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Interaction of CO_2 with a Series of Detached Organic Films

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Synopsis

Data obtained from gaseous sorption isotherms of CO_2 on eight organic films at three temperatures and three pressures were evaluated for evidences of chemisorption and physical adsorption. The rates of sorption, affected by both temperature and pressure, were analyzed by calculating the parameters of the Elovich equation and those of Barrer's solution of Fick's law for diffusion. Through a consideration of the Elovich parameters, the sorption coefficients, the limiting diffusion coefficients, and the activation energies for diffusion it appears that the rate of interaction of CO_2 with these organic films is primarily a diffusion-controlled process.

INTRODUCTION

It was anticipated that investigations of the surface properties of a series of eight unpigmented coatings might supply information that would lead to an understanding of filiform corrosion. Consequently, water vapor sorption by detached samples of these films was reported,[1] in which a rate effect in the water sorption was qualitatively observed. In a later investigation,[2] equilibrium adsorption-desorption isotherms were obtained for water vapor on the eight films, from which were calculated pore size distributions based upon the assumption that the hysteresis effect observed is caused by capillary condensation and the lowering of vapor pressure over a concave meniscus. Most recently, a very pronounced rate effect on the sorption of CO_2 on this series of films has been observed. Quantitative measurements of these rates and a theoretical interpretation of the results are given in the present paper.

MATERIALS AND EXPERIMENTAL PROCEDURE

The eight organic polymer films cast by the Barrington Laboratory of the American Can Company were removed from tin plate by the mercury amalgamation technique. The eight films along with some of their physical properties are listed in Table I.

The sorption data were determined by an eight-place gravimetric apparatus previously described.[1] The eight films were simultaneously exposed to controlled pressures of carbon dioxide purified by fractionation

TABLE I
Specifications of Films Examined

Film number	Type	Applied weight, mg./cm.^{2}	Free film thickness $\times 10^4$, cm.	Filiform corrosion performance[a]
1	Oleoresinous (common resin–oil coating)	0.85	7.9	6
2	Phenolic (100% phenolic, oil-soluble heat-hardening resin-oil coating)	0.66	8.9	8
3	Vinyl (vinyl chloride–vinyl acetate copolymer, solution coating)	1.01	10.2	1
4	Vinyl (same as coating 3)	0.50	5.6	2
5	Alkyd (conventional glycerol–phthalic acid, oil-modified coating)	0.85	7.9	3
6	Epoxy (epichlorhydrin–dihydric phenol heat-hardening coating)	0.66	7.1	4
7	Hydrocarbon (polyisobutylene coating)	0.70	8.6	5
8	Hydrocarbon (phosphoric acid-catalyzed polyisobutylene coating)	0.78	8.9	7

[a] Higher number indicates better ability to prevent filiform corrosion.

before use. Sorption of CO_2 was investigated extensively at combinations of three different pressures (117.5, 326.5, and 461.0 torr) and three different temperatures (−76.5, −63.5, and −45.3°C.). Temperatures were controlled with slush baths and measured with an ammonia vapor pressure thermometer.

The rate of CO_2 sorption was followed for about 30 hr. in each experiment. Sorption was so slow that equilibrium isotherms could not be measured effectively. In most cases extrapolation of the rate curve allowed the equilibrium value to be estimated, and, for a few samples, sorption had essentially ceased by the end of the rate run at the higher temperatures. In an attempt to achieve equilibrium isotherms, runs were made at 0 and 25°C. Even at these temperatures, only two films, 1 and 8, achieved equilibrium within a reasonable time. The others continued to gain weight after 24 hr., especially the phenolic film, whose rate of uptake was slowest in all runs.

RESULTS

The sorption rate curves of CO_2 on the eight organic films were of similar shape. The plots shown in Figure 1 are representative of the data ob-

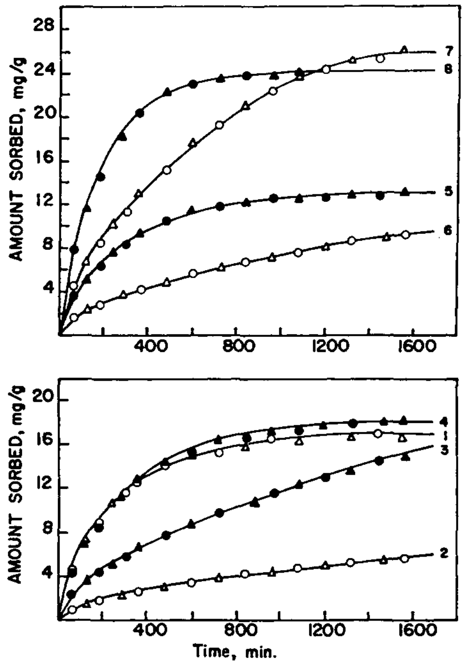

Fig. 1. Rate of CO_2 sorption on the eight organic films.

tained. Two runs plotted for each film show the degree of reproducibility. As the temperature was raised the general trend was for faster rates but less overall uptake of gas. Total amount sorbed increased with pressure in all cases.

Where it was possible to extrapolate to equilibrium values at both −63.5 and −45°C., isotherms were plotted and isosteric heats were calculated using the Clausius-Clapeyron equation. The required pressures at the two different temperatures were read from the isotherm plots at positions corresponding to a constant amount sorbed. Table II summarizes the

TABLE II
Isosteric Heats of Sorption for CO_2 on Organic Films Between −45.3 and −63.5°C.[a]

Sample no.	Isosteric heat for various amounts sorbed, kcal./mole 2 mg./g.	4 mg./g.	6 mg./g.	8 mg./g.	10 mg./g.	12 mg./g.	14 mg./g.	16 mg./g.	18 mg./g.	20 mg./g.
1	3.2	4.1	4.8	5.5	6.1	—	—	—	—	—
4	4.7	4.4	4.5	4.8	5.2	5.5	5.4	—	—	—
5	3.4	3.8	4.7	5.5	—	—	—	—	—	—
7	2.8	2.8	2.8	2.9	3.2	3.6	4.2	4.7	4.8	4.6
8	4.8	4.7	4.8	4.9	5.2	5.6	6.2	—	—	—

[a] $H_{\text{sublimation}}$ for CO_2 at −56.2°C. is 5.8 kcal./mole.

results of these calculations. No attempt was made to fit the equilibrium data to a theoretical isotherm because of the small number of values available.

Chemisorption Kinetics

A preliminary investigation in this laboratory indicated that the rate effect of the CO_2 interaction could be satisfactorily interpreted on the basis of activated chemisorption. Proceeding from this premise, the CO_2 rate data from this investigation were tested with the empirical Elovich equation[3] which fits a large body of chemisorption data:

$$dq/dt = a \exp \left\{ -\alpha q \right\} \qquad (1)$$

where q is the amount sorbed at time t, and a and α are constant during any one experiment. Thus, the rate decreases exponentially with the amount of gas adsorbed. Assuming that $q = 0$ at $t = 0$, the Elovich equation in its integrated form is:

$$q = (1/\alpha) \ln (t + t_0) - (1/\alpha) \ln t_0 \qquad (2)$$

with $t_0 = 1/a\alpha$. Equation (2) has the form of a straight line and when q is plotted as a function of $\ln (t + t_0)$, it provides a test of the Elovich equation. In this investigation the method of Sarmousakis and Low[4] was used. Here the Elovich parameters are calculated at various times along the rate curve and the constancy of the parameters throughout an experiment along with temperature and pressure coefficients of these values is a measure of the degree to which the equation fits the data. When q, the amount sorbed, equals zero, it is seen from eq. (1) that a represents the initial rate of adsorption. Since mass action of the gas governs this initial rate a is proportional to the gas pressure and increases with rising tempera-

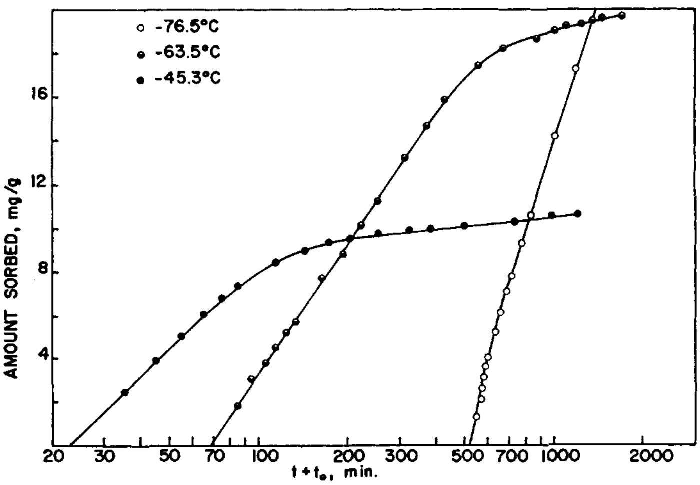

Fig. 2. Elovich plots for CO_2 sorption on sample 1 at 461.0 torr.

TABLE III
Values of a from Elovich Equation for CO_2 on Organic Films

Temp., °C.	Pressure, torr	a, mg./g.-min.							
		Film 1	Film 2	Film 3	Film 4	Film 5	Film 6	Film 7	Film 8
−76.5	117.5	0.015	0.0035	0.0088	0.013	0.011	0.0040	0.015	0.024
	326.5	0.030	0.0063	0.016	0.034	0.023	0.0082	0.024	0.064
	461.0	0.037	0.0072	0.018	0.046	0.024	0.0074	0.026	0.076
−63.5	117.5	0.040	0.0062	0.0094	0.044	0.022	0.0066	0.023	0.072
	326.5	0.096	0.0086	0.020	0.094	0.062	0.014	0.050	0.16
	461.0	0.11	0.0095	0.025	0.11	0.090	0.016	0.058	0.22
−45.3	117.5	0.10	0.0067	0.022	0.088	0.060	0.024	0.062	0.18
	326.5	0.20	0.012	0.046	0.22	0.14	0.051	0.15	0.38
	461.0	0.25	0.016	0.065	0.28	0.23	0.063	0.18	0.35

TABLE IV
Values of α from Elovich Equation for CO_2 on Organic Films.

Temp., °C.	Pressure, torr	α, g./mg.							
		Film 1	Film 2	Film 3	Film 4	Film 5	Film 6	Film 7	Film 8
−76.5	117.5	0.12	0.42	0.28	0.14	0.18	0.32	0.13	0.073
	326.5	0.064	0.36	0.13	0.66	0.093	0.28	0.050	0.045
	461.0	0.050	0.28	0.079	0.48	0.063	0.17	0.028	0.033
−63.5	117.5	0.21	0.68	0.18	0.24	0.30	0.26	0.098	0.16
	326.5	0.15	0.28	0.094	0.14	0.16	0.16	0.062	0.096
	461.0	0.12	0.22	0.072	0.12	0.16	0.14	0.047	0.082
−45.3	117.5	0.56	0.46	0.31	0.40	0.65	0.54	0.26	0.50
	326.5	0.23	0.24	0.16	0.26	0.32	0.30	0.17	0.19
	461.0	0.16	0.20	0.14	0.22	0.32	0.26	0.12	0.11

ture. It is thought that α represents the rate of sorption site decay for a given site concentration and rate of sorption. Experimentally, α normally decreases slightly with increasing initial pressure. With rising temperature, α decreases depending on the gas–solid system studied.

Tables III and IV give the values for the Elovich parameters calculated in this investigation. At −76.5°C., where the rate is slowest and thus the experimental accuracy the greatest, the average deviation during any experiment varied ± 5% for both a and α. At higher temperatures the deviations were somewhat greater.

From these values of a and α in Tables III and IV, t_0's were calculated and Elovich plots of q versus $\ln (t + t_0)$ were made according to eq. 2. Figure 2 shows the Elovich plot behavior obtained with film 1 at three temperatures and constant pressure. Linear sections are obtained with abrupt discontinuities appearing at the higher temperatures. Other films showed similar behavior.

Diffusion

A second interpretation of the rate effect in sorption of CO_2 is that a slow diffusion process is taking place. Consequently, the rate data were treated by diffusion theory. Of specific interest in diffusion studies is the diffusion coefficient D, which appears in Fick's laws of diffusion.[5]

The technique used to determine the diffusion coefficient and its concentration dependence from experimental data depends upon the diffusion system under study. Two basic experimental methods are used when investigating the diffusion of gases through membranes. The first method involves permeation, a steady-state procedure in which the rate of penetrant transfer through a membrane is determined.

The second technique, a sorption method, is a transient state procedure in which the mass of penetrant gained or lost by the membrane when exposed to different, but constant, vapor activity is followed gravimetrically. This is the experimental technique used in this study. As gas penetrates the film from both sides, the rate of weight increase and the final equilibrium values are recorded. Barrer[6] solved Fick's laws of diffusion for the general case of sorption kinetics. When the boundary conditions for the experimental technique used here are applied, the result is:

$$q/q_e = 1 - (8/\pi^2) \sum_{m=0}^{\infty} [2/(2m + 1)^2] \exp \{-(2m + 1)^2\pi^2 Dt/L^2\} \qquad (3)$$

where D is the diffusion coefficient, L is the film thickness, $m = 0, 1, 2, \ldots$, q is the weight change (sorption or desorption) at time t, and q_e is the equilibrium weight change.

Equation (3) can be simplified if attention is turned to the value of t/L^2 for which $q/q_e = {}^1/_2$. The equation can then be solved directly for D, and Crank[5] gives the approximate expression:

$$D = 0.049/(t/L^2)_{1/2} \qquad (4)$$

The error in this approximate method for determining D is given by Crank as 0.001%. If D is concentration-dependent, eq. (4) would give an average diffusion coefficient, $\bar{D}$. It is also possible to deduce an average diffusion coefficient from the initial slope of the reduced sorption curve, that is q/q_e versus t/L. Thus in the early stages, for a constant diffusion coefficient D and sheet thickness L, Crank derived the expression:

$$q/q_e = (4/\sqrt{\pi})(Dt/L^2)^{1/2} \tag{5}$$

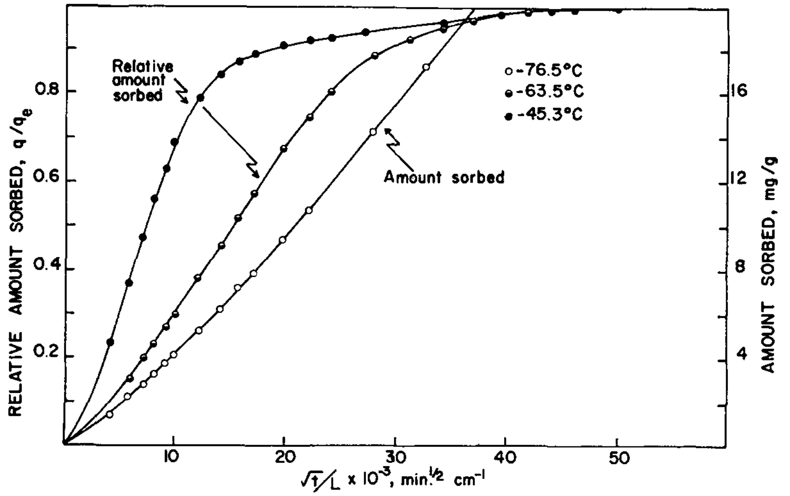

Fig. 3. Reduced sorption curves for CO_2 sorption on sample 1 at 461.0 torr.

If the initial slope S of the reduced sorption curve is observed in a sorption experiment in which D is concentration dependent, then the average diffusion coefficient $\bar{D}$ is approximately:

$$\bar{D} = (\pi/16)S^2 \tag{6}$$

By taking the slope at $q/q_e = {}^1/_2$, it is seen that eqs. (5) and (6) are equivalent.

These diffusion expressions hold only for Fickian diffusion, defined experimentally when the reduced sorption curve is linear over most of its course. Sorption which is non-Fickian is defined as that which does not give an initially linear reduced sorption curve. The calculation of diffusion coefficients in these cases is thus confused. The sorption half times are known, however, and an average sorption coefficient $\bar{R}$ has been defined by Hunt et al.:[7]

$$\bar{R} = 0.0049/(t/L^2)_{1/2} \tag{7}$$

$\bar{R} = \bar{D}$ for reduced sorption curves which are linear through their half-times. It can be further stated that:

$$\lim_{a\to 0} \bar{R} = \lim_{a\to 0} \bar{D} = D_0 \tag{8}$$

TABLE V

Values of the Average Sorption Coefficients $\bar{R}_s$ and Limiting Division Coefficients D_0 for CO_2 on Organic Films

Temp., °C.	Pressure, torr	R_s and $D_0 \times 10^{12}$, cm.²/sec.[a]							
		Film 1	Film 2	Film 3	Film 4	Film 5	Film 6	Film 7	Film 8
−76.5	461.0	(10.33)	(20.7)	(6.87)	(8.20)	(7.17)	(2.20)	(12.87)	(20.38)
	326.5	(7.93)	(1.73)	(5.27)	(6.13)	(5.70)	(1.78)	(9.38)	(16.50)
	117.5	(4.03)	(0.995)	(2.53)	(2.77)	(2.80)	(1.03)	(4.63)	(7.78)
−63.5	461.0	3.48	(2.68)	(9.00)	1.47	2.93	(3.67)	1.82	5.57
	326.5	3.20	(2.22)	(6.90)	1.34	2.70	(2.97)	1.68	4.90
	117.5	2.40	(1.27)	(3.30)	0.917	1.90	(1.62)	1.39	3.52
	D_0	1.08	—	—	0.35	0.74	—	0.66	1.55
−45.3	117.5	15.12	(3.65)	3.68	4.77	12.15	2.60	7.50	23.07
	326.5	13.60	(2.93)	3.48	4.73	10.20	2.40	6.13	18.52
	461.0	9.77	(1.53)	2.68	3.23	7.72	1.90	4.22	11.08
	D_0	4.17	—	1.26	1.05	3.90	0.91	1.98	3.90

[a] Numbers in parentheses are the slope of the curve q versus $\sqrt{t/L}$. $\bar{R}_s$ values could not be calculated since equilibrium sorption values were not known.

where a is the activity of the vapor and D_0 is a limiting diffusion coefficient.

Reduced sorption curves were plotted for the CO_2 rate data. A few representative curves for film 1 at three temperatures and constant pressure are shown in Figure 3. In cases where the equilibrium value of amount sorbed was not reached, the instantaneous amount sorbed was plotted versus $\sqrt{t/L}$. The overall shape of the curve in this case will be the same, linearity still being achieved if diffusion is taking place.

All of the reduced sorption curves showed long sections of linearity but deviated from linearity near the origin. Thus the initial slope could not be used to calculate diffusion coefficients. However, the linear portion of the plots extended through $q/q_e = 0.5$ in all cases. Therefore, eq. 7 was used to calculate average sorption coefficients, $\bar{R}_s$. The results of these calculations are collected in Table V. Listed also are the limiting diffusion coefficients, D_0, obtained by extrapolating the pressure-dependent $\bar{R}_s$ values to zero CO_2 activity. In the cases where the equilibrium value of amount sorbed was not known, the slope of the curve q versus $\sqrt{t/L}$ is given in parentheses instead of $\bar{R}_s$. The square of this slope is roughly proportional to the sorption coefficient since deviation from Fickian diffusion was slight, and thus trends can still be seen. An overall average precision for these determinations was ±3.5%.

DISCUSSION

A major problem in this investigation was to elucidate the mechanism of the interaction of carbon dioxide with the eight polymer films. This involved a critical comparison of how well the data fit the two possible rate-controlling mechanisms, chemisorption or diffusion.

Referring to Tables III and IV, it can be seen that the normally observed temperature and pressure dependence of the Elovich parameter a was found. That is, a for all samples increased markedly with both temperature and pressure. The variations of α however are somewhat anomalous although α decreases rather strongly with pressure. It should decrease with pressure, but only slightly, since the slow sorption rate is believed to be dependent only on the concentration of surface sites. Furthermore, the temperature variation of α is quite erratic. Low[8] states that the temperature coefficient of α may be positive or negative depending on the gas–solid system. Examination of Table IV shows α to increase consistently with temperature for films 1, 5, and 8, to decrease for film 2, but to vary randomly for the remaining four films. Variations of the temperature coefficients among the eight films would be expected as their surfaces are no doubt considerably different in nature. However, the erratic nature of four of the films may be interpreted as a complete transition of type of interaction. This seems quite unlikely for these films.

Elovich plots of amount sorbed versus ln $(t + t_0)$ were made by using back-calculated values of t_0 rather than values obtained by trial and error.

These values were in the range of hundreds of minutes. The resulting Elovich plots do show linear regions but abrupt changes in slope are in evidence. Although linear segments were obtained, these changes in slope may again be interpreted as a complete transition of type of interaction taking place during a particular experiment. The high values of t_0 obtained also casts doubt on the validity of adding a value to the time which is itself larger than the actual time of most of the experiment. Almost any log plot could be straightened by adding large enough numbers to the values from which the logarithms are derived. The t_0 values added to the time correspond to experimental times during which 50–75% of the sorption had already taken place. The fit of the rate data to the Elovich equation is questionable, but chemisorption cannot be ruled out completely without an alternate explanation.

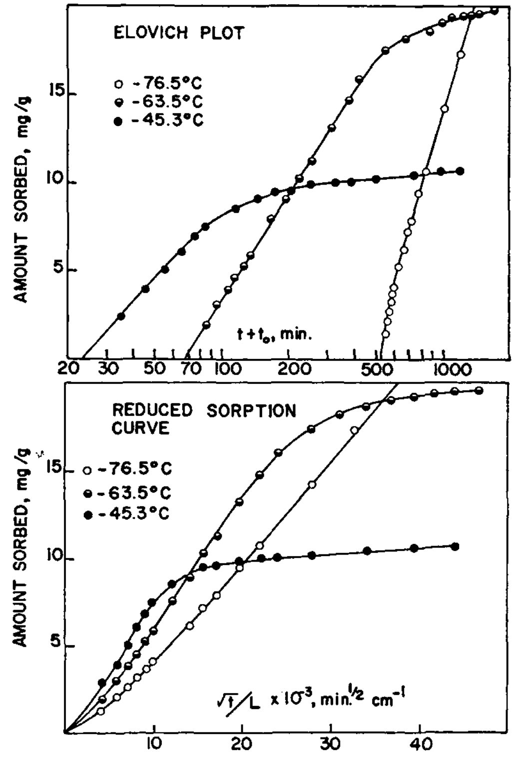

Fig. 4. Comparison between chemisorption theory and diffusion theory, for film 1 at 461 torr.

Diffusion theory states that the amount sorbed plotted against the square root of time should give a straight line over most of the course of the experiment, leveling out at large times as the process terminates. As Figure 3 demonstrates, extended straight-line portions are indeed found in these reduced sorption curves, covering 60–75% of the amount sorbed.

Examination of these reduced sorption curves together with the Elovich plots resulted in a striking comparison. If one looks at q plotted against either log $(t + t_0)$ or $\sqrt{t}/L$, very similarly shaped curves are obtained, the breaks occurring at the same actual experimental times. This is demonstrated in Figure 4 for film 1. This figure is simply a comparison between Figures 2 and 3, the only change being that the abscissa for Figure 3 is changed from q/q_e to q so that it will be consistent with Figure 2. The similarity was seen in all samples throughout the range of conditions studied. This means that treatment by both theories has reduced the data to roughly the same condition. In the case of diffusion, direct data points are used, the only modification being that the square root of time is plotted instead of time directly. For the Elovich treatment, a constant added to the time was required, the size of which casts some doubt on its validity.

The isosteric heats of sorption listed in Table II are seen to rise with coverage and to roughly approach the heat of sublimation of CO_2. The rise of isosteric heats is usually interpreted as being caused by lateral interaction of the sorbate molecules on a homogeneous surface. If the sorption process were chemisorption, a heterogeneous surface would be expected, some sites forming bonds with the adsorbate molecules more easily than others. This is what is normally observed in chemisorption, resulting in isosteric heats that decrease with coverage. Also, the heat values are very low compared to almost all chemisorption processes known, and the apparent approach to the heat of sublimation value of CO_2 strongly indicates a physical adsorption process. These isosteric heat values cannot be taken as absolutely correct due to the problem of nonreversibility. A strong hysteresis effect was found for water vapor sorption on these samples.[2] Hence a strong possibility exists that there will also be hysteresis for CO_2 sorption. However, the trends shown by the isosteric heat values will still be valid and the actual numerical values should not be in serious error.

With the heat of adsorption values pointing toward physical rather than chemical adsorption and with the rate data lending itself to interpretation in terms of diffusion as well or better than in terms of chemisorption, it is concluded that the process actually taking place is diffusion controlled physical adsorption. This conclusion is well substantiated in the literature where cases of sorption of gases on polymer films showing a rate effect are interpreted as diffusion processes.

The use of sorption techniques to measure diffusion coefficients of gases in polymers is a well-established technique, especially for those systems which exhibit coefficients smaller than 10^{-9} cm.^{2}/sec.,[9] Kumins and Roteman[10] determined diffusion coefficients of 6.3×10^{-8} cm./sec. at 91°C. and 99 torr to 1.6×10^{-10} cm.^{2}/sec. at 1°C. and 85 torr for CO_2 on vinyl films. The values obtained in this study for vinyl films are listed in Table V, films 3 and 4. If the downward trend of diffusion coefficients with temperature in the work of Kumins and Roteman is assumed to continue, the diffusion coefficients for films 3 and 4 would indeed be in agreement and they lend support to the belief that diffusion is actually the rate-controlling mechanism.

An insight into the mechanism of diffusion in polymer films is given by the transition-state theory according to Glasstone et al.[11] Diffusion is pictured as taking place discontinuously, depending on the random motion of the polymer segments, a void or hole being formed by their movement. If this occurs in the vicinity of the diffusant, the gas can then occupy this free space. The transition state is then the molecular sized void and the activation energy is considered to be that necessary to cause the polymer segments to move in such a way as to form this opening. The energy of separation of the diffusant from its neighbors is assumed to be negligible. In accordance with the transition theory, Glasstone et al. give:

$$D = A \exp \{-E_a/RT\} \tag{9}$$

where D is the diffusion coefficient, A is a constant, and E_a is the activation energy.

By using eq. (9) in the definite integral form and the D values from Table V, activation energies for the diffusion process listed in Table VI were calculated. If the isosteric heats of sorption given in Table II are compared to these activation energies, it is seen that for films 1 and 5, the activation energies are slightly greater. Thus it appears that for these two films, the diffusing molecule has to acquire more energy than is necessary for the sublimation of CO_2 (assuming that the heats of sorption do indeed approximate the heat of sublimation of CO_2) to enable it to move from one equilibrium position to the next as it migrates into the sample. This additional energy is needed for the work which must be done in order to make a passage for the CO_2 molecule. The activation energies for the other films listed in the tables are approximately the same as the heat of sublimation of CO_2, or in the case of film 8, slightly less. This can be interpreted on the basis that no energy is required to form the passage for the CO_2 molecule and for film 8, that CO_2 is capable of diffusing without completely subliming. In all cases, the energies of passage formation required are relatively small, of the order of van der Waals forces or less, indicating that the

TABLE VI
Activation Energies for Rate of Diffusion of CO_2 in Organic Films Between −45.3 and −63.5°C.

Film no.	Activation energy, kcal./mole
1	7.0
2	—
3	—
4	5.7
5	8.7
6	—
7	5.7
8	4.8

size of the pores through which the gas diffuses is of the same order as the size of the CO_2 molecule.

SORPTION OF CO_2 AND FILIFORM CORROSION

Both the type and quantity of information, such as listed in Table I on filiform corrosion performance, negates the validity of a statistical analysis of the effect of CO_2 on filiform corrosion. However, CO_2 has been shown[12] to be an inhibiting factor on the rate of filiform corrosion where an atmosphere of 5% CO_2 offers maximum inhibition to filiform. Consequently, it is deduced that the rate of CO_2 diffusion may exert an effect on filiform corrosion as it occurs in normal atmosphere. Except for the phenolic film, it appears that the greater the rate of CO_2 diffusion the greater the film inhibits filiform corrosion. Since the phenolic film is outstandingly high in inhibiting filiform, it is assumed that other factors besides CO_2 diffusion are involved in the rate-controlling steps in filiform corrosion.

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Résumé

Les résultats obtenus au départ de l'isotherme de sorption gazeuse d'anhydride carbonique sur 8 films organiques à trois températures et trois pressions ont été évalués pour montrer la chemisorption et l'adsorption physique. Les vitesses de sorption, affectées à la fois par la température et la pression ont été analysées, en calculant le paramètre de l'équation dé Elovich et celle de la solution de Barrer de la loi de Fick pour la diffusion. Par la consideration des paramètres de Elovich, des coefficients de sorption, les coefficients de diffusion limite et les énergies d'activation de diffusion, on montre que la vitesse d'interaction du CO_2 avec ces films organiques est primairement un processus contrôlé par diffusion.

Zusammenfassung

Aus Gassorptionsisothermen für CO_2 an acht organischen Filmen bei drei Temperaturen und drei Drucken erhaltene Daten wurden zur Bestimmung der Chemiesorption und physikalischen Adsorption ausgewertet. Die Abhängigkeit der Sorptionsgeschwindigkeit von Temperatur und Druck wurde einer Analyse durch Berechnung der Parameter der Elovich-Gleichung und derjenigen der Lösung des Fick'schen Diffusionsgesetzes von Barrer unterzogen. Eine Betrachtung der Elovich-Parameter, der Sorptionskoeffizienten, der Grenzdiffusionskoeffizienten und der Aktivierungsenergien der Diffusion zeigt, dass die Geschwindigkeit der Wechselwirkung von CO_2 mit diesen organischen Filmen primär ein diffusionsbestimmter Prozess ist.

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