Diffusion in Glassy Polymers. I. Effects of Initial Concentration upon the Sorption of Organic Vapors in Polymers

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(Received October 17, 1960)

Kishimoto et al.1) have recently shown for a number of glassy polymer-organic vapor systems that when such a system is studied by the differential absorption technique, the sorption kinetics exhibits three types of non-Fickian anomalies as the initial concentration for each differential step increases. These non-Fickian anomalies are sigmoid type, pseudo-Fickian type and two-stage type. They also found that for amorphous systems the differential absorption process changes to the normal Fickian type in the vicinity of a penetrant concentration at which the given polymer-vapor mixture undergoes glass transition at the temperature of the experiment. The study reported in the present paper is concerned with integral absorption experiments in which the initial concentrations are taken in the regions corresponding to these four different types of differential absorption processes. It is expected that such a study will provide us with information about how small the concentration increment of each step should be in order that the absorption process may exhibit the behavior regarded as being characteristic of the initial concentration of the experiment. We have from existing literatures a vast amount of available experimental data for the integral absorption of vapors in polymeric solids2−16).

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1) A. Kishimoto, H. Fujita, H. Odani, M. Kurata and M. Tamura, *J. Phys. Chem.*, **64**, 594 (1960).

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

3) G. S. Park, ibid., **46**, 684 (1950).

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

5) S. Prager and F. A. Long, *J. Am. Chem. Soc.*, **73**, 4072 (1951).

6) G. S. Park, *Trans. Faraday Soc.*, **47**, 1007 (1951).

7) A. T. Hutcheon, R. J. Kokes, J. L. Hoard and F. A. Long, *J. Chem. Phys.*, **20**, 1232 (1952).

8) R. J. Kokes, F. A. Long and J. L. Hoard, ibid., **20**, 1711 (1952).

9) G. S. Park, *J. Polymer Sci.*, **11**, 97 (1953).

10) S. Prager, E. Bagley and F. A. Long, *J. Am. Chem. Soc.*, **75**, 1255 (1953).

11) F. A. Long and R. J. Kokes, ibid., **75**, 2232 (1953).

12) R. J. Kokes and F. A. Long, ibid., **75**, 6124 (1953).

13) F. A. Long and L. J. Thompson, *J. Polymer Sci.*, **15**, 413 (1955).

14) M. J. Hayes and G. S. Park, *Trans. Faraday Soc.*, **51**, 1134 (1955).

15) A. Kishimoto and K. Matsumoto, *J. Phys. Chem.*, **63**, 1529 (1959).

16) H. Fujita, A. Kishimoto and K. Matsumoto, *Trans. Faraday Soc.*, **56**, 424 (1960).

However, the majority of them deal with experiments started from zero initial concentration, and data from non-zero concentrations are yet limited to a very few systems.

The systems chosen in this work are atactic polystyrene + benzene and cellulose nitrate + acetone, both at 25°C. Successive differential absorptions of these systems have been described in detail in Ref. 1. In the following pages we present data from experiments with the polystyrene system in greater detail, and only partial data are given for the cellulose nitrate system.

Experimental

Materials.—The atactic polystyrene used was a commercial product "Lustrex hi-flow 77-234" and had a viscosity-average molecular weight of 2.2×10^5. The cellulose nitrate was a sample obtained from Fuji Photo Co. The intrinsic viscosity in acetone at 20°C and the nitrogen content (determined by the Lunge method) were 2.51 dl./g. and 11.95%, respectively. The polymer films used for sorption experiments were obtained by the same procedure reported elsewhere[1]. The penetrants were of A. R. grade.

Apparatus and Procedure.—The sorption apparatus used was practically the same as that reported elsewhere[1]. For absorption experiments the integral absorption technique was employed; i. e. a given polymer film was suspended from a sensitive quartz spring in a sorption tube and was equilibrated with the vapor of a given penetrant at a desired pressure p_i (including zero). Then the pressure was suddenly increased to a higher pressure p_f and the absorption process was followed by measuring the extention of the spring as a function of time. Although the term "integral" was previously referred to experiments with pressure differences ($\Delta p=p_f-p_i$) of relatively large magnitudes[1], results reported in this paper also include those obtained from "differential" absorptions in which Δp is sufficiently small. All the measurements were conducted at 25°C. This temperature is well below the glass transition temperatures of the respective polymers in their dry state[17].

Results and Discussion

Atactic Polystyrene—Benzene System.—As described in the previous paper[1], the successive differential absorptions for this system changed with the initial concentration according to the following scheme.

Sigmoid type → pseudo-Fickian type → two-stage type → Fickian type.

We studied integral absorptions for this system by choosing the initial concentrations in the regions corresponding to these four types of differential absorption.

Integral Sorptions from Initial Concentrations Corresponding to Differential Absorptions of Sigmoid Type. — Figure 1 gives data of integral absorptions from zero pressure, and also includes partial results from the desorption runs; the solid lines refer to absorption and the dashed lines to desorption. These data were taken on films 2.40×10^{-3} cm. thick.

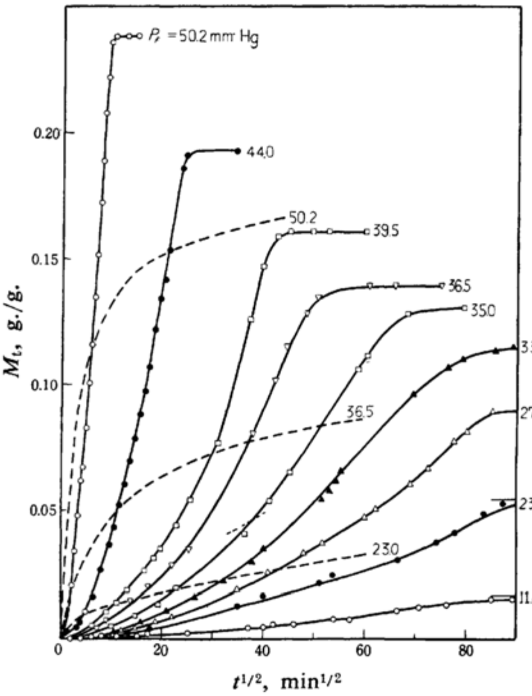

Fig. 1. Integral absorptions from and desorptions to zero pressure for atactic polystyrene at 25°C. p_f is the final pressure of a particular run. M_t is the weight of vapor absorbed or desorbed by mass of the polymer at time t. Solid lines, absorption; Dashed lines, desorption. Film thickness $=2.40\times10^{-3}$ cm.

The integral absorption processes are all non-Fickian over the entire range of vapor pressures studied. It is seen that even for the largest pressure interval the shape of the absorption curve is sigmoid. In all cases, the initial rate of desorption is greater than that of the corresponding absorption.

Long and Kokes[11] found that the integral absorptions from zero pressure were Fickian type when the final pressures were above the value corresponding to the equilibrium concentration at which the given polymer-penetrant mixture undergoes glass transition at the temperature of the experiment. However, it is seen from Fig. 1 that this is not the case with our atactic polystyrene—benzene system. The equilibrium concentration for $p_f=50.2$ mmHg is well above the critical concentration, 0.191

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[17] H. Mark and A. V. Tobolsky, "Physical Chemistry of High Polymeric Systems", Interscience Pub. Inc., New York (1950), p. 347.

g./g., for this system to undergo glass transition at 25°C[1]. Nevertheless, the absorption for this pressure is evidently non-Fickian.

In Fig. 1 it is also noted that the absorption curves show a pronounced dependence upon the pressure difference. Many experimental results[1,4,8,9,11,13,18] show that when a given polymer-penetrant mixture is in the glassy state, the absorption processes depend not only upon the concentration of penetrant but also upon other factors, probably the time. Under such circumstances we are not able to evaluate the mutual diffusion coefficient of a given system by using the method which uses measurements of the initial rate of absorption[15,19]. We here choose the value of $1/(t/l^2)_{1/2}$ to measure the overall rate of each absorption curve, where l is the thickness of the film, t is time, and $(t/l^2)_{1/2}$ is the value of t/l^2 when the amount of vapor in the film reaches one half of the final equilibrium value.

The values of $1/(t/l^2)_{1/2}$ determined from the data of Fig. 1 are plotted semi-logarithmically against C_f, the concentration of benzene at absorption equilibrium, in Fig. 2. For comparison the values calculated from the data of Park for the same kind of system[6] are included. It is seen that above 0.12 g./g. of C_f our data for $\log[1/(t/l^2)_{1/2}]$ increase almost linearly with increasing C_f and the shape of this plot is similar to that obtained from Park's data. However, the relative positions of the two curves are different from each other. This discrepancy may be attributed to the difference in thickness of the films used in the two studies*.

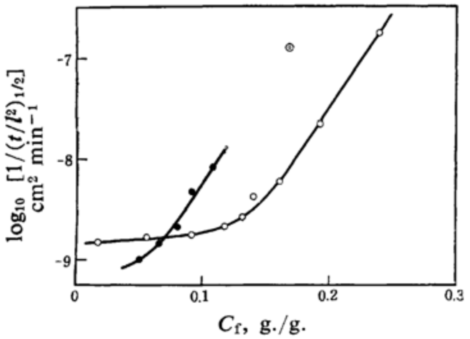

Fig. 2. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and final equilibrium concentration C_f for atactic polystyrene–benzene at 25°C. $(t/l^2)_{1/2}$ is the values of t/l^2 when the amount of vapor in polymer reaches one half of the final equilibrium value; l is the thickness of film and t is time. $C_i=0$. ○, $l=2.40\times10^{-3}$ cm.; ◎, $l=1.61\times10^{-2}$ cm.: ●, Park's data. $l=1.80\times10^{-2}$ cm. (These values have been calculated from the results given in Table I of Park's paper.[6]).

Integral absorptions from the initial concentration $C_i=0.095$ g./g. to several higher C_f were also investigated by using films of 2.40×10^{-3} cm. thick. Although the results are not given here, the absorption processes were of sigmoid type and the dependence of $1/(t/l^2)_{1/2}$ upon the difference between the initial and final concentrations, $\Delta C(=C_f-C_i)$, was similar to that obtained for the series with $C_i=0$.

In a summary it is concluded that in the region of initial concentrations C_i where differential absorptions are of sigmoid type, absorption rates depend markedly upon the final concentration, C_f, or the concentration increment, C_f-C_i, and this dependence is not affected so appreciably by the value of C_i.

Integral Absorptions from Initial Concentrations Corresponding to Differential Absorptions of Pseudo-Fickian Type.—Integral absorptions from $C_i=0.118$ and 0.132 g./g. were investigated by using films of 2.40×10^{-3} cm. thick. Although the results are not given here, the curves are very similar to those from zero initial concentration reported by Park for the polystyrene–methylene chloride system at 25°C[9] and also those by Long and Kokes for the same system at 30°C[11]. That is, for so small values of Δp as to give only 0.010～0.015 g./g. concentration increment, the shape of absorption curves was of pseudo-Fickian type, but for larger values of Δp the absorption curves changed to the sigmoid type and this feature persisted up to the largest of the Δp investigated.

The values of $1/(t/l^2)_{1/2}$ increase with ΔC, but to a less extent than in the case of integral absorptions from initial concentrations corresponding to differential absorption of sigmoid type.

Integral Absorptions from Initial Concentrations Corresponding to Differential Absorptions of Two-stage Type.—Integral absorptions from $C_i=0.160$, 0.169 and 0.181 g./g. were studied with films of 2.40×10^{-3} cm. thick. Figure 3 gives data from a series of absorption experiments from $C_i=0.160$ g./g. For small Δp the curves are similar in shape and show distinctly the two-stage characteristics, but as Δp increases the two-stage character becomes less apparent and the inflection point on the second stage portion shifts markedly to the short time region. These

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

[19] R. M. Barrer, *J. Phys. Chem.*, **61**, 178 (1957); R. M. Barrer and R. R. Ferguson, *Trans. Faraday Soc.*, **54**, 989 (1958).

* As seen in Fig. 2, the point obtained from an experiment with a film of 1.61×10^{-2} cm. thick appears at a smaller value of C_f than do the plots obtained with a film of 2.40×10^{-3} cm. thick.

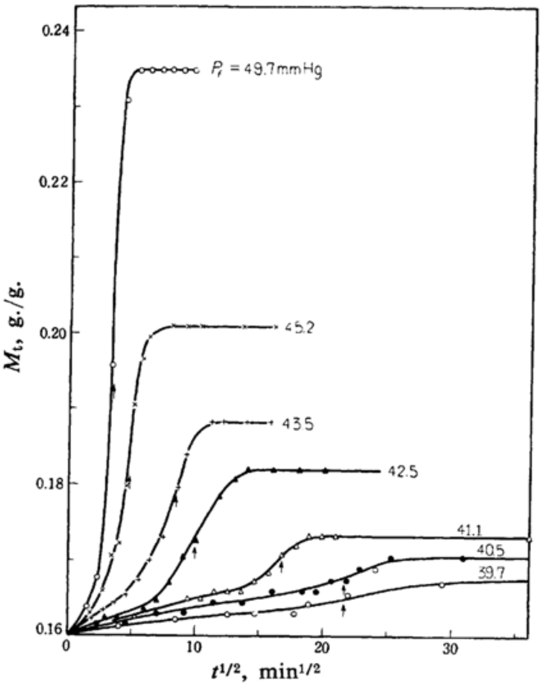

Fig. 3. Integral absorptions from a fixed non-zero initial pressure to different final pressures for atactic polystyrene–benzene at 25°C. Initial pressure $p_i = 39.3$ mmHg. Film thickness $= 2.40 \times 10^{-3}$ cm.

results are similar to those published by Long and Richman for the cellulose acetate–methyl iodide system at 40°C[20]. The data with $C_i = 0.169$ and 0.181 g./g. showed the general trend similar to that obtained for $C_i = 0.160$ g./g. Thus we see that the integral absorptions also depend strongly on Δp when the experiments start from initial concentrations where differential absorption curves exhibit the two-stage behavior.

For small values of Δp the contribution of the first stage absorptions to the total concentration increment is significant, but the time taken to attain the quasi-equilibrium of the first stage is much shorter than that taken for the total absorption process. Therefore, for this type of absorption curve we may use the quantity $1/(t/l^2)_{1/2}$ as an approximate measure of the overall rate of absorption. The values of this quantity determined from the data of Fig. 3 and the similar data at $C_i = 0.169$ and 0.181 g./g. are plotted semi-logarithmically against ΔC in Fig. 4. It is seen that the dependences of $1/(t/l^2)_{1/2}$ on ΔC for the three C_i values are hardly different from one another and that they are all so marked that an extremely small pressure increment must be used in this region of C_i in order to obtain an absorption curve characteristic of a given initial concentration.

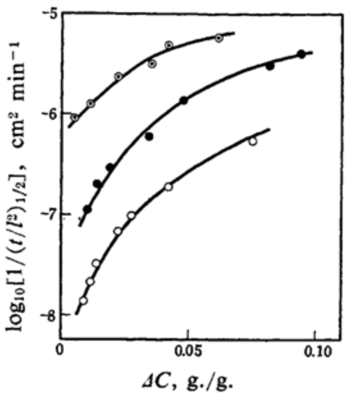

Fig. 4. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and concentration difference ΔC for absorption of benzene in atactic polystyrene at 25°C. ○, $C_i = 0.160$ g./g.; ●, $C_i = 0.169$ g./g.; $C_i = 0.181$ g./g. Film thickness $= 2.40 \times 10^{-3}$ cm.

Integral Absorptions from Initial Concentrations Corresponding to Differential Absorptions of Fickian Type.—According to our previous investigation[1], the critical concentration of benzene in polystyrene at which the system undergoes glass transition at 25°C is 0.191 g./g. Choosing this concentration as C_i we carried out integral absorption experiments for sample films which covered a five-hold range of thickness. We also performed similar experiments with $C_i = 0.235$ g./g. for two films of different thicknesses. The results of these measurements are as follows:

a) Both absorption and desorption curves are initially linear; for absorption this linearity holds over about 70% of the total concentration increment and for desorption this is limited to about 50% of the total concentration increment.

b) Above the linear regions both absorption and desorption curves are concave against the time axis.

c) Desorption is always slower than absorption irrespective of the magnitude of ΔC.

d) With the increase of ΔC absorption becomes faster and this is also the case for desorption.

These are the features of the true Fickian diffusion in which the diffusion coefficient increases with increasing concentration[21]. However, it was found that;

e) Data from varying thickness experiments could not be reduced to a single curve when plotted against the variable t/l^2; for the same

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[20] F. A. Long and D. Richman, *J. Am. Chem. Soc.*, **82**, 513 (1960).

[21] H. Fujita, A. Kishimoto and H. Odani, *Suppl. Progr. Theor. Phys.*, **10**, 210 (1959).

value of ΔC thicker films gave curves which are located to the left of the curve obtained for thinner films, the behavior very similar to that exhibited by integral absorption curves started with zero initial concentration.

Because of this last feature it is concluded that even in the region of benzene concentrations where the given mixture is considered to be in the rubbery state the absorption process of benzene in atactic polystyrene is not altogether controlled by the purely Fickian mechanism.

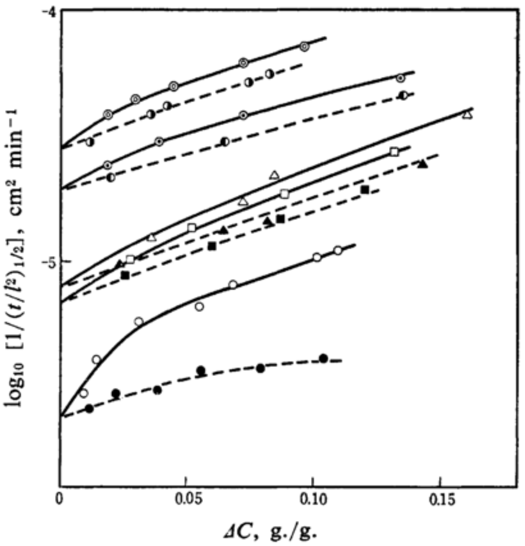

Fig. 5. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and ΔC for atactic polystyrene —benzene at 25°C.

	l, cm.	Absorptions	Desorptions
(a) $C_i=0.191$ g./g.	2.40×10^{-3}	○	●
	7.67×10^{-3}	□	■
	1.12×10^{-2}	△	▲
(b) $C_i=0.235$ g./g.	1.15×10^{-2}	⊙	◐
	1.70×10^{-2}	◎	◑

In Fig. 5 are plotted the values of $1/(t/l^2)_{1/2}$ determined from these measurements as a function of ΔC, with l and C_i as parameters. It is seen that for both C_i the thicker films give higher values of $1/(t/l^2)_{1/2}$ when compared at the same values of ΔC. This is substantially equivalent to the feature (e) stated above. Finally, one may remark that the dependence of $1/(t/l^2)_{1/2}$ on ΔC in this region of C_i is much milder than those obtained in the regions of C_i where differential absorptions are non-Fickian.

It is generally conceived that when the system is in the glassy state there must be a time delay in the establishment of the equilibrium value of the diffusion coefficient and/or of the concentration on the sample surface. This may cause the absorption process of the system not to obey the purely Fickian diffusion mechanism. In the case treated above it is considered that the polymer-vapor mixtures were in the rubbery state at the start of the absorption experiments. Nevertheless, the absorption processes measured exhibited a non-Fickian feature (the film thickness effect). This appears to indicate that even when the mixture is in the rubbery state the diffusion of penetrant does not follow the Fickian mechanism if the penetrant concentration is not sufficiently above the critical concentration corresponding to the temperature of the experiment. Kishimoto and Matsumoto[22] have recently shown with polyvinyl acetate and polymethyl acrylate that integral absorptions of organic vapors into these amorphous polymers cannot be interpreted in terms of the purely Fickian mechanism when the temperatures of the systems are only 10 to 20°C above the glass transition temperatures of respective polymers. Although the effect of rising temperature may not exactly be equivalent to that of increasing diluent concentration, our observations of the non-Fickian feature at concentrations above the critical concentration appear to have a close correlation to those of Kishimoto and Matsumoto. A more detailed study of the sorption behavior in the region of initial concentrations above the critical concentration is now in progress in this laboratory and will be reported in a forthcoming article.

In a summary, it may be concluded as follows: The sorption rate of benzene into atactic polystyrene depends strongly on the concentration of benzene in the region of low C_i, the dependence becomes milder with increasing concentration of benzene and almost vanishes in the concentration region somewhat above the critical concentration for this system. Just above the critical concentration, the effect of sample thickness still exists, though the differential absorption curves in this region appear to have the shape expected from the purely Fickian mechanism.

Cellulose Nitrate — Acetone System.—The successive differential absorption curves for this system change their shape according to the following scheme[1]:

Sigmoid type → pseudo-Fickian type → two-stage type → sigmoid type.

We studied the integral sorptions from zero initial concentration and also from a non-zero initial concenration corresponding to a differential absorption of two-stage type.

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[22] A. Kishimoto and K. Matsumoto, private communication.

Integral Absorptions and Desorptions from and to Zero Initial Concentration.—Integral absorptions and desorptions from and to zero pressure were studied in the range of acetone pressure from 8.5 to 147 mmHg. The features of the curves obtained exactly resemble those for the atactic polystyrene—benzene system. That is, the integral absorption processes are all non-Fickian of sigmoid type over the entire range of vapor pressures studied and the initial rate of desorption is greater than that of the corresponding absorption for all cases. The absorption curves show a pronounced dependence on the pressure difference and the general feature of this dependence is very similar to that observed for the atactic polystyrene—benzene system.

In accordance with the atactic polystyrene—benzene system, we choose the quantity $1/(t/l^2)_{1/2}$ as a measure of absorption rate. Figure 6 gives the plots of $\log[1/(t/l^2)_{1/2}]$ against C_f, and the corresponding data for the atactic polystyrene—benzene system are also indicated for the sake of comparison. It is seen that the values of $1/(t/l^2)_{1/2}$ increase rapidly in the region of medium C_f and the shape of the curve in this region is quite similar to that for atactic polystyrene—benzene system. Also it will be seen that in the region of high C_f the plots approach a constant value. These observations suggest that there is no close correlation between the dependence of integral absorption rates upon the concentration of penetrant and the molecular features of the polymer, such as crystallinity and chain stiffness.

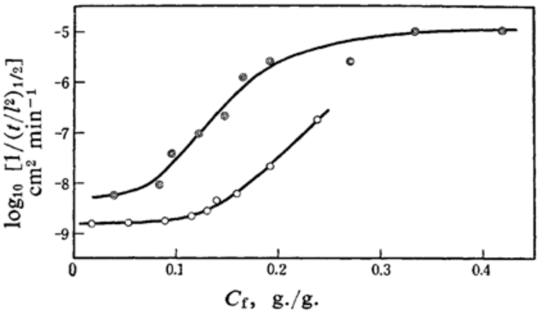

Fig. 6. Logarithmic correlation plots of $1/(t/l^2)_{1/2}$ and C_f for cellulose nitrate—acetone and for atactic polystyrene—benzene at 25°C. $C_i=0$. Film thickness $=2.40\times10^{-3}$ cm. ◎, cellulose nitrate—acetone; ○, atactic polystyrene—benzene.

Integral Absorptions from a Non-zero Initial Concentration Corresponding to a Differential Absorption of Two-stage Type.—Figure 7 gives data from integral absorption experiments obtained with $C_i=0.192$ g./g. It is observed that the general feature of these curves is very similar to that for the atactic polystyrene—benzene system shown in Fig. 3. However, we may notice some differences between the two. First, absorption rates of the first stage of the two-stage sorption process for the cellulose nitrate—acetone system are much faster than those for the atactic polystyrene—benzene system. Second, in the former system the two-stage character first becomes increasingly apparent as Δp increases, accompanied with a marked shift of the inflection point to the short time region and a rapid enhancement of the second stage rate.

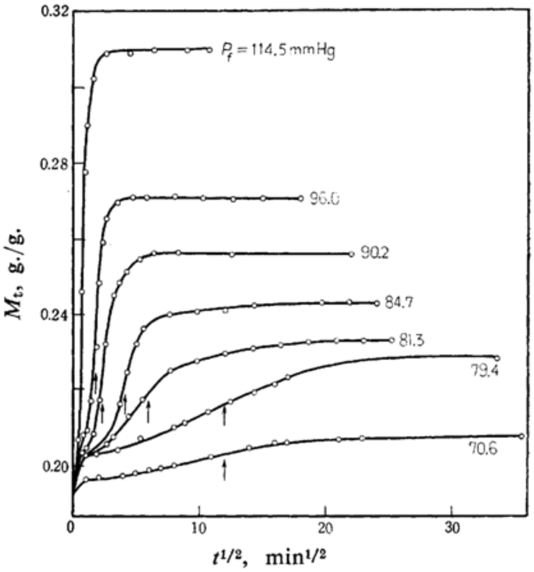

Fig. 7. Integral absorptions from a fixed non-zero initial pressure to different final pressures for cellulose nitrate—acetone at 25°C. $p_i=63$ mmHg. Film thickness $=2.40\times10^{-3}$ cm.

In a summary, it may be concluded that in the glassy state the dependence of integral absorption rates upon penetrant concentration for the cellulose nitrate—acetone system does not differ markedly from that for the atactic polystyrene—benzene system.

We wish to thank Professor H. Fujita and Dr. A. Kishimoto of this University for advice given during the course of this investigation. The study reported in this paper was supported in part by the Ministry of Education to which grateful acknowledgment is made.

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