Kinetics of Non-Isothermal Sorption in Molecular Sieve Crystals

A mathematical model is developed to describe non-isothermal sorption kinetics and used to interpret experimental uptake curves for CO_2 in 4A zeolite and for CO_2 and nC_5H_{12} in 5A zeolite. The model assumes that the dominant mass transfer resistance is intracrystalline diffusion while the major resistance to heat transfer is the external heat transfer between the adsorbent sample and the surroundings. It gives a good representation of the kinetic behavior over a wide range of conditions. Both the extreme cases of isothermal diffusion and complete heat transfer control are demonstrated experimentally. Intermediate situations, in which the uptake rate is controlled by the combined effects of diffusion and heat transfer, are demonstrated as well. The parameters derived from the model are consistent, reproducible, and agree well with *a priori* estimates. The model provides a useful theoretical basis for the analysis of rapid sorption processes for which the non-isothermal approximation is invalid.

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SCOPE

The traditional method of measuring diffusivities in porous adsorbents is to measure the transient sorption curve generated when a sample of the adsorbent is exposed to a change in ambient sorbate concentration. Such curves are generally analyzed according to a simple isothermal diffusion model. This is a valid approximation when diffusion is slow compared with heat transfer, but for rapidly diffusing systems, the sorption kinetics may be appreciably influenced by thermal effects.

Presented here is a non-isothermal model for an assemblage of spherical adsorbent particles. The principal mass transfer resistance is intraparticle diffusion while the major resistance to heat transfer is the external heat transfer between the adsorbent and the ambient fluid. The model is restricted to small differential changes in sorbate concentration, since a linear equilibrium relationship and constant diffusivity are assumed. These assumptions are physically reasonable for many systems.

The model is used to analyze experimental sorption curves for CO_2 in 4A and 5A zeolites and for nC_5H_{12} in 5A. The conditions of the experimental study were selected to illustrate the main features of the theory. Both the extreme cases of isothermal diffusion and complete heat transfer control, as well as intermediate cases involving combined heat transfer and diffusion control, are demonstrated. The model provides both a useful criterion for the validity of the isothermal approximation and a theoretical basis for the analysis of uptake curves for rapidly diffusing systems for which isothermal conditions cannot be achieved.

CONCLUSIONS AND SIGNIFICANCE

The model shows that the kinetic behavior of the system is determined by two dimensionless parameters, α and β. The parameter α is the ratio of the time constants for diffusion and heat transfer, while β depends on the heat of sorption, the thermal capacity, and the temperature coefficient of the equilibrium position. By comparing theoretical uptake curves calculated from the non-isothermal model with the curves for isothermal diffusion, a criterion for the validity of the isothermal approximation is established.

The model provides a consistent interpretation of experimental kinetic data for a wide range of conditions. In particular, when uptake curves for CO_2 in small (7.3 μm) 4A crystals are analyzed according to the non-isothermal model, the time constants yield diffusivities consistent with the values obtained with larger crystals (in which diffusion is practically isothermal). Isothermal analysis leads to apparent diffusivities which are smaller for the smaller crystals. Apparent diffusivities which vary with crystal size have been reported in the literature for several systems, and the intrusion of thermal effects is a possible explanation.

The effect of sample configuration on the uptake rate has been demonstrated experimentally. For certain systems, it is possible to pass from the region of near isothermal diffusion to complete heat transfer control, simply by increasing the depth of the adsorbent sample. Constancy of the uptake curves measured with different sample configurations provides a useful experimental test for the absence of significant thermal effects. But, agreement between differentially measured uptake curves determined over different step sizes and consistency between adsorption and desorption curves is not a valid criterion of isothermal behavior. The intrusion of thermal effects is not always evident simply from the form of the uptake curves. It seems possible that such effects may be responsible for some of the anomalies in the published literature.

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The classical method of studying sorption kinetics involves following the transient sorption curve generated when a sample of the adsorbent is subjected to a change in ambient sorbate concentration. The uptake curves have generally been interpreted in terms of a diffusion model on the assumption that the system can be considered as isothermal. See, for example, Barrer (1971), Loughlin, Derrah and Ruthven (1971). This is a valid approximation when diffusion is slow but, in faster diffusing systems, the sorption kinetics may be appreciably influenced by thermal effects. The significance of thermal effects has been demonstrated experimentally by Eagan, Kindl and Anderson (1971), Kondis and Dranoff (1971) and by Doelle and Riekert (1977). Temperature rises as high as 20-30°C were observed during the sorption of propane in zeolite 5A and butane in 13X. However, with the exception of the work of Armstrong and Stannet (1966), which appears to have been overlooked in most subsequent studies, there has been little theoretical analysis.

The problem of non-isothermal sorption has recently attracted the attention of several different research groups. An approximate analysis based on a linear driving force representation of the mass transfer rate equation was developed by Chihara et al. (1976) while a solution in terms of the moments of the uptake curves was obtained by Kocirik, Zikanova and Karger (1979). A more detailed theoretical analysis was presented by Brunovska et al. (1978) who solved numerically the simultaneous diffusion and heat conduction equations for a porous spherical particle of finite thermal conductivity subjected to a step change in sorbate concentration at the external surface. The diffusivity was assumed independent of temperature, external heat transfer resistance was neglected, and the isotherm was considered to be of the Langmuir form.

There are, in principle, two distinct effects which should be considered in the analysis of non-isothermal sorption: 1) the temperature dependence of the diffusivity and 2) the temperature dependence of the equilibrium. For zeolitic sorbents, the temperature dependence of diffusivity generally follows an Arrhenius expression with the activation energy commonly several kilocalories. The assumption of a constant diffusivity is therefore a valid approximation only when temperature changes are small. The effect of the temperature dependence of diffusivity (the dominant effect in the initial stages of the uptake) is to increase the rate of adsorption and decrease the rate of desorption, relative to an isothermal process. In later stages, the effect of the temperature dependence of the equilibrium becomes dominant. This effect retards both adsorption and desorption rates to similar extents. Non-isothermal adsorption curves, therefore, generally show an initial rapid uptake followed by a slow approach to equilibrium in the long time region.

A theoretical analysis which takes account of the temperature dependence of both the diffusivity and the equilibrium has been developed by Lee (1976). By reducing the size of the step over which the uptake curve is measured, the effect of the temperature dependence of the diffusivity may be eliminated, but the effect of the temperature dependence of the equilibrium position remains. The problem of theoretical analysis is greatly simplified by restricting consideration to small differential changes in sorbate concentration. Under these conditions, the equilibrium relationship can be considered linear and the diffusivity constant.

There are, in principle, three distinct resistances to heat transfer which should be considered 1) thermal conduction through the zeolite crystals, 2) heat transfer or conduction between the individual particles (or zeolite crystals) within the adsorbent sample (or pellet) and 3) heat transfer between the sample and the surrounding atmosphere. A simple analysis of the time constants for these processes shows that for small crystals (~ 10 μm) and for commonly used sample quantities (10-50 mg) the external heat transfer resistance will always be much more important than either intraparticle conduction or inter-particle heat transfer. Under most practical conditions it is therefore a good approximation to consider the sample temperature to be uniform and to take account only of the external heat transfer resistance.

In our work, a mathematical model based on the above simplifications is developed and then used to interpret experimental uptake curves for several different systems under non-isothermal conditions.

THEORETICAL ANALYSIS

The assumptions of the mathematical model, which is similar to the model of Armstrong and Stannett but in spherical geometry, are as follows:

1) The sample consists of an assemblage of uniform spherical particles (zeolite crystals).

2) Thermal conduction through an individual particle and heat transfer between the particles within the sample is rapid, so that the only significant heat transfer resistance is at the external surface of the sample. This implies a constant temperature through the sample, although, as a result of the heat of adsorption, there will be a time dependent difference in temperature between the adsorbent and the surroundings. External heat transfer is assumed to be governed by Newton's Law.

3) Intraparticle diffusion is the only significant resistance to mass transfer. The sorbate concentration at the surface of each particle in the sample is therefore always in equilibrium, at the temperature of the sample, with the sorbate concentration in the ambient fluid.

4) The diffusivity is assumed constant and the equilibrium relationships are linear, (i.e., $\partial c^*/\partial T$ constant).

With the appropriate definition of the particle radius, this model is applicable to either a sample of individual adsorbent crystals, under conditions of intracrystalline diffusion control, or to a macroporous adsorbent pellet under conditions of intrapellet (macropore) diffusion control. Another practical and important case, that of an assemblage of crystals in which the mass transfer rate is controlled by diffusion into the sample bed, will be dealt with in a subsequent paper.

Subject to these approximations, the system may be described by the following set of differential equations:

$$\frac{\partial Q}{\partial \tau} = \frac{1}{\eta^2} \cdot \frac{\partial}{\partial \eta} \left(\eta^2 \cdot \frac{\partial Q}{\partial \eta} \right) \tag{1}$$

$$\overline{Q} = 3 \int_0^1 Q \eta^2 \cdot d\eta \tag{2}$$

$$\rho(-\Delta H) \frac{d\overline{Q}}{d\tau} = \frac{\rho C_p}{c_\infty - c_0} \cdot \frac{dT}{d\tau} + \frac{ha}{(c_\infty - c_0)} \cdot \frac{(T - T_0)}{(D/r^2)} \tag{3}$$

$$Q(1, \tau) = \frac{c_s - c_0}{c_\infty - c_0} = 1 + \left(\frac{\partial c^*}{\partial T} \right) \left(\frac{T - T_0}{c_\infty - c_0} \right) \tag{4}$$

with the initial and boundary conditions:

$$Q(\eta, \tau) = 0, \quad (\tau < 0); \quad \left. \frac{\partial Q}{\partial \eta} \right|_{\eta = 0} = 0 \tag{5}$$

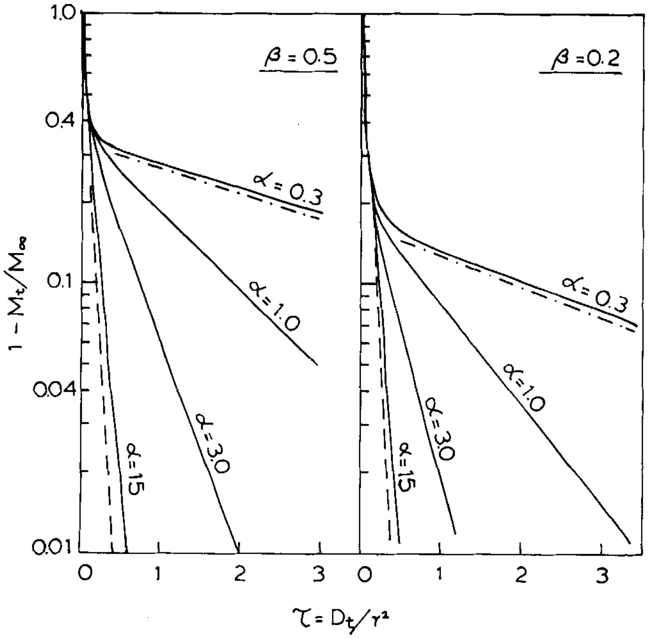

Figure 1. Theoretical uptake curves calculated from Eqns. (6) and (8) for representative values of α and β. Also shown is the limiting curve for isothermal diffusion (Eqn. 9) – – – –, and the curve for heat transfer control (Eqn. 10) for $\alpha = 0.3$ —·—·—·.

TABLE 1. DETAILS OF ZEOLITE CRYSTALS

Zeolite	Mean crystal diameter (μm)	Composition	Origin
4A	34 21.5 7.2	Na form, as synthesized	Synthesized by Yucel using Charnell's method
5A	34	As above after ~65% Ca++ exchange	Synthesized by Yucel using Charnell's method
5A	3.6	~65% Ca++	Linde 5A Lot 550045

Note: Size fractions were separated using 'Nitek' microsieves.

The solution to this set of equations may be obtained by Laplace transformation. Inversion by the method of residues yields the expressions for the dimensionless sorption curve and the temperature history of the sample in terms of the dimensionless parameters $\alpha \equiv ha/\rho C_p$ and $\beta \equiv (\Delta H/C_p) \cdot (\partial c^*/\partial T)$:

$$\overline{Q} = \frac{\bar{c} - c_0}{c_\infty - c_0} = 1 - \sum_{n=1}^{\infty} \frac{9[(q_n \cot q_n - 1)/q_n^2]^2 \exp(-q_n^2\tau)}{\frac{1}{\beta} + \frac{3}{2}[q_n \cot q_n(q_n \cot q_n - 1)/q_n^2 + 1]} \tag{6}$$

$$(T - T_0)\left(\frac{\partial Q^*}{\partial T}\right) = 1 - Q_s = \sum_{n=1}^{\infty} \frac{-3[(q_n \cot q_n - 1)/q_n^2] \exp(-q_n^2\tau)}{\frac{1}{\beta} + \frac{3}{2}[q_n \cot q_n(q_n \cot q_n - 1)/q_n^2 + 1]} \tag{7}$$

where q_n is given by the roots of:

$$3\beta(q_n \cot q_n - 1) = q_n^2 - \alpha \tag{8}$$

A family of uptake curves, calculated from Equations (6) and (8), for several values of α and β is shown in Figure 1. The limiting case of isothermal behavior is obtained when either $\alpha \to \infty$ or $\beta \to 0$. Under these conditions the roots of Equation (8) become simply $q_n = n\pi$ and Equation (6) reduces to the familiar form:

$$\overline{Q} = 1 - \frac{6}{\pi^2} \Sigma \frac{1}{n^2} \exp(-n^2\pi^2\tau) \tag{9}$$

When diffusion is very rapid, the kinetics are controlled entirely by heat transfer. The limiting behavior may be derived by considering the asymptotic form of Equation (6) for small values of α. Replacing $(q\cot q - 1)$ in Equation (8) by the series expansion $-(q2/3 + q^4/45 + \ldots)$ shows that, for small α, the first root of Equation (8) is given by $q_1^2 = \alpha/(1 + \beta)$. The asymptotic form of the uptake curves is then obtained from the first term of the summation of Equation (6) which becomes:

$$\overline{Q} = \frac{m_t}{m_\infty} = 1 - \frac{\beta}{(1 + \beta)} \exp(-\alpha\tau/(1 + \beta))$$

$$= 1 - \frac{\beta}{1 + \beta} \exp\left[\frac{-hat}{\rho C_p(1 + \beta)}\right] \tag{10}$$

This is equivalent to the expression derived by King and Cassie (1940).

For all values of α and β the uptake curves reduce, in the long time region, to simple exponential curves. For certain values of α and β, the shapes of the curves are quite similar to the curve for isothermal diffusion (Equation 9), so it is not always easy to detect the intrusion of thermal effects simply from the shape of the uptake curves. In practice, thermal effects may be minimized by using the smallest possible quantity of adsorbent spread over as large an area as possible. Further, since α varies directly with the external area of the sample, varying the size or configuration of the sample provides a convenient experimental test for thermal limitations.

It has been previously assumed (for example Loughlin, Derrah and Ruthven 1971) that 1) thermal effects may be detected by varying the size of the concentration step over which the uptake curves is measured and 2) that agreement between the uptake curves measured over different concentration steps and for adsorption and desorption provides evidence that the system can be considered as isothermal. This is correct when the diffusivity is temperature dependent. However, if the interval over which the uptake curve is measured becomes sufficiently small, the effect of the temperature dependence of diffusivity vanishes. The uptake curves then are independent of step size and the same for adsorption and desorption, even though there may still be an appreciable thermal affect arising from the temperature dependence of the equilibrium position. Under these conditions, identity of the sorption curves for different step sizes does not provide unequivocal evidence of isothermal behavior.

Comparing the time constants from Equations (6) and (9) shows that the system may be considered iso-

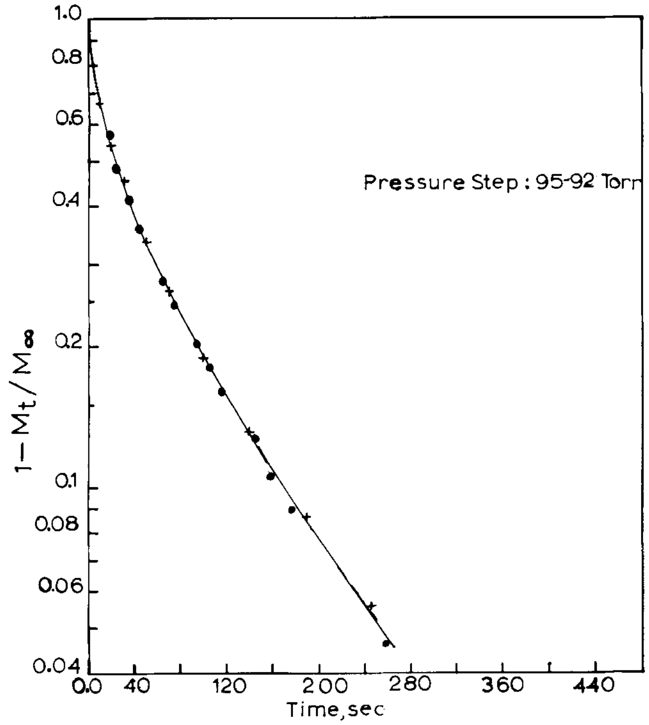

Figure 2. Uptake curves for sorption of CO_2 in 4A zeolite (34μm) crystals at 273K, measured over the same pressure steps. ●, 36mg sample; + 13mg sample. Theoretical curve is calculated for isothermal diffusion with $D/r^2 = 1.3 \times 10^{-3}$ sec^{-1}.

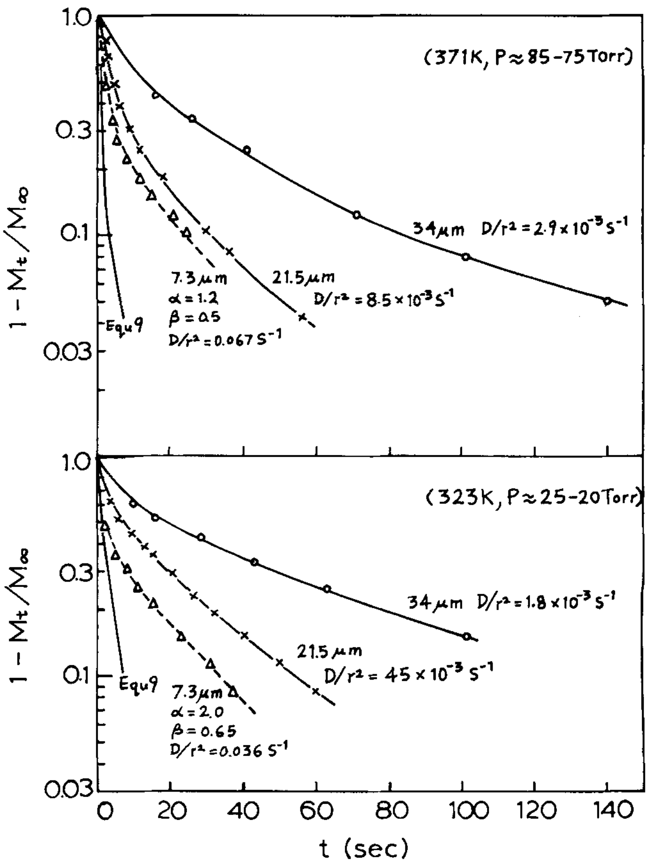

Figure 3. Uptake curves for CO_2 in different size fractions of 4A zeolite crystals. In the larger crystals (21.5 and 34μm), sorption is nearly isothermal. Theoretical curves are calculated from the isothermal diffusion model with the indicated values of D/r^2. Sorption in the 7.3μm crystals is non-isothermal and the theoretical curves (– – – –) are calculated from the non-isothermal model (Eqns. 6 and 8) with the indicated values of α, β and D/r^2. The limiting curves for isothermal diffusion, calculated according to Eqn. (9) for the 7.3μm crystals, with the same diffusional time constants (D/r^2 = 0.067 and 0.036 s^{-1}), are also indicated for comparison.

thermal if $\alpha/(1+\beta) >> \pi^2$. This condition is unnecessarily severe, since if the value of β is sufficiently small, thermal effects are important only in the very last stages of the uptake curve. By directly comparing the uptake curves calculated from Equation (6) with the isothermal curves (Equation 19), it may be shown that the error in the time constant arising from the use of the isothermal approximation will not exceed 15% over the range 0-85% uptake (provided that $\alpha/\beta > 60$). This condition is equivalent to and somewhat less severe than the criterion developed by Chihara, Suzuki and Kawazoe (1976) from the linear driving force approximation. For small values of β, the criterion may be relaxed somewhat further.

EXPERIMENTAL

Sorption curves were measured gravimetrically using a Cahn vacuum microbalance system. We followed the change in weight of a small sample of adsorbent when subjected to a small differential step change in sorbate pressure. Details of the zeolite crystals are given in Table 1. In the systems studied, heats of sorption are relatively large and thermal effects are important. The experimental data illustrate the main features of the non-isothermal model.

CO_2-4A

Uptake curves for CO_2 in 34μm 4A crystals, measured over similar pressure steps, with two different depths of adsorbent sample are shown in Figure 2. There is good agreement between the uptake curves showing that, under these conditions, the system is essentially isothermal and the macro-diffusional resistance of the sample is negligible. For a more accurate comparison with the experimental data, we calculated the theoretical curve for isothermal diffusion for an assemblage of

TABLE 2. PARAMETERS OBTAINED FROM NON-ISOTHERMAL ANALYSIS OF SORPTION CURVES FOR CO_2 IN 4A ZEOLITE (FIGURE 3)

		Non-isothermal analysis					Isothermal analysis
T (K)	Crystal radius (μm)	D/r^2 (sec^{-1})	D (cm$^2 \cdot$ sec^{-1})	$(ha/\rho C_p)$ (sec^{-1})	β	α	D/r^2 (sec^{-1})
371 (~80 Torr)	34	2.9×10^{-3}	8.4×10^{-9}	0.08	0.5	28	2.7×10^{-3}
	21.5	8.5×10^{-3}	9.8×10^{-9}			9.4	8×10^{-3}
	7.3	0.067	8.9×10^{-9}			1.2	0.015
323 (~22 Torr)	34	1.8×10^{-3}	5.2×10^{-9}	0.073	0.65	41	1.7×10^{-3}
	21.5	4.5×10^{-3}	5.18×10^{-9}			16.2	4.4×10^{-3}
	7.3	0.036	4.8×10^{-9}			2.0	0.012

TABLE 3. ANALYSIS OF UPTAKE CURVES FOR CO_2-5A UNDER CONDITIONS OF HEAT TRANSFER CONTROL (EQN. 10)

$p_1 - p_2$ (Torr)	c (mol/cavity)	From equilib. βC_p (cal · g^{-1} · deg^{-1})	From uptake curves $ha/\rho C_p$ (s^{-1})	β	C_p (cal · g^{-1} · deg^{-1})
		(34 μm) Thick bed 34mg 371K			
263-232	4.05	0.38	0.052	0.96	0.40
150-140	3.26	0.35	0.052	0.92	0.38
102-95	2.77	0.30	0.049	0.82	0.37
74-69	2.40	0.25	0.046	0.64	0.39
44-39	1.91	0.18	0.048	0.49	0.37
			Av. 0.049		Av. 0.38
		(34 μm) Thick bed 37mg 323K			
213-205	8.0	0.24	0.034	0.92	0.26
147-131	7.43	0.29	0.037	1.04	0.28
88-83	6.74	0.33	0.036	1.22	0.27
50-45	5.72	0.36	0.034	1.3	0.28
30-27	4.87	0.4	0.035	1.38	0.29
			Av. 0.036		Av. 0.28
		(34 μm) Thick bed 34mg 273K			
234-204	10.1	0.24	0.031	0.67	0.36
119-108	9.57	0.26	0.031	0.79	0.33
43-39	8.57	0.33	0.031	1.13	0.30
20-17	7.56	0.51	0.032	1.56	0.33
4.3-3.6	5.22	0.76	0.03	2.33	0.33
			Av. 0.032		Av. 0.32
		(34 μm) Thin bed 12.5mg 273K			
43-37	9.0	0.34	0.053	0.47	0.72
21-18	8.5	0.48	0.062	0.67	0.72
12-8	7.52	0.65	0.061	0.79	0.83
4.6-4.2	6.66	0.75	0.058	1.08	0.71
			Av. 0.06		Av. 0.8
		Linde 5A (3.6μm) Thick bed 38mg 273K			
114-98	8.2	0.26	0.022	0.74	0.35
63-55	7.8	0.29	0.022	0.89	0.33
27-23	6.9	0.42	0.020	1.2	0.34
8.5-8.2	5.5	0.62	0.020	2.0	0.31
4.4-3.7	4.2	0.76	0.023	2.3	0.33
			Av. 0.022		Av. 0.34

cubic particles with the size distribution of this sample (see Ruthven and Loughlin 1971), rather than from Equation (9). This curve fits the experimental curve well.

Further evidence that, for this system, sorption rates are controlled by intra-crystalline diffusion, comes from a comparison of the uptake curves for different crystal size fractions (Figure 3). The sorption curves for the 34μm and 21.5μm crystals can be well represented by the theoretical curves for isothermal diffusion. The time constants (D/r^2) are in the ratio of the square of the crystal radii, so that essentially the same diffusivities are obtained for both crystal sizes. Sorption rates in the 7.3μm sample are higher than in the large crystals, but not as high as would be expected from the difference in crystal size. This apparent anomaly can be explained by the intrusion of heat transfer resistance. The uptake curves were matched to the non-isothermal model (Equations 6 and 8), using values of β calculated from the equilibrium isotherms and values of $(ha/\rho C_p)$ determined from measurements for similar systems under conditions of complete heat transfer control (Equation 10). This yields values of D/r^2, and hence values of D, which are consistent with the near isothermal data for the larger crystals (see Table 2).

If non-isothermal effects are ignored, and the uptake curves for the 7.3μm crystals are matched to the isothermal model, erroneously low values of D/r^2 are obtained. This results in diffusivities which seem to decrease with decreasing crystal size. Diffusivities which vary in this way with crystals size have been reported by Karger and Caro (1976), Gupta, Ma and Sand (1971), Satterfield and Frabetti (1967), and Brandt and Rudloff (1964), and the intrusion of thermal effects offers a possible explanation.

CO_2-5A

Diffusion in the 5A zeolite is much faster than in 4A because of the larger effective window aperture. Heat transfer limitations become more significant, even in the larger crystals. Sorption curves were measured over a wide range of conditions in the Linde 5A crystals (3.6μm) and in the Ca^{++} exchanged (5A) form of the 34μm crystals (~ 65% Ca^{++}). Two different sample bed configurations were used: a "thin bed" of about 10-12 mg spread as thinly as possible over the entire area of the sample pan, and a "thick bed" sample of about 35 mg on a smaller pan.

For the thick bed, sorption rates were essentially controlled by heat transfer under all conditions. The sorption curves,

TABLE 4. COMPARISON OF PARAMETERS CALCULATED FROM THERMALLY CONTROLLED UPTAKE CURVES (DATA OF TABLE 3)

Heat capacities

Sample	T (K)	Wt of sample (mg)	Wt of pan (mg)	Estimated C_p (cal · g^{-1} deg^{-1})	Experimental C_p
Thick bed	273	34	20	0.31	0.32
	371			0.36	0.38
Thin bed	273	12	35	0.8	0.8

Note: Heat capacity of sieve (cal·gm^{-1}·deg^{-1}) is 0.19 at 273K and 0.22 at 371K. Heat capacity of pan is 0.21 at 273K and 0.225 at 371K.

Heat transfer coefficients

Sample	T (K)	Theoretical estimates $h' \times 10^4$ (cal · cm^{-1} · sec^{-1} · deg^{-1})	$h'' \times 10^4$	$h \times 10^4$	Experimental $ha/\rho C_p$ (s^{-1})	a/ρ (cm^2 · g^{-1})	Total external area (cm^2) = (a/ρ) × wt of sample
Thick bed	273	1.54	0.9	2.44	0.032	42	1.4
	371	2.54	2.25	4.79	0.049	39	
Thin bed	273	3.22	0.9	3.12	0.06	153	1.9

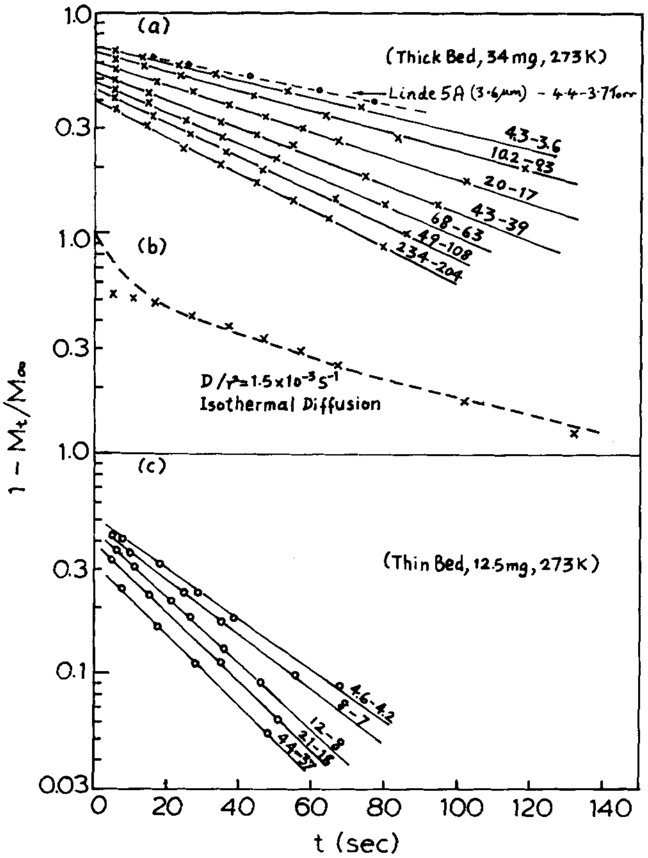

Figure 4. Experimental sorption curves for CO_2 in 5A zeolite (34μm crystals) at 273K, under conditions of complete heat transfer control: (a) 34 mg sample (thick bed); uptake curve for Linde 5A crystals over the pressure step 4.4-3.7 Torr is also indicated for comparison; (b) comparison of experimental curve for pressure step 20-17 Torr from (a) with theoretical curve for isothermal diffusion; (c) 12.5 mg sample (thin bed) (Numbers on curves denote pressure steps in Torr).

measured over similar pressure steps with similar adsorbent sample quantities (34-40mg), for the small Linde 5A crystals and the large Charnell crystals, showed very little difference, despite the order of magnitude difference in crystal size. This is convincing evidence of the absence of any significant intracrystalline diffusional resistance, under the experimental conditions. Representative sorption curves are shown in Figure 4 and comparative data are given in Tables 3 and 4.

The uptake curves (both adsorption and desorption) show a rapid initial uptake followed by a slow exponential approach to equilibrium, in accordance with Equation 10. Because of the larger external area/volume ratio for the thin bed sample, the heat transfer rate is faster. And, the uptake is controlled by the combined effects of both heat transfer and diffusion, rather than by heat transfer alone (as for the thick bed). Depending on the precise conditions, one or other of these effects may be dominant. This is illustrated in Figure 5.

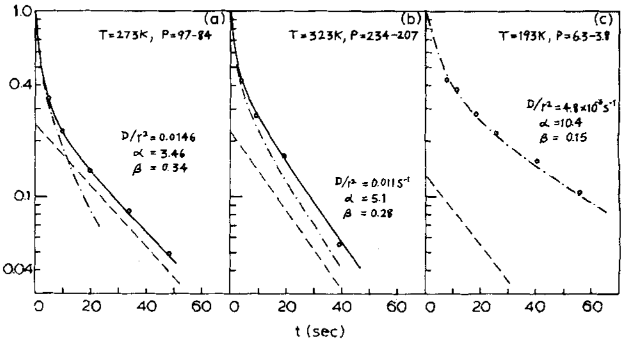

Figure 5. Sorption curves for CO_2 in the thin bed sample (~12 mg) of 5A zeolite (34μm crystals): (a) and (b) show curves in which the intrusion of heat transfer resistance causes significant deviation from the isothermal diffusion curve; at 193K diffusion is slower and the uptake curve shown in (c) is practically isothermal; theoretical non-isothermal curves calculated from Eqns. 6 and 8 with the indicated parameters, ———; isothermal curves for same values of D/r^2 —·—·; asymptotic curves for heat transfer control, – – – – –. At 193K the isothermal and non-isothermal curves are nearly coincident. Points are experimental.

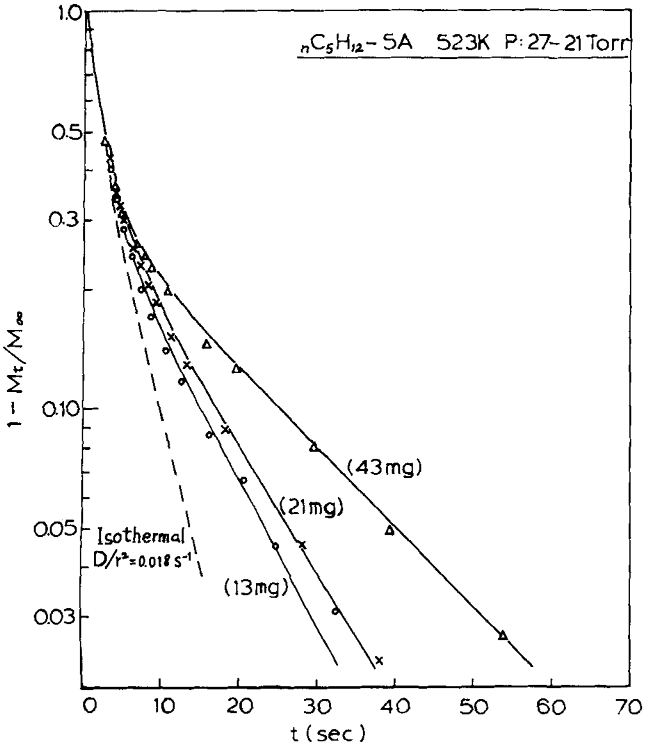

Figure 6. Uptake curves for *n*-pentane-Linde 5A at 250°C, measured over pressure step ~27-21 Torr, with different sample bed depths. Theoretical non-isothermal curves (———) are calculated from Eqns. 6 and 8 with the parameters given in Table 5. The isothermal curve (– – – – –) is from Eqn. 9 with the same value of $D/r^2 (= 0.018$ sec$^{-1})$.

In the long-time region, all curves represented by Equation (6) or (9) approach an exponential decay. Therefore, for certain values of the parameters $ha/\rho C_p$ and β the curves for complete heat transfer control (Equation 10) may appear similar to the curves for isothermal diffusion, except in the initial region, as illustrated in Figure 4b. For rapidly diffusing systems, the initial uptake rate is difficult to measure with accuracy, so it may be difficult in practice to distinguish unequivocally between heat transfer and diffusion control simply from the form of an individual uptake curve.

However, such a distinction is relatively easy when a series of curves measured over different pressure steps is available. The curves are plotted in semilogarithmic coordinates and values of the apparent parameters β and $ha/\rho C_p$ are calculated according to Equation 10 from the slopes and intercepts. Values of $\beta C_p (\equiv \Delta H \partial c^*/\partial T)$ are calculated from the equilibrium data and values of the effective heat capacity C_p may then be found from the kinetic data for each run. If the uptake curves are indeed thermally controlled, the values of both heat capacity and heat transfer coefficient should be independent of pressure. Confirmation may be obtained by comparing the values of heat transfer coefficients and heat capacities derived in this way with the values estimated from physical data. The results of such calculations are summarized in Table 3. Only representative data are given; the mean values are averages of about 20 runs at each temperature.

The parameters (C_p and $ha/\rho C_p$) derived from the analysis of the uptake curves are compared in Table 4 with values estimated *a priori*. The total effective heat capacity is estimated from C_p = heat capacity of sieve + (Wt of pan/Wt of sieve) × heat capacity of pan. The values estimated in this way are close to the experimental values. The overall heat transfer coefficient h is estimated as the sum of the contributions from radiation (Stefan's Law with emissivity 0.8: $h' = 4.4 \times 10^{-12}\ T^3$) and from conduction in a stagnant fluid ($Nu = 2$ or $h'' = k/R$), where k is the thermal conductivity of the gas (independent of pressure) and R is the equivalent radius of the adsorbent sample, estimated from sample wt/density $= (4/3)\ \pi R^3$). Using the estimated heat transfer coefficient, together with the experimental values of C_p and $ha/\rho C_p$, gives a value for the total external surface area of the sample. This value is comparable with the geometric area.

Table 5. Parameters for Non-Isothermal Uptake Curves for n-Pentane-5A at 523K, Pressure Step ~27-21 Torr (see Figure 6)

Sample wt (mg)	β	α	$ha/\rho C_p$ (s^{-1})	D/r^2 (s^{-1})
13	0.23	7.6	0.136	0.018
21	0.25	5.1	0.092	
43	0.29	3.4	0.061	

It is evident that the model of complete heat transfer control fits the kinetic data for the thick bed sample over the entire range of conditions and the parameters derived from this model are similar for the two different crystal sizes and in good agreement with estimated values. When data for the thin bed sample are analyzed in this way, the values obtained for C_p and $ha/\rho C_p$ show regular trends with pressure. Detailed analysis shows that except for a limited range of pressure at 0°C (5-50 Torr) the diffusional resistance was significant. So, the uptake rate in the thin bed is controlled by both diffusion and heat transfer. The behavior of the thin bed sample is illustrated in Figure 5. At 273K and 323K, the initial portions of the uptake curves lay close to the isothermal diffusion curve, but the deviation from isothermal behavior becomes pronounced in the long-time region. These non-isothermal diffusion curves are well represented by the theoretical model (Equations 6 and 8). At the lowest temperature (193K), diffusion is slower and, since the sorbate concentration is approaching the saturation limit, the value of β is small. Under these conditions the uptake curve is practically isothermal.

n-Pentane-Linde 5A (3.6μm crystals) at 250°C

The sorption curves for this system provide a clear illustration of the effect of varying the depth of the adsorbent sample. Desorption curves, measured over essentially the same pressure step with three different depths of sample are shown in Figure 6. Up to about 75% completion, the curves for the three samples are similar and quite close to the isothermal curve, calculated from Equation 9. However, there are considerable deviations in the later portions of the curves. As may be expected, the smallest sample, which has the highest external area/volume ratio, lies closest to the isothermal curve. The greatest deviation is shown by the largest sample. All three curves are well approximated by the theoretical non-isothermal curves, calculated according to Equations 6 and 8, with the parameters given in Table 5.

The value of D/r^2 derived from the non-isothermal model (0.018 sec^{-1}) agrees well with the value obtained by isothermal analysis of the initial region of the curves. The values of β are consistent with the values estimated from equilibrium data, using experimental values of the effective heat capacity. Values of $ha/\rho C_p$ agree well with those obtained at the same temperature for faster diffusing systems, under conditions of complete heat transfer control.

CONCLUSION

The non-isothermal model provides a consistent interpretation of the uptake behavior over a wide range of conditions. The effects of varying the adsorbent crystal size, the configuration of the adsorbent sample and the sorbate concentration (which affects the parameter β through the term $\partial c^*/\partial T$) are correctly predicted. The parameters derived from the model agree well with *a priori* estimates.

Most of the sorption kinetic data reported in the literature have been interpreted assuming isothermal behavior. When diffusion is rapid or heat transfer slow, significant departures from isothermal behavior may occur. The intrusion of heat transfer resistance is not always obvious simply from the shape of the uptake curve, since for certain values of the parameters α and β, the form of the non-isothermal curve resembles closely the form of the curve for isothermal diffusion. Analysis of such an uptake curve according to the isothermal assumption will lead to an erroneous value for the diffusional time constants.

For systems such as hydrocarbons in 13X zeolite or in mordenite, diffusion is rapid and heats of sorption are relatively large. Under these conditions, the uptake behavior is likely to be significantly modified by heat effects. The uptake curves for such systems show the form typical of thermal limitation, a rapid initial uptake followed by a slow final approach to equilibrium. See, for example, Satterfield and Frabetti (1967) and Satterfield and Katzer (1971). It is probable that some anomalies in the published diffusivity data may arise from failure to take adequate account of heat transfer limitations. A similar conclusion was reached by Zikanova and Kocirik (1979), in their recent study of cyclohexane sorption in 13X zeolite compacts.

The non-isothermal model provides a convenient basis for the analysis of non-isothermal uptake curves. The model makes it possible to determine a reliable criterion for validity of the isothermal approximation. Thermal effects may be minimized in practice by using the smallest possible quantity of adsorbent sample spread over as wide an area as possible, and by maximizing the effective thermal capacity, possibly by adding inert material to the sample. Varying the configuration and particle size of the adsorbent provides a convenient direct experimental test for the significance of heat transfer resistance. However, even if heat transfer resistance cannot be entirely eliminated, it is possible to derive reliable diffusional time constants from the uptake curves using the non-isothermal model, provided that diffusion is not so fast that the uptake is entirely controlled by heat transfer (Equation 10).

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NOTATION

a = external surface area per unit volume of adsorbent sample
$c(\eta, \tau)$ = adsorbed phase concentration
$c_s(\tau)$ = adsorbed phase concentration at crystal surface
c_0 = initial (steady state) adsorbed phase concentration
c_∞ = final steady state adsorbed phase concentration
c^* = equilibrium adsorbed phase concentration
C_p = effective heat capacity of adsorbent sample (including containing pan)
D = intracrystalline diffusivity
h = external heat transfer coefficient
q_n = roots of Equation (8)
$Q(\eta, \tau)$ = dimensionless adsorbed phase concentration $\equiv (c - c_0)/(c_\infty - c_0)$
$\overline{Q}(\tau)$ = average value of Q defined by Equation (2) ($\equiv$ fractional uptake m_t/m_∞)
$Q_s(\tau)$ = dimensionless adsorbed phase concentration at crystal surface $\equiv (c_s - c_0)/(c_\infty - c_0)$
Q^* = equilibrium value of Q (for specified ambient concentration)
r = equivalent radius of zeolite crystal
T = temperature
T_0 = initial (and final) steady state temperature

Greek Letters

η = dimensionless radial coordinate
τ = dimensionless time Dt/r^2
ρ = effective density of adsorbent sample
$-\Delta H$ = heat of adsorption
α = dimensionless parameter $ha/\rho C_p$
β = dimensionless parameter $\equiv (\Delta H/C_p)\ (\partial c^*/\partial T)_p$

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