nature of their scatter.

Figures 3 and 4 show that, for the tetrahydrofuran-water system, the raw data indeed require the appearance of inflection points and, as a result, the correction of this anomaly by our method is necessitated. It is quite possible that for more accurate data inflection points will not appear, in which case no correction is needed.

The application of the present method to binary systems with two azeotropes—which are very rare—is quite straightforward. The curve of the boiling temperature versus composition exhibits, in this case, a maximum and a minimum and the application of this "sectionwise-fitting" is a natural extension. Similarly, heat of mixing data for systems which exhibit both negative and positive values may be correlated by "sectionwise-fitting" using this method.

ACKNOWLEDGMENT

Thanks to Professor Alexander Apelblat for his contribution to this work, and to Elisha Elijah for his splendid cooperation in editing this paper.

NOTATION

c = number of adjustable parameters
C_k = the derivatives at $X = Y_k$
f_k = analytical representation in the kth interval ($Y_k < X < Y_{k+1}$)
L_k = $Y_{k+1} - Y_k$
M_k = number of data points at interval k
n = number of boundaries
NC = number of constraints to avoid inflection points
$S.O.S.$ = σ^2 = sum of squares, Eq. 4
T_k = value of the dependent variable f at Y_k
X = independent variable
X_{km} = X of the mth experimental point between Y_k and Y_{k+1}
Y_k = the boundaries of intervals

Greek Letters

λ_j, λ_j' = Legrange multiplier
ϕ_j = constraint
θ_{km} = experimental temperature at X_{km}

Subscript

k = the k interval

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Manuscript received June 8, 1981; revision received March 8, and accepted March 23, 1982.

R & D NOTES

Kinetic Analysis of a Non-Isothermal Reactor: Comments on a Note by Cooper and Alley

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Cooper and Alley (1981) have recently published a technique for analyzing non-isothermal kinetic data for a plug flow reactor (PFR). The data needed for this analysis are the concentration and the temperature profiles along the length of the reactor. Since the temperature varies along the length of the reactor, a plot of $ln(f_x/f_o)$ vs. x where f_x and f_o represent the mole fractions of the reactant at length x and at the entrance of the reactor, respectively, against x will not be linear. Cooper and Alley present a transformation of the independent variable, x, such that the plot of $ln(f_x/f_o)$ versus the transformed x yields a straight line. The slope of this line represents k_o, the rate coefficient evaluated at the inlet temperature. Cooper and Alley have assumed previous knowledge of the value of the activation energy, and used this value in defining the transformation factors. They pointed out that knowledge of the activation energy, E, is necessary to use this technique. Further, they have stated that if the value of E is not available, a second set of measurements, starting at a different initial temperature may

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be needed to estimate E, and subsequently, k_o and A, the pre-exponential factor.

The purpose of this note is twofold: we intend to show that the transformation factors derived by Cooper and Alley are valid for constant volume batch reactors and constant linear velocity PFR only, and that a different set of transformation factors are necessary to analyse variable volume batch reactor and variable linear velocity PFR (subject to the same assumptions made by Cooper and Alley), and that a priori knowledge of E is not necessary for the use of this technique, i.e., both A and E can be calculated from the temperature and concentration profiles from a single experiment.

Cooper and Alley have used the Lagrangian approach in their analysis of the plug flow reactor. They treat each differential element (of volume Adx) as a batch reactor, and follow the state of this element with respect to time. Unfortunately, Cooper and Alley have used the equation for constant volume batch reactor, which is not valid in this case, since the superficial velocity, u, is changing along the length of the reactor. The proper equation to use in this case is:

$$\frac{1}{V}\frac{d(VC)}{dt} = -kC \tag{1}$$

where

$V = Au$
A = cross-sectional area of the PFR
u = superficial velocity, function of temperature

Following the derivation of Cooper and Alley, and using Eqs. 1 and 2

$$\frac{U_x}{U_o} = \frac{T_x}{T_o} \tag{2}$$

We obtain

$$ln\,\frac{Uf|_{t'}}{Uf|_o} = -\frac{k_o}{U_0}t' \tag{3}$$

where

$$t' = \sum_{i=1}^{n} F'_i \frac{\Delta x_i}{U_i}$$

and $F'_i = \dfrac{T_o}{T_i} e^{\frac{-E}{RT_o}\left(\frac{T_o}{T_i} - 1\right)}$

Note that the transformation factor, F'_i, calculated from Eq. 1 differs from that of Cooper and Alley by the multiplying factor T_o/T_i.

Clearly, if the temperature variation along the reactor is significant, the use of the Cooper and Alley transformation factor will not result in a linear relationship between $ln(Uf)|_{t'}$ and t' whereas our transformation defined in Eq. 3 will.

We shall now show that an a priori knowledge of E is not required for using this technique. We shall prove that if one guesses a value for E other than the true value, the resulting plot of $ln(f/f_o)$ vs. t' will not be linear. Therefore, one can iterate on the value of E until a linear plot is obtained.

Assume that the true (but unknown) value of the activation energy is given by E, and the guessed value is $E + \Delta E$. We shall use the constant volume batch reactor, and the corresponding transformation factors developed by Cooper and Alley as an example, but the same arguments can be used for a variable volume batch reactor (and a corresponding PFR) using the transformation factors shown in Eq. 3. The transformation factor based on the true and guessed activation energies will be denoted by F_i and F'_i, respectively.

Thus, we get

$$F'_i \equiv e^{-\frac{E + \Delta E}{RT_o}\left(\frac{T_o}{T_i} - 1\right)} \tag{4}$$

We also have,

$$k_i = k_o e^{\frac{-E}{RT_o}\left(\frac{T_o}{T_i} - 1\right)} = k_o F_i \tag{5}$$

Following the derivation of Cooper and Alley, subject to the same assumptions, we get

$$ln\,\frac{f_t}{f_o} = -kdt$$

$$= -\sum_i k_o F_i \Delta t_i$$

But

$$F_i = F'_i e^{\frac{\Delta E}{RT_o}\left(\frac{T_o}{T_i} - 1\right)} \tag{6}$$

$$\therefore\ ln\,\frac{f_t}{f_o} = -\Sigma k_o F'_i e^{\frac{\Delta E}{RT_o}\left(\frac{T_o}{T_i} - 1\right)} \Delta t_i \tag{7}$$

Define

$$\Delta t'_i = F'_i \Delta t_i \tag{8}$$

$$\therefore\ ln\,\frac{f_{t'}}{f_o} = -\Sigma k_o \Delta t'_i e^{\frac{\Delta E}{RT_o}\left(\frac{T_o}{T_i} - 1\right)} \tag{9}$$

$$\neq -\ \Sigma k_o \Delta t'_i \tag{10}$$

Thus,

$$ln\,\frac{f_{t'}}{f_o} \neq -k_o t' \tag{11}$$

This demonstrates that unless $\Delta E = 0$, the plot of $ln\,f_{t'}/f_o$ vs. t' will not be linear. Thus one can iterate on the guessed value of E until a straight line is obtained. The slope of this line yields k_o, as mentioned by Cooper and Alley.

NOTATION

A = pre-exponential factor (s^{-1}) or cross-sectional area of reactor (m^2)
c = concentration (gmol/L)
E = activation energy (kcal/gmol)
F_i = transformation factor for the ith increment of reactor distance, as defined by Cooper and Alley (1981)
F'_i = transformation factor for the ith increment of reactor distance, as derived in this work.
f_i = mole fraction at the ith increment of reactor distance
f_o = mole fraction at the entrance of the reactor
f_x = mole fraction, equal to f_i for $x = i\Delta x$
i = index for number of distance increments
k = first-order reaction rate constant (s^{-1})
k_o = first order rate constant at the inlet temperature, T_o (s^{-1})
R = gas constant (0.001987 kcal/gmol·K)
T = absolute temperature (K)
T_i = absolute temperature at the ith increment of reactor distance (K)
T_o = absolute temperature at reactor inlet (K)

u = superficial velocity (m/s)
u_o = superficial velocity at reactor entrance (m/s)
t = time (s)
t' = transformed time (s)
ΔE = deviation from true activation energy (kcal/gmol)
Δt, $\Delta t'$ = incremental time, incremental transformed time (s)
Δx = incremental reactor distance (m)

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Manuscript received March 8, 1982; revision received May 7, and accepted May 28, 1982.

Mechanical Mixing Efficiency Parameter for Static Mixers

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INTRODUCTION

Static mixers or motionless mixers (Middleman, 1977, p. 327) are a special type of mixer that achieve intermaterial area (a_v) increase (Ottino et al., 1979) without any moving parts. Static mixer uses include both laminar and turbulent flow regimes (Koch bulletin KSM-2), mixing of high and low viscosity fluids, such as in-line blending of solvents, polymer blending, gas-gas mixing, and dispersion of immiscible fluids. Our description here is restricted to mixing of similar fluids in laminar flows. These types of mixers are designed to produce increase in intermaterial area per unit volume, a_v (reduction in striation thickness, s), by flow reorientation and material subdivision in such a way that a_v increases predictably in each of the repetitive flow units of the mixer. The consecutive flows are produced by a periodic pattern of non-moving solid surfaces inserted in the flow.

The repetitive flow pattern implies that flow parameters follow some kind of periodic function in which inverse time decay of stretching efficiency by shear (Ottino et al., 1981) is avoided or kept at some constant average value. It is apparent that degree of subdivision and pressure drop are inversely related. The cost of high intermaterial area generation is large pressure drops. Presently, there is no criterion for a rational comparison of these competitive effects. Here we propose to use a recently developed mixing theory for such a comparison.

THEORY

A structured continuum mixing description is based on a lamellar structure assumption (Ottino et al., 1979) and a derived point description of the state of mixing based on intermaterial area per unit volume, a_v. The transport equation for the property a_v is given as

$$\frac{\partial \ln a_v}{\partial t} + v \cdot \mathrm{grad}(\ln a_v) = e(x,t)(D{:}D)^{1/2} \tag{1}$$

where $e(x,t)$ is a mixing efficiency such that $e(x,t) < 1$. For a continuous flow mixer in steady state Eq. 1 produces the bound (Ottino et al., 1981)

$$\frac{d}{dz} \ll \ln a_v \gg < \frac{\overline{(D{:}D)}^{1/2}}{\bar{v}_z}, \tag{2}$$

where the mean values $\ll \gg$ and — of any function $f(x,t)$ are defined as

$$\ll f \gg = \frac{\int_A f v_n dA}{\int_A v_n dA}, \quad \bar{f} = \frac{\int_A f dA}{\int_A dA}, \tag{3}$$

and where A denotes the cross sectional area of the mixer. A mechanical mixing efficiency parameter, $\overline{\mathrm{eff}(z)}$, is defined with respect to the upper bound (Eq. 2) as

$$\frac{d}{dz} \ll \ln a_v \gg = \overline{\mathrm{eff}(z)} \frac{\overline{(D{:}D)}^{1/2}}{\bar{v}_z} \tag{4}$$

$\overline{\mathrm{eff}(z)}$ can be roughly interpreted as a ratio of energy used to create intermaterial area to energy dissipated by viscous action (Ottino et al., 1981).

Applications to macroscopic systems are done by relating $\overline{D{:}D}$ with the so-called viscous dissipation per unit volume per unit time, $\tau{:}D$, by means of a constitutive equation representing the rheological behavior of the structured continuum. Viscous dissipation is a bound of mechanical mixing. Values of $\overline{\tau{:}D}$ can be obtained from macroscopic balances or experimental measurements.

APPLICATION TO STATIC MIXERS

The theory will be applied to compare two commonly used static mixers: a Kenics Static Mixer and an ISG Ross Mixer (Schott et al., 1975). The Kenics Static Mixer consists of a circular pipe within which are fixed a series of short helical elements of alternating left and right-hand pitch. Due to this geometry it is possible to achieve an intermaterial area output (adapted from Tadmor and Gogos *op. cit.*, p. 442) given approximately by

$$\frac{\ll a_v \gg}{\ll a_{v_o} \gg} \simeq 2^N \tag{5}$$

where N is the number of flow units the material has passed through. Since we refer to intermaterial area delivered it is natural to use a mixed cup average $\ll \gg$, definition 3. The ISG Ross mixer using another geometry for flow reorientation and subdivision delivers intermaterial area according to (Tadmor and Gogos *op. cit.*, p. 441)

$$\frac{\ll a_v \gg}{\ll a_{v_o} \gg} \simeq 4^N \tag{6}$$

where N is the number of flow units.
