[Contribution from the Department of Chemistry, Cornell University]

Two-stage Sorption and Desorption of Organic Vapors in Cellulose Acetate[1,2]

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The rate of sorption of vapors of acetone and methanol into films of cellulose acetate exhibits a two-stage behavior in that, when the initial concentration of penetrant in the film is above a minimum value, the sorption rate is initially rapid and then abruptly decreases. A very similar phenomenon occurs for desorption. During the fast initial stage of sorption and desorption the vapor penetrates the entire polymer film to give a quasi-equilibrium concentration of vapor which amounts to about 10% of the true equilibrium change of concentration for the experiment. The sorption and desorption for this rapid initial stage follow Fick's law and diffusion coefficients can be calculated. The resulting diffusion coefficients are independent of film thickness and, at a given initial concentration, are the same for sorption and desorption but increase with the concentration of penetrant in the film. The temperature coefficient of this diffusion is very small. The second, slow stage of sorption and desorption does not obey Fick's law. For constant concentration intervals the initial rate of second stage sorption is independent of the initial concentration of penetrant. A tentative explanation of these results is that the Fickian, initial stage sorption involves only an elastic expansion of the polymer network without affecting the interchain bonds, and that the rate-determining step for the slow stage is the breaking of these bonds rather than ordinary diffusion. On this hypothesis the quasi-equilibrium represents a balance between osmotic forces and the elastic forces of the polymer network.

Several recent studies[3-6] have led to the conclusion that the diffusion of organic vapors into polymers which are at temperatures below their second-order transition is anomalous in the sense that Fick's law (assuming the normal boundary conditions) does not apply. This anomalous or non-Fickian diffusion is particularly apparent for diffusion of organic vapors into cellulose nitrate and acetate[5,7,8] and we wish to report on a fairly detailed study of this phenomenon for the latter polymer. Some aspects of the problem have been discussed in a preliminary communication.[9]

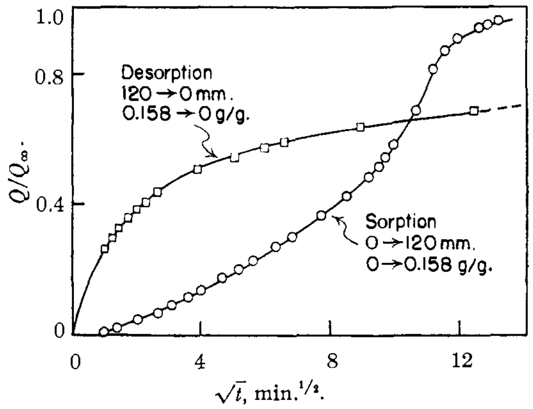

Fig. 1.—Integral sorption and desorption of acetone in cellulose acetate at 30°. Film thickness is 4×10^{-3} cm.

Most conclusions about anomalous diffusion in polymers have been drawn from studies of *integral* sorption and desorption of vapors into thin films. These measurements give weight increase or decrease of the film as a function of time and it can be shown that Fick's law with the usual assumption of equilibrium surface concentration of the vapor predicts an initially linear plot of Q, the change in film weight, *vs.* root time. Furthermore, for the usual case where the diffusion coefficient increases with concentration of penetrant, the initial slope of a Q *vs.* $\sqrt{t}$ plot for sorption over the concentration interval $0 \rightarrow c_f$ is greater than the slope for desorption over the reverse interval, $c_f \rightarrow 0$. The most striking aspect of anomalous diffusion (see Fig. 1) is that the Q–$\sqrt{t}$ slopes are not initially linear and that the initial slope for desorption is much greater than for sorption in spite of the fact that other evidence usually indicates that the apparent diffusion coefficient increases with concentration.

In studies of Fickian diffusion of organic vapors in polymers and in particular in studies of the change from anomalous to Fickian diffusion in the region of the second order transition,[3,4] it has been useful to make *interval* rather than *integral* sorption and desorption experiments, *i.e.*, experiments where the interval between the initial and final concentrations, c_i and c_f, is small and where c_i is in general not zero. Most of the studies to be reported here involve such *interval* experiments.

Experimental

Sorption and desorption measurements were made with an apparatus very similar to that of Prager and Long.[10] Polymer films were suspended from a quartz spiral balance of sensitivity about 1.5 mg./mm. in a weighing chamber which could be evacuated. For interval sorption studies the film was permitted to equilibrate with organic vapor present in the weighing chamber at a constant pressure, p_i. At zero time the pressure of vapor was suddenly increased from p_i to p_f, the final value of pressure, and the weight change of the film was then followed as a function of time. Measurements of the weight of the dry film and of the equilibrium weight for the pressures p_i and p_f permit direct calculation of the corresponding concentrations c_i and c_f (grams penetrant per gram of polymer). For interval desorption studies the procedure is essentially the reverse of the above, *i.e.*, the film is equilibrated at the higher pressure, p_f, and then the pressure of vapor is suddenly reduced to the lower value p_i. For integral sorption and desorption studies p_i is always zero.

The entire sorption apparatus, weighing chamber, vapor reservoirs and manometer, was mounted in an air-bath which was thermostated to ±0.2°.

The molecular orientation of the cellulose acetate films was determined by measuring the optical birefringence of a cross-sectional strip of the film using the method described

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[1] Sponsored by Office of Ordnance Research, U. S. Army.

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

[3] R. J. Kokes, F. A. Long and J. L. Hoard, *J. Chem. Phys.*, **26**, 1711 (1952).

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

[5] G. S. Park, *J. Polymer Sci.*, **11**, 97 (1953).

[6] J. Crank, *ibid.*, **11**, 151 (1953).

[7] L. Mandelkern and F. A. Long, *ibid.*, **4**, 457 (1951).

[8] P. Drechsel, J. L. Hoard and F. A. Long, *ibid.*, **10**, 241 (1953).

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

[10] S. Prager and F. A. Long, This Journal, **73**, 4072 (1951).

by Long and Kokes.[4] For cellulose acetate the measured birefringence, Δn, is negative if the preferred orientation is in the plane of the film. A knowledge of the film orientation is needed because the rate of diffusion of vapors into cellulose acetate and nitrate is strongly dependent on the amount of orientation of the film and the diffusion process itself causes a change in the orientation.[8]

The cellulose acetate used in these studies was designated by the manufacturer as Hercules PH-1. Its acetyl content is 37.9% and it has an intrinsic viscosity of 1.62 in acetone at 25°. Films were cast from acetone solutions on clean mercury surfaces. Film thicknesses varied from 0.002 to 0.020 cm. Final traces of casting solvent were removed by several days leaching in water followed by drying in a vacuum oven at 60°. Although films cast on mercury are more nearly isotropic than those cast on glass,[8] the freshly prepared cellulose acetate films invariably show a Δn value of from -2 to -4×10^{-4} indicating a small degree of preferred orientation in the plane of the films.

The organic penetrants, acetone and methanol, were reagent grade and were extensively dried with anhydrous calcium sulfate. This drying is essential since water diffuses rapidly into polymer films and, when present, causes accelerated diffusion of organic vapors.[11]

Diffusion Equations.—The relevant form of Fick's law for studies of sorption and desorption is

$$\frac{\mathrm{d}c}{\mathrm{d}t} = \frac{\mathrm{d}}{\mathrm{d}x}\left(D\,\frac{\mathrm{d}c}{\mathrm{d}x}\right) \qquad (1)$$

where c is penetrant concentration, t is time, D is diffusion coefficient and x is distance in the direction of diffusion, *i.e.*, normal to the plane of the polymer film. The usually assumed boundary condition is that the concentration of the penetrant at the surface of the film is the equilibrium value for the particular pressure of vapor in the gas phase. This equation has not been solved analytically for the case of interest here where the diffusion coefficient is a function of concentration. However, until the concentration at the film center changes a polymer film can be treated as an "infinite solid" and the Boltzmann solution of Fick's law for this case may be used. This leads to the following equations for weight change during the initial stages of Fickian sorption and desorption

$$Q_s/Q_\infty = K_s\sqrt{t}/l \qquad (2)$$

$$Q_d/Q_\infty = K_d\sqrt{t}/l \qquad (3)$$

where Q_s and Q_d are weight changes for sorption and desorption, respectively. Q_∞ is the equilibrium weight change, l is film thickness and K_s and K_d are constants.

If values of K_s and K_d are determined for a pair of *integral* sorption–desorption experiments between the concentrations 0 and c_f, Crank and coworkers[12,13] have shown that a good approximation to the integral diffusion coefficient for the concentration c_f is given by the equation

$$\bar{D}(c_f) = \frac{\pi}{32}\,(K_s^2 + K_d^2) \qquad (4)$$

If desired, values of the differential diffusion coefficient, D, may be obtained from the defining equation

$$\bar{D}(c) = \frac{1}{c}\int_0^c D\,\mathrm{d}c \qquad (5)$$

Finally if as is usual with diffusion of organic vapors into polymers the diffusion coefficient increases with concentration, the slope K_s for sorption over a given concentration interval is larger than the slope K_d for desorption over the same concentration interval.

A slightly better approximation for $\bar{D}(c)$ can be obtained by making sorption and desorption studies over a series of narrow concentration intervals. For this case, a modified form of eq. 4 holds[3]

$$c_f\bar{D}(c_f) = c_i\bar{D}(c_i) + \frac{\pi}{32}\,(c_f - c_i)[K_s^2(c_i, c_f) + K_d^2(c_f, c_i)] \qquad (6)$$

where c_i and c_f are initial and final concentrations for the interval experiment. A consideration of this equation yields the result that the term $\pi/32[K_s^2(c_i,c_f) + K_d^2(c_f,c_i)]$ is equal to the average differential diffusion coefficient, D_{ave}, for the concentration range c_i to c_f and hence in the limit of c_i very close to c_f can be taken to give D for the concentration c_i. Incidentally as the interval c_i to c_f becomes smaller the slopes K_s and K_d become more nearly the same and in the limit of an infinitesimal interval will be equal even though D is a function of concentration.

Two-stage Sorption and Desorption.—Figure 1 gives typical results for integral sorption and desorption of organic vapors in cellulose acetate, in this case for acetone between concentrations of 0 and 0.16 g. per g. polymer. The anomalous or non-Fickian aspects are apparent. Similar plots are obtained for other values of c_f and are also found for diffusion of methylene chloride[5,7] and methanol. If the sorption data of Fig. 1 are plotted as Q *vs.* t, a pronounced inflection is observed at a value of Q_s/Q_∞ of about 0.5, leading from the analysis by Prager[14] to the conclusion that no possible dependence of D on concentration will explain the results. Most attempts to explain this anomalous behavior have focused on the increasing value of the slope of the Q–$\sqrt{t}$ plot and on the inflection in the Q–t plots. A recent detailed analysis by Crank[6] suggested at least two possible explanations, neither of which was found to be wholly satisfactory.

Additional information on the anomalous sorption of acetone in cellulose acetate can be gained by successive *interval* sorption measurements. Figure 2 gives partial data for one set of such experiments. Each interval involves an increase in acetone pressure of about 33 mm. and a corresponding increase in acetone concentration of about 0.04 g./g. For each of the experiments Fig. 2 shows only about the first 20% of the total sorption; at later times all of the curves show an increasing slope similar to the sorption curve of Fig. 3, which is a plot of the overall sorption for run F of Fig. 2.

The striking feature of Fig. 2 is the change in character which occurs between curves B and C. For the first two intervals, A and B, the sorption starts out with a low, almost constant slope which increases in the later stages. The sorption for interval C and all subsequent ones starts with a high rate which lasts for only one or two minutes and during which about 10 to 15% of the total sorption occurs. Then the slope abruptly *decreases* to a low value similar to the initial slope of

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[11] F. A. Long and L. J. Thompson, *J. Polymer Sci.*, **14**, 321 (1954).

[12] J. Crank and G. S. Park, *Trans. Faraday Soc.*, **45**, 240 (1949).

[13] J. Crank and M. G. Henry, *ibid.*, **45**, 636 (1949).

[14] S. Prager, Thesis, Cornell University, 1951.

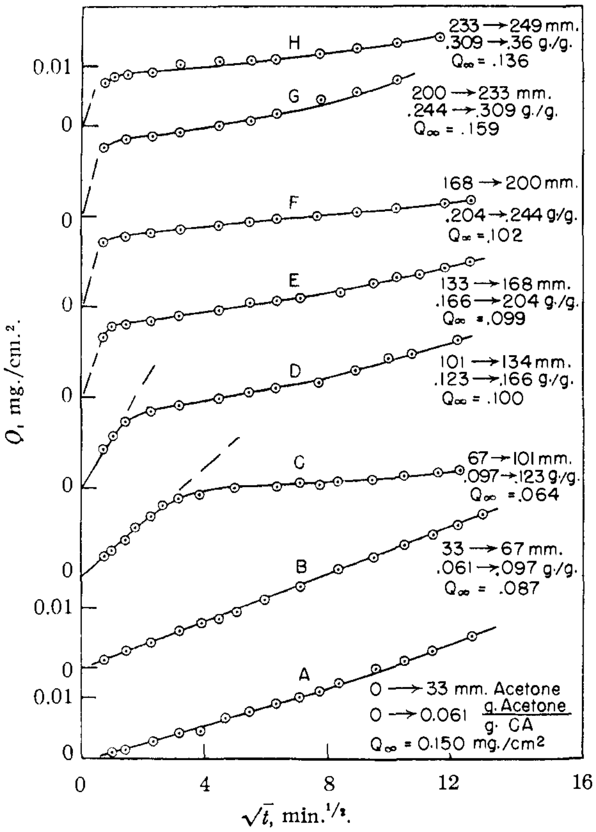

Fig. 2.—Successive interval sorptions of acetone into cellulose acetate at 30°. Film thickness is 3.8×10^{-3}. Figures with each curve give the pressure and concentration interval and the equilibrium weight increase.

curves A and B. As shown in Fig. 3, at times later than those of Fig. 2 this second slope increases in the manner typical of anomalous integral sorption. For convenience in later discussions we shall refer to the initial rapid takeup of curves C to H as the "initial stage" of the sorption and shall designate the $Q-\sqrt{t}$ slope for this stage as S_1; we shall refer to the later, slower takeup as the "second stage" and designate the *initial* slope of this second stage as S_2. These slopes are illustrated in Fig. 3.

Experiments similar to those of Fig. 2 have been done with four different films of cellulose acetate varying in thickness from 3.8×10^{-3} to 16.5×10^{-3} cm. In all cases the general character of the results is the same: at concentrations above about 0.08 g./g. of acetone the sorption curves show a rapid initial stage followed by a slower second stage. Table I summarizes the results of these experiments and lists the values of the slopes S_1 and S_2. A notable aspect of the slopes is their different dependence on concentration. For these almost constant concentration intervals the initial stage slopes increase rapidly with increasing concentration of acetone in the polymer. In contrast the second stage slopes appear to be almost constant, independent of concentration.

Compared either to the results for Fickian diffusion or to integral experiments of the type of Fig. 1, the unexpected aspect of Fig. 2 is the rapid initial stage sorption and it is important to determine what is occurring during this. One obvious possibility is that this initial stage takeup involves only surface adsorption. Two results argue conclusively against this. One is the fact that for films of constant surface area the amount of acetone taken up during the initial stage is directly proportional to film thickness. Thus for a concentration interval of from $c_i = 0.16$ to $c_f = 0.20$, a film of thickness 3.8×10^{-3} cm. absorbs 0.013 mg./cm.^{2} during the initial stage whereas a film of thickness 13.8×10^{-3} cm. absorbs 0.040 mg./cm.^{2}. A second point is that for a given concentration interval the time to complete the initial stage increases with film thickness. It thus appears that in the initial stage sorption the acetone penetrates the entire polymer film to give a quasi-equilibrium concentration of penetrant.

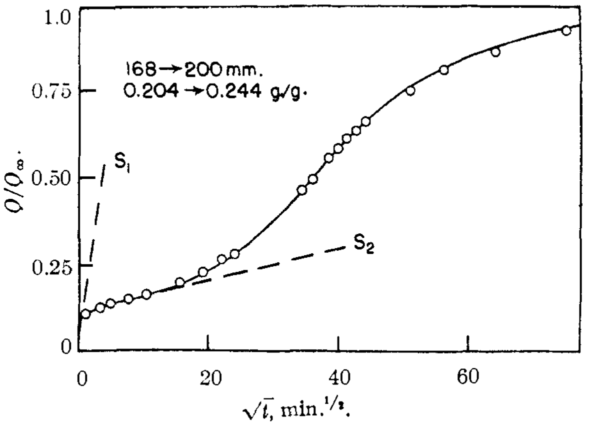

Fig. 3.—Complete sorption curve for run F of Fig. 2. The initial stage and second stage slopes, S_1 and S_2, are indicated.

Table I

Interval Sorption Data, Acetone–Cellulose Acetate, 30°

Film thickness in cm. $\times 10^3$: $A = 4.1$; $B = 3.8$; $C = 16.5$; $D = 13.8$.

Film	p_i, mm.	Δp, mm.	c_i, g./g.	Δc, g./g.	Slopes, mg./cm.^{2}/min.$^{1/2}$ $\times 10^{3}$[a] S_1	S_2
A	0	30.4	0.0	0.0305	...	1.55[b]
B	0	33.3	.0	.0606	...	1.70[b]
A	30.3	30.3	.0305	.0601	...	1.40[b]
B	33.3	33.4	.0606	.0367	...	1.98[b]
A	60.3	31.1	.0906	.0335	4.38	3.53
B	66.6	34.0	.0973	.0257	4.53	0.45
A	102.0	31.7	.1302	.0326	9.49	1.02
B	99.7	34.6	.1230	.0426	9.11	0.98
C	87.7	31.5	.1175	.0425	8.43	..
C	119.2	33.6	.1500	.0375	17.7	3.66
D	119.5	31.1	.1500	.0350	19.5	1.77
A	133.2	29.3	.1628	.0362	18	1.03
B	133.5	34.5	.1656	.0385	18	0.75
A	161.6	30.2	.1990	.0453	21	1.25
B	168.0	32.0	.2041	.0410	27	0.54
A	190.3	31.9	.2443	.0573	25	1.7
B	200.0	34.4	.2451	.0634	31	1.01
B	232.6	16.8	.3085	.0550	...	0.5

[a] These and subsequent slopes of the same dimensions are calculated using total surface area; this is twice the "film area." [b] Two-stage phenomenon not observed; slopes are for initial portion of curve.

Further evidence for the quasi-equilibrium character of the initial stage sorption is given by Fig. 4 which compares the rate of acetone sorption during the initial stage with the change in film dimensions during the same time period. The experiment involves two films which were actually adjacent segments of a larger film and hence of similar thickness and orientation. The upper curve of Fig. 4 is a Q *vs.* t plot for the initial stage of acetone takeup for the pressure interval 126 to 159 mm. The lower curve gives for the other film segment the increase in film length for the same time period with a similar acetone pressure interval, 122 to 156 mm. Quite evidently the film as a whole expands during the initial stage sorption of acetone. The calculated value of Δx for isotropic expansion of the film, assuming additivity of volumes, is 0.08 mm. for the initial stage takeup whereas the observed value is 0.05 mm. Considering that the films have some preferred orientation in the plane of the film so that the preferred expansion is normal to the plane, this agreement is quite satisfactory and supports the conclusion that the acetone penetrates the film to give a quasi-equilibrium.

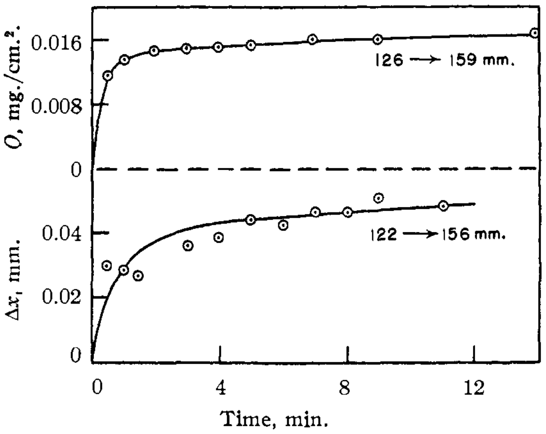

Fig. 4.—Comparison of initial change of film length, Δx, with weight of acetone takeup for similar pressure intervals, 30°. Film thickness is 4.7 × 10^{-3} cm.; length is 3.6 cm.

Several other experimental results argue that, in contrast to the non-Fickian second stage, the initial stage diffusion is Fickian. One such result is that for a given concentration interval the value of the slope, S_1, in mg./cm.²/min.$^{1/2}$ is independent of film thickness. Since the diffusion coefficient is proportional to S^2, this implies a diffusion coefficient which is independent of film thickness. A second result which is illustrated in Fig. 5 is that for a given initial concentration of acetone a desorption experiment gives the same initial stage phenomenon with, in fact, the same absolute value of the slope, S_1. Finally as Fig. 5 also shows, the initial stage process for either sorption or desorption gives a linear Q *vs.* $\sqrt{t}$ plot and this is the expected result for Fickian diffusion. We conclude that above a fairly definite initial concentration of acetone both the sorption and desorption of acetone in cellulose acetate are two stage processes and also that the initial stage involves Fickian diffusion to a quasi-equilibrium concentration of the acetone.

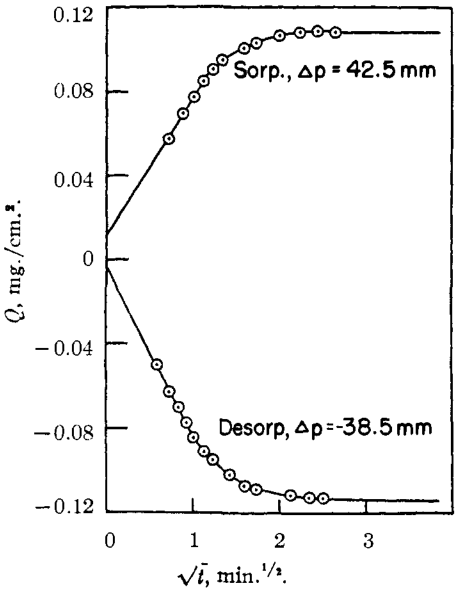

Fig. 5.—Sorption and desorption of acetone from same initial concentration, 30°. Film thickness = 13.8 × 10^{-3} cm.; p_i = 160 mm.; c_i = 0.195 g./g.

Experiments with other systems indicate that this two stage behavior is a common aspect of sorption and desorption of organic vapors in polymers. Data similar to those of Table I will be given later for the system methanol–cellulose acetate. In addition similar if less extensive results have been obtained[15] for methylene chloride–cellulose acetate, acetone–cellulose nitrate, acetone–polystyrene and methylene chloride–polystyrene. Apparently whenever anomalous diffusion is observed with integral sorption–desorption experiments the two stage phenomenon can also be observed.

Initial Stage Diffusion Coefficients.—A detailed study of the initial stage of the sorption and desorption of acetone in cellulose acetate was carried out with a thick film of polymer (l = 13.8 × 10^{-3} cm.). The film was equilibrated at a given pressure p_i. Then the pressure was suddenly increased to $p_i + \Delta p$ and the initial sorption kinetics determined. When the quasi-equilibrium was reached, the pressure was dropped back to p_i and the desorption kinetics *from the quasi-equilibrium* were measured. At each value of p_i the experiments were done for a series of Δp values. Figure 6 is a Q *vs.* $\sqrt{t}$ plot of data for a typical experiment at p_i = 100 mm. and Δp = 40 mm. The early parts of the plots for both sorption and desorption are linear. Furthermore the slopes of the linear portions for sorption to and desorption from the quasi-equilibrium are very nearly equal. This is the expected result since the initial and quasi-equilibrium concentrations are very similar, 0.128 and 0.133 g./g., respectively. Even though, as will be shown later, the diffusion coefficient is an increasing function of concentration, the slopes for sorption and desorption are nearly equal simply because the concentration change is so slight.

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[15] F. A. Long, L. Mandelkern, P. Drechsel, A. Di Pietro and E. Bagley, unpublished results.

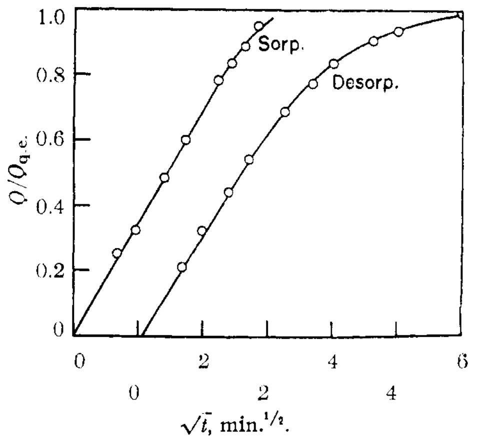

Fig. 6.—Sorption and desorption of acetone to and from quasi-equilibrium, 30°. Film thickness is 13.8×10^{-3} cm.; p_i = 100 mm.; Δp = 40 mm.

Table II summarizes the data on these initial stage sorption and desorption experiments. The first two columns gives values of p_i and Δp. The third column gives values of the initial concentration of acetone, c_i, corresponding to the initial pressure, p_i. The fourth and fifth columns give values of Δc(q.e.) and Δc(e), the concentration increases to the quasi-equilibrium and to the true equilibrium, respectively. The former is roughly 10% of the latter in all cases. The sixth and seventh columns of the table give S_1(s) and S_1(d) the slopes of Q *vs.* $\sqrt{t}$ plots for sorption to the quasi-equilibrium and desorption from it.

Table II

Sorption to Quasi-equilibrium, Acetone–Cellulose Acetate, 30°

Film thickness, l = 13.8×10^{-3} cm.; film weight, m = 73.54 mg.

p_i, mm.	Δp_i, mm.	$10^2 c_i$, g./g.	Δc (q.e.), $\times 10^2$	Δc(e)[a] $\times 10^2$	Slopes, mg./min.$^{1/2}$ S_1(s)	Slopes, mg./min.$^{1/2}$ S_1(d)	$10^6 D$, cm.^{2}/min.
100.0	29.4	12.85	0.34	3.00	0.104	0.081	5.2
100	40.0	12.85	.49	4.15	.146	.119	5.1
100	49.5	12.85	.53	5.30	.193	.129	6.7
100	49.8	12.85	.53	5.40	.159	.131	5.2
100	60.5	12.85	.62	6.75	.195	.158	5.5
99.4	60.6	12.77	.63	6.75	.197	.158	5.5
							5.5
119.5	31.1	14.94	.43	3.45	.170	...	10.8
119.5	31.1	14.94	.43	3.45	.149	...	8.3
120.0	40.5	15.00	.53	4.75	.236	.214	12.4
120.9	49.6	15.11	.67	6.20	.272	.267	11.2
121.4	58.1	15.17	.81	7.70	.314	.307	10.2
							10.6
139.2	30.5	17.00	.37	3.80	.217	.140	16.8
140.0	39.7	17.10	.49	5.60	.324	.246	23.8
140.0	49.4	17.10	.62	7.20	.352	.344	21.8
140.5	59.1	17.17	.71	8.75	.351	.298	14.6
							19.3
159.0	37.3	19.58	.48	5.70	.304	.262	24.2
159.3	42.5	19.62	.58	6.60	.320	.332	21.9
159.3	46.9	19.62	.59	7.10	.384	.372	28.4
159.3	59.6	19.62	.85	10.30	.450	.460	19.8
							23.5
66.6	34.0	9.70	.61	3.35	.038	...	0.27

[a] Calculated from equilibrium isotherm.

From the slope values of Table II diffusion coefficients can be calculated from the equation

$$D(c_i) = \frac{\pi}{32} \frac{l^2}{Q^2_{q.e.}} [S_1(s)^2 + S_1(d)^2] \qquad (7)$$

where l is film thickness and $Q_{q.e.}$ is the weight change to or from the quasi-equilibrium. This equation is actually the same as discussed earlier since $K_s \equiv lS_1(s)/Q_{q.e.}$. In accord with the earlier discussion the resulting D value is the *differential* diffusion coefficient for the concentration c_i since in these cases c_f for the quasi-equilibrium is very similar to c_i. The last column of Table II gives D values calculated from eq. 7. From these it is evident that D is independent of the value of Δp but increases with the value of p_i itself. Both of these are the expected results. The independence of Δp is a reflection of the fact that for all Δp's the c_f value at the quasi-equilibrium is only slightly larger than c_i. The increase of D with p_i (and hence with c_i) indicates that the diffusion coefficient increases with concentration. This is the usual observation for Fickian diffusion of organic vapors into polymers.[3]

The initial stage D values of Table II are quite large and a point of interest is to compare them with coefficients for Fickian diffusion of acetone in polyvinyl acetate. From the data of Kokes, Long and Hoard[3] the approximate differential diffusion coefficient of acetone into PVAc at 30° and a concentration of 0.129 g./g. is $D = 1.6 \times 10^{-6}$ cm.^{2}/min. This is clearly of the same order of magnitude as the initial stage diffusion coefficient for acetone into cellulose acetate which, at this same concentration and temperature, is $D = 5.5 \times 10^{-6}$ cm.^{2}/min.

From the results for interval sorption to the quasi-equilibrium it would be expected that interval desorption experiments would give similar results and this is true. A set of experiments was made in which a film of cellulose acetate was initially equilibrated at p_i = 161 mm. Then the pressure was dropped suddenly to $p_i - \Delta p$ and the desorption kinetics followed down to the *desorption quasi-equilibrium.* At this point the pressure was increased back to p_i and the sorption kinetics measured. The observed results for values of Δp varying from 20 to 70 mm. were very similar in character to those of Table II. Plots of Q *vs.* $\sqrt{t}$ were initially linear for both desorption and sorption. For each value of Δp the desorption and sorption slopes were nearly equal. Just as with experiments to the sorption quasi-equilibrium, values of the slopes increased with Δp. The calculated D values for p_i = 161 mm. were constant, independent of Δp. The average value of D for these desorption experiments is $D = 2.7 \times 10^{-5}$ cm.^{2}/min. which is very close to the average value listed in Table II for sorption experiments from a p_i value of 159 mm.

Figure 7 summarizes values of the initial stage D as a function of concentration of acetone in the polymer. The data are from studies with six different films of varying thickness and varying amounts of molecular orientation. It is evident that D increases with concentration of acetone and also that D at a given concentration is larger for films with a more negative value of the optical birefringence, Δn. The fact that the diffusion coefficient is smaller for an *increase* in molecular orientation in the direction of diffusion is in accord with the conclusions of Drechsel, Hoard and Long.[8] However, these investigators reported data for integral sorption experiments and hence were really talking about rate of sorption for the second stage. The data of Fig. 7 show that the rate of sorption during the initial, Fickian stage also depends on orientation.

In their integral sorption studies, Drechsel, Hoard and Long found that diffusion of acetone into cellulose acetate and nitrate caused increased orientation in the direction of diffusion and this in turn caused a decrease in sorption rate. In the present studies the same behavior was observed for the second stage diffusion of acetone. However repeated initial stage sorptions and desorptions to and from the quasi-equilibrium, as for example in the experiments listed in Table II, did not cause any change in the molecular orientation of the film and no significant changes in rate during such series were observed. This implies that the behavior of the polymer itself differs in the two stages.

Interval sorption of methanol in cellulose acetate shows a two-stage behavior similar to that of acetone. Table III gives a direct comparison of the two vapors for very similar concentration intervals. The films used for this comparison were adjacent segments of the same large polymer films. The data show that an "initial stage" enters at a lower concentration for methanol than for acetone. Other experiments show that with methanol the minimum concentration for two-stage behavior is about 0.04 g./g. whereas for acetone it is about 0.08 g./g. At the lower concentrations listed in Table III the initial stage D value for methanol is larger than for acetone but the concentration dependence is smaller so that at the higher concentrations the D values are actually larger for acetone. These results are at least consistent with Fickian diffusion in polyvinyl acetate where the D for methanol is larger than for acetone but shows a smaller rate of increase with concentration.[3]

TABLE III

COMPARISON OF TWO-STAGE DIFFUSION OF METHANOL AND ACETONE IN CELLULOSE ACETATE AT 30°

$l = 4.2 \times 10^{-3}$ cm.; $\Delta n = -6.1$

Concn. interval, g./g.	$10^3 S_1$, mg./cm.^{2} min.$^{1/2}$	Δc(q.e.)	$10^6 D$, cm.^{2}/min.	$10^3 S_2$, mg./cm.^{2} min.$^{1/2}$
Methanol				
0.070 → 0.116	18	0.0085	2.0	1.4
.116 → .173	30	.0091	4.9	1.6
.173 → .240	24	.0082	4.1	2.0
Acetone				
0.078 → 0.111	No initial stage	$10^3 S$ =	2.7	
.111 → .171	8.4	.0062	1.0	2.6
.171 → .242	42[a]	.0064	20[a]	2.1
.242 → .315	..	.0063	..	2.1

[a] Too fast to measure; calculated from other data with thicker films.

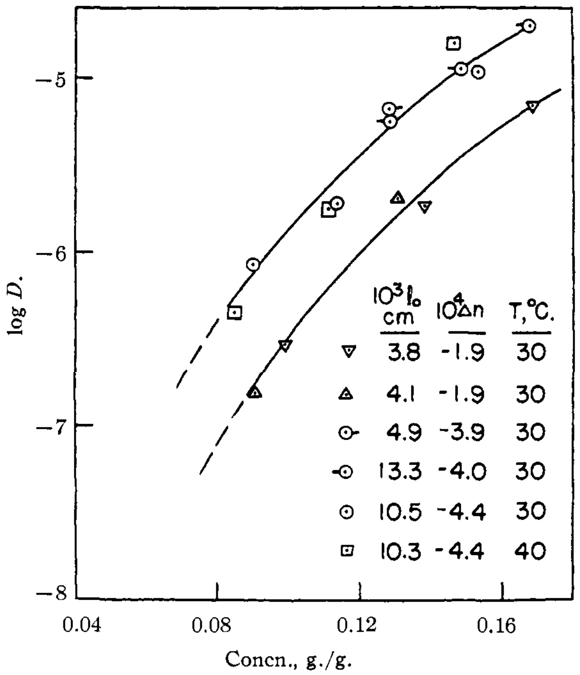

Fig. 7.—Diffusion coefficients, cm.^{2}/min., for initial stage sorption and desorption of acetone in cellulose acetate. Tabulation gives film thickness, optical birefringence of film and temperature of experiment.

A few experiments on initial stage sorption have been done with acetone–cellulose acetate at 40°. The resulting D values are plotted in Fig. 7 and are seen to fall closely on the curve for D values at 30°. This implies that the energy of activation, E_d, for this Fickian diffusion is close to zero. This is surprising since for polymers above their second-order transition the E_d values for diffusion of organic vapors are normally quite high. Thus for diffusion of acetone into polyvinyl acetate at $c_i = 0$, E_d is 38 kcal. per mole and even at $c_i = 0.10$ g./g. the E_d value is 26 kcal. per mole.[3] However a qualitative explanation of the observed low E_d can be given. For diffusion above the second-order transition one can consider that the large temperature coefficient (and hence large E_d) involves both an increase in the diffusion rate at constant volume and an increase in rate caused by expansion with temperature of the polymeric material. It is reasonable that with polymers the expansion term is the major one. When a polymer is below its second-order transition the temperature coefficient of volume expansion is much smaller than when it is above. For Fickian diffusion into a polymer which is below its second-order transition temperature one would thus expect a smaller contribution from the polymer expansion and hence a lower temperature coefficient.

The Second-stage of Sorption and Desorption.—The second stage of the sorption–desorption process is experimentally more difficult to study than the initial stage. The rates are slower and are more sensitive to conditioning of the polymer. However, several facts appear to be fairly well established. As shown in Fig. 3, the second stage for an interval sorption experiment quite generally starts out with an almost constant slope, S_2, which then increases considerably in the later phases of the sorption. For interval desorption the initial slope for the second stage appears to have a value very similar to that for sorption but the slope does not later increase. As Table I shows, the value of S_2 is essentially independent of the initial concentration, c_i, and also independent of film thickness. (The latter is not surprising and only implies that the film is behaving as an "infinite solid.") A few preliminary experiments indicate that S_2 does increase with the size of the pressure or concentration interval but this point needs further investigation. As shown in Table III the S_2 slopes for methanol and acetone, studied with similar concentration intervals, are very similar. Actually the values for methanol are slightly smaller but in view of the difficulties in measuring S_2 the difference is not significant. This similarity of S_2 values for the two vapors is in contrast to the distinctly different rate of sorption of methanol during the initial, Fickian stage. The implication is that the initial rate of the second stage is primarily a property of the polymer itself rather than of the diffusing vapor.

Discussion

The phenomenon of two-stage sorption and desorption appears to be a general one for interval sorption or desorption of organic vapors in polymers which are below their second-order transition. The experimental results are all in accord with the conclusion that the initial stage goes to a quasi-equilibrium and involves Fickian diffusion with a diffusion coefficient which depends on the polymer, the nature of the penetrant and its concentration. In contrast the second stage is independent of the concentration of penetrant although it does appear to depend on the size of the concentration interval. The observation that the rate of sorption in the initial stage increases with concentration whereas that for the second stage does not offers a quite reasonable explanation of the fact that the initial stage does not enter below a fairly definite minimum concentration and it may be concluded that below the minimum concentration (curves A and B of Fig. 2) only the second stage is being observed. The observation (Table III) that the minimum concentration for entrance of the two stage process is lower for methanol than for acetone is consistent with this since at lower concentrations the initial stage diffusion coefficient for methanol is higher than for acetone.

The fact that the Fickian initial stage terminates rather abruptly at a quasi-equilibrium and is followed by a much slower process clearly indicates that two different rate determining steps enter. A possible explanation for this can be given by assuming that the cellulose acetate is characterized by inter-chain bonds ("effective" cross-links) which prevent rapid macro movement of one chain relative to another but which still permit some elastic expansion of the network, perhaps by extension of the chain segments between the inter-chain bonds. On this basis the initial stage diffusion involves this elastic expansion and the rate-determining step is ordinary Fickian diffusion of the penetrant. The quasi-equilibrium would then represent a balance between the osmotic force of the pressure increment and the elastic force of the polymer network. This is consistent with the fact that, for a given initial concentration, the weight sorbed at the quasi-equilibrium increases linearly with the pressure increment, Δp.

The assumption of a balance between osmotic and elastic forces at the quasi-equilibrium permits a semi-quantitative calculation of the latter and hence a check on the reasonableness of the assumption. Consider for example the second entry of Table II where the pressure increment of acetone is 40 mm. From the equilibrium isotherm, the observed Δc of 0.0049 for the quasi-equilibrium corresponds to an interval pressure increment of 4.7 mm. The calculated osmotic pressure is

$$\pi = \frac{RT}{V_1} \ln \frac{40}{4.7} = 710 \text{ atm.}$$

using 75 ml./mole for the molar volume of acetone. Assuming additivity of volumes the relative volume change to the quasi-equilibrium is $\Delta V/V = 0.0067$ and this with the above osmotic pressure leads to a compressibility of $\beta = 1 \times 10^{-5}$ atm.$^{-1}$. This seems to be a reasonable value. For comparison, Bridgman's value for cellulose acetate[16] for a pressure of 2.5×10^3 atm. is $\beta = 1.9 \times 10^{-5}$ atm.$^{-1}$

An item of indirect support for this hypothesis is given by the stress–strain studies of Haward[17] with plasticized cellulose acetate which show a small amount of instantaneous elasticity followed by slow, non-ideal elasticity. In fact the shape of Haward's extension–time curves for cellulose acetate is quite similar to the sorption curve of Fig. 3.

From this general picture the rate-determining step for the second stage of sorption or desorption is macro rearrangement of the polymer network which can presumably occur only by breaking interchain bonds. The lack of concentration dependence of the initial second stage slope then implies that the rate of breaking inter-chain bonds is essentially independent of the amount of penetrant present and this is not unreasonable. From this standpoint a "diffusion coefficient" for the second stage has a very different meaning from that which it has for Fickian diffusion since for the second stage it is primarily a property of the polymer. The fact that S_2 increases in the later stages of sorption suggests that after some inter-chain bonds are broken, breaking of others becomes easier perhaps because of the expansion forces discussed by Crank.[6] This permits explanation of the time dependent nature of D for the second stage as well as for the dependence of rate of takeup on film thickness which has been reported by Mandelkern and Long[7] and by Park.[5] However, it should be emphasized that this hypothesis is still rather speculative and that further experiments are needed to confirm it.

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(16) P. W. Bridgman, *Proc. Am. Acad. Arts Sci.*, **76**, 71 (1947).

(17) R. N. Haward, *Trans. Faraday Soc.*, **38**, 394 (1942); **39**, 267 (1943).