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Heat Effects in ZLC Experiments

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Abstract. The problem of nonisothermal desorption in a zero length column (ZLC) experiment is considered theoretically. Simple analytical expressions for the ZLC desorption curve are derived for certain limiting situations in which the governing equations reduce to a linear form. More general numerical solutions are calculated for a wide range of experimental conditions assuming both negligible mass transfer resistance and finite mass transfer resistance controlled by intraparticle diffusion. A simple criterion for negligible thermal effects is developed. It is shown that when the ZLC technique is applied to the measurement of diffusion in unaggregated zeolite crystals, as originally intended, heat effects are generally insignificant. However, when applied to the measurement of macropore diffusion in relatively large adsorbent particles heat effects can become important and may cause major modification of both the desorption rate and the shape of the desorption curve. A recent experimental ZLC study carried out with commercial adsorbent particles, under conditions of macropore diffusion control, showed an anomalous dependence of the desorption rate on both temperature and particle size. These effects can be qualitatively explained by the nonisothermal model. A more precise quantitative representation of these experiments will require a more refined model incorporating a nonlinear equilibrium isotherm as well as intraparticle diffusional resistance.

Keywords: diffusion zeolite, ZLC, heat effects

Introduction

Because of its simplicity the ZLC (zero length column) technique (Eic and Ruthven, 1988) has been widely accepted as a method for measuring intracrystalline or intraparticle diffusion in adsorbents and catalysts. A major advantage claimed for this method is that the use of a very small adsorbent sample with a relatively high gas flow rate makes it easy to maintain essentially isothermal conditions. The isothermal approximation is indeed valid when the measurement is performed with unaggregated zeolite crystals, as originally envisaged. However, under certain experimental conditions, particularly when large macroporous particles are used, significant departures from isothermality can occur, leading to an interesting variety of desorption curves. Indeed, this study was triggered by Guimaraes' experimental observations which, for strongly adsorbed species on relatively large composite adsorbent particles, showed consistent but anomalously shaped desorption curves. The objective of this paper is to explore such behavior and to develop a simple criterion to guide the selection of experimental conditions for diffusion measurements.

Theoretical Model

The experimental set-up for ZLC measurements has been described in earlier publications (Eic and Ruthven, 1988; Hufton et al., 1994). We consider a

ZLC system in which heat transfer is sufficiently rapid to maintain the temperature of the gas in the ZLC cell at a constant value (T_o). However, as a result of the heat of desorption, depending on the rate of heat transfer, a temperature difference may develop between the adsorbent and surrounding gas.

The major assumptions used to develop the mathematical model are:

- ideal gas behavior
- mass transfer is sufficiently rapid that local equilibrium is maintained at all times (although thermal equilibrium between fluid and solid is not assumed)
- linear equilibrium isotherm with vant Hoff temperature dependence of the Henry's Law constant
- temperature variation through an adsorbent particle is neglected and the resistance to heat transfer is represented by an overall coefficient (Eq. (10)).

The heat balance may be written:

$$C_s \frac{dT}{dt} = \frac{d\bar{q}}{dt}(-\Delta H) + ha(T_o - T) \tag{1}$$

where $a = 3/R$ is the external area per unit particle volume. C_s is the volumetric heat capacity of the adsorbent which is assumed to be independent of loading. Since the experiments are performed at low loadings the contribution of the adsorbed phase to the heat capacity is minor, this is a valid approximation.

The corresponding mass balance is

$$-V_s \frac{d\bar{q}}{dt} = Fc(t) \tag{2}$$

where $c(t)$ represents the time dependent concentration of sorbate in the effluent gas stream and F is the purge flow rate. As a simple limiting case we further assume that the mass transfer resistance between the adsorbent and the gas is small so that adsorption equilibrium is maintained at all times according to a linear equilibrium isotherm:

$$q = \bar{q} = K(T) \cdot c \tag{3}$$

The temperature dependence of the equilibrium constant is assumed to follow the usual vant Hoff relation:

$$K = K_\infty e^{-\Delta H/\mathbf{R}T} \tag{4}$$

so that

$$\begin{aligned} \frac{d\bar{q}}{dt} &= K\frac{dc}{dt} + c\frac{dK}{dT}\cdot\frac{dT}{dt} \\ &= K\left[\frac{dc}{dt} - \frac{|\Delta H|}{\mathbf{R}T^2}\cdot\frac{dT}{dt}c\right] \end{aligned} \tag{5}$$

In the last bracket we have explicitly recognized the fact that adsorption is an exothermic process so ΔH will be negative.

The transient response of the system is given by the simultaneous solution of Eqs. (1)–(5) with the initial conditions:

$$t = 0, \quad c = 0, \quad T = T_o, \quad \frac{dT}{dt} = -\frac{|\Delta H| F c_o}{V_s C_s} \tag{6}$$

In dimensionless form the equations become

$$\frac{d\theta}{d\tau} + \alpha\frac{dQ}{d\tau} = \gamma(1-\theta) \tag{7}$$

$$\begin{aligned} &\frac{dQ}{d\tau} + C(\tau) = 0; \\ &C(\tau) = \left[\frac{d\theta}{d\tau} - \gamma(1-\theta)\right]\Big/\alpha \end{aligned} \tag{8}$$

$$Q(\theta, \tau) = \exp\left[\delta\left(1 - \frac{1}{\theta}\right)\right]\cdot C(\tau) \tag{9}$$

with the initial conditions

$$\begin{aligned} &\tau = 0, \quad C = 1, \quad Q = 1, \\ &\frac{dQ}{d\tau} = -1, \quad \Bigg|\frac{d\theta}{d\tau} = \alpha \end{aligned} \tag{10}$$

and the dimensionless variables defined by

$$C = c/c_o, \quad Q = \bar{q}/q_o, \quad \theta = T/T_o, \quad \tau = Ft/K_oV_s$$
$$\delta = |\Delta H|/\mathbf{R}T_o, \quad \gamma = (ha/C_s)/(F/K_oV_s),$$
$$\alpha = \frac{|\Delta H| K_o c_o}{C_s T_o}$$

α is the dimensionless adiabatic temperature change.

By simple algebra Eqs. (7)–(9) can be reduced to the form of a pair of partially coupled ordinary differential equations:

$$\begin{aligned} &\left\{\frac{d\theta}{d\tau} - \gamma(1-\theta)\right\}\left\{\frac{\delta}{\theta^2}\cdot\frac{d\theta}{d\tau} - \exp\left[\delta\left(1-\frac{1}{\theta}\right)\right]\right\} \\ &= \frac{d^2\theta}{d\tau^2} + \gamma\frac{d\theta}{d\tau} \end{aligned} \tag{11}$$

$$\frac{d\ln C}{d\tau} = \frac{\delta}{\theta^2}\cdot\frac{d\theta}{d\tau} - \exp\left[\delta\left(1-\frac{1}{\theta}\right)\right]$$

$$= \frac{\frac{d^2\theta}{d\tau^2}+\gamma\frac{d\theta}{d\tau}}{\frac{d\theta}{d\tau}-\gamma(1-\theta)} \tag{12}$$

From these forms it is clear that, in principle, Eq. (11) may be integrated directly to yield the temperature response $\theta(\tau)$ and the concentration response may then be found either from Eq. (8) or by integration of Eq. (12). However, Eq. (11) is clearly nonlinear so it is unlikely that a simple general analytic solution can be found. Approximate analytic solutions may, however, be obtained for some important limiting cases.

In the long time limit, except when $\gamma \to 0$ (adiabatic case), $\theta \to 1.0$ and $d\theta/d\tau \to 0$ so, from Eq. (12) the slope of the long time asymptote is given by

$$\left.\frac{d\ln C}{d\tau}\right|_{\tau\to\infty} \to -1 \tag{13}$$

as for the isothermal case.

When the heat of sorption is small ($\delta \to 0$) Eq. (11) reduces to

$$\frac{d^2\theta}{d\tau^2} + (\gamma+1)\frac{d\theta}{d\tau} - \gamma(1-\theta) = 0 \tag{14}$$

The solution of this equation, satisfying the initial condition (Eq. (10)) is

$$1-\theta = \frac{\alpha}{\alpha-1}(e^{-\tau}-e^{-\alpha\tau}) \tag{15}$$

Substitution in Eq. (12) shows that, under these conditions, the concentration response approaches the isothermal case:

$$C = e^{-\tau} \tag{16}$$

In the adiabatic limit $\alpha \to 0$ and Eqs. (11) and (12) reduce to

$$\frac{d^2\theta}{d\tau^2} + \exp\left[\delta\left(1-\frac{1}{\theta}\right)\right]\cdot\frac{d\theta}{d\tau} - \frac{\delta}{\theta^2}\cdot\left(\frac{d\theta}{d\tau}\right)^2 = 0 \tag{17}$$

$$\frac{d\ln C}{d\tau} = \frac{d^2\theta/d\tau^2}{d\theta/d\tau} \tag{18}$$

Provided that the adiabatic temperature change (α) is small relative to δ i.e.,

$$\frac{\Delta T_{\text{ad}}}{T_o} = \alpha \ll \frac{|\Delta H|}{\mathbf{R}T_o} = \delta \tag{19}$$

the factors $\exp[\delta(1-1/\theta)]$ and $1/\theta^2$ will not depart greatly from unity and Eq. (17) then reduces to

$$\frac{d^2\theta}{d\tau^2} + \frac{d\theta}{d\tau} - A\left(\frac{d\theta}{d\tau}\right)^2 = 0 \tag{20}$$

where $A = \delta/\theta^2$ can be treated as a constant. This equation can be solved directly by the substitutions $p = d\theta/d\tau$, $d^2\theta/d\tau^2 = p\,dp/d\theta$, whence we find

$$\frac{d\theta}{d\tau} = \frac{-\alpha e^{-\tau}}{1+\alpha A(1-e^{-\tau})} \tag{21}$$

Integrating with the initial condition $t = 0,\ \theta = 1$ we find

$$1-\theta = \frac{1}{A}\ln\left[1+\alpha A(1-e^{-\tau})\right] \tag{22}$$

In the long time limit

$$(e^{-\tau}\to 0) \quad \text{and} \quad 1-\theta \to \frac{\ln(1+\alpha A)}{A} \cong \alpha \tag{23}$$

since αA is, according to Eq. (19), small. Substitution in Eq. (14) followed by integration yields as the expression for the concentration response:

$$C = \frac{e^{-\tau}}{1+\alpha A(1-e^{-\tau})} \tag{24}$$

Equations (22) and (24) thus provide simple analytical approximations for the temperature and concentration response in the adiabatic limit. The long time asymptote for C evidently has the same slope as for the isothermal case, in accordance with Eq. (13).

A more general solution for the long time asymptote under adiabatic conditions may be obtained by recognizing that the temperature falls relatively rapidly to the limiting value given by $1-\theta \cong \alpha$ (the adiabatic temperature change) and thereafter remains constant. The asymptotic form of the desorption curve ($\tau \to \infty$)

then follows from Eqs. (8) and (9) with $\theta = 1 = \alpha$:

$$\beta \frac{dC}{d\tau} + C = 0; \qquad \frac{d \ln C}{d\tau} = -\frac{1}{\beta} \tag{25}$$

where $\beta = \exp[\frac{\delta\alpha}{1-\alpha}]$.

This solution applies only for $\alpha < 1$. For $\alpha > 1$ the model predicts that the temperature will fall to the absolute zero (and all desorption will stop) before the adiabatic temperature drop is achieved. This analysis shows that for modest deviations from isothermal behavior, the important parameter governing the equilibrium behavior is the product $\delta\alpha$. Since γ measures the ratio of the time constants for heat transfer and convection the correlation, of deviations from isothermal behavior in terms of the combined parameter $\alpha\delta/\gamma$ is evidently a reasonable choice.

Results and Discussion

In order to obtain a more general understanding of the form of the concentration and temperature response curves (Eqs. (7)–(9)) were integrated numerically, subject to the initial conditions represented by Eq. (10). The resulting response curves (C vs. τ and θ vs. τ) for representative values of the parameters (α, γ, δ) are shown in Figs. 1–5. The families of curves are of similar general form but the shapes of the individual response curves, for both temperature and concentration, vary greatly depending on the magnitude of the nonisothermality. For high values of γ (rapid heat transfer) the departure from isothermality is minimal and occurs only in the initial region. The corresponding concentration response curves approach the simple exponential decay characteristic of an isothermal system (Eq. (16)). For smaller values of γ the temperature response develops a prolonged minimum with a corresponding plateau in the concentration response. For very small values of γ the behavior approaches the adiabatic limit defined by Eqs. (22) and (24) and the temperature declines monotonically towards the adiabatic limit (α). The effect of increasing δ (the dimensionless heat of sorption) is to elongate the plateau region. The long time asymptotes of all concentration curves show the behavior required by Eq. (13) or Eq. (25) (adiabatic case).

Effect of Concentration

The effect of concentration, as measured by α, is shown in Fig. 3. For these particular parameter values ($\delta = 10$, $\gamma = 0.1$) the curves for increasing α span the entire range from nearly isothermal ($\alpha = 0.1$) to almost adiabatic (for $\alpha = 100$).

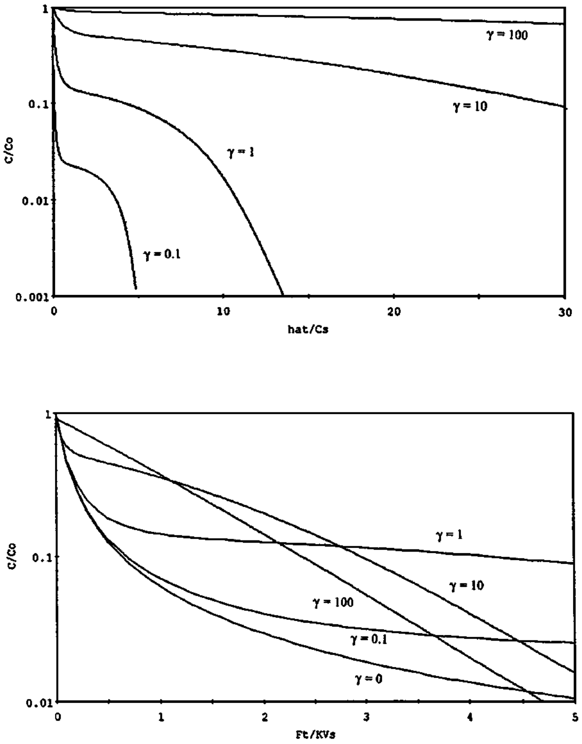


Figure 1. Theoretical nonisothermal desorption curves calculated from the nonisothermal equilibrium theory for $\alpha = 1.0$, $\delta = 10$ for a range of γ values. The curves are plotted against two different dimensionless time parameters ($ha\,\tau/C_s$ and Ft/KV_s) and show the change in shape with increasing heat transfer resistance from $\gamma = 100$ (nearly isothermal) to $\gamma = 0$ (adiabatic).

Effect of Mass Transfer Resistance

A limited investigation of the effect of finite mass transfer resistance was undertaken in which Eq. (2) was replaced by the following set of partial differential equations describing the desorption process under conditions of diffusion control:

$$\frac{\partial q}{\partial t} = D\left[\frac{\partial^2 q}{\partial r^2} + \frac{2}{r}\frac{\partial q}{\partial r}\right] \tag{26}$$

$$-D\frac{\partial q}{\partial r}\bigg|_{\nu=R} = \frac{FR}{3V_s} \cdot \frac{q}{K(T)} \tag{27}$$

$$\bar{q} = \frac{3}{R^3}\int_0^R qr^2\, dr \tag{28}$$

$$\frac{\partial q}{\partial r}\bigg|_{r} = 0; \quad q\big|_{r=R} = Kc_o \tag{29}$$

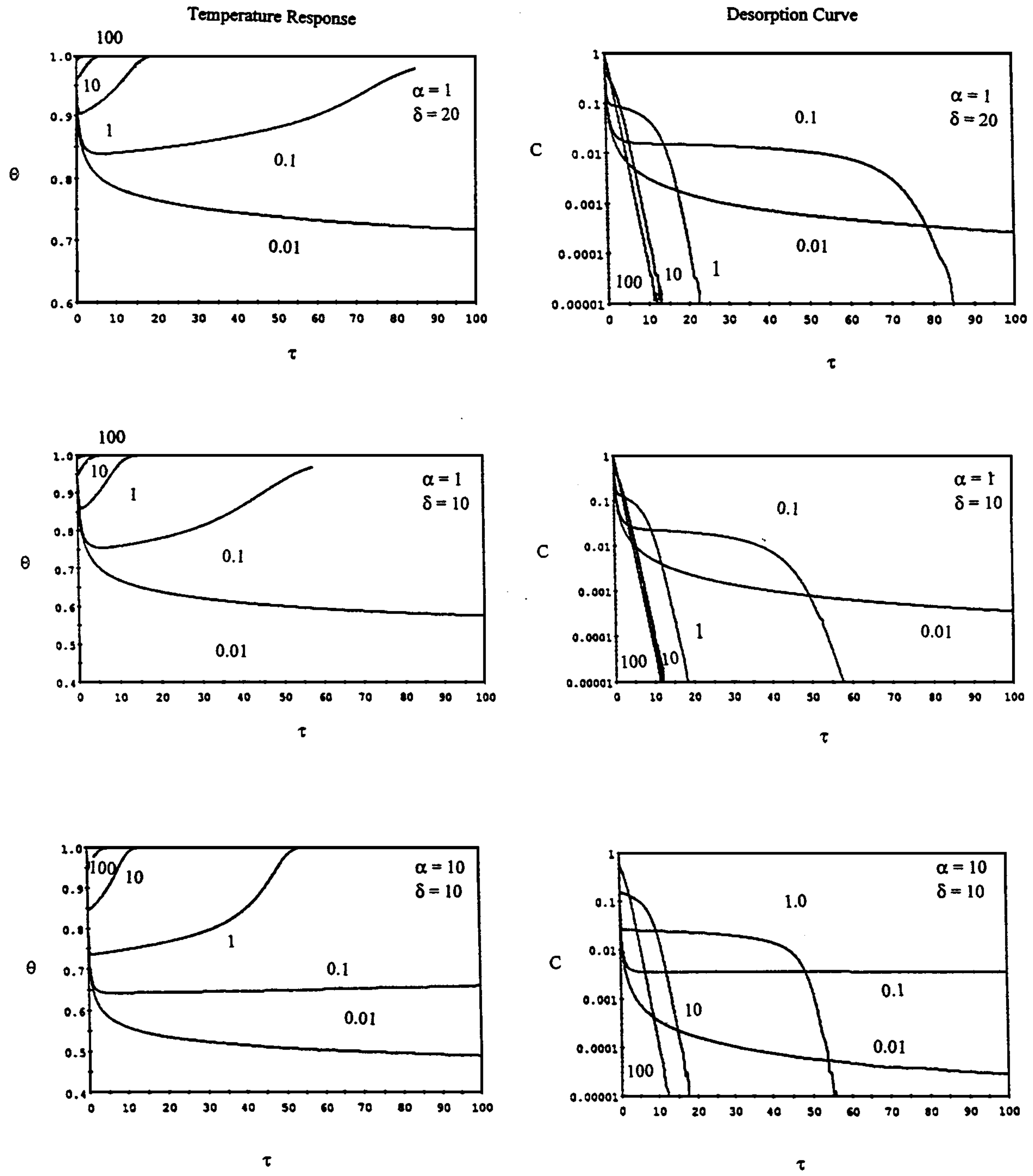


Figure 2. Representative theoretical desorption and temperature response curves calculated from the nonisothermal equilibrium theory for a range of parameter values. The parameter shown for each curve is γ.

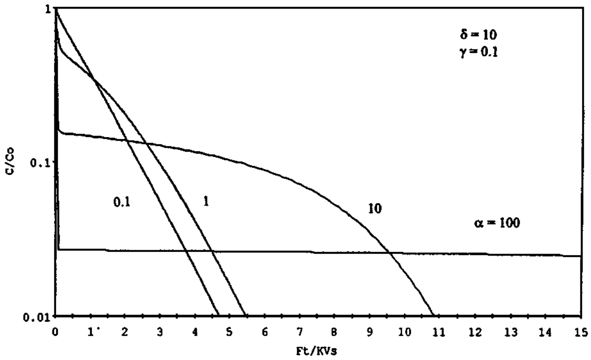


Figure 3. Theoretical desorption curves, calculated from the nonisothermal equilibrium model, showing the transition from near isothermal to strongly heat limited with increasing concentration (α).

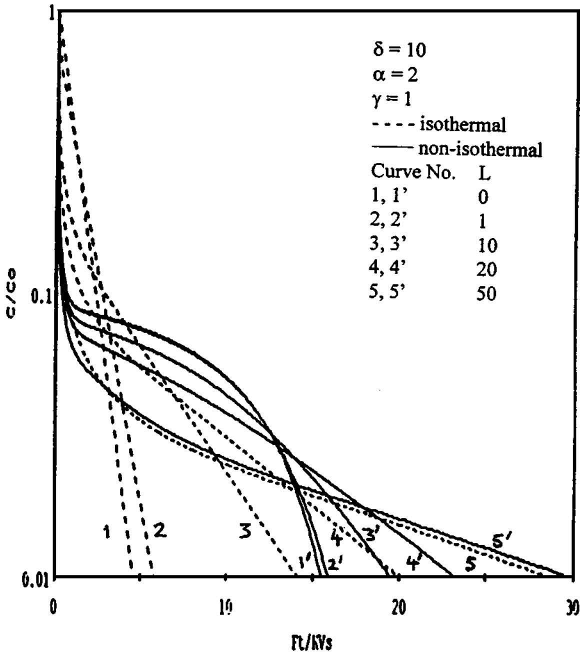


Figure 4. Theoretical desorption curves calculated numerically from the full numerical simulation, including the effects of both heat and mass transfer resistance, showing the effect of increasing diffusional resistance as measured by the parameter L. ($\alpha = 2$, $\delta = 10$, $\gamma = 1$, $L = 0, 1, 10, 20, 50$).

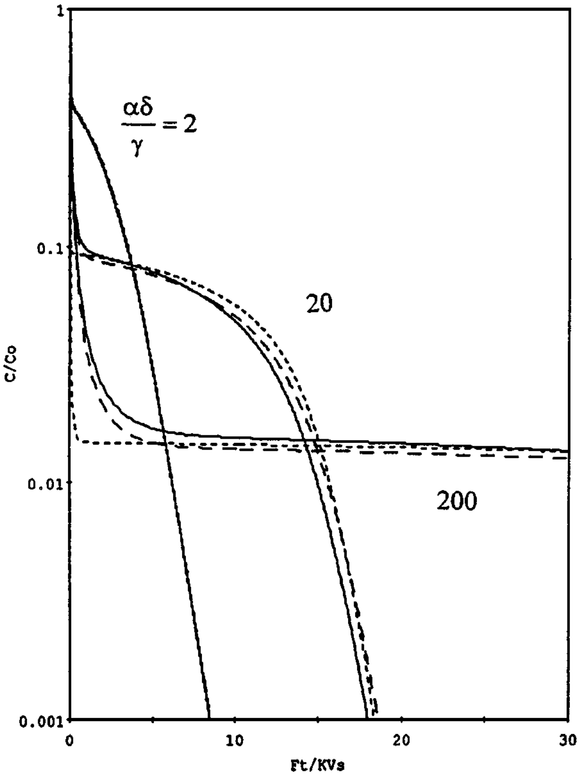


Figure 5. Theoretical desorption curves calculated from the nonisothermal equilibrium model showing that, for similar values of $(\alpha\delta/\gamma)$ 2,20,200, the desorption curves are similar, regardless of differences in the individual parameter values: (——) $\delta = 20$, $\alpha = 1$, $\gamma = 0.1$, 1.0, 10; (------) $\delta = 10$, $\alpha = 2$, $\gamma = 0.1$, 1.0, 10; (.........) $\delta = 10$, $\alpha = 20$, $\gamma = 0.01$, 0.1, 1.0.

This gives the dimensionless variable $L = \frac{1}{3} \cdot \frac{F}{V_s} \cdot \frac{R^2}{K_o D}$ as an additional parameter in the model. The temperature dependence of D is neglected.

A set of theoretical desorption curves calculated according to the isothermal and nonisothermal models for a range of different L values (for $\delta = 10$, $\alpha = 1.0$ and $\gamma = 1$) is shown in Fig. 4. The curves for $L = 0$ correspond to the equilibrium limit and thus coincide with the earlier simplified model. Under these conditions there is a large difference between the isothermal and nonisothermal curves. As L increases the effect of mass transfer resistance becomes more pronounced and we see that the difference between the curves derived from the isothermal and nonisothermal models becomes less pronounced. For $L > 20$ the effect of the nonisothermality is evidently minimal.

Criterion for Negligible Heat Effects

From a practical perspective it is important to establish a simple criterion that can be used to assess the significance of heat effects for any particular set of operating conditions. To develop such a criterion we used the arbitrary condition that we consider the heat effect to be insignificant if, over the range of 0 to 99% completion of the desorption step, the time required to achieve any given degree of completion, as measured by the adsorbed phase loading, does not exceed the isothermal time for this same degree of desorption by more than 10%. By comparing the results of numerous numerical simulations over a wide range of parameter values we were able to demonstrate that the relevant parameter is the combined group $(\alpha\delta/\gamma) = (\frac{\Delta H}{\mathbf{R}T_o})^2 \cdot \frac{c_0 F\mathbf{R}}{haV_s}$ that heat effects increase strongly with the heat of sorption and the sorbate concentration and decrease with the heat transfer parameter is intuitively obvious. However, it is less obvious that the equilibrium constant cancels, and therefore has no effect, and that the magnitude of the nonisothermal effect *increases* with the space velocity (F/V_s). This arises because, under equilibrium conditions, the (isothermal) desorption rate depends directly on this quantity.

Some justification for the use of this combined parameter is provided by Fig. 5 which shows a series of desorption curves calculated, assuming negligible mass transfer resistance, for various values of α, δ and γ chosen to give the same values of the combined group $(\alpha\delta/\gamma)$. It is clear that the curves for different values of this combined group are quite different but for a constant value of this group the curves are all quite similar regardless of the individual values of α, δ and γ.

For the equilibrium theory case $(L = 0)$ the criterion for insignificant thermal effects reduces to $\alpha\delta/\gamma < 1.0$. However, the effect of mass transfer resistance is to reduce the desorption rate, thus making heat effects less significant (for a given value of $\alpha\delta/\gamma$). From a series of numerical simulations in which the effect of intraparticle diffusional resistance was included in the nonisothermal model the maximum tolerable value of $\alpha\delta/\gamma$ as a function of L was established—as shown in Fig. 6.

An approximate estimate of the heat transfer coefficient between the adsorbent particles and the gas phase can be obtained from the (conservative) assumption that $\mathrm{Nu} = 2.0$ or $h = \gamma/R$. Since $a = 3/R$ (for spherical particles) it follows that $\gamma \propto 1/R^2$. We thus reach the somewhat surprising conclusion that the intrusion of thermal effects becomes more pronounced with larger adsorbent particles. Of course, this is true only under conditions of insignificant mass transfer resistance (L small). When diffusional resistance to mass transfer is important (L large) we find that both L and the critical value of the combined parameter $(\alpha\delta/\gamma)$ increase in proportion to R^2 so, under these conditions, changing the particle size does not greatly alter the relative importance of heat and mass transfer resistances. Similarly, variation of the flow rate (or rather the ratio F/V_s) does little to alter the heat and mass transfer resistance when the system is operating at large L in the kinetically controlled regime since both $\alpha\delta/\gamma$ and L are directly proportional to F/V_s.

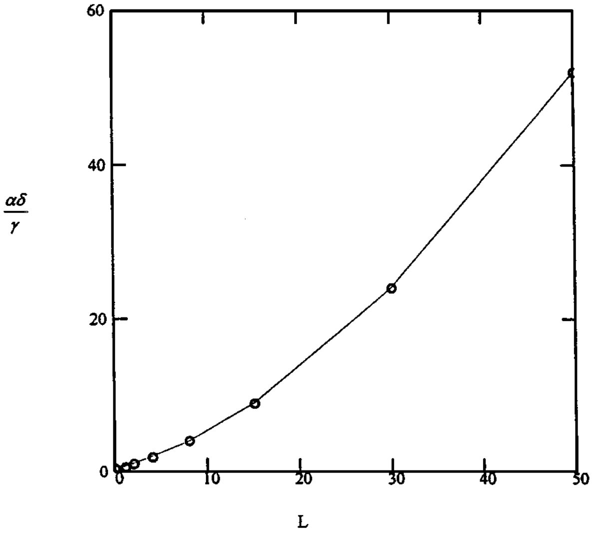


Figure 6. Plot of $\alpha\delta/\gamma$ vs. L showing criterion for negligible thermal effects as a function of diffusional resistance to mass transfer (as measured by L).

In order to assess the practical input of heat effects in ZLC systems we have made approximate estimates of the parameter values for three representative systems. These are summarized in Table 1. Even for a system such as benzene in NaX crystals for which the heat of adsorption is high and the possibility of heat effects seems at first sight plausible, it is evident that the value of $\alpha\delta/\gamma$ is so small that thermal effects will be entirely negligible. The very small value for $\alpha\delta/\gamma$ for this system results mainly from the high value of γ, which in turn arises from the use of small (100 μm) particles (crystals). Indeed, this conclusion would appear to be generally valid, under all practically reasonable conditions, for any ZLC system involving small zeolite crystals (as opposed to macroscopic particles).

In contrast, for the system N_2-5A at 200 K, for which the heat of sorption is much smaller, the criterion $\alpha\delta/\gamma < 1$ is only just satisfied. This is a direct consequence of the use of much larger (macroscopic) particles in these experiments. For the system *p*-xylene-NaX pellets we find that the criterion is violated and significant heat effects are to be expected.

Table 1. Significance of heat effects in ZLC experiments.

System	V_s (cm^3)	R (cm)	K	c_o (mol/cm^3)	F (STP) (cm^3/s)	$-\Delta H$ (kcal/mol)	α	δ	γ	$\frac{\alpha\delta}{\gamma}$
N_2-5A pellets 200 K He carrier (Xu and Ruthven, 1993)	0.003	0.1	10^3	10^{-6}	0.33	5.5	0.17	14	3.2	0.74
C_6H_6-NaX crystals 400 K He carrier (Brandani et al., 1996)	10^{-3}	5×10^{-3}	10^7	10^{-9}	0.5	19	3.6	24	5×10^6	1.7×10^{-5}
C_6H_8-BaY pellets 423 K N_2 carrier (Guinmaraes, 1996)	0.003	0.14	10^6	3×10^{-7}	0.6	17	75	20	180	8.3

Heat transfer coefficient is estimated from $\mathrm{Nu} = 2$ or $h = \lambda/R$, $ha = 3\lambda/R^2$. This should be a minimum value. Heat capacity of solid $C_s \cong 0.2$ $cal/cm^3 \cdot$ deg.

This is attributable to the use of relatively large particles together with a relatively high value for c_o. It thus appears that although when applied, as originally intended, to the study of intracrystalline diffusion the ZLC technique can be regarded as operating under essentially isothermal conditions, this is not necessarily true when the technique is used to study macropore diffusion in larger adsorbent particles. In such studies it is clearly essential to examine carefully the possible intrusion of heat effects before any conclusions concerning diffusional time constants can be derived from the experimental desorption curve. To minimize the possibility of thermal control it is desirable to keep the sorbate concentrations as small as possible.

Comparison with Experimental Data. This study was prompted by some surprising observations in a recent experimental ZLC study of the desorption of the desorption of p-xylene from a commercial pelleted Y zeolite adsorbent of the type used in the *Parex* process (Guinmaraes, 1997). It was found that the desorption curves for different particle size fractions, measured under similar experimental conditions (Fig. 7(a)), could not be properly interpreted using an isothermal model. The experimental curves show apparently faster mass transfer rates for the larger particles (higher slope of the $\ln(c/c_o)$ vs. t plot in the long time region) than for the smaller particles whereas, under isothermal conditions, depending on the nature of the rate limiting mass transfer resistance, the mass transfer rate for the smaller particles should always be greater than or equal to that for the larger particles. Furthermore, for a given particle size, the desorption rate appeared to be faster at the lower temperature (see Fig. 8(a)). This is again contrary to what is to be expected under isothermal conditions.

Examination of the parameter values corresponding to these experiments (Table 1) shows that the parameter $\alpha\delta/\gamma$ is indeed relatively large, suggesting that the intrusion of heat effects is probably significant. Unfortunately, the conditions of these experiments were well outside the Henry's Law region and the assumption of negligible mass transfer resistance is probably not fulfilled, so the simple nonisothermal equilibrium theory is not directly applicable. Nevertheless, the simplified theory correctly reproduces the qualitative trends shown by the experimental data, as may be seen from Figs. 7(b) and 8(b) which show the theoretical curves, calculated from the simplified model with parameter values corresponding approximately to the experimental conditions. To obtain a more precise representation of these experiments the model should be refined to include a non-linear equilibrium relation and finite resistance to mass transfer.

Conclusions

A simple theoretical analysis has been developed to represent ZLC desorption behavior under nonisothermal conditions. Even under the restrictive assumptions of the model (linear equilibrium, negligible resistance to mass transfer) the desorption curves show a rich variety of different shapes depending on the magnitudes of the various parameters. Although the assumptions of isotherm linearity and negligible mass transfer resistance are almost certainly not fulfilled the model provides a qualitative interpretation of recent experimental desorption curves for a high heat macro-controlled system, suggesting that under these conditions the intrusion of heat effects is indeed significant. Further refinement of the model to include a nonlinear isotherm and finite mass transfer resistance can

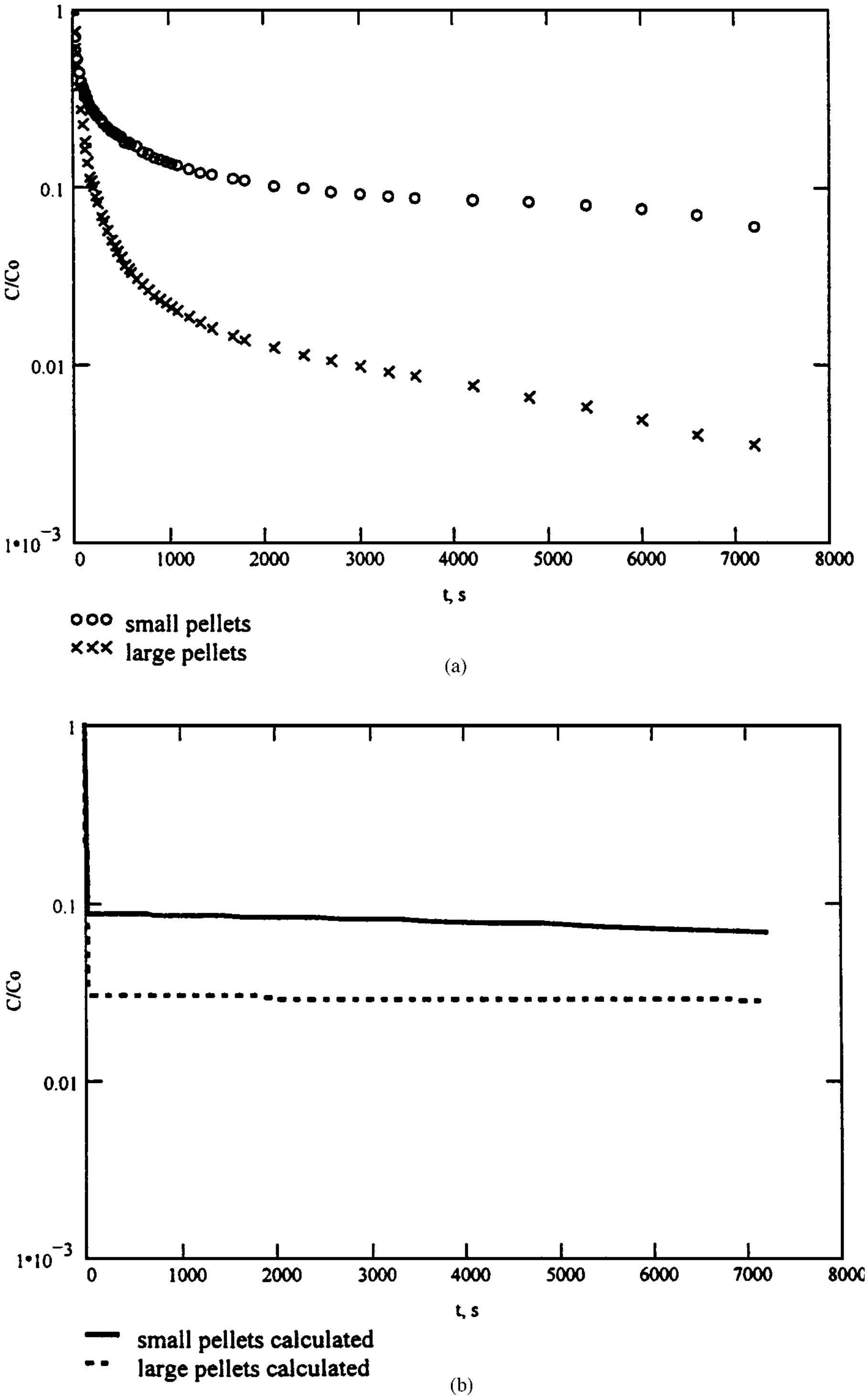
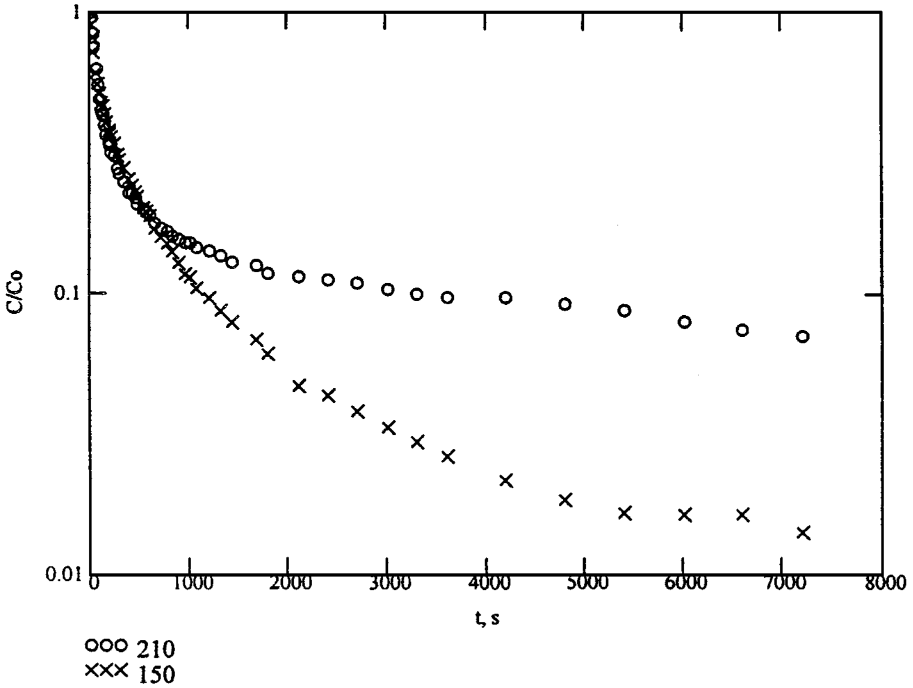
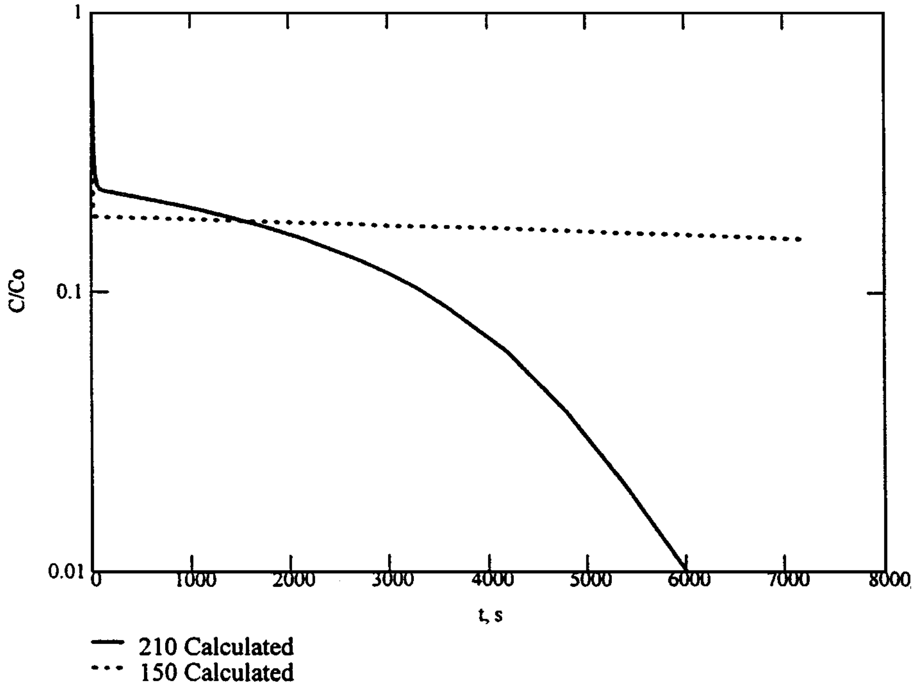


Figure 7. Effect of particle size: (a) Experimental curves for desorption of *p*-xylene at 150°C with N_2 carrier (102 ml/min STP) for "large" particles (equivalent radius 1.4 mm), (×) and "small" particles (equivalent radius 0.7 mm), (○). (b) Theoretical desorption curves calculated from the nonisothermal equilibrium model with $\alpha = 75$, $\delta = 20$, $\gamma = 60$, $F/KV_s = 10^{-3}\ \mathrm{s}^{-1}$, $\alpha = 150$ (small particles) and $\alpha = 600$ (large particles). These values are approximately representative of the real system.



(a)



(b)

Figure 8. Effect of temperature: (a) Experimental curves for desorption of *p*-xylene at 150°C (×) and 210°C (o) with N_2 carrier (34 ml/min STP). Equivalent radius 1.4 mm. (b) Theoretical desorption curves calculated from the nonisothermal equilibrium model with the following parameters: At 150°C; (-----) $\delta = 20$, $\gamma = 180$, $\alpha = 75$, $F/KV_s = 3 \times 10^{-4}\ \text{s}^{-1}$, At 210°C (——); $\delta = 17.5$, $\gamma = 15$, $\alpha = 5$, $F/KV_s = 4 \times 10^{-3}\ \text{s}^{-1}$. These values are approximately representative of the experimental system.

probably be achieved in order to provide a better quantitative representation of the experimentally observed behavior. However, the main value of the simple model developed here is that it provides a very simple criterion that can be used to assess a priori the significance of heat effects in a ZLC experiment under any specified conditions, and thus to provide guidance in the choice of conditions for ZLC diffusion measurements.

Notation

a	External area/volume for adsorbent particle ($= 3/R$)	cm^{-1}
A	Parameter δ/θ^2	—
c	Fluid phase concentration	mol/cm^3
c_o	Fluid phase concentration	mol/cm^3
C	Dimensionless variable c/c_o	—
C_s	Volumetric heat capacity of adsorbent particle	J/cm^3 · deg
D	Intracrystalline (or intra-particle) diffusivity	cm^2 · s^{-1}
F	Purge gas flow rate	cm^3 · s^{-1}
h	Heat transfer coefficient	J/cm^2· deg · s
ΔH	Heat of adsorption	J/mol
K	Dimensionless Henry constant	—
K_*	Pre-experimental factor (in Eq. (4))	—
K_o	Value of K for initial equilibrium state (T_o)	—
L	Dimensionless parameter $= \frac{1}{3}\frac{F}{V_s}\frac{R^2}{K_o D}$	—
q	Adsorbed phase concentration	mol/cm^3
$\bar{q}$	Adsorbed phase concentration averaged over a particle.	mol/cm^3
q_o	Adsorbed phase concentration at equilibrium with c_o at T_o	mol/cm^3
Q	Dimensionless variable $\bar{q}/q_o$	—
R	Particle (crystal) radius r radial coordinate	cm
$\mathbf{R}$	Gas constant	J/mol · deg
t	Time	s
T	Temperature	deg
V_s	Adsorbent volume	cm^3
α	$\frac{\lvert\Delta H\rvert K_o c_o}{C_s T_o}$	—
δ	$\frac{\lvert\Delta H\rvert}{\mathbf{R} T_o}$	—
γ	$\frac{ha}{C_s}\cdot\frac{K_o V_s}{F}$	—
θ	T/T_o	—
τ	$\frac{Ft}{K_o V_s}$	—
λ	Thermal conductivity of carrier gas	J/cm · deg · s
Nu	Nusselt Number $= 2Rh/\lambda$	—

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