proach a limiting association number somewhere between three and four. This again is indicative of the similarity of these two liquids. On the other hand, triethylsilanol is definitely less associated than either trimethylsilanol or *t*-butyl alcohol, while 3-ethylpentanol-3 exhibits essentially no association. This result is not entirely unexpected since one would anticipate that the more highly hindered ethyl derivatives should be less associated than their methyl analogs.

Dipole Moments.—The dipole moments of trimethylsilanol, triethylsilanol, and 3-ethylpentanol-3 were evaluated from the dielectric properties of the pure liquids.[22] The experimental data are summarized in Table V in which V is the molar volume of the liquid at 20°, tan δ is the loss factor, ϵ is the dielectric constant at 20° and 1000 cycles and μ is the dipole moment in Debye units.

Table V

Dielectric Properties

	V	tan δ	ϵ	μ
$(CH_3)_3SiOH$	111.2	<0.0002	7.17 ± 0.03	2.01 ± 0.10
$(CH_2CH_2)_3SiOH$	152.9	.0004	2.66 ± .02	0.62 ± .08
$(CH_3CH_2)_3COH$	138.0	.002	3.24 ± .02	1.13 ± .05

The dipole moment *t*-butyl alcohol has been reported to be 1.74 *D* (Onsager moment).[23] The dipole moments vary considerably from the values which would be predicted for the unassociated liquids. This result is to be expected on the basis of the data obtained in careful studies of the dielectric properties of alcohols.[24,25] Such behavior may be attributed to strong forces of association in the liquid state, as indicated by the high values of the entropies of vaporization and the high degree of association in cyclohexane solution.

Acknowledgment.—The authors express their appreciation to Dr. S. W. Kantor and Dr. J. D. Hoffman for their many helpful suggestions.

[22] L. Onsager, This Journal, **58**, 1490 (1936).

[23] S. R. Phadke, N. L. Phalnikar and B. V. Bhide, *J. Indian Chem. Soc.*, **22**, 239 (1945).

[24] G. Oster and J. G. Kirkwood, *J. Chem. Phys.*, **11**, 174 (1943).

[25] D. W. Davidson and R. H. Cole, *ibid.*, **19**, 1484 (1951).

Schenectady, N. Y.

[Contribution from the Department of Chemistry, Cornell University]

Diffusion of Benzene and Methylene Chloride Vapors into Polystyrene[1,2]

By F. A. Long and R. J. Kokes

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The rates of sorption and desorption of vapors of benzene and methylene chloride in films of polystyrene have been studied at 30 and 40° and at a variety of pressures. With low concentrations of either vapor the diffusion is anomalous in that the diffusion does not obey Fick's law with the usual assumption of equilibrium concentration of penetrant at the film surface. By studying sorption and desorption of benzene over narrow concentration intervals it is found that there is a critical concentration of benzene in the polymer above which diffusion is Fickian and below which it is anomalous. At both 30 and 40° the observed critical concentration for change in character of diffusion agrees closely with the critical concentration found by Fox for the second-order transition of polystyrene–solvent mixtures. In the region of anomalous diffusion, *i.e.*, below the second-order transition, the diffusion of either benzene or methylene chloride causes macromolecular orientation in the direction of diffusion and this orientation influences the rate of sorption.

Several recent studies[3-7] of the diffusion of small molecule species into polymer films have shown that in some cases Fick's law

$$\frac{dc}{dt} = \frac{d}{dx}\left[D(c)\frac{dc}{dx}\right] \quad (1)$$

with the usually assumed boundary conditions, $C = C_{eq}$ at $x = 0$ and $x = l$ for all t, is obeyed whereas in other cases it is not. (In the above C is concentration of small molecule in the polymer in grams per gram, l is film thickness, x is distance in the film, t is time and $D(c)$ is the diffusion coefficient. C_{eq} is equilibrium concentration for the particular pressure of vapor under study.) A particularly interesting result obtained with acetone–polyvinylacetate is that with this system diffusion is normal above the second-order transition temperature for the polymer–solvent mixture whereas below this temperature the diffusion is anomalous, *i.e.*, Fick's law with the above boundary conditions is not obeyed.[8]

To distinguish between normal and anomalous diffusion two criteria have been used. One is that for the initial diffusion into a polymer film, *i.e.*, until concentration at the film center changes appreciably, a plot of weight of vapor takeup or loss, Q, *versus* $\sqrt{t}$ for either sorption or desorption should be linear if diffusion follows Fick's law with the above boundary conditions. A second criterion is that a plot of Q *versus* time for vapor sorption should show no inflections.

A suggestion that the influence of second-order transition on diffusion may be general is found in the facts that the diffusion at 25 to 45° of hydrocarbons into polyisobutylene ($T_g = -70°$) is normal[6] whereas diffusion at 30° of vapors into cellulose acetate[5] and nitrate[7] is highly anomalous and with these cellulosics the second-order transition presumably occurs at temperatures above 100°.[9] In order to obtain further evidence on this point we have studied the diffusion of two vapors,

[1] Work supported by a grant from Office of Ordnance Research.

[2] Presented in part at 122nd Meeting of American Chemical Society, Atlantic City, N. J., September, 1952.

[3] J. Crank and G. S. Park, *Trans. Faraday Soc.*, **45**, 240 (1949); **47**, 1072 (1951).

[4] G. S. Park, *ibid.*, **48**, 11 (1952).

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

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

[7] P. Drechsel, F. A. Long and J. L. Hoard, *J. Polymer Sci.*, **10**, 241 (1953).

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

[9] L. Mandelkern and P. J. Flory, This Journal, **73**, 3206 (1951).

benzene and methylene chloride, into polystyrene at concentrations above and below that for the second-order transition.

With the cellulosic polymers it has been shown that the rate of diffusion is highly dependent on molecular orientation of the polymer and also that the diffusion process itself induces molecular orientation.[7] We have therefore made studies of the influence of diffusion on the molecular orientation of polystyrene to see if similar effects enter with this non-polar polymer.

Studies on the diffusion of several small molecules into polystyrene at 25° have previously been reported by Park and co-workers[3,4,10,11] and in particular it has been shown that with methylene chloride the sorption is anomalous in that at higher pressures Q *versus* $\sqrt{t}$ plots show slopes which increase with time.[4] Park has also reported a comparison of diffusion coefficients obtained from sorption–desorption studies and from permeability studies for the system methylene chloride–polystyrene.[4]

Materials and Procedure.—The polystyrene used for these studies had a viscosity average molecular weight of 110,000 and T_g for the dry polymer was 97°. Polymer films were cast from methyl ethyl ketone on a mercury surface and were eventually dried in a vacuum oven at 75° for about five days. For the sorption experiments segments of known area were cut from these films and the film thicknesses were calculated from measured weights and areas using 1.05 as the density of polystyrene at 30°. Film thickness varied in the different experiments from 0.001 to 0.010 cm.

Measurements of rates of sorption and desorption were done in the apparatus described by Prager and Long.[6] Two somewhat different procedures, designated as *regular* and *interval* experiments, were used. For *regular* sorption–desorption experiments a dry polymer film was suspended in the evacuated chamber; at zero time the diffusing vapor was admitted at the given pressure and then the kinetics of vapor takeup were measured. After equilibrium was attained the chamber was rapidly evacuated and the kinetics of desorption back to zero pressure were observed. For *interval* experiments the procedure differed from the above in that sorption started not with dry polymer but with a film equilibrated at a pressure, P_i. Then for a sorption study the pressure was suddenly increased to a higher pressure, P_f. After equilibration at P_f the interval desorption was studied by reducing the chamber pressure down to P_i. The object of the interval experiments was to permit sorption–desorption studies to be made over narrow pressure intervals as a function of initial pressure.

The molecular orientation of the polymer films was determined by measuring the birefringence of a film section in a polarizing microscope equipped with a quarter-wave plate and a first-order red plate.[12] The film sections used were actually uniform strips, about 0.5 mm. wide, cut from the film concerned. The exact width of the strip was measured in a microscope equipped with an eyepiece micrometer and the strip was then examined edgewise under the polarizing microscope. The direction in the film of the electric vector of the slow ray was established with the first-order red plate and quantitative measurements of the birefringence were obtained with a Senarment compensator (quarter wave plate) and a monochromatic light source (580 mμ).

To relate the observed birefringence to the molecular orientation, preliminary experiments were made on prestretched films of polystyrene. In this way it was determined that a positive value of the birefringence ($n_{\parallel} - n_{\perp}$), where $n_{\parallel}$ and $n_{\perp}$ are the refractive indices for the ray with the electric vector vibrating parallel and perpendicular, respectively, to the plane of the film, indicates molecular orientation *normal* to the film, *i.e.*, in the direction of diffusion.

In order to amplify the molecular orientation which is induced by diffusion at temperatures below that of the second-order transition, use has been made of so-called cycling experiments. In a typical cycling experiment several *regular* ($P_i = 0$) sorption–desorption runs are carried out on the same segment of film and measurements are made both of the kinetics of sorption for successive cycles and of the birefringence after several cycles. Since desorption of benzene to give a completely dry film takes an excessively long time, final removal of this solvent was accelerated by adding some methylene chloride leaching vapor. Specifically, after roughly 75% of the benzene in the film had desorbed spontaneously, about 80 mm. pressure of methylene chloride was added and the system allowed to stand overnight. Then a few hours evacuation sufficed to remove both the residual benzene and the leaching vapor. In all cases the total amount of vapor in the film was kept low enough so that the swollen polymer was never above its second-order transition.

Sorption and Desorption.—Sorption and desorption of benzene into polystyrene have been studied at two temperatures, 30 and 40°, both of which are well below T_g for the dry polymer. At both temperatures diffusion is anomalous when the concentration of benzene in the polymer is low. Figures 1 and 2 show typical results. Figure 1 gives a Q *vs.* t plot for a *regular* experiment and shows a decided inflection in the sorption curve. Furthermore the desorption is initially very rapid but becomes abnormally slow in the later stages. The general character of Fig. 1 is very similar to the anomalous sorption and desorption of acetone

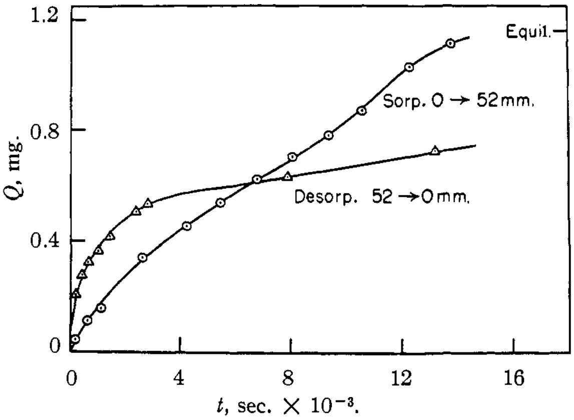

Fig. 1.—Weight change *vs.* time for sorption and desorption of benzene in polystyrene at 30°. Dry film weighs 8.24 mg. and is 1.39×10^{-3} cm. thick.

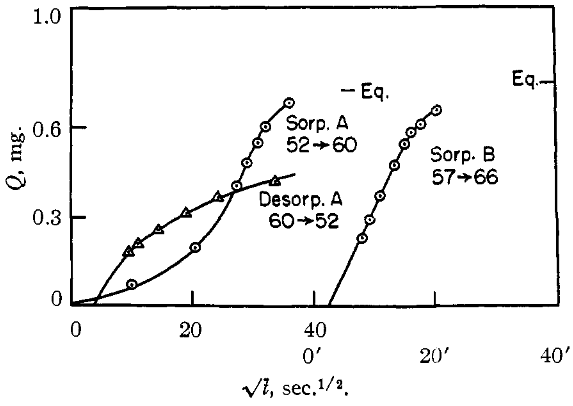

Fig. 2.—Interval experiments, benzene–polystyrene at 30°: film areas, 8.11 cm.^{2}; film weights, A is 16.7 mg., B is 17.6 mg.

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(10) G. S. Park, *Trans. Faraday Soc.*, **46**, 684 (1950).

(11) G. S. Park, *ibid.*, **47**, 1007 (1951).

(12) A. F. Rogers and P. F. Kerry, "Thin-section Mineralogy," McGraw–Hill Book Co., Inc., New York, N. Y., 1933.

or methylene chloride into cellulose acetate and cellulose nitrate.[5,7]

Figure 2 gives Q *vs.* $\sqrt{t}$ plots for interval experiments at 30°. The curves for film A again show anomalous behavior in that for both sorption and desorption the initial slopes are far from linear. Very similar results have been reported for *interval* sorption and desorption of acetone in polyvinyl acetate at temperatures below the second-order transition.[8]

If it is assumed that the anomalous diffusion of benzene in polystyrene is due to the fact that the polymer is below its second-order transition, then one should be able to obtain normal diffusion by increasing either the temperature or the benzene concentration enough so that the polymer–benzene mixture is above the second-order transition. Furthermore one would expect, just as was found with acetone–polyvinylacetate, that at a temperature below T_g for the dry polymer the concentration when diffusion changes from anomalous to normal should be the same as the concentration for which the temperature of the experiment is T_g for the mixture. To study these points for the benzene–polystyrene system we have made at both 30 and 40° a series of *interval* sorption–desorption studies starting from different initial benzene concentrations. That a sharp changeover in type of diffusion does occur is illustrated in Fig. 2. For an interval sorption from 52 to 60 mm. (film A) the Q *vs.* $\sqrt{t}$ plot is decidedly non-linear but for the slightly higher interval of 57–66 mm. (film B) the plot is obviously linear for the initial stages of the sorption.[13]

A detailed list of both *regular* and *interval* experiments at 40° is given in Table I. The table gives pressure ranges, equilibrium values of Q/w_0 the ratio of solvent weight to dry film weight, values of the dry film thickness, l_0, and values of $t_{1/2}$ the time for half the equilibrium weight change. The final column of the table indicates by Anom. and F. whether the diffusion is anomalous or Fickian, using the criteria discussed previously. The results for the *interval* sorption experiments show clearly that there is a critical value of the initial pressure below which diffusion is anomalous and above which it is Fickian. At 40° the approximate value of P_i where this changeover occurs is 71 mm. and this corresponds to a critical volume fraction of benzene (assuming additivity of volumes for benzene and polystyrene) of 0.138. Similar interval experiments at 30° lead to a value of the critical volume fraction for Fickian diffusion of 0.160.[14]

TABLE I

SORPTION OF BENZENE IN POLYSTYRENE, 40°

Pressure range, mm.	(Q/w_0) eq.	$10^3\ l_0$, cm.	$10^{-3} t_{1/2}$, sec.	$10^9\ t_{1/2}/l_0^2$, sec./cm.^{2}	Diffusion character
0–57	0.092	3.32	75.6	6.9	Anom.
0–61	.102	2.48	45.6	7.4	Anom.
0–68.5	.120	2.86	32.4	3.9	Anom.
0–88	.178	1.33	1.25	0.11	F.
57–82	.150	3.32	4.86	..	Anom.
61–73	.132	2.48	5.04	..	Anom.
68.5–78	.141	2.86	0.82	..	Anom.
73–86	.169	2.48	1.56	..	F.
86–68	.120	2.48	0.36	..	F.
89–103	.227	3.32	0.05	..	F.

Figure 3 compares the values of v_g, the critical volume fraction for diffusion, with values of v_c, the critical volume fraction for the second-order transition of plasticized polystyrene. In this figure the straight line and circled points are those of Fox[15] for v_c *vs.* T_g for the system diethylbenzene–polystyrene (using a portion of the same polystyrene as was used in the present study). Since it is known that the value of T_g depends almost solely on the volume fraction of plasticizer and not on the nature of the latter,[15] the solid line of Fig. 3 can be assumed to apply generally. The triangular points of Fig. 3 are the observed values of v_g where diffusion of benzene into polystyrene changes character. The fact that these points fall well on the v_c line clearly indicates that the second-order transition of the polymer determines whether the diffusion is Fickian or anomalous.

A few sorption–desorption studies have also been made with acetone and methylene chloride for comparison with the benzene results. With acetone several *regular* experiments were made at 30° with pressures such that the equilibrium volume fraction was always below the v_g value of 0.160 found for benzene. In all cases the observed diffusion was anomalous. Typical results are shown in Fig. 4 where it is evident that the Q *vs.* $\sqrt{t}$ plots are non-linear.

Figure 5 gives sorption results with methylene chloride at several pressures and in this case also the equilibrium volume fractions are in all cases less than 0.160. The curves of Fig. 5 are very similar to those reported by Park at 25° for this same system.[4] At low pressures the Q *vs.* $\sqrt{t}$ plots for sorption are apparently linear which by our criteria implies Fickian diffusion. At higher pressures the curves are initially non-linear indicating anomalous diffusion. Evidence of anomaly even at the lower pressures comes from the comparison of sorption and desorption rates given in Fig. 6. Again the Q *vs.* $\sqrt{t}$ plot for sorption is essentially linear implying Fickian diffusion by our criteria. However the desorption plot is decidedly non-linear indicating anomalous diffusion and also the initial slope for desorption is considerably higher than that for sorption, a result that is quite inconsistent with the studies of Park[10] which show that the diffusion coefficient for methylene chloride in polystyrene increases with increasing concentration of the small molecule. We conclude that the diffusion of methylene chloride (at volume fractions

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(13) The fact that the Q *vs.* $\sqrt{t}$ plots of Fig. 2 and subsequent figures do not always extrapolate to zero Q at zero time is simply an indication of the sensitivity of these plots to the precise determination of the true zero time. For example, the intersection of the Desorp. A curve of Fig. 2 with the Q axis corresponds to t = 15 sec. an error in determining zero time of $^1/_4$ minute.

(14) It is noteworthy in Table I that the *regular* experiment from 0 to 88 mm., *i.e.*, to a pressure well above that for the critical concentration, shows Fickian behavior. Similar results were obtained with acetone and polyvinylacetate at temperatures below T_g for this system.[9]

(15) T. G. Fox, *Phys. Rev.*, **82**, 652 (1952).

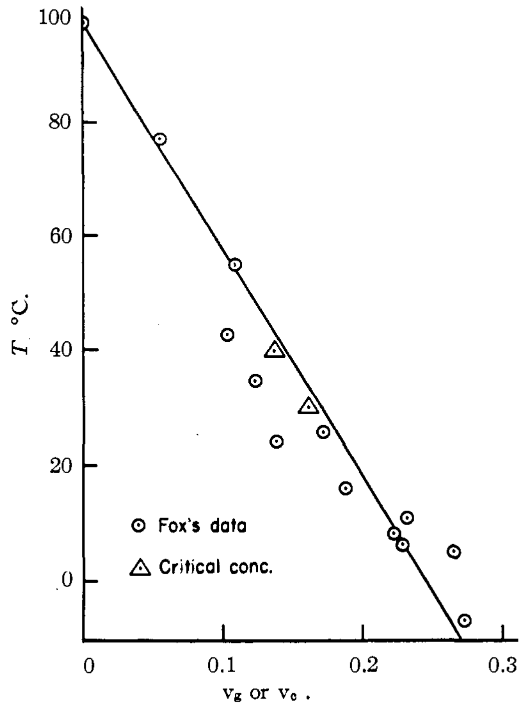

Fig. 3.—Comparison of concentration for second-order transition with critical concentration for diffusion.

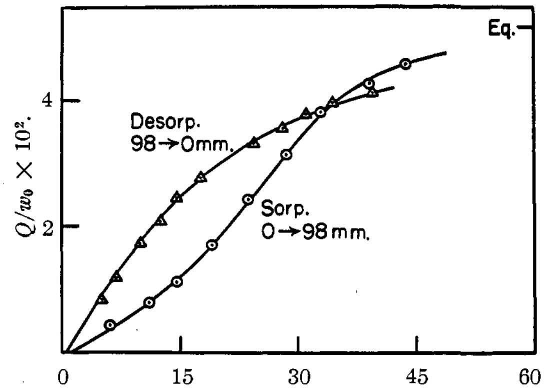

Fig. 4.—Sorption and desorption of acetone by polystyrene at 30°. Film thickness is 1.60 × 10^{-3} cm.

below the critical) is also anomalous but less strikingly so than that for acetone and benzene.

A possible explanation of the less anomalous character of the diffusion of methylene chloride is that it is a considerably smaller molecule than the other two. With the very small molecule, water, diffusion even into cellulose acetate is Fickian and, in contrast to the behavior of larger molecules, the diffusion does not cause orientation of the polymer network.[16] It is thus possible that diffusion anomalies will generally be less apparent with small diffusing molecules than with large.

Diffusion Coefficients.—Although eq. (1) has not been solved analytically for the case of a diffusion coefficient which varies with concentration, two approximate methods have been developed for obtaining D from sorption and desorption data.[3,17]

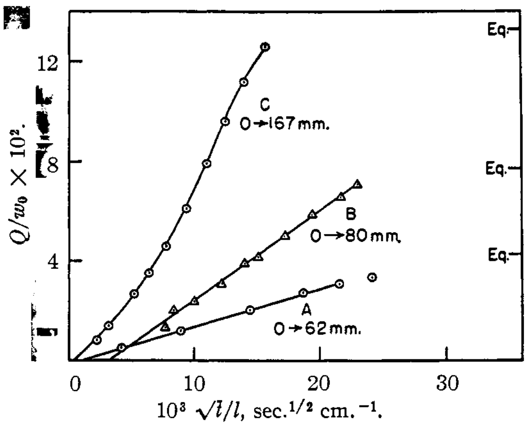

Fig. 5.—Sorption of methylene chloride by polystyrene at 30°: film thickness, A is 2.7 × 10^{-3} cm., B is 1.36 × 10^{-3} cm., C is 5.0 × 10^{-3} cm.

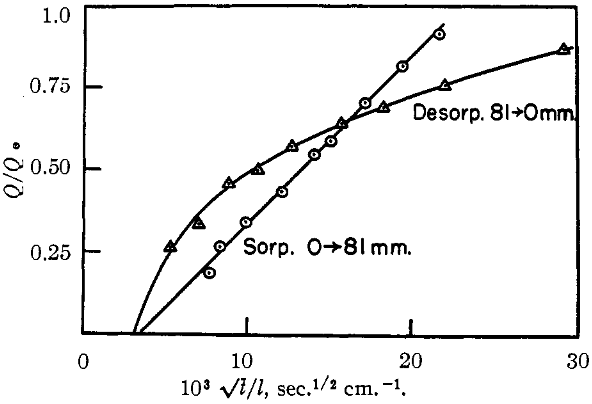

Fig. 6.—Sorption and desorption for methylene chloride and polystyrene at 30°. Film thickness is 1.36 ×10^{-3} cm.

One method involves obtaining initial slopes of Q/Q_{eq} *vs.* $\sqrt{t}/l$ plots for both sorption and desorption and then calculating $\bar{D} \equiv 1/c \int_0^c D\, dc$ from the relation

$$\bar{D} = \pi/32\,(K_s^2 + K_d^2)$$

where K_s and K_d are the above slopes for sorption and desorption, respectively. Then D can be obtained by graphical differentiation of the $\bar{D}$ *vs.* c curve. This method has been applied to diffusion in polyisobutylene and polyvinylacetate.[6,8] Clearly the method is not applicable unless the diffusion is Fickian, *i.e.*, unless the Q *vs.* $\sqrt{t}/l$ plots are initially linear.

Another procedure which has been used by Park for sorption data alone consists of obtaining an average D by assuming that a given sorption can be approximated with a constant diffusion coefficient.[10] This average D (called $\bar{D}$ by Park) is obtained from the value of the half-time for the sorption using the equation

$$D_{av} = 0.0494 l^2/t_{1/2}$$

Then the D_{av} values at various concentrations are used to obtain approximate values of $\bar{D}$ from which D values are obtained as before. Since this method utilizes only the value of $t_{1/2}$ it can be applied to data even for anomalous diffusion although there is obviously some uncertainty about

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(16) F. A. Long, E. Bagley and L. Thompson, unpublished work.

(17) J. Crank and M. S. Henry, *Trans. Faraday Soc.*, **45**, 636 (1949).

the interpretation of the D values obtained when eq. 1 (with the usual boundary conditions) does not hold.

Using the second of these methods Park[4,10] has calculated D values for the diffusion at 25° of a variety of small molecules into polystyrene, among them benzene and methylene chloride. To obtain some comparison of our data with these we have calculated D values from the methylene chloride sorptions of Fig. 5 along with other data not listed there. The results are given in Table II. The calculated diffusion coefficients increase with concentration in agreement with the results of Park. The values of D from this work at 30° are fairly close to those of Park at 25°, *i.e.*, somewhat smaller than would be predicted from Park's data. Furthermore the increase of D with concentration listed in Table II is not as large as reported by Park. Even so the agreement between the two studies is about as good as can be expected since our methylene chloride studies are somewhat incomplete for calculation of diffusion coefficients.

TABLE II

CALCULATED VALUES OF DIFFUSION COEFFICIENT FOR METHYLENE CHLORIDE AT 30°

$10^2 Q/w_p$	$D \times 10^9$, cm.^{2} sec.$^{-1}$
0	0.63
4	1.81
8	4.92
12	9.7

We have not attempted to calculate diffusion coefficients for benzene partly because of inadequate data at low volume fractions of benzene and partly because of the highly anomalous character of the sorption. A comparison of values of $t_{1/2}/l_0^2$ from the present experiments with extrapolated values from Park[4] again indicates that our experiments with benzene at 30° give about the same values of D_{av} as reported by Park at 25°.

Orientation Accompanying Diffusion.—It has previously been postulated[7] that anomalous diffusion is, at least in part, a consequence of molecular orientation which is induced in the polymer by the diffusion process itself; hence simultaneous studies have been made of the orientation induced by successive sorption and desorption of benzene into a polystyrene film and of the rates of the successive sorption steps. Figure 7 gives Q *vs.* t plots for the parts of successive sorption–desorption cycles at 30°. With the low pressure of benzene which was used, 52 mm., the polymer–solvent mixture was at all times below its second-order transition.

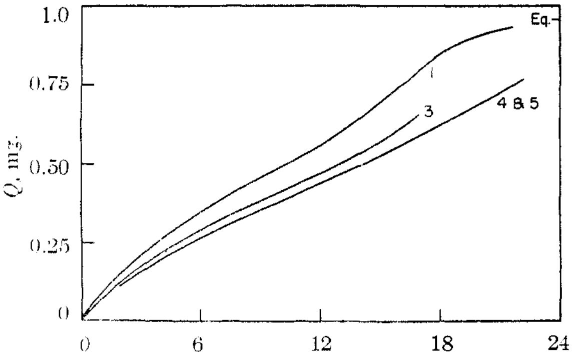

Fig. 7.—Rates of sorption of benzene for successive cycles at 30°. Pressure range 0 → 50 mm. Film weighs 7.25 mg. and is 1.41 × 10^{-3} cm. thick.

It is apparent in Fig. 7 that for the third sorption step the rate is distinctly slower than the first. (The rate for the second cycle was intermediate between the first and third.) However, for the fourth and fifth cycles the rate is essentially unchanged. The decrease in sorption rate for successive cycles is qualitatively similar to the results for acetone–cellulose nitrate; however, with the latter system the observed decrease in rate was much larger (15-fold increase in $t_{1/2}$ for five cycles) and the change in rate did not diminish for the later cycles.[7]

Measurements of the optical birefringence of the film used in the above study showed that the successive cycles caused an increase in orientation parallel to the direction of diffusion. The initial value of $(n_{\parallel} - n_{\perp})$ was -0.8×10^{-4} and after five cycles the value was $+2.6 \times 10^{-4}$ which means that the film changed from a very slight orientation in the plane of the film to a small orientation normal to the film.[18] This result is similar to that observed with cycling studies on cellulosic polymers. However, with polystyrene, although the rate of sorption becomes constant after about four cycles, the orientation does not. Specifically the above film was subject to four additional cycles and the observed birefringence increased (for the total of nine cycles) to $+4.6 \times 10^{-4}$ even though the rate of sorption did not change from the value for the fifth cycle. Apparently the rate of diffusion varies with orientation only for small amounts of the latter.

Cycling studies were also made at 30° for the methylene chloride–polystyrene system. For this system the change in orientation was very similar to that caused by diffusion of benzene. Thus for a set of four cycles at 30° with the methylene chloride vapor pressure going from 0 to 81 mm. the values of $(n_{\parallel} - n_{\perp})$ changed from -0.8×10^{-4} to $+2.0 \times 10^{-4}$. However the rate of sorption in this case actually *increased* slightly in going from the first to the second step and then showed no change for further cycles. Very similar results were observed for cycles between 0 and 62 mm. pressure.

We have no explanation for the differences between the results with benzene and methylene chloride. Quite possibly the smaller size of the methylene chloride molecule is a factor. However, the more important point is that for both systems the observed changes in rate upon cycling are quite small, very much smaller than observed with cellulose nitrate.

In spite of these conflicting kinetic data the results obtained so far for diffusion into polymers

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(18) An indication of the actual change in orientation needed to cause this change in birefringence is given by the studies on stretched films of polystyrene by Buchdahl and Nielson (*J. Applied Phys.*, **21**, 488 (1950)) who report that polystyrene films stretched 50% in length at 105° and suddenly chilled show an average change in birefringence of $\Delta n = 48 \times 10^{-4}$.

are quite consistent (at least for molecules of the size of acetone and benzene). Whether the polymer is polar like cellulose nitrate or polyvinylacetate or non-polar like polystyrene and independent of the character of the diffusing molecule, diffusion is Fickian if the polymer is above its second-order transition and anomalous if the polymer–solvent mixture is below T_g. Furthermore for systems below T_g the diffusion process causes increased orientation in the direction of diffusion. This change in the character of the diffusion at T_g is undoubtedly a result of the marked change in the mobility of polymer segments which occurs at the second order transition. Presumably above T_g the polymer-penetrant system can adjust to changes in penetrant concentration with sufficient rapidity that the normal process of hole formation is the rate-determining step and hence the diffusion is Fickian. The anomalous diffusion which occurs below T_g can formally be explained by postulating that the diffusion coefficient is a function of variables other than concentration. A more specific suggestion is that, because of the low segment mobility below T_g, the diffusion coefficient does not immediately reach its equilibrium value as the penetrant concentration changes, leading to a D which depends on time as well as concentration. As Crank and Park[3] have pointed out such an added dependence of D on time can easily lead to the sort of anomalous diffusion that is observed.

ITHACA, N. Y.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA, LOS ANGELES]

The Conversion of Ortho–Parahydrogen by Cuprous Acetate in Quinoline[1]

BY W. K. WILMARTH AND MAX K. BARSH

RECEIVED AUGUST 25, 1952

The conversion of ortho–parahydrogen by cuprous acetate in quinoline has been studied over the temperature range 60–100°. The rate of the conversion can be represented by the equation: $-d(p - H_2)/dt = 6.6 \times 10^{11} \exp. (-16{,}000/RT)$ (l. mole^{-1} min.$^{-1}$)^2(CuOAc)^2(H$_2$). It has been experimentally verified that the same activated intermediate is formed during the cuprous acetate-catalyzed hydrogenation of cupric acetate and the conversion process. This conclusion has been further substantiated by a calculation of the rate of hydrogenation from the rate constant for the parahydrogen conversion. The exchange of deuterium gas with a solution of cuprous acetate in quinoline has also been observed.

It was shown by Calvin[2] and subsequently by Wilmarth[3] that homogeneous catalytic hydrogenation of solutions of cupric acetate occurred at 100° and 38 cm. pressure, and that the autocatalytic reaction was catalyzed by one of the reduction products, the cuprous species. Other investigations by Tyson and Vivian[4a] and Fobes and Tyson[4b] on the magnetic properties of hydrogenated pyridine solutions of cupric and nickelous disalicylaldehyde, seemed to indicate that the hydrogenation of the cupric compound in pyridine solution did not involve reduction to a cuprous species, but instead involved the reduction of the salicylaldehyde to salicylyl alcohol. A comparison, however, of the similarities of the copper solution reactions in pyridine and quinoline, such as color change during hydrogenation and chemical nature of the solvent, led one to suspect that the reactions described by Calvin,[2] Wilmarth,[3] and Tyson and Vivian[4a] probably involved the same mechanism and reaction products. The possibilities that either the cuprous compounds were paramagnetic, or that the measurements of Tyson and Vivian[4a] were in error, were investigated by Wilmarth, Barsh and Dharmatti.[5]

Magnetic susceptibility measurements demonstrated that the cupric species was paramagnetic but that both the pure cuprous species and the direct hydrogenation products of the cupric species were diamagnetic. This was in contradiction to the results of Tyson and Vivian[4a] and of Fobes and Tyson,[4b] but was in substantial agreement with the conclusions of Calvin[2] and of Wilmarth.[3]

Calvin[2] also reported that ortho–parahydrogen conversion was not observed during hydrogenation with para-rich hydrogen, but that when the reduced solution was allowed to stand overnight, conversion did occur.

The main purpose of this investigation was to study the rates of conversion of ortho–parahydrogen by solutions of cuprous acetate in quinoline and, if possible, to relate the conversion process to the hydrogenation process. The latter was achieved through a study of the rate of ortho–parahydrogen conversion during and after hydrogenation, with para-rich hydrogen, of a solution of cuprous and cupric acetates in quinoline.

In addition, an exploratory study was made of the exchange of deuterium gas with a solution of cuprous acetate in quinoline.

Theoretical Considerations

In the presence of a suitable catalyst in a homogeneous system, ortho- and parahydrogen reach equilibrium as

$$(p\text{-H}_2) + \mathrm{C} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} (o\text{-H}_2) + C \qquad (1)$$

where C is the concentration of the catalyst. At equilibrium the ratio of k_1 to k_2 at room temperatures is known to be 3. The rate at which the

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[2] M. Calvin, *Trans. Faraday Soc.*, **34**, 1181 (1938).

[3] W. K. Wilmarth, Ph.D. Dissertation, University of California, Berkeley, 1942.

[4] (a) G. N. Tyson, Jr., and R. E. Vivian, THIS JOURNAL, **63**, 1403 (1941); (b) M. A. Fobes and G. N. Tyson, Jr., *ibid.*, **63**, 3530 (1941).

[5] W. K. Wilmarth, M. K. Barsh and S. S. Dharmatti, *ibid.*, **74**, 5035 (1952).