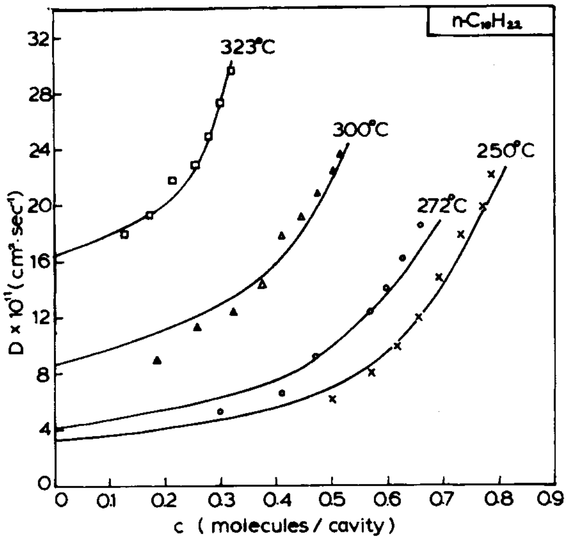

Figure 2. Concentration dependence of differential diffusivities for n-decane in 5A zeolite, calculated from the experimental uptake curves.

Loughlin, 1974). It therefore seems that the surface barrier resistance observed in the liquid phase at lower temperatures is indeed due to the blocking effect of the solvent, rather than to an intracrystalline barrier.

Extrapolation of the present limiting differential diffusivity data suggests that at 295 K $D_o \approx 2 - 6 \times 10^{-15}$ cm$^2 \cdot$ s^{-1}. This is considerably lower than the apparent integral diffusivities observed by Caro et al. However, in view of the strong positive concentration dependence of the differential diffusivity these results are not necessarily inconsistent.

A more detailed report of our studies will be published shortly.

NOTATION

c = sorbate concentration
D = intracrystalline diffusivity
D_o = corrected diffusivity (Eq. 3)
m_t/m_∞ = fractional approach to equilibrium in an uptake experiment
P = equilibrium sorbate pressure
r = equivalent radius of zeolite crystals
t = time
α = constant of proportionality for surface resistance model (Caro et al., 1980)

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Extrapolating Conversions to Zero External Gradients in Vapor Phase Catalytic Recirculation Reactors

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In vapor phase catalytic studies, recirculation reactors are often used in obtaining kinetic data. These reactors provide the high mass flows in the catalyst bed typical of industrial conditions and minimize the temperature and concentration gradients external to the catalyst. An example for these type of reactors which has recently become popular is the Berty reactor (Berty et al., 1969) with the blower and return line enclosed in an autoclave. In our recent study of cyclohexane dehydrogenation kinetics at atmospheric pressure with the Berty reactor (Schneider et al., 1978), we have found external temperature gradients to be significant. In this communication a method for extrapolating conversions to zero external gradients is outlined and shown to be significantly superior to the method traditionally used.

Extrapolation to zero external gradients is commonly done by plotting conversion (X) vs. the reciprocal mass velocity (ϕ) over the catalyst bed. As the mass velocity approaches infinity ($\phi \rightarrow 0$), external gradients are essentially eliminated. Therefore, a polynomial fit for a plot of X vs. ϕ would yield conversion at zero external gradients (X^∞) upon intersection with the ordinate. Our analysis here was carried out with the objective of developing a functional relationship based on theoretical considerations to see if the corresponding extrapolation is superior to the one outlined above.

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In the absence of internal gradients, observed reaction rate is a function of conditions at the catalyst surface, i.e.

$$r_o = r\,(C_{1s}, C_{2s} \ldots, C_{Ns}, T_s) \tag{1}$$

In the presence of external gradients, surface concentrations and temperature will be a function of flow conditions in the catalyst bed. First we will show how reaction rate can be expressed as a function of conversion and the mass velocity in the reactor bed.

At steady state the rate at which the reacting species are transported between the bulk phase and the catalyst surface can be written in terms of the appropriate mass transfer coefficient and the stoichiometric coefficient as

$$\frac{K_i(C_{ib} - C_{is})}{\nu_i} = \frac{k_\alpha(C_{\alpha b} - C_{\alpha s})}{\nu_\alpha} \tag{2}$$

Product rates are related to the input rates by

$$N_i = N_{io} - \frac{\nu_i}{\nu_\alpha} N_{\alpha o} X \tag{3}$$

where X is the conversion for the key component, α. Summing Eq. 3 over each component, one obtains

$$N_T = N_o - \frac{\Delta\nu}{\nu_\alpha} N_{\alpha o} X \tag{4}$$

With Eqs. 3 and 4 and the perfect gas law, bulk concentrations can be written as

$$C_{ib} = \frac{y_{io} - \frac{\nu_i}{\nu_\alpha} y_{\alpha o} X}{1 - \frac{\Delta\nu}{\nu_\alpha} y_{\alpha o} X} \frac{P_T}{R_g T_b} \tag{5}$$

Reaction rate can be written as

$$r_o = \frac{k_\alpha(C_{\alpha b} - C_{\alpha s})}{-\nu_\alpha} \frac{A_p}{V_p} \tag{6}$$

$$= \frac{N_{\alpha o} X}{-\nu_\alpha} \frac{\rho_p}{} \tag{7}$$

Combining Eqs. 2, 5 and 7 one obtains

$$C_{is} = \frac{y_{io} - \frac{\nu_i}{\nu_\alpha} y_{\alpha o} X}{1 - \frac{\Delta\nu}{\nu_\alpha} y_{\alpha o} X} \frac{P}{R_g T_b} - \frac{\nu_i}{\nu_\alpha} \frac{1}{k_i} \frac{V_p}{A_p} \frac{\rho_p}{m} N_{\alpha o} X \tag{8}$$

$$C_{\alpha s} = \frac{y_{\alpha o} - y_{\alpha o} X,}{1 - \frac{\Delta\nu}{\nu_\alpha} y_{\alpha o} X} \frac{P}{R_g T_b} - \frac{1}{k_\alpha} \frac{V_p}{A_p} \frac{\rho_p}{m} N_{\alpha o} X \tag{9}$$

From heat balance on a catalyst particle, it follows

$$T_b = T_s + \frac{V_p}{A_p} \frac{\rho_p}{m} \frac{\Delta H_R}{h} N_{\alpha o} X \tag{10}$$

Assuming k_α/h is independent of the flow conditions, Eq. 10 can be written as

$$T_s = T_b - \kappa \frac{X}{k_\alpha} \tag{11}$$

where

$$\kappa = \frac{V_p}{A_p} \frac{\rho_p}{m} \Delta H_R\, N_{\alpha o} \frac{k_\alpha}{h}$$

Using the correlation of Petrovich and Thodos (1968) the mass transfer coefficient can be related to the mas velocity in the bed by

$$k \,\alpha\, G^{0.641} \tag{12}$$

Since T_b is held constant, by combining Eqs. 1, 8, 9, 11 and 12 one could obtain

$$r_o = R\,(X, \xi) \tag{13}$$

where

$$\xi = X/G^{0.641} \tag{14}$$

At infinite fan speed

$$\begin{aligned} G &= \infty \\ \xi &= o \\ X &= X^\infty \end{aligned} \tag{15}$$

Forming a Taylor's series expansion about $\xi = o$ and $X = X^\infty$

$$\begin{aligned} r_o = R(X^\infty, o) &+ \left.\frac{\partial R}{\partial X}\right|_{\substack{X=X^\infty \\ \xi=o}} (X - X^\infty) + \left.\frac{\partial R}{\partial \xi}\right|_{\substack{X=X^\infty \\ \xi=o}} \xi + \\ &\tfrac{1}{2} \left.\frac{\partial^2 R}{\partial X^2}\right|_{\substack{X=X^\infty \\ \xi=o}} (X - X^\infty)^2 + \tfrac{1}{2} \left.\frac{\partial^2 R}{\partial \xi^2}\right|_{\substack{X=X^\infty \\ \xi=o}} \xi^2 \\ &+ \left.\frac{\partial^2 R}{\partial X \partial \xi}\right|_{\substack{X=X^\infty \\ \xi=o}} (X - X^\infty)\xi + \ldots . \end{aligned} \tag{16}$$

Combining Eqs. 7 and 16 one obtains

$$\begin{aligned} X = \lambda_1 &+ \lambda_2 (X - X^\infty) + \lambda_3 \xi + \lambda_4 (X - X^\infty)^2 \\ &+ \lambda_5 \xi^2 + \lambda_6 (X - X^\infty)\xi + \ldots . \end{aligned} \tag{17}$$

where λ's are all constants. Equations 17 can further be rearranged to

$$\begin{aligned} X = \beta_1 &+ \beta_2 \xi + \beta_3 X^2 + \beta_4 \xi^2 + \beta_5 X \xi \\ &+ \beta_6 X^3 + \ldots + \beta_9 \xi^3 + \ldots . \end{aligned} \tag{18}$$

where β's are constants. If up to 2nd order terms in the series expansion are retained.

$$X \cong \beta_1 + \beta_2 \xi + \beta_3 X^2 + \beta_4 \xi^2 + \beta_5 X \xi \tag{19}$$

From the conditions given by Eq. 15, it follows that X^∞ could be obtained from the solution of

$$\beta_3 X^{\infty 2} - X^\infty + \beta_1 = o \tag{20}$$

β's can be determined from the fit of data. For example, if a Berty reactor is employed, by using the available characteristic curves for the fan (Berty et al., 1969), the mass velocity can be calculated for any fan speed provided that either the corresponding pressure drop across the catalyst bed or the ratio of the catalyst bed to particle diameter is known.

If only the first two terms are retained in Eq. 18, one would have

$$X \cong \beta_1 + \beta_2 \xi \tag{21}$$

TABLE 1. RATE EXPRESSION USED (CYCLOHEXANE DEHYDROGENATION) AND REACTION PARAMETERS

$$r_o = Z\,e^{-E_a/R_g T_s} C_{\alpha s}$$

with

$$T_s = T_b - \kappa \frac{X}{k_\alpha}$$

where

$$\kappa = \frac{V_p}{A_p} \frac{\rho_p}{m} \Delta H_R\, N_{\alpha o} \frac{k_\alpha}{h}$$

and

$$C_{\alpha s} = \frac{1 - x}{1 + 3x} \frac{P_T}{R_g T_b} - \frac{1}{k_\alpha} \frac{V_P}{A_P} \frac{\rho_P}{m} N_{\alpha o} X$$

$T_b = 553$ K

$P_T = 1.013 \times 10^5$ N/m^2

$Z = 1.514 \times 10^{11}$ s^{-1}

$E_a = 1.605 \times 10^8$ J/mol

$\frac{k_\alpha}{h} = 4.05 \times 10^{-2}$ m^3·K/J

$\Delta H_R = 2.092 \times 10^8$ J/mol

$N_{\alpha o} = 3.72 \times 10^{-8}$ mol/s

$m = 0.04$ kg

$\rho_P = 1.0 \times 10^3$ kg/m^3

$V_P/A_P = 1.0 \times 10^{-3}$ m

TABLE 2. EXTRAPOLATION RESULTS

Extrapolation Equation	X^∞ (Actual) = 0.50 Conversion Range $0.29 \le x \le 0.36$ X^∞ (Extrapolated)	X^∞ (Actual) = 0.73 Conversion Range $0.48 \le x \le 0.56$ X^∞ (Extrapolated)
$X \cong \beta_1 + \beta_2\xi$	0.49	0.76
$X \cong \beta_1 + \beta_2\xi + \beta_3 X^2 + \beta_4\xi^2 + \beta_5\xi X$	0.51	0.72
$X \cong \sigma_1 + \sigma_2\phi$	0.40	0.63
$X \cong \sigma_1 + \sigma_2\phi + \sigma_3\phi^3 + \sigma_4\phi^3 + \sigma_5\phi^4$	0.41	0.68

TABLE 3. EXTRAPOLATION RESULTS

Extrapolation Equation	X^∞ (Actual) = 0.87 Conversion Range $0.68 \le x \le 0.79$ X^∞ (Extrapolated)	X^∞ (Actual) = 0.33 Conversion Range $0.19 \le x \le 0.23$ X^∞ (Extrapolated)
$X \cong \beta_1 + \beta_2\xi$	0.91	0.32
$X \cong \beta_1 + \beta_2\xi + \beta_3X^2 + \beta_4\xi^2 + \beta_5\xi X$	0.88	0.33
$X \cong \gamma_1 + \gamma_2\psi$	0.87	0.28
$X \cong \gamma_1 + \gamma_2\psi + \gamma_3\psi^2 + \gamma_4\psi^3 + \gamma_5\psi^4$	0.88	0.30
$X \cong \sigma_1 + \sigma_2\phi$	0.83	0.26
$X \cong \sigma_1 + \sigma_2\phi + \sigma_3 \phi^2 + \sigma_4\phi^3 + \sigma_5\phi^4$	0.84	0.27

with $\beta_1 = X^\infty$

To test the proposed extrapolation scheme, conversions at different mass velocities were calculated for a recirculation reactor with a specified feed composition, temperature, pressure and space velocity. To do this surface concentrations and temperature which appear in Eq. 1 were expressed in terms of a single variable, i.e., conversion, by substituting from Eqs. 8, 9 and 11. This expression was then combined with Eq. 7 and conversions at different mass velocities were solved for numerically with the conversion corresponding to zero external gradients being evaluated at $G \rightarrow \infty$. The rate expression used was for cyclohexane dehydrogenation reaction represented by irreversible first order kinetics. Table 1 lists the reaction parameters used in the calculations.

In extrapolating to X^∞, regression analysis was carried out for fifteen calculated conversions. Different combinations of activation energy and preexponential factor qualitatively gave the same results.

Calculations show that extrapolation based on Eq. 18 is significantly better than extrapolation based on

$$X = \sigma_1 + \sigma_2\phi + \sigma_3\phi^2 + \ldots + \sigma_{n+1}\phi^n + \ldots \qquad (22)$$

where $\sigma_1 = X^\infty$ and $\phi = 1/G$

The difference in the ability of the two extrapolation schemes to predict the correct X^∞ becomes apparent when conversions corresponding to significant external gradients are used in the regression analysis. This is seen in Table 2 where extrapolation based on Eq. 18 is adequate whereas extrapolation based on Eq. 22 is inadequate. In fact, for all cases tested, extrapolation based on retaining only the first two terms in Eq. 18 (i.e., Eq. 21) is superior to extrapolation based on retaining the first five terms in Eq. 22. Table 2 also shows that Eq. 21 would be adequate for extrapolation if the conversion data are sufficiently close to X^∞.

Calculations also show that even under severe external gradients the improvement in the accuracy of extrapolation by retaining the third order terms is not significant (in the order of 1–2%).

One problem with higher order equations is the non-uniqueness of the solution. In the regression analysis carried out for calculated conversions (error-free data), uniqueness did not become a problem because the coefficients for the higher order conversion terms (i.e., β_3 and β_6 in Eq. 18) were very small. However, this may not be the case if the extrapolation is carried out for error-containing data. An approach which may circumvent this problem would be the formulation

$$X = \gamma_1 + \gamma_2\psi + \gamma_3\psi^2 + \ldots \gamma_{n+1}\psi^n + \ldots \qquad (23)$$

where

$$\psi = 1/G^{0.641} \qquad (24)$$

and $\gamma_1 = X^\infty$

This formulation is suggested from the functional dependence shown in Eq. 13. Calculations show that extrapolation based on Eq. 23 is as good as the one based on Eq. 18 if X^∞ is high (>0.8). At lower conversions ($X^\infty < 0.5$), although extrapolation based on Eq. 23 is not as effective as the one based on Eq. 18, it is still significantly more effective than extrapolation based on Eq. 22. These results are given in Table 3.

Probably the most important problem with higher order equations derived from Eq. 18 in extrapolating live, error-containing data is statistical. This is due to the difficulty in being able to estimate parameters independently of one another, i.e., the joint confidence interval problem. For example, Eq. 19 with Eq. 14 may be rewritten as

$$X = \beta_1 + \beta_2 \frac{X}{G^{0.641}} + \left(\beta_3 + \frac{\beta_4}{G^{1.282}} + \frac{\beta_5}{G^{0.641}}\right) X^2 \qquad (25)$$

The parameters needed in Eq. 20 for estimation of X^∞ and β_1 and β_3. However, β_3 in turn is only one part of the coefficient for X^2 in Eq. 25 and a unique, accurate estimation of β_3 from error-containing data should be difficult indeed.

Such problems with higher-order equations, plus the satisfactory performance of Eq. 21

$$X = \beta_1 + \beta_2\xi = \beta_1 + \beta_2 \frac{X}{G^{0.641}}$$

lead one to speculate that perhaps this relationship is capable of providing the most accurate estimate of X^∞ for live, error-containing data.

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J. B. Cropley is gratefully acknowledged for many helpful suggestions. Grace Kovenklioglu helped with the regression analysis.

NOTATION

A_p = catalyst particle surface area, m^2

C_{ib}, C_{is} = concentrations in the bulk phase and on the catalyst surface for component i, mol/m^3

$C_{\alpha b}, C_{\alpha s}$ = concentrations in the bulk phase and on the catalyst surface for the key component α, mol/m^3

E_a = activation energy, J/mol
G = mass velocity in the reactor bed, $kg/m^2 \cdot s$
h = heat transfer coefficient, $J/m^2 \cdot s \cdot K$
ΔH_R = heat of reaction, J/mol(23)
k_i, k_α = mass transfer coefficients for components i and α, m/s
m = catalyst weight in the reactor, kg
N_i = effluent rate for component i, mol/s
$N_{io}, N_{\alpha o}$ = inlet rates for components i and α, mol/s
N_o = total inlet rate, mol/s
N_T = total effluent rate, mol/s
P_T = total pressure, N/m^2
R_g = gas constant, $J/mol \cdot K$
r_o = observed reaction rate based on unit catalyst volume, $mol/s \cdot m^3$
T_b = bulk phase temperature in the reactor, K
T_s = temperature at the catalyst surface, K
V_p = catalyst particle volume, m^3
X = conversion for the key component α, $(N_{\alpha o} - N_\alpha)/N_{\alpha o}$
X^∞ = conversion corresponding to zero external gradients
$y_{io}, y_{\alpha o}$ = mole fraction at the inlet for components i and α
X = preexponential factor, s^{-1}

Greek Letters

α = key component, cyclohexane
$\beta_1 \ldots \beta_9$ = constants in Eq. 18
$\gamma_1 \ldots \gamma_{n+1}$ = constants in Eq. 23
κ = constant in Eq. 11
$\lambda_1 \ldots \lambda_6$ = constants in Eq. 17
ν_i, ν_α = stoichiometric coefficients for component i and α
$\Delta\nu$ = sum of the stoichiometric coefficients
ξ = parameter defined by Eq. 14
ρ_p = density of the catalyst particle, kg/m^3
$\sigma_1 \ldots \sigma_{n+1}$ = constants in Eq. 22
ϕ = reciprocal mass velocity $(1/G)$, $m^2 \cdot s/kg$
ψ = parameter defined by Eq. 24

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Evaporation of Water through Surfactant Layers

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A recent model using Fick's law to describe gas diffusion in a surfactant film and into the water, with local equilibrium solubility conditions at the interfaces, effectively described the observed phenomena for three rather different experiments (Ly et al., 1979). In the present paper we extend that model to mass transfer of H_2O through surface-active films. Blank (1979) has discussed the possibility of applying Fickian diffusion analysis to permeation through monolayers, but did not have at hand the necessary mathematical model required for a full evaluation. The present work is a step toward the development of such a mathematical model.

Figure 1 pictures a surfactant layer of thickness δ covering a semi-infinite volume of water. The concentration gradients sketched are for water evaporating into air, although the case of condensation and mass transfer *to* the liquid water is also described by the model. Letting subscripts a and s refer to quantities in the air and surfactant regions respectively, we write the diffusion equations for concentration of water $c(x,t)$ as a function of position x and time t,

$$\frac{\partial c_s}{\partial t} = D_s \frac{\partial^2 c_s}{\partial x^2} \quad 0 \le x \le \delta \tag{1}$$

$$\frac{\partial c_a}{\partial t} = D_a \frac{\partial^2 c_a}{\partial x^2} \quad \delta \le x \le \infty \tag{2}$$

The initial condition specifies that for $t \le 0$ the water vapor in the air is in equilibrium with the surfactant film (but not with the underlying bulk water),

$$c_a(x, t = 0) = c_i \tag{3}$$

$$c_s(x, t = 0) = c_i/K \tag{4}$$

The distribution coefficient K, which is related to the Henry's law constant, is discussed more completely below.

When the surfactant film is formed on the liquid water for $t > 0$ we assume local equilibrium is instantaneously established at the interface to give the boundary condition

$$c_s(x = 0, t) = c^* \tag{5}$$

where c^* is the solubility of H_2O in the film. Equilibrium is assumed to hold locally at the air/surfactant interface,

$$c_a(x = \delta, t) = K\, c_s\, (x = \delta, t), \tag{6}$$

and the flux is continuous there,

$$-D_s \left. \frac{\partial c_s}{\partial x} \right|_{x=\delta} = -D_a \left. \frac{\partial c_a}{\partial x} \right|_{x=\delta} \tag{7}$$

Far enough into the air, the concentration remains unchanged,

$$c_a(x \to \infty, t) = c_i \tag{8}$$

For a three-phase equilibrium between air, water, and the non-volatile surfactant, the concentration of water vapor in the air

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