

# Heat Effects in Sorption of Organic Vapors in Rubbery Polymers

PING WANG,\* JERRY H. MELDON, and NAKHO SUNG†

Laboratory for Materials and Interfaces, Chemical Engineering Department, Tufts University, Medford, Massachusetts 02155

## SYNOPSIS

During supposedly isothermal sorption/desorption of gases or vapors by solid polymers, latent heat effects alter local temperatures with the result that diffusion behavior may appear to be non-Fickian. Even when sorption curves are seemingly Fickian, spurious values of the diffusion coefficient,  $D$ , may still be inferred. These phenomena are examined in an experimental and theoretical study of incremental sorption/desorption of acetone vapor in the fluoroelastomer, vinylidene fluoride/hexafluoropropylene copolymer. A theoretical analysis developed earlier to model water vapor sorption in wool and cellulose is shown to successfully reconcile measured mass transfer rates and temperature changes.

© 1996 John Wiley & Sons, Inc.

## INTRODUCTION

Isothermal sorption/desorption experiments are a common means of measuring the diffusivity,  $D$ , of a gaseous penetrant in a solid material. However, it is not generally recognized that omnipresent latent heat effects may complicate the determination of  $D$ . Because diffusion time scales typical of organic vapors dissolved in rubbery polymers are often comparable to or smaller than those of heat transfer between the solid and vapor phases, heat effects accompanying sorption are slowly dissipated, and neglecting them may produce large errors in  $D$ .

The primary effect of a perturbation in solid temperature is on vapor solubility. In sorption, elevated temperatures reduce solubility, which slows mass uptake. In desorption, reduced temperatures increase solubility, slowing devolatilization. In both cases, the result is artifactual lowering of the apparent  $D$ .

A secondary effect is associated with the dependence of  $D$  on temperature. The increase in apparent  $D$  manifests itself primarily at the start of sorption/

desorption. Its significance decreases as the increment in vapor activity decreases.<sup>1</sup> Because of the small activity increments in the experimental study,  $D$  was treated as a constant in the theoretical analysis outlined below.

The phenomena investigated here were first analyzed rigorously in a study of water vapor sorption in wool and polymers.<sup>2,3</sup> Because of water's large heat of vaporization, its heat of sorption,  $\Delta H_s$ , is much greater than those characteristic of organic vapors in polymers, which is probably why heat effects in the latter systems have generally been neglected. However, our recent studies of organic vapor sorption in rubbery polymers<sup>4,5</sup> have demonstrated significant heat effects and correspondingly abnormal sorption behavior, especially at high vapor activities.

Investigations of heat effects<sup>2,3,6-8</sup> have heretofore focussed on the determination of correct  $D$  values from sorption/desorption data, and calculation of time courses of solid-phase temperature. Large temperature excursions were measured during recently reported integral desorption measurements.<sup>9</sup> Apparently no previous investigation has reconciled model predictions with both experimentally measured mass transfer rates and temperature data, as we do here. In addition, we explore the utility of a single dimensionless parameter that emerges from

\* Current address: Department of Chemical and Biochemical Engineering, University of Iowa, Iowa City, IA 52242.

† To whom correspondence should be addressed.

Journal of Applied Polymer Science, Vol. 59, 937-944 (1996)

© 1996 John Wiley & Sons, Inc.

CCC 0021-8995/96/060937-08

the analysis, as an index of the significance of heat effects in inferring diffusion coefficients from sorption/desorption data.

## MATHEMATICAL MODEL

In incremental sorption measurements, a sorbent sample initially equilibrated with a gas phase of pure penetrant is exposed to consecutive step increases in the latter's activity. The sample's mass,  $M$ , is monitored as it approaches a new equilibrium value following each step change. Data for  $M(t)$  are used to determine  $D$ . Because of the substantial solubility of vapors in polymers,  $D$  may vary considerably with dissolved penetrant concentration,  $C$ . Thus, step changes in activity are generally minimized to justify assumption of constant  $D$  in the analysis which follows.<sup>10</sup>

A plane sheet of polymer of thickness  $2L$  is assumed to be in equilibrium with gas comprised of penetrant at pressure  $P_i$  and temperature  $T_o$ , at which the equilibrium  $C$  value is  $C_i$ . At time  $t = 0$ , the penetrant's pressure is instantaneously changed to  $P_f$ , and it is maintained there until equilibrium is again established, this time with  $C = C_f$ . The polymer's temperature changes with time due to  $\Delta H_s$ , but it is ultimately restored to  $T_o$  by heat transfer between polymer and gas, with the latter behaving as an infinite sink. It is further assumed that the polymer surface instantaneously equilibrates with the gas—i.e., that the surface concentration is fixed by equilibrium with  $P_f$  at the prevailing surface temperature.

(The step change in pressure also causes the bulk gas temperature to change. However, the temperature change is generally small, and so quickly dissipated by heat transfer between the gas and chamber wall—normally jacketed by a constant temperature fluid—that bulk gas may be considered isothermal.)<sup>11</sup>

The differential equation governing diffusion in polymer is then:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (1)$$

and the associated initial and boundary conditions are:

$$C(x,0) = C_i \quad (2)$$

$$C(L,t) = C_\infty[T(L,t)] \quad (3)$$

$$\frac{\partial C}{\partial x}(0,t) = 0, \quad (4)$$

where subscript  $\infty$  denotes sorption equilibrium, e.g.,  $C_\infty(T_o) = C_f$ .

To obtain an analytical solution to eq. (1), which is coupled to a differential energy balance, the system must be linear—a goal already served by use of an average  $D$  value over the increment in  $C$ . Thus, the  $T$ -dependence of  $C_\infty$  is linearized as:

$$C_\infty(T) = C_\infty(T_o) - \omega(T - T_o) \quad (5)$$

where  $\omega$ , referred to as the temperature coefficient of regain, is defined by:

$$\omega \equiv - \left( \frac{\partial C}{\partial T} \right)_{T=T_o, P=P_f} \quad (6)$$

(Truncation of the Taylor expansion about  $T_o$  is another reason the step change in vapor activity must be small.)

In setting up the energy balance, it is assumed that sample temperature is always uniform, albeit a function of time. This is reasonable since: (1) the Lewis number,  $Le \equiv D\rho c_p/k$  ( $\rho$  is density,  $c_p$  is heat capacity, and  $k$  is thermal conductivity), is estimated to be of order  $10^{-4}$ , and so internal thermal equilibration is much faster than mass transfer; and (2) the Biot number,  $Bi \equiv hL/k$ , is of order  $10^{-2}$ , and so internal thermal equilibration is also much faster than external heat transfer. Thus, while  $T$  varies with time, it is considered independent of position in the polymer, and the governing ordinary differential equation is:

$$\rho c_p L \frac{dT}{dt} = - \frac{\rho L}{1 + C_i} [\Delta H_s + c_p^*(T - T_o)] \frac{dC}{dt} - h(T - T_o) \quad (7)$$

subject to the initial condition:

$$T(0) = T_o \quad (8)$$

where  $h$  is the coefficient of heat transfer between solid surface and bulk gas,  $\rho$  the density of polymer phase including penetrant dissolved at the start of

an incremental experiment),  $c_p$  is the polymer phase heat capacity (assumed independent of  $C$  on a mass basis), and  $c_p^*$  the penetrant's heat capacity; the underline denotes average concentration.

The sensible heat term,  $c_p^*(T - T_o)$  (accounting for the temperature change on sorption), makes eq. (7) nonlinear. However, it is negligibly small and, therefore, eliminated.

Treating  $h$ ,  $D$ , and all other parameters as constants transforms the differential equations into the coupled linear set solved by Armstrong et al.,<sup>3</sup> and later applied by Ruthven and Lee<sup>7</sup> to sorption in zeolites. The solution, obtained using Laplace transforms,<sup>7,12</sup> is:

$$\frac{M}{M_\infty} = 1 - 2 \sum_{n=1}^{\infty} \frac{\exp - (\lambda_n^2 Dt/L^2)}{(1 + \frac{2}{\beta}) \lambda_n^2 \cot^2(\lambda_n) + \lambda_n \cot(\lambda_n) + \lambda_n^2} \quad (9)$$

$$\frac{T - T_o}{T^* - T_o} = 2 \sum_{n=1}^{\infty} \frac{(\beta + 1) \exp - (\lambda_n^2 Dt/L^2)}{(\beta + 2) \lambda_n \cot(\lambda_n) + \beta [\lambda_n \tan(\lambda_n) + 1]} \quad (10)$$

where the eigenvalues,  $\lambda_n$ , satisfy:

$$\cot(\lambda_n) = \frac{\beta \lambda_n}{\alpha - \lambda_n^2} \quad (11)$$

The two dimensionless groups are defined as follows:

$$\alpha \equiv \frac{hL}{\rho c_p D} \quad (12)$$

$$\beta \equiv \frac{\omega \Delta H_s}{(1 + C_i) c_p} \quad (13)$$

$M$  and  $M_\infty$  are the respective weight changes up to time  $t$  and at equilibrium; i.e.,

$$\frac{M}{M_\infty} = \frac{C - C_i}{C_f - C_i} \quad (14)$$

(note that  $\alpha = Bi/Le$ ); and  $T^* - T_o$  is the adiabatic ( $h \rightarrow 0$ ) temperature change, calculated as follows:

$$T^* - T_o = \frac{\beta(C_f - C_o)}{\omega(\beta + 1)} \quad (15)$$

Because polymers swell upon sorption of organic vapors,  $L$  varies with time. An analysis with  $L$  fixed at its swollen value at the start of an experiment

remains applicable to sorption data. However, mutual diffusion coefficient  $D_{12}$  ( $1 =$  penetrant,  $2 =$  polymer), is not the  $D$  so obtained; but may be calculated according to:<sup>13,14</sup>

$$D_{12} = \frac{D}{(1 - \phi_1)^r} \quad (16)$$

where  $\phi$  denotes volume fraction.

The appropriate value of  $r$  is  $2/3$  in isotropic swelling (as assumed in calculations), and  $2$  in unidimensional ( $x$ -axis) swelling;  $4/3$  is otherwise recommended. Equation (16) was originally derived for initially dry polymer. Accordingly,  $\phi_1$  is defined here as the ratio of the increment in volume of sorbed penetrant, to total volume of polymer plus penetrant at initial equilibrium.

In addition, when  $D$  is concentration dependent, the value inferred from sorption measurements corresponds to concentration  $C_+$  defined by:

$$C_+ \equiv C_i + k(C_f - C_i) \quad (17)$$

with  $k = 0.7$  when  $D$  increases with  $C$ , and  $0.56$  when  $D$  decreases with  $C$ .<sup>10</sup>

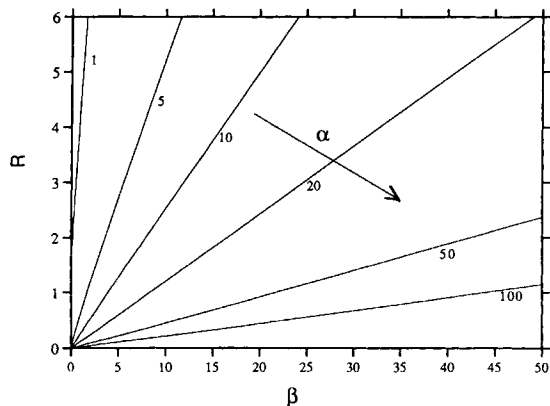
A common means of inferring  $D$  from sorption/desorption data is to plot  $-\ln(1 - M/M_\infty)$  vs.  $t$ . According to eq. (9), at sufficiently large  $t$ , the data will approach a straight line of slope  $\lambda_1^2 D/L^2$ , where  $\lambda_1$  is the lowest eigenvalue determined by eq. (11). Thus,  $D$  can be calculated from the slope, using the  $\lambda_1$  value based on  $\alpha$  and  $\beta$ . The "Fickian" solution to eq. (1)<sup>7</sup>, i.e., that decoupled from heat effects, is an infinite series with exponential terms analogous to those in eq. (9), but with  $\lambda_n = (2n-1)\pi/2$ . Based on it, the limiting slope would be erroneously interpreted as  $\pi^2 Dt/4L^2$  (where  $D = "D_{\text{Fick}}"$ ). Accordingly, we define the following correction factor:

$$R \equiv \frac{D}{D_{\text{Fick}}} - 1 = \left( \frac{\pi}{2\lambda_1} \right)^2 - 1 = f(\alpha, \beta) \quad (18)$$

Figures 1 and 4 show that spurious heat effects, as measured by  $R$ , are promoted by low  $\alpha$  (slow heat dissipation) and high  $\beta$  (large heat of sorption). The key parameter is  $\alpha/\beta$ , with the effects increasing as this ratio decreases.<sup>3,7</sup>

## EXPERIMENTAL PROCEDURE

Measurements were undertaken of sorption and desorption of acetone vapor in Fluorel<sup>®</sup> (3M Corp.),

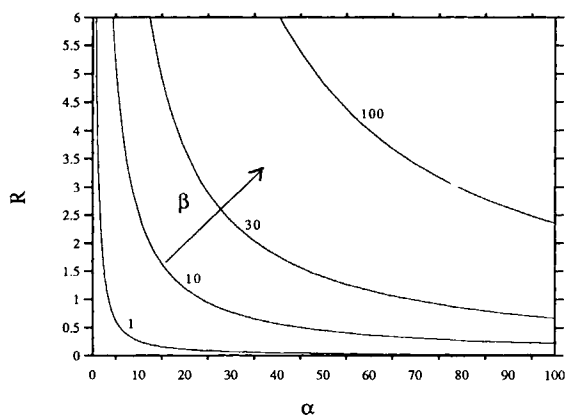


**Figure 1** Calculated dependence of correction factor, *R*, upon  $\beta$ , with  $\alpha$  as parameter.

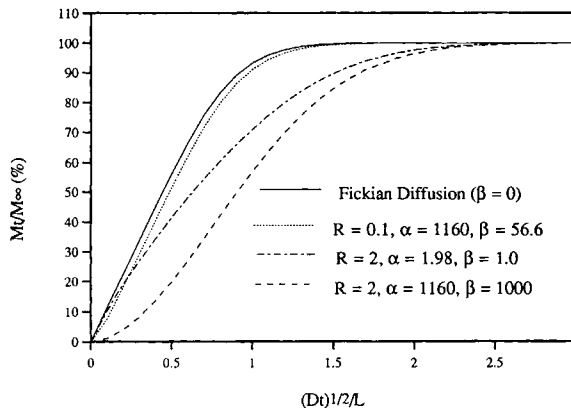
a copolymer of vinylidene fluoride and hexafluoropropylene. Samples were cut from compounded rubber sheets of nominal thicknesses 10 and 20 mils (1 mil =  $2.54 \times 10^{-3}$  cm), immersed in acetone to leach out plasticizers and other processing aids, and dried prior to diffusion measurements.

During sorption/desorption, samples were suspended from a quartz spring housed in a glass chamber jacketed with water at a temperature controlled to  $\pm 0.1^\circ\text{C}$ . Sample weight was monitored by observing spring extension with a cathetometer.

Due to difficulties in simultaneously measuring temperature and weight changes, paired polymer samples were suspended in the same chamber. The temperature of one was measured with a thermocouple attached to one surface. Because heat transfer between thermocouple and polymer was faster than between thermocouple and vapor, thermocouple readings largely reflected polymer temperature. Independent measurements established that due to the



**Figure 2** Calculated dependence of correction factor, *R*, upon  $\alpha$ , with  $\beta$  as parameter.

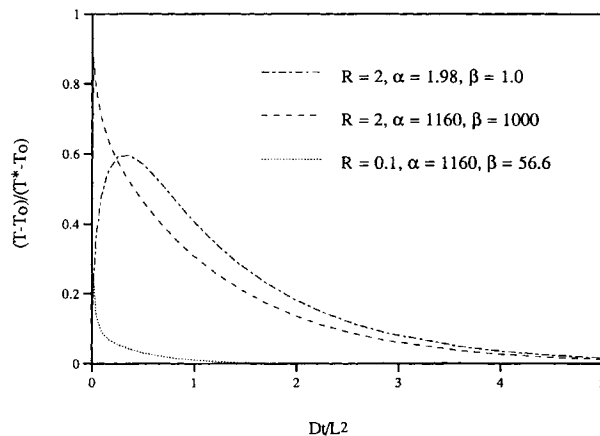


**Figure 3** Theoretical sorption curves calculated on the basis of different  $(\alpha, \beta)$  values; theoretical correction factor, *R*, also indicated.

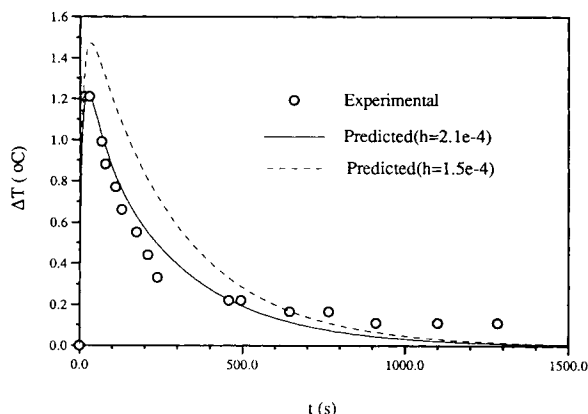
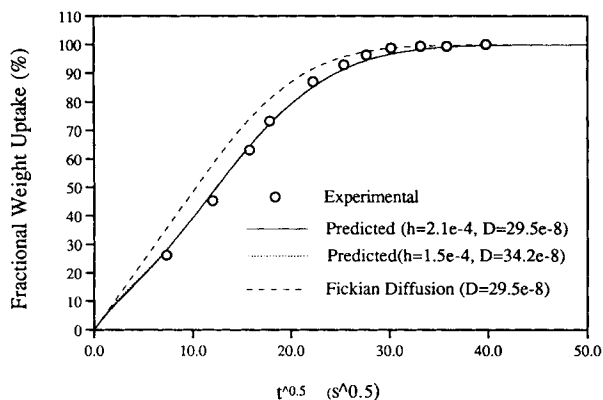
slight influence of gas temperature on readings, values of  $\Delta T$  (solid/gas temperature difference) were underestimated by  $\sim 10\%$ . Accordingly,  $\Delta T$  data reported here include 10% corrections.

### DISCUSSION OF RESULTS

Acetone sorption/desorption and temperature data are shown in Figures 5–7 for several activity increments (along with theoretical curves as explained below). Mass uptake/loss curves have a sigmoidal character; but close inspection suggests incipient two-stage behavior with an early plateau. Temperature curves confirm significant heat effects. The analysis that follows reconciles the two sets of data. To do so, it was first necessary to assign values to the relevant parameters.



**Figure 4** Theoretical dimensionless temperature–time courses calculated on the basis of different  $(\alpha, \beta)$  values; theoretical correction factor, *R*, also indicated.



**Figure 5** Comparison of theoretical and experimental data for acetone sorption dynamics;  $T_0 = 25^\circ\text{C}$ ; initial activity = 0.47 (see Table I for details). (a) Sorption curves; note that the two curves with different  $(h, D)$  combinations overlap. (b) Temperature changes.

The heat of sorption,  $\Delta H_S$ , was determined from sorption isotherms. It is generally safe to approximate it by acetone's latent heat of condensation,  $-\Delta H_{vap}$ , which  $\Delta H_S$  approaches at high activities; at low activities, small  $D$  and  $\omega$  values make heat effects negligible.

The so-called regain coefficient,  $\omega$ , was calculated from:

$$\begin{aligned} \omega &\equiv -\left(\frac{\partial C}{\partial T}\right)_P = -\frac{C}{\phi_1\phi_2} \left(\frac{\partial \phi_1}{\partial T}\right)_P \\ &= -\frac{C}{\phi_1\phi_2} \left(\frac{\partial \phi_1}{\partial \ln a_1}\right)_P \left(\frac{\partial \ln a_1}{\partial T}\right)_P \quad (19) \end{aligned}$$

where  $a_1$  (penetrant activity) is equivalent to  $P/P^\circ$ , and  $P^\circ$  is penetrant vapor pressure.

The Clausius-Clapeyron equation transforms eq. (19) into:

$$\omega \approx \frac{C\Delta H_{vap}}{\phi_1\phi_2 R_g T^2 (\partial \ln a_1 / \partial \phi_1)_P} \quad (20)$$

where  $R_g$  is the gas constant.

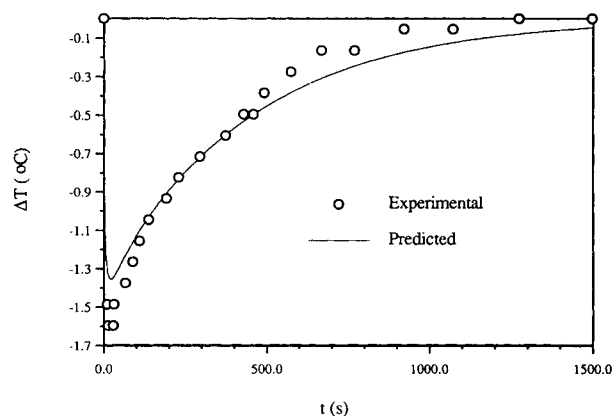
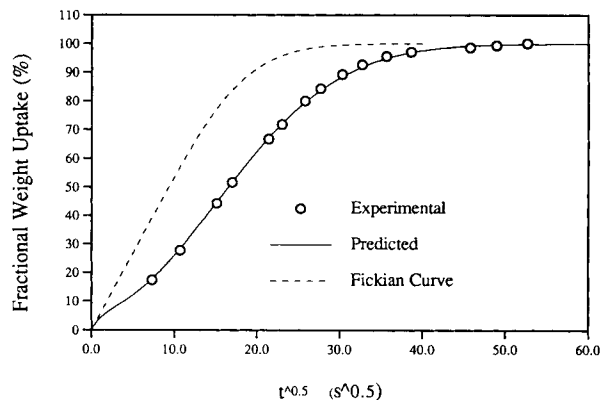
Values of  $(\partial \ln a_1 / \partial \phi_1)_P$  were obtained by fitting to sorption equilibrium data reported earlier,<sup>5</sup> a modified Flory-Rehner equation:

$$\begin{aligned} \ln a_1 &= \ln(1 - \phi_1) + \phi_2 + \chi\phi_2^2 \\ &\quad + K[\phi_2^{1/3} - \phi_2/2] \quad (21) \end{aligned}$$

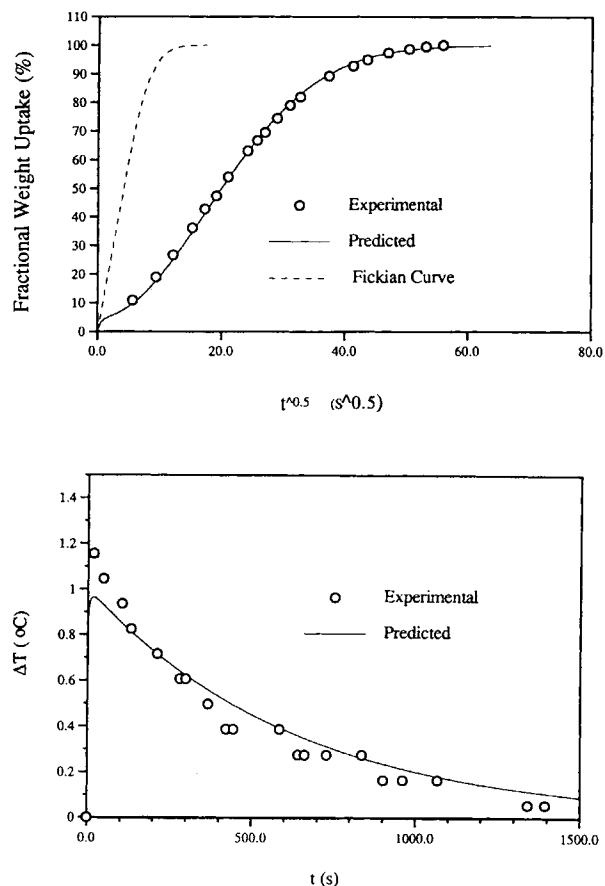
where:

$$K = \frac{V_1}{M_c V_2} \left(1 - \frac{2M_c}{M_2}\right) \quad (22)$$

$V$  denotes molar volume,  $V$  specific volume,  $M$  molecular weight, and subscript  $C$  the polymer segment between crosslinks. A good fit to the data was obtained only when  $\chi$ , the solvent-polymer interaction



**Figure 6** Comparison of theoretical and experimental data for acetone desorption dynamics;  $T_0 = 25^\circ\text{C}$ ; initial activity = 0.80 (see Table I for details). (a) Desorption curves. (b) Temperature changes.



**Figure 7** Comparison of theoretical and experimental data for acetone sorption dynamics;  $T_0 = 25^{\circ}C$ ; initial activity = 0.87 (see Table for I for details). (a) Sorption curves. (b) Temperature changes.

parameter, was allowed to vary with penetrant concentration. The following relationship was assumed:

$$\chi = \chi_0 + \chi_1\phi_2 + \chi_2\phi_2^2 \quad (23)$$

**Table I** Physicochemical Parameters ( $25^{\circ}C$ )

$a_i$ ( $P_i/P^0$ )	$C_i$ (g/100 g)	$C_{\infty}$ (g/100 g)	$D \times 10^9$ ( $cm^2/s$ )	$D_{12} \times 10^9$ ( $cm^2/s$ )	$Q$ (cal/g)	$\omega \times 10^3$ (g/g/ $^{\circ}C$ )	$\alpha$	$\beta$	$R$
0.47	7.16	10.2	2.95	3.06	117	5.81	18.0	2.10	0.28
0.56	10.2	13.3	5.06	5.23	119	8.46	10.8	2.97	0.70
0.65	13.3	17.0	7.33	7.61	120	12.7	7.68	4.29	1.47
0.74	17.4	21.9	7.22	7.53	121	20.0	8.07	6.42	2.05
0.81	21.9	27.4	6.97	7.30	121	31.5	8.65	9.55	2.80
0.87 <sup>a</sup>	29.8	37.0	23.5	24.7	121	64.1	2.71	17.6	16.7
0.80 <sup>b</sup>	34.6	27.2	4.78	4.58	121	31.1	13.7	8.11	1.46

Dry polymer thickness = 0.024 cm; polymer density = 1.8 g/cm<sup>3</sup>; polymer heat capacity = 0.24 cal/g/ $^{\circ}C$ .

<sup>a</sup> Because heat effects were so large, diffusion coefficients are unreliable.

<sup>b</sup> Desorption experiment.

A least-squares fit to the  $25^{\circ}C$  sorption data yielded  $\chi_0 = 1.596$ ,  $\chi_1 = -3.319$ ,  $\chi_2 = 1.514$ , and  $K = -0.034$ . The negative  $K$  indicates that while the modified Flory–Rehner equation suffices for present purposes, the adjusted parameters themselves cannot be used to deduce significant information.

A heat transfer coefficient,  $h$ , was inferred by inserting experimental  $dT/dt$  and  $dC/dt$  values into eq. (7). An average value of  $2.1 \times 10^{-4}$  cal/cm<sup>2</sup>/s/ $^{\circ}K$  was obtained, for both 10- and 20-mil polymer samples. This is 40% higher than the value used in a study of water vapor sorption,<sup>2</sup> which had been predicted from radiation theory (assuming an emissivity of 1.0) and verified by independent heat transfer measurements. Assuming the fluoroelastomer's emissivity is the same as natural rubber's, 0.8,<sup>15</sup> it is estimated that  $h$  due to radiation is  $1.2 \times 10^{-4}$ . An additional contribution due to free convection<sup>16</sup> is estimated to be  $0.3 \times 10^{-4}$ . The residual discrepancy between apparent and estimated  $h$  values is puzzling. However, the higher adjusted value was retained because it produced superior fits to sorption/desorption and temperature data, as discussed below.

Rather than using plots of  $\ln(1 - M/M_{\infty})$  vs.  $t$ , diffusion coefficients were obtained by least squares fits of eq. (9) to each set of sorption/desorption data. These  $D$  values, together with  $h$ , were then inserted in eq. (10) to predict, without further parameter adjustment, the corresponding temperature–time curves. In addition,  $D_{12}$  values were calculated from eq. (16). Table I summarizes the assumed material parameters and calculated diffusion coefficients.

Experimental and calculated mass and temperature curves in Figures 5–7 show that agreement is generally excellent. In addition, sensitivity to  $h$  is illustrated in Figure 5. Figure 5 (a) shows that when

$h$  is set at  $1.5 \times 10^{-4}$  cal/cm<sup>2</sup>/s/°K, the  $D$  value that optimizes the fit to mass uptake data is  $3.42 \times 10^{-8}$  cm<sup>2</sup>/s. This may be compared to an adjusted  $D$  of  $2.95 \times 10^{-8}$  cm<sup>2</sup>/s when  $h = 2.1 \times 10^{-4}$ . Each  $h$ - $D$  combination produced essentially the same excellent fit to the weight data. However, Figure 5(b) reveals that when the lower  $h$  was used to predict temperatures, the fit was markedly worse.

Notably, when diffusivity correction factor  $R > 4$ , there is poor agreement between calculated and measured temperature changes, and  $D$  adjusted to fit sorption data is unreasonably high. There are at least two possible causes. One is that when  $\alpha$  is sufficiently low, mass transfer is heat-transfer controlled. Sorption equilibrium is then achieved instantaneously within the heat transfer time frame, and weight and temperature changes are insensitive to  $D$ . Alternatively, when  $\beta$  is sufficiently large, temperature changes are so great as to invalidate the underlying assumptions of constant  $D$ ,  $\omega$ , and material properties.

## CONCLUSIONS

The availability of both temperature and mass uptake data serves both to ascertain the presence of heat effects and to provide a severe test of consistency of theory and experimental data.

The significance of heat effects decreases as sample thickness,  $L$ , increases, because  $\alpha$  then increases (i.e., mass transfer slows down relative to heat dissipation).

Temperature changes as small as the 1°C excursions reported here may be quite significant, especially at higher activity levels, because  $\omega$ , and therefore  $\beta$ , increase rapidly with penetrant activity (Table I).

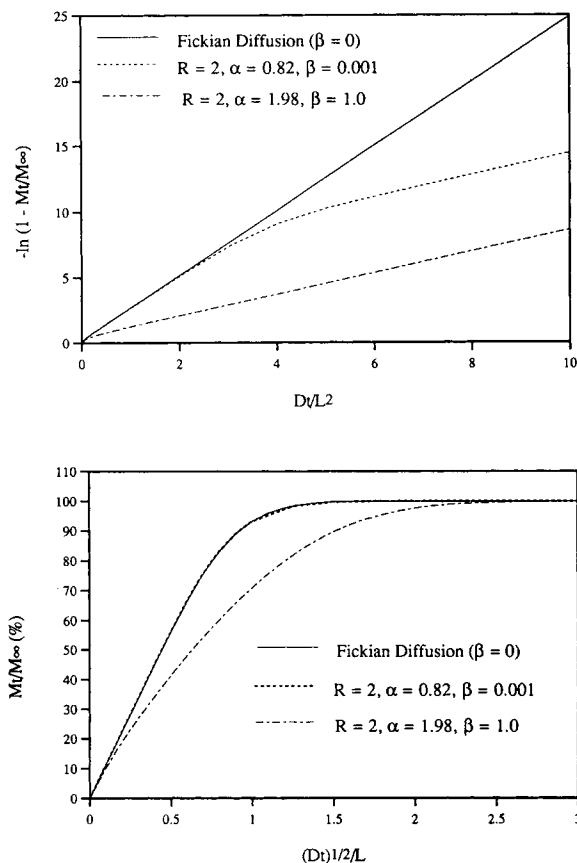
When  $R < 0.1$ , diffusion behavior is essentially Fickian, and nonisothermal effects may be neglected. When  $0.1 < R < 4$ , heat effects are significant, the behavior may appear to be non-Fickian, and reliable diffusion coefficients may be inferred using the analysis outlined here. When  $R > 4$ , heat effects are so large that reliable diffusion coefficients cannot be inferred from sorption/desorption data.

Armstrong et al.<sup>3</sup> suggested that when  $\alpha/\beta > 10$ , heat effects are negligible; and when  $\alpha/\beta < 1$ , the effects are so strong that sorption is heat-transfer controlled. Our own theoretical calculations (e.g., Figs. 1 and 2) are generally consistent with these criteria. However, as shown in Figure 8, there is a notable difference between the degrees to which the

effects manifest themselves in: (1) overall sorption curves ( $M/M_\infty$  vs.  $\sqrt{t}$ ), and (2) asymptotic, long-time behavior ( $\ln[1 - M/M_\infty]$  vs.  $t$ , as  $t \rightarrow \infty$ ).

Figure 8(a) and (b) each compare Fickian ( $\beta = 0$ ) curves with pairs of theoretical curves calculated using  $(\alpha, \beta)$  values—(0.82, 0.001) and (1.98, 1)—such that  $\alpha/\beta = 820$  and 1.98, respectively, yet  $R$  [defined by eq. (18)] equals 2 in each case. According to Armstrong et al., no heat effects should be apparent in the former case. Indeed, the relevant overall sorption curve overlaps with a Fickian curve [Fig. 8(b)], whereas the curve for (1.98, 1) does not. Nonetheless, the long-time behavior of each [Fig. 8(a)] diverges from that of the Fickian curve, consistently with  $R = 2$ .

Thus, heat effects, however small in terms of overall sorption behavior, may still control the asymptotic approach to equilibrium. However, because of their very small magnitude, the deviations from Fickian behavior shown in Figure 8(a) when  $\beta = 0.001$ , would almost certainly escape experi-



**Figure 8** Comparison of Fickian curve with theoretical sorption curves calculated based on two  $(\alpha, \beta)$  combinations that each yield  $R = 2$ . (a) Overall sorption curves. (b) Emphasis on long-time behavior.

mental detection. Moreover, focussing on long-time asymptotic behavior carries the risk of overlooking tell-tale nonlinearities in the earlier stages of sorption/desorption (e.g., Figs. 5–7).

This work was supported in part by funding provided by the Natick Research, Development and Engineering Center (through Dr. Eugene Wilusz) under the auspices of the U.S. Army Research Office Scientific Services Program administered by Battelle (Contract No. DAAL03-91-C-0034). The authors are also indebted to Dr. N. Schneider of Geo Centers, Inc., for valuable discussions.

## REFERENCES

1. L.-K. Lee and D. M. Ruthven, *J. Chem. Soc. Faraday Trans. I*, **75**, 2406 (1979).
2. A. A. Armstrong, Jr. and V. Stannett, *Makromol. Chem.*, **90**, 145 (1966).
3. A. A. Armstrong, Jr., J. D. Wellons, and V. Stannett, *Makromol. Chem.*, **95**, 78 (1966).
4. L. S. Waksman, N. S. Schneider, and N.-H. Sung, *Barrier Polymers and Structure*, ACS Symposium Series 424, American Chemical Society, Washington, DC, 1990, p. 377.
5. P. Wang and N.-H. Sung, *ACS PMSE*, **69**, 372 (1993).
6. G. King and A. B. D. Cassie, *Trans. Faraday Soc.*, **36**, 445 (1940).
7. D. M. Ruthven and L.-K. Lee, *AIChE J.*, **27**, 654 (1981).
8. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon Press, Oxford, 1975.
9. M. M. Gou, W. J. Koros, and G. Goldman, *J. Appl. Polym. Sci.*, **51**, 1685 (1994).
10. J. S. Vrentas, J. L. Duda, and Y. C. Ni, *J. Polym. Sci. Phys. Ed.*, **15**, 2039 (1977).
11. P. Nordon and I. C. Watt, *J. Polym. Sci. A*, **43**, 267 (1960).
12. J. M. Contompasis, M. S. Thesis, Tufts University, Medford, MA, 1990.
13. J. Crank and G. S. Park, *Diffusion in Polymers*, Academic Press, New York, 1968, Chap. 1.
14. G. F. Bilovits and C. J. Durning, *Chem. Eng. Commun.*, **82**, 21 (1989).
15. M. F. Modest, *Radiation Heat Transfer*, McGraw-Hill, New York, 1993, Append. B.
16. D. K. Edwards, V. E. Denny, and A. F. Mills, *Transfer Processes*, 2nd ed., McGraw-Hill, New York, 1977, p. 167.

Received April 10, 1995

Accepted September 25, 1995