temperature which is just below that for the glass transition of the polymer-penetrant mixture. This pressure gives a vapor activity at 20° of 0.29 very similar to that used in the 30 and 40° studies with PVA.[16] As expected, when the vapor takeup for this system was plotted as weight gain *versus* root time the curve was not linear but showed the same sort of sigmoid character as had been found earlier for sorption of acetone into PVA at 13 and 20° and also for sorption of acetone into cellulose acetate at 30 and 40°.

The PVA films then were removed from the sorption apparatus at predetermined times, microtomed and the resulting slices examined as before by microradiography. The qualitative character of the calculated concentration gradients for the methyl iodide was much like that of Fig. 4 of the previous paper.[16] There was, however, one notable difference. In contrast to the results for 30 and 40°, it was found at 20° that for the early stages of the sorption the surface concentrations of methyl iodide were well below the equilibrium sorption value and also that the surface concentrations increased with time. Unfortunately these experiments were difficult and tedious, partly because of the low temperature, partly because of the necessity of working at low vapor pressures so as to stay in the glassy state. Since previous studies had shown that cellulose acetate at 30 and 40° exhibited all of the usual anomalous diffusion properties of glassy polymers, it was decided to make more detailed studies with methyl iodide and cellulose acetate at 40°.

Integral sorption of methyl iodide into films of cellulose acetate shows the characteristic sigmoid behavior. This is illustrated in Fig. 1 for 200 mm. of methyl iodide at 40°. Studies at pressures of 100 and 300 mm. give similarly shaped curves. If the cellulose acetate is equilibrated with methyl iodide at pressures of over about 200 mm., a subsequent *interval* sorption to a higher pressure leads to a typical two-stage sorption curve. Figure 2 illustrates this for three such experiments, all starting with films which had been equilibrated with 300 mm. of methyl iodide. The two-stage be-

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[16] D. Richman and F. A. Long, THIS JOURNAL, **82**, 509 (1960).

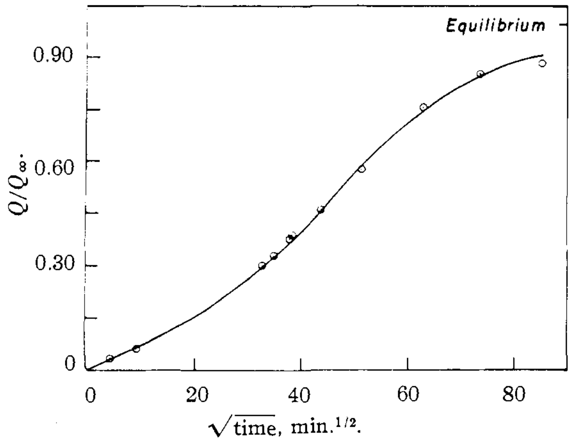

Fig. 1.—Sorption of 200 mm. of methyl iodide into dry cellulose acetate at 40°. Film width is 1.3 × 10^{-2} cm.

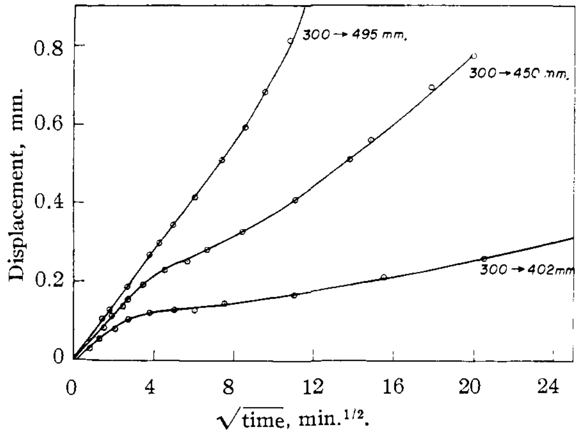

Fig. 2.—Sorption into cellulose acetate at 40° for three pressure intervals of methyl iodide. Film widths are 5.1 × 10^{-3} cm. for two lowest intervals and 1 × 10^{-2} for largest interval.

havior is apparent for the two smaller pressure intervals; it has virtually disappeared for the highest pressure interval. These various results will be considered in detail later. However, they are obviously similar to the behavior found for acetone in cellulose acetate, for acetone in glassy PVA and for several vapors into glassy polystyrene and may thus be considered as typical for a glassy polymer.

Figure 3 gives densitometer traces from a microradiographic study of microtomed slices of the methyl iodide–cellulose acetate films. Figure 4 gives the calculated concentration–distance curves for the traces of Fig. 3. All of these curves are for relatively small amounts of sorption; even for the curve of Fig. 4c, only 30% of the final, equilibrium takeup has occurred. The striking feature of the curves of Fig. 4 is that the surface concentrations are much lower than the equilibrium value of 0.16 g./g. for 200 mm. of methyl iodide and are increasing with time. This result is in sharp contrast to that for diffusion into a non-glassy polymer where the surface concentration is essentially the equilibrium value at all times.[16]

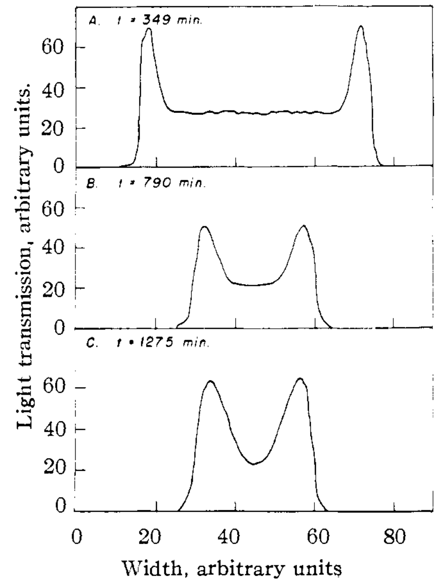

Fig. 3.—Densitometer traces for microtomed slices of cellulose acetate after exposure at 40° to 200 mm. of methyl iodide. Slice thicknesses are roughly 80 μ; film widths vary from 0.9 × 10^{-2} to 1.3 × 10^{-2} cm.

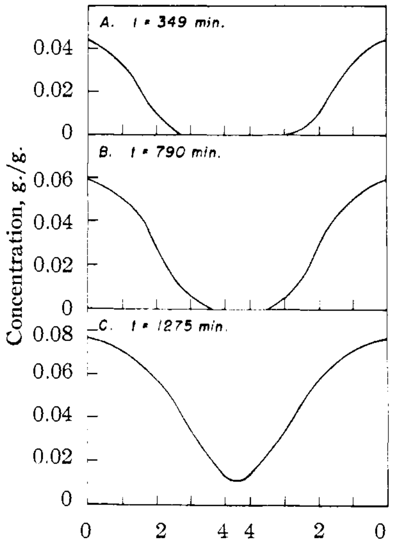

Fig. 4.—Concentration–distance curves calculated from the data of Fig. 3 for diffusion of methyl iodide into cellulose acetate.

Figure 5 gives a plot of surface concentrations as a function of time for two separate groups of experiments with cellulose acetate at 200 mm. of methyl iodide. The agreement of the values for the two sets of films is about as good as expected from the estimated experimental errors. The data indicate that for the early stages of sorption, the surface concentration C_s in g./g. increases linearly with time and can be approximated by an equation of the type

$$C_s = C_0 + Kt \qquad (1)$$

where C_0 is surface concentration at $t = 0$ and K is a constant. Although the accuracy was much lower, an equation of this same form also fitted the observed changes in surface concentration for

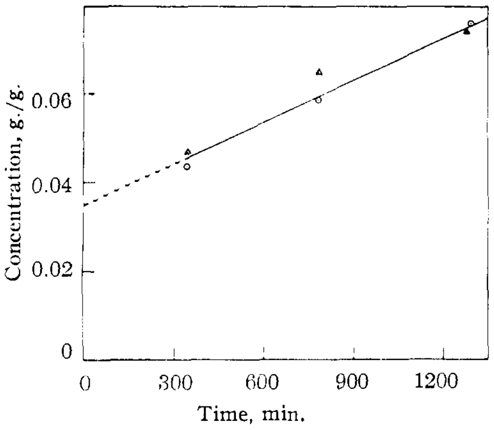

Fig. 5.—Surface concentration as a function of time for sorption of 200 mm. of methyl iodide into cellulose acetate at 40°. Equilibrium concentration is 0.16 g./g.

methyl iodide diffusing into polyvinyl acetate at 20°.[17]

Figure 3c shows that for 30% of the total sorption and with a film of 0.9 mm. width, the surface concentration has not reached half of the equilibrium value and yet the vapor already has penetrated to the center of the film. This clearly implies that for the later stages of the sorption the concentration gradients will become rather small and the main cause of further sorption will be the increase in surface concentration. This explanation is similar to the early speculations on the phenomenon of two-stage sorption and in fact can be directly applied to this latter case. The first stage of a two-stage sorption presumably will be the entire takeup which can occur for normal diffusion from the instantaneously established initial surface concentration. The second stage will then be for the slow increase in surface concentration and should be characterized by virtually zero concentration gradient within the film. Experimentally it is found that the time to complete the first stage for the two-stage sorption of methyl iodide into cellulose acetate is invariably so short as to make examination of this stage by microtoming virtually impossible. It is, however, possible to microtome and examine for times which are just at the start of the second stage of the sorption. As Fig. 6B illustrates, it is found that there are no perceptible concentration gradients in the interior of the film. The shape of the curve is very like those for the final stages of either an integral or interval sorption as may be seen by comparison with Fig. 6A and 6C. These results give direct confirmation to the previously proposed explanation for two-stage behavior. When combined with data of Fig. 4 and 5 and with similar data for PVA at 20°, they lead to the definite conclusion that slow establishment of the surface concentration is characteristic of the diffusion of organic vapors into glassy polymers.[18]

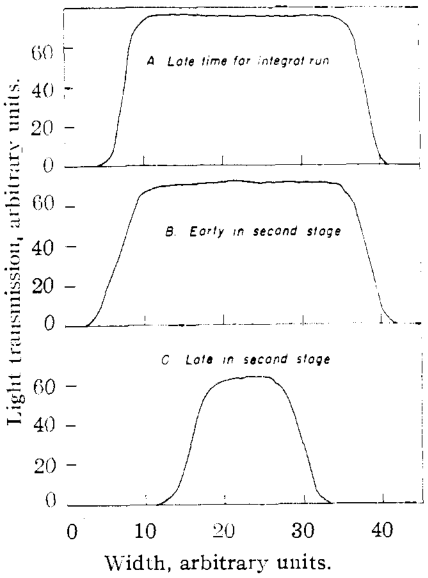

Fig. 6.—Densitometer traces for sorption of methyl iodide into cellulose acetate at 40°. Slices are roughly 80 μ thick. Curve A: 0 ⟶ 300 mm. methyl iodide; film width 1.1×10^{-2} cm. Curve B: 302 ⟶ 446 mm. methyl iodide; film width 1.3×10^{-2} cm. Curve C: 300 ⟶ 444 mm. methyl iodide; film width 6.4×10^{-3} cm.

Discussion

Given the complex integral and interval sorption behavior which is exhibited by organic vapors with glassy polymers, the question now is, can these phenomena be explained by a general form of Fick's Law which explicitly recognizes the observed changes in surface concentration? Before approaching this problem we need an adequate analytical expression for the time dependence of the surface concentration C_s for glassy polymers. From Fig. 5 we know that C_s starts at an initial value C_0 and then for a while increases linearly with time. We also know that C_s must ultimately approach the equilibrium concentration C_{eq} asymptotically. Finally, we infer from the general behavior that the rate of increase of C_s itself increases with the magnitude of the concentration difference $C_{eq} - C_0$. A simple assumed expression which accommodates these points is

$$C_s = C_0 + (C_{eq} - C_0)(1 - e^{-\beta t}) \qquad (2)$$

By expansion of the exponential it is seen that this leads for the initial period to the linear relationship of equation 1. It also follows that the constants of equations 1 and 2 are related by $K = \beta(C_{eq} - C_0)$.

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(17) Our extrapolation of the line of Fig. 5 to zero time implies that the surface concentration reaches a sensible value, C_0, at the very start of a sorption experiment. Since we are unable to make accurate measurements of surface concentrations for short times, we cannot eliminate the possibility that there is actually a gradual buildup of surface concentration during, say, the first 100 minutes. However, the notion that there is a virtually instantaneous buildup to concentration C_0 is by no means implausible. This kind of behavior is quite clearly indicated by the observed two-stage sorption for "plasticized" films (see Figs. 2 and 8). Hence the idea of an initially rapid attainment of a surface concentration which is dictated by a limited elastic expansion of a polymer network is entirely reasonable for a dry polymer also.

(18) Additional qualitative evidence on the slow changes of surface concentration can be obtained from the relative rates of sorption and desorption. It is observed with glassy polymers (in contrast to the situation with non-glassy polymers) that initial rates of sorption for a pressure interval $p_1 \rightarrow p_2$ are always much smaller than the initial rate of desorption for the reverse interval $p_1 \rightarrow p_1$. Since there is no evidence that diffusion coefficients ever decrease with increasing concentration, about the only possible explanation is that the equilibrium surface concentrations are established slowly.

The next step is to incorporate this time dependence of surface concentration into the boundary conditions for diffusion and to solve the appropriate form of Fick's Law. This cannot be done for the general case of a diffusion coefficient which depends on concentration. It is, however, not a bad approximation to replace the known concentration dependent diffusion coefficient by a constant D which will represent an average for the true $D(c)$ over the concentration interval concerned. This approach is similar to that used by Crank and Park[19] who considered the case of a surface concentration which varied as $C_{eq}(1 - e^{-\beta t})$.

For the particular case of an integral sorption the boundary conditions for a film of thickness $2l$ centered at the origin, are

$$C = 0, t = 0; \ -l < x < l$$

$$C = C_0 + (C_{eq} - C_0)(1 - e^{-\beta t}), x = \pm l; \ t > 0$$

The solution to the diffusion equation then may be obtained by superposing the known solutions for the cases of constant surface concentration and time dependent surface concentration as given by Crank.[20] This gives for the amount of penetrant Q in g./cm.^{2} which has entered the film

$$\frac{Q}{2l\rho_0} = C_0 - \frac{8C_0}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{-D(2n+1)^2\pi^2 t/4l^2}}{(2n+1)^2} + (C_{eq} - C_0) - (C_{eq} - C_0)e^{-\beta t}(D/\beta l^2)^{1/2}\tan\left(\frac{\beta l^2}{D}\right)^{1/2} - \frac{8(C_{eq} - C_0)}{\pi^2}\sum_{n-0}^{\infty}\frac{e^{-D(2n+1)^2\pi^2/4l^2}}{(2n+1)^2\left[1 - (2n+1)^2\left(\frac{D\pi^2}{4\beta l^2}\right)\right]} \quad (3)$$

where ρ_0 is the density of the dry polymer.

Examination of the above expression immediately indicates the cause of "anomalous" diffusion behavior. The weight gain is made up of two parts, the penetrant which enters due to diffusion down the concentration gradient set up by the initial surface concentration (the first two terms of equation 3), and the penetrant which enters as a result of the time dependence of the surface concentration (the last three terms of (3)). When D/l^2 is of the same order of magnitude as β, the two processes occur at the same rate and so a single "anomalous" sorption process is observed. When D/l^2 is much greater than β, the diffusion down the initial gradient is complete before there is any significant change in surface concentration. As a result there will be two distinct steps in the sorption curve, essentially as found in "two-stage" sorption.

To illustrate how both of these types of behavior can follow from equation 3 we have made numerical calculations on sorption as a function of time using the two sets of parameters which are listed below. The chosen value for the half-width is representative of the film widths used in the experimental study. The values of C_0 and β are simply the experimental values, as given by Fig. 5, for sorption of 200 mm. of methyl iodide into cellulose acetate. The equilibrium concentration of sorbed vapor, C_{eq} is also just the experimental value for this same system. The two D values are typical ones for diffusion of a molecule like methyl iodide into a dry polymer (Case A) and into a polymer containing a fair amount of vapor (Case B).

Case A:

$D = 1 \times 10^{-8}$ cm.^{2}/min.; $l = 5 \times 10^{-3}$ cm.

$C_0 = 0.035$ g./g.; $C_{eq} = 0.16$ g./g.; $\beta = 1.66 \times 10^{-4}$ min.$^{-1}$

Case B:

$D = 1 \times 10^{-6}$ cm.^{2}/min.; other parameters as in Case A

The calculated sorption curves are given in Fig. 7. The lower value of D leads to typical "anomalous" sorption as observed for integral sorption experiments. The higher value of D gives a curve which is very similar to that found for "two-stage" sorption from an interval experiment. It is safe to conclude that equation 3 with the particular boundary conditions can explain the characteristic curve shapes for sorption of organic vapors in glassy polymers.

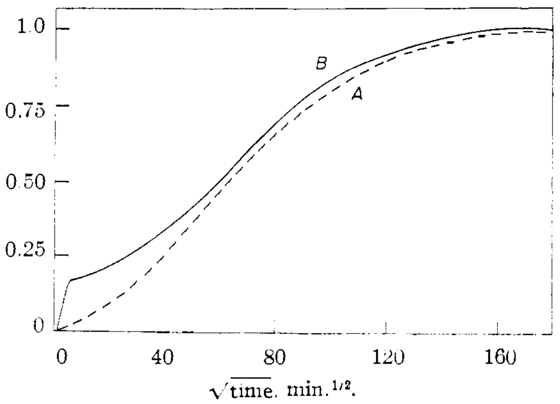

Fig. 7.—Calculated sorption for diffusion of methyl iodide into cellulose acetate using equation 3 with parameters as listed for Cases A and B.

The comparison of theory with actual experimental results is most satisfactorily carried out for the case of two stage behavior since for this case all the necessary constants are available from the sorption curve. Furthermore the assumption of a constant value for the diffusion coefficient is particularly plausible when the concentration interval is narrow. To obtain a solution of the diffusion equation which fits the experimental conditions it is necessary to modify the boundary conditions to take into account the presence of vapor in the polymer due to the previous equilibrium. This may be done by changing the first boundary condition for equation 3 to

$$C = C_1, t = 0; \ -l < x < l$$

and the second to

$$C = C_0 + (C_{eq} - C_0)(1 - e^{-\beta t}), x = \pm l; \ t > 0$$

The solution then is

$$\frac{Q}{2l\rho_0} = (C_0 - C_i) - \frac{8(C_0 - C_i)}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{-D(2n+1)^2\pi^2 t/4l^2}}{(2n+1)^2} + (C_{eq} - C_0) - (C_{eq} - C_0)e^{-\beta t}\left(\frac{D}{\beta l^2}\right)^{1/2}\tan\left(\frac{\beta l^2}{D}\right)^{1/2} - \frac{8(C_{eq} - C_0)}{\pi^2}\sum_{n=0}^{\infty}\frac{e^{-D(2n+1)^2\pi^2 t/4l^2}}{(2n+1)^2\left[1 - (2n+1)\left(\frac{\pi^2 D}{4\beta l^2}\right)\right]} \quad (4)$$

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(19) J. Crank and G. Park, *Trans. Faraday Soc.*, **47**, 1072 (1951).

(20) J. Crank, "Mathematics of Diffusion," Oxford Press, London, 1956.

here C_i is the initial concentration of equilibrated vapor in the polymer, C_0 is the concentration at the quasi-equilibrium and C_{eq} is the concentration at final equilibrium.

Bagley[21] has extensive data for the two-stage sorption of acetone into cellulose acetate and we have applied equation 4 to a set of his results for sorption over a pressure interval of 67 to 101 mm. acetone at 30°. We have taken for D the value which Bagley has calculated from the "first-stage" data assuming that this stage goes to a quasi-equilibrium. All the other parameters of equation 4 are listed by Bagley with the exception of β. The present development implies that the initial slope for the second stage is given by $S_2 = \beta(C_{eq} - C_0)$ so that β is calculable from Bagley's value for S_2. The experimental data and the results from the calculation are shown in Fig. 8. The agreement is quite good.

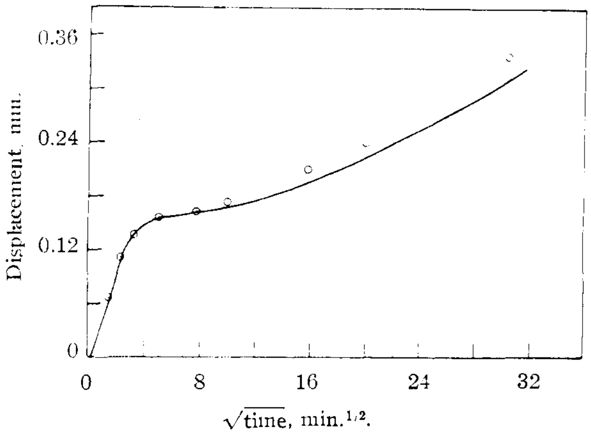

Fig. 8.—Sorption of acetone into cellulose acetate at 30° for pressure interval 66.6 ⟶ 100.6 mm. Solid line is calculated and points are experimental.

Comparison of theory and experiment for the single sigmoid type of behavior is less easily made since this comparison requires a knowledge of both the diffusion coefficient and the rate of change of the surface concentration. However, if knowledge of the latter is available, as for example from a microradiographic study, it is then possible to calculate an average value of the diffusion coefficient. The equation for this can be obtained by combining the solutions given by Crank[20] in his equations 3.15 and 3.17; it can also be obtained directly by applying the method of LaPlace Transforms to the diffusion equation for the boundary condition, $C_s = C_0 + Kt$. The result is

$$\frac{Q}{2l\rho_0} = \frac{\sqrt{D}C_0}{\pi^{1/2}l}\left[t^{1/2} + \frac{2K}{3C_0}t^{3/2}\right] + \frac{C_0\sqrt{Dt}}{l}\sum_{n=1}^{\infty}(-1)^n\, i\,\mathrm{erfc}\,\frac{nl}{\sqrt{Dt}} + \frac{2K}{3}\left(\frac{D}{\pi}\right)^{1/2}\sum_{n=1}^{\infty}(-1)^n\, 16t^{3/2}\, i^3\,\mathrm{erfc}\,\frac{nl}{\sqrt{Dt}} \qquad (5)$$

For small values of Dt/l^2 the i erfc and i^3 erfc terms may be neglected giving

$$Q = 2\pi^{-1/2}\rho_0C_0D^{1/2}\left[t^{1/2} + \frac{2K}{3C_0}t^{3/2}\right] \qquad (6)$$

Hence for early times a plot of weight sorbed *versus* the time function in brackets should give a linear plot with a slope which depends on $D^{1/2}$. A plot of this sort was made for the sorption of methyl iodide at 40° and 200 mm. pressure into cellulose acetate using the values of K and C_0 as given for this case by Fig. 5. The plot was indeed linear and led to a value of $D = 2 \times 10^{-8}$ cm.^{2}/min. This value was then used in equation 3 to give the calculated sorption curve of Fig. 9. The calculated curve agrees well at early times but falls slightly below the experimental points at the later stages. This last is quite possibly a reflection of the fact that D increases with concentration rather than remaining constant at its early time value as we have perforce assumed.

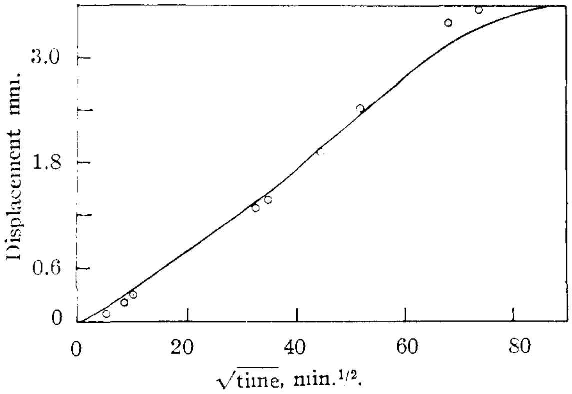

Fig. 9.—Integral sorption of 200 mm. of methyl iodide into cellulose acetate at 40°; —, calculated; ⊙, experimental.

These quantitative interpretations of anomalous sorption are closely related to the earlier qualitative discussions of Park[11] and of Bagley and Long[9] both of whom pointed to the role of a slow rate of relaxation for glassy polymers. On the basis of Bagley's results for the dependence of second stage slopes on pressure increments,[21] it is in fact quite plausible to interpret the parameter β as a measure of the rate of stress relaxation of polymer structure and to conclude that this rate is proportional to the applied stress, *i.e.*, to the size of the pressure or concentration increment to which the system is subjected. This interpretation permits a very natural explanation of the observations of Ryskin[4,5] and others that at very low pressures sorption of organic vapors into glassy polymers appears to follow the ordinary formulation of Fick's Law. For a sufficiently small increment of pressure and hence value of β an experiment can be sensibly complete (to a quasi-equilibrium sorption) before any sorption due to relaxation is observed. This effect should be the more pronounced the thinner the polymer film and the experiments of Park[11] are qualitatively in accord with this expectation. Another illustration of this is to be seen in the experiments of Fig. 2 where for the lowest pressure interval the two-stage behavior is very distinct. In contrast for the experiment with the highest pressure interval, which also involves the thinnest film,

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(21) E. Bagley, Thesis, Cornell University, 1954.

the two-stage behavior has essentially disappeared. However, it must be emphasized that these explanations as well as the specific interpretation of the parameter β are somewhat speculative and need to be checked by further experiments.

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Free Radicals by Mass Spectrometry. XVII. Ionization Potential and Heat of Formation of Vinyl Radical

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The vertical ionization potential of vinyl radical is found to be 9.45 v. by direct electron impact on radicals produced by the thermal decomposition of methyl vinylmercury. From the appearance potential of vinyl ion from ethylene, $D(C_2H_3-H) = 105 \pm 3$ kcal./mole, $\Delta H_f(C_2H_3) = 65 \pm 3$ kcal./mole, $\Delta H_f(C_2H_3^+) = 283 \pm 3$ kcal./mole and $D(C_2H_2-H)$ in vinyl radical is 41 ± 3 kcal./mole.

Introduction

As pointed out recently by Cottrell,[2] the published electron impact measurements of the C–H bond dissociation energy in ethylene show a large discrepancy, the two values being $D(C_2H_3-H) = 91.5$ kcal./mole[3] and 122 kcal./mole.[4] The corresponding values for $\Delta H_f(C_2H_3)$ are 51.6 and 82 kcal./mole. There are a number of reasons for preferring a value for $D(C_2H_3-H)$ somewhat larger than $D(C_2H_5-H)$ (~ 96[2]) but not larger than $D(C_6H_5-H)$, for which values in the range 102–107 have been obtained.[2] When used to calculate the dissociation energy of the central C–C bond in 1,3-butadiene, the two values of $\Delta H_f(C_2H_3)$ lead to $D(C_2H_3-C_2H_3) = 77$ and 138 kcal./mole, both of which appear quite improbable by comparison with other C–C bonds.[5] Recently[6] support for the higher value for $\Delta H_f(C_2H_3)$ has been withdrawn, on the basis of a revised value for $\Delta H_f(t\text{-butyl}^+)$. Since considerable evidence supports a value of $\Delta H_f(C_2H_3^+) \sim 283$ kcal./mole,[4] it would appear that a direct determination of the ionization potential of the C_2H_3 radical should be of assistance in resolving this discrepancy in the data for $\Delta H_f(C_2H_3)$.

Experimental

Although the vinyl radical had been detected by mass spectrometry in the thermal decomposition of divinyl ether,[7] considerable difficulty was encountered in producing the radical in yields sufficient to permit measurement of the ionization potential. A much higher yield of vinyl has now been obtained by the pyrolysis of methyl vinylmercury. This compound was prepared by the reaction between vinylmagnesium bromide and methyl mercuric iodide in tetrahydrofuran.[8] It was purified by repeated vacuum distillation until the mass spectrum showed only negligible traces of impurities, mainly di-methyl and divinylmercury.[9]

Pyrolysis of methyl vinylmercury in a fused silica capillary furnace leading to the ionization chamber of a mass spectrometer[10] resulted in the formation of vinyl and methyl radicals, as shown by large increases in the mass 27 and mass 15 peaks when using electrons of low energy. Other products were acetylene, ethane and a small amount of methane. No significant amounts of the dimerization products 1,3-butadiene and propylene were found. At furnace temperatures above 900°, the yield of vinyl radicals decreased rapidly, with the formation of large quantities of acetylene.

The method of comparison of the ionization efficiency curve for vinyl radical with that for the added standard gas, in this case krypton, was the same as that employed to measure the ionization potentials of propyl and butyl radicals.[11] As a check on the calibration procedure, a number of curves also were obtained for the acetylene which was formed in the reaction.

In mixtures of ethylene and krypton, the ionization efficiency curves for krypton and for the $C_2H_3^+$ ion from ethylene were measured down to the "vanishing" point, where the ion current was 0.01% of the ion current with 50 v. electrons. The voltage difference between these curves at corresponding ion currents was found to decrease from 0.25 v. at 0.1% of the 50 v. ion current to 0.05 v. at 0.01%. Owing to this lack of parallelism, $A(C_2H_3^+)$ was evaluated by extrapolation of a plot of voltage difference against ion current[12] as shown in Fig. 1. The average of a number of determinations, 14.00 ± 0.05 v., was essentially the same as that obtained by the "vanishing current" method.[13] Unless some drastic alteration in the shape of this curve occurs in the region of very small ion currents below 0.01%, it is difficult to see how the extrapolated voltage difference (Fig. 1) can differ from 0.00 v. by more than ± 0.05 v. Owing to the curvature observed, however, a larger limit of error has been assigned, and $A(C_2H_3^+)$ from ethylene has been taken as 14.00 ± 0.1 v., in excellent agreement with 14.04 ± 0.1 v. as found by Field[4] and with the average of two earlier determinations of 14.2 ± 0.1[14] and 13.92 v.[15]

Results and Discussion

The average of several sets of ionization efficiency curves for the vinyl radical and for krypton gave 9.45 ± 0.05 v. for the ionization potential of vinyl radical. On the same scale, the curves for the acetylene formed in the reaction gave 11.42 ± 0.05 v. for $I(C_2H_2)$, in good agreement with three identical values of 11.41 v. obtained by electron impact,[16] by photoionization[17] and by spectros-

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