Limitations of the Equilibrium Theory of Countercurrent Devices

In the analysis of countercurrent adsorption processes, an equilibrium theory in which local equilibrium between the fluid and the adsorbent phases is assumed has been used in the past to determine the composition of the pinch state that would be obtained for long columns. It is shown that this equilibrium theory is deficient and that certain mass transfer parameters, which are lost in the procedure by which the model equations for the equilibrium theory are formulated, can have a profound effect on the composition of the pinch.

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Introduction

Separation of multicomponent mixtures by means of mass transfer between a flowing fluid phase and another immiscible fluid or solid phase, which may be stationary or moving, is an operation of central importance to the chemical process industries. Absorption, extraction, adsorption, and distillation are prime examples. Models of varying degrees of complexity have been proposed for these processes and analyzed in the literature. In the analysis of such processes it is common practice to examine the relative importance of various terms appearing in a detailed model (e.g., various mass transfer resistances) and to simplify the model to a level that is acceptable for the process being studied. One such scheme involves a hitherto unrecognized pitfall and the purpose of this communication is to illustrate this by an analysis of a countercurrent adsorption process. In such a process, as the length of the adsorption column increases without bound, it is well known that an increasing fraction of the column length lies close to a "pinch" state in which the two phases are in mutual equilibrium, and that this fraction of the length tends to unity as the total length tends to infinity. Transition regions, adjacent to one or both ends of the column, where there are significant departures from equilibrium, then occupy only a small fraction of the total length. On the scale of this length they therefore appear as thin boundary layers. While the variation in conditions within the boundary layers is of interest, it is of prime practical importance to determine the composition of the pinch state, since from this alone the performance of a column of unbounded length can be predicted.

Rhee et al. (1971) have put forward a scheme for determining the composition of the pinch state. As the boundary layer regions located at one or both ends of a very long column are very short compared to the total length of the column, they proposed that these regions be treated as boundary discontinuities or shocks. Accordingly, the pinch state, where the two phases are in mutual equilibrium, will prevail everywhere in the interior of the column. As a result of this postulate of existence of local equilibrium everywhere in the interior of the column, this scheme is often referred to as the "equilibrium theory" approach. But without following the concentration variations in the boundary layers, the steady state mass balance equations do not determine the composition of the pinch state. To identify the pinch state composition, Rhee et al. view the problem as a transient one and employ the method of characteristics to identify the final steady state that will be obtained.

In contrast, we have calculated the steady concentration profiles in columns of finite length by solving directly the steady state equations that retain the details of the interphase mass transfer process in the boundary layer regions. By doing this for a sequence of columns of successively increasing length, and examining the limiting form as the length increases without bound, we can identify directly the pinch state that is approached as the length tends to infinity.

It will be shown through illustrative examples that the results of these direct calculations are not, in general, the same as the predictions of the equilibrium theory of Rhee et al.

Countercurrent Adsorption Process

Consider a process in which a flowing gas stream containing several adsorbable species and an excess amount of an inert (nonadsorbing) species is contacted with a countercurrently moving solid adsorbent phase. Although one can readily write an elaborate model taking into account axial dispersion, interphase transport resistance on the fluid side, and intraparticle

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diffusional resistance, we shall confine attention to a simpler model as a starting point for our analysis. We shall assume isothermal conditions and neglect axial dispersion. Further, as the dominant mass transfer resistance in such processes is usually on the solid side of the gas-solid interface, we shall neglect the gas-side mass transfer resistance. Finally, we shall approximate the intraparticle diffusional resistances through an effective mass transfer coefficient for each species. As the solid phase effective diffusivities of the various species in a multicomponent system will differ from each other, one can expect the effective mass transfer coefficients for these species to differ also.

The unsteady mass balances for the ith species in the fluid and solid phases can then be written as

$$A_x\epsilon \frac{\partial C_i}{\partial t} + q_f \frac{\partial C_i}{\partial z} + A_x a_v k_i (n_i^e - n_i) = 0$$

$$A_x(1-\epsilon)\frac{\partial n_i}{\partial t} - q_s \frac{\partial n_i}{\partial z} - A_x a_v k_i (n_i^e - n_i) = 0$$

$$0 < z < L, \quad t > 0, \quad i = 1, M$$

Here A_x denotes the cross-sectional area of the column, assumed to be a constant; a_v denotes the external surface area of the pellets per unit volume of the bed and k_i is the effective mass transfer coefficient for the ith species; q_f and q_s denote the volumetric flow rates of the gas and the solid, respectively, and are assumed to be constant; n_i^e denotes the concentration of the ith species in the solid phase that would be in equilibrium with the gas phase, and it is determined by a suitable equilibrium isotherm. For the sake of our illustration, we assume that the Langmuir isotherm holds for all the species so that

$$n_i^e = NK_iC_i \Bigg/ \left(1 + \sum_{j=1}^{M} K_jC_j\right), \quad i = 1, M$$

where N is the maximum adsorption capacity of the solid per unit volume and K_i is the equilibrium constant for the adsorption of species i. The boundary conditions for this system of differential equations are given by

$$\text{At } z = 0\text{: } C_i = C_i^o, \quad i = 1, M$$

$$\text{At } z = L\text{: } n_i = n_i^L, \quad i = 1, M$$

Accumulation in the gas phase inside the pores of the solid has been neglected in the above differential equations, as it is usually small compared to the amount adsorbed.

The above equations can be cast in dimensionless form to obtain

$$\frac{\partial y_i}{\partial \tau} + \frac{\partial y_i}{\partial \xi} + \alpha_i(x_i^e - x_i) = 0 \tag{1}$$

$$\nu \frac{\partial x_i}{\partial \tau} - \frac{1}{\mu}\frac{\partial x_i}{\partial \xi} - \alpha_i(x_i^e - x_i) = 0$$

$$0 < \xi < 1, \quad \tau > 0, \quad i = 1, \mathrm{M} \tag{2}$$

$$x_i^e = \tilde{K}_i y_i \Bigg/ \left(1 - \sum_{j=1}^{M} \tilde{K}_j y_j\right) \tag{3}$$

$$\text{At } \xi = 0, \quad y_i = y_i^o, \quad i = 1, M \tag{4}$$

$$\text{At } \xi = 1, \quad x_i = x_i^1, \quad i = 1, M \tag{5}$$

Here

$$x_i = n_i/N; \quad y_i = C_i/C_o; \quad x_i^e = n_i^e/N$$

$$\tilde{K}_i = K_iC_o; \quad \nu = (1-\epsilon)N/\epsilon C_o; \quad \mu = q_fC_o/q_sN$$

$$\alpha_i = A_x a_v k_i NL/q_fC_o; \quad \xi = z/L; \quad \tau = q_ft/A_x\epsilon L$$

$$y_i^o = C_i^o/C_o; \quad x_i^1 = n_i^L/N$$

Although we have presented the transient equations above, we are mainly concerned with the steady state performance of the column. Increasing the length of the column while keeping all other physical parameters constant is equivalent to an increase in the dimensionless mass transfer coefficients α_i, and the question at issue here is the performance of the column in the limit $\alpha_i \rightarrow \infty$, i.e., in the limit of a very long column. In this limit one can anticipate that a pinch state where the fluid and solid phases are essentially in equilibrium will be approximated closely in most of the length of the column with relatively thin boundary layers at one or both ends. Our objective is to determine the composition of this pinch state. If this is known, the compositions of the effluent fluid and solid streams (i.e., $y_i(1)$ and $x_i(0)$] can be computed readily from simple mass balances.

$$x_i(0) = x_i^p + \mu(y_i^o - y_i^p) \tag{6}$$

$$y_i(1) = y_i^p + \mu^{-1}(x_i^1 - x_i^p), \quad i = 1, M \tag{7}$$

where the superscript p denotes the pinch state. In what follows we shall discuss two approaches to the estimation of the pinch state composition, the equilibrium approach and the direct approach.

Equilibrium Theory Approach

One may argue that as all the α_i's tend to infinity, the fluid and the solid phases must be very close to being in equilibrium with each other almost everywhere in the column, major departures from equilibrium being confined to relatively short regions at one or both ends of the column. Since these boundary layer regions are very short compared to the total length of the column, it was proposed by Rhee et al. that they may be treated as boundary discontinuities or shocks. Thus

$$x_i = x_i^e, \quad i = 1, M \quad \text{almost everywhere in } 0 < \xi < 1 \tag{8}$$

Addition of Eqs. 1 and 2 then yields

$$\frac{\partial y_i}{\partial \tau} + \nu\frac{\partial x_i^e}{\partial \tau} + \frac{\partial y_i}{\partial \xi} - \frac{1}{\mu}\frac{\partial x_i^e}{\partial \xi} = 0$$

$$0 < \xi < 1, \quad \tau > 0, \quad i = 1, M \tag{9}$$

In this approach, often referred to as the equilibrium theory approach (the name being derived from the assumption of local equilibrium described by Eq. 8), one then solves Eq. 9 using Eq. 3 to eliminate the x_i^e's. The system of PDE's in Eq. 9 is usually hyperbolic for commonly encountered systems. It turns out that the boundary conditions, Eqs. 4 and 5, cannot be satisfied simultaneously in the equilibrium theory approach. To overcome this difficulty, the existence of boundary discontinuities at one or both ends of the column is permitted, and the system of equations is solved using the method of characteristics. A detailed discussion of the boundary conditions and the method of characteristics has been presented by Rhee et al. (1971) and will not be repeated here. In our subsequent discussion, we shall simply present the results of the equilibrium theory approach and the reader is referred to the article by Rhee et al. for the details of the solution procedure. It is interesting to note that although the calculation of the pinch state is inherently a steady state problem, in the equilibrium theory it is necessary to attack a dynamic problem to obtain any kind of solution. This is because, under steady state conditions, Eq. 9 is satisfied by any uniform state (in which the fluid and solid phases are in equilibrium) prevailing over the entire length of the column.

We must emphasize that in the equilibrium theory, the only parameter (other than those associated with the adsorption isotherm) that affects the steady state composition of the pinch state is the dimensionless flow ratio μ. It is precisely in this regard that the limitation of the equilibrium theory arises. It will be shown below that there are other parameters that can have a profound influence on the composition of the pinch state, and that these parameters are lost in the procedure by which the model equations for the equilibrium theory are developed. Consequently the equilibrium theory leads to the correct pinch state composition only in rather restricted circumstances.

Direct Approach

Under steady state conditions, model Eqs. 1 and 2 reduce to

$$\frac{dy_i}{d\xi} + \alpha_i(x_i^e - x_i) = 0 \tag{10}$$

$$\frac{1}{\mu}\frac{dx_i}{d\xi} + \alpha_i(x_i^e - x_i) = 0, \quad 0 < \xi < 1, \quad \tau > 0, \quad i = 1, M \tag{11}$$

Combining Eqs. 10 and 11 we can write

$$\frac{dy_i}{d\xi} = \frac{1}{\mu}\frac{dx_i}{d\xi}, \quad i = 1, M$$

so that, for each species,

$$x_i(\xi) = x_i(\xi^*) + \mu[y_i(\xi) - y_i(\xi^*)] \tag{12}$$

where ξ^* is any location in the bed. The straight line defined by Eq. 12 in the x_i vs. y_i plane is commonly referred to as the operating line. One can also project the equilibrium relation, Eq. 3, onto the x_i^e vs. y_i plane to give an equilibrium curve, but only if one knows how all the $y_j (j \neq i)$ vary with y_i. Thus the projected equilibrium curve will depend on the solution itself.

Let us first consider the case of a single species ($M = 1$) adsorbing onto a solid. In this case the above statement is irrelevant and the equilibrium curve is uniquely defined *a priori*. As the operating conditions (namely μ and α_1) are changed, the operating line is shifted around in the x_1 vs. y_1 plane. It can easily be shown that, for any finite and positive values of μ and α_1, the operating and equilibrium curves cannot intersect in the interval bounded by $y_1 = y_1^o$ and $y_1 = y_1^{eq}$ where y_1^{eq} denotes the dimensionless fluid phase concentration of species 1 that would be in equilibrium with an adsorbent having a dimensionless adsorbate concentration of $x_1(1)$. Further, as α_1 increases, the operating line approaches the equilibrium line until finally, when $\alpha_1 \rightarrow \infty$ these two lines contact each other at $y_1 = y_1^o$, $y_1 = y_1^{eq}$, or some intermediate value of y_1. The point of contact then gives the x_1 and y_1 values corresponding to the pinch state. In this case of a single species adsorbing onto a solid, the only operating parameter that determines the composition of the pinch state is μ, just as in the equilibrium theory. We note that this approach, based on operating and equilibrium lines, and the equilibrium theory approach of Rhee et al. always yield identical results for the composition of the pinch state in this simple case.

Let us now consider a multicomponent system. In most of the practical situations, x_i^e depends not only on y_i, but also on y_j, $j = 1, M, j \neq i$. Thus in order to construct the projected equilibrium curves, x_i^e vs. y_i, $i = 1, M$, it is necessary to determine how a change in the concentration of the ith species in the adsorption column affects the concentrations of all the other species. From Eqs. 10 and 12 we can write

$$\frac{dy_j}{dy_i} = \frac{\alpha_j}{\alpha_i}\left[\frac{x_j(\xi^*) + \mu y_j(\xi) - \mu y_j(\xi^*) - x_j^e(\xi)}{x_i(\xi^*) + \mu y_i(\xi) - \mu y_i(\xi^*) - x_i^e(\xi)}\right] \tag{13}$$

For a given flow ratio μ, in order to compute the composition of the pinch state one has to consider the limit $\alpha_j \rightarrow \infty$, $j = 1, M$. But, inspection of Eq. 13 reveals that even in the limit $\alpha_j \rightarrow \infty$, $j = 1, M$, the equilibrium curves continue to depend on the details of the mass transfer process through the ratios (α_j/α_i). ($\alpha_j/\alpha_i = k_j/k_i$ is simply the ratio of the mass transfer coefficients and is therefore independent of the length of the column.) Clearly there exist $(M - 1)$ independent α_j/α_i ratios, so there are M parameters [namely, $(M - 1)$ mass transfer ratios and the flow ratio μ], in addition to those constants associated with the equilibrium isotherms, that can influence the composition of the pinch state. In contrast, the $(M - 1)$ mass transfer ratios are never considered in the equilibrium theory approach and hence their effect on the pinch state composition is completely lost. In the next section we shall illustrate this through some examples for a two-component ($M = 2$) system.

For a single species adsorbing on a solid, it was possible to make a definitive statement that the equilibrium and operating lines cannot cross each other in an interval bounded by $y_1 = y_1^o$ and $y_1 = y_1^{eq}$. In the case of a multicomponent system it is, in general, not possible to make such strong statements. It is indeed possible that the projected equilibrium curves and the operating lines can cross each other for some of the species. The only definitive statement that can be made is that such crossings cannot occur for all the species simultaneously for any finite μ and α_j's. In fact, only in the limit when $\alpha_j \rightarrow \infty$, $j = 1, M$ will the operating lines and the projected equilibrium curves contact each other for every species at the same time. This unfortunately is too broad a statement to allow us to develop an effective procedure for estimating the pinch state composition. The purpose of the above discussion is simply to establish that the mass transfer ratios will in general affect the pinch state composition and that the equilibrium theory approach does not predict this.

For the purpose of this study, we have determined the pinch state composition directly by a brute force numerical method. For given value of the flow ratio μ, the $(M - 1)$ mass transfer ratios α_j/α_1, and the constants associated with the equilibrium isotherms, we simply solve the two-point boundary value problem described by Eqs. 10 and 11 subject to the boundary conditions in Eqs. 4 and 5, assuming some finite value for α_1. The method of orthogonal collocation in conjunction with interpolation using piecewise Hermite polynomials yielded satisfactory numerical results. Once the composition profiles in the column were determined for this value of α_1, the calculations were repeated for larger and larger values, at each stage using the composition profiles for the previous value of α_1 as an initial estimate. This procedure was repeated until the solution contained a segment where the composition was constant and essentially corresponded to equilibrium, spanning at least 90% of the column length. Further increases in α_1 then merely extended the length of this segment without changing its composition significantly. This is illustrated in Figure 1, where the gas phase composition profiles in the column for two different values of α_1 are shown. The parameter values used in the simulations are indicated in the figure itself. Note that, for the sufficiently large values of α_1 shown in this figure, the gas phase composition in the center segment is essentially independent of α_1. Further, it was found from the computational results that the fluid and solid phases were essentially in mutual equilibrium in this segment. Thus the pinch composition was generated directly as the composition in this segment. Our procedure is, therefore, simply to solve the equations for a column of finite length, then successively increase the length until the pinch develops. In practice, it was found that the pinch composition changed little after the segment representing the pinch grew to about 50% of the column length.

Model Results

The results presented here were obtained for a two-component system. If the two species do not interact with one another through the equilibrium isotherm, i.e., x_1^e and x_2^e do not depend on y_2 and y_1, respectively, then the two-component adsorption problem can effectively be viewed as two independent single-species adsorption problems. In that case, it is easy to see that the ratio α_1/α_2 is irrelevant in the computation of the pinch state composition. Further, the direct method and the equilibrium theory approach can be shown to give identical results.

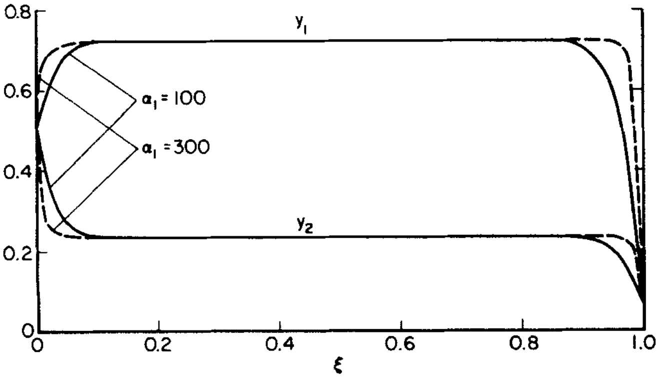

Figure 1. Gas phase composition profiles in column for various values of α_1.

$\alpha_1/\alpha_2 = 1.0$; $\mu = 0.60$; $y_1^o = y_2^o = 0.50$; $y_1^{eq} = y_2^{eq} = 0.05$.

For the purpose of our illustration, let us now consider the Langmuir isotherm, Eq. 3. Clearly, x_1^e and x_2^e depend on y_2 and y_1, and so adsorption of these two species is coupled. Without loss of generality, we shall assume that species 2 is adsorbed more strongly than species 1. In all the results presented below, we have set $\tilde{K}_1 = 3$ and $\tilde{K}_2 = 6$.

Example 1: Coadsorption of two species

$$y_1^o = y_2^o = 0.50, \quad y_1^{eq} = y_2^{eq} = 0.05$$

Here y_1^{eq} and y_2^{eq} denote the dimensionless concentrations of species 1 and 2, respectively, that would be in equilibrium with the entering solids. Thus $x_1^1 = 0.10345$ and $x_2^1 = 0.2069$. In this case the entering solid is lean in both species 1 and 2 relative to the entering fluid, and the process occurring in the column is coadsorption of both species.

For this problem, the equilibrium theory approach predicts three possible regimes for the pinch state.

$$y_1^p = y_1^{eq} = 0.05, \quad y_2^p = y_2^{eq} = 0.05, \quad 0 < \mu < 0.55$$
$$y_1^p = 0.723, \quad y_2^p = 0.236, \quad 0.55 < \mu < 0.90$$
$$y_1^p = y_1^o = 0.50, \quad y_2^p = y_2^o = 0.50, \quad \mu > 0.90$$

Thus, for small μ values the pinch state is the same as the state of the entering solid, and for large μ values the pinch state is the same as the state of the entering fluid. For $0.55 < \mu < 0.90$ a constant state that is different from either of the entering streams is obtained as the pinch state. The composition of the pinch state is independent of the value of μ in this region.

Direct calculations were made as described above for various values of μ and the ratio α_1/α_2. It was found that the results computed for the case $\alpha_1/\alpha_2 = 1.0$ coincided exactly with those predicted by the equilibrium theory. However, it was found that the pinch state composition does indeed depend on the α_1/α_2 ratio. Figure 2 shows the composition of the pinch state as a function of μ for $\alpha_1/\alpha_2 = 1.0$ and $\alpha_1/\alpha_2 = 3.0$. The direct calculation shows three possible regimes for the pinch state composition. For small values of μ $(0 < \mu < \mu_*)$ the pinch state is the same as the state of the entering solid and for large values of μ $(\mu > \mu^*)$ the pinch state is the same as the state of the entering fluid. However, the values of μ_* and μ^* depend on the α_1/α_2 ratio, as can be seen in Figure 2. The change in the pinch state composition in the vicinity of $\mu = \mu_*$ and $\mu = \mu^*$ was found to be discontinuous for all α_1/α_2 ratios tested $(0.10 \leq \alpha_1/\alpha_2 \leq 10)$, and it is only this feature that is predicted correctly by the equilibrium theory for this example. In the region $\mu_* < \mu < \mu^*$, the composition of the pinch state is independent of μ only for $\alpha_1/\alpha_2 = 1.0$, otherwise it varied markedly with μ. This is illustrated in Figure 2.

The solid lines in Figure 3 show the variation of the pinch state composition with α_1/α_2 for $\mu = 0.60$. A very pronounced variation in y_1^p with α_1/α_2 is clearly evident. It readily follows from Eqs. 6 and 7 that the adsorbate composition in the effluent solid phase [i.e., $x_1(0)$ and $x_2(0)$], and the composition of the effluent fluid phase [i.e., $y_1(1)$ and $y_2(1)$] will also vary with α_1/α_2. These variations are shown in Figure 4 for $\mu = 0.60$.

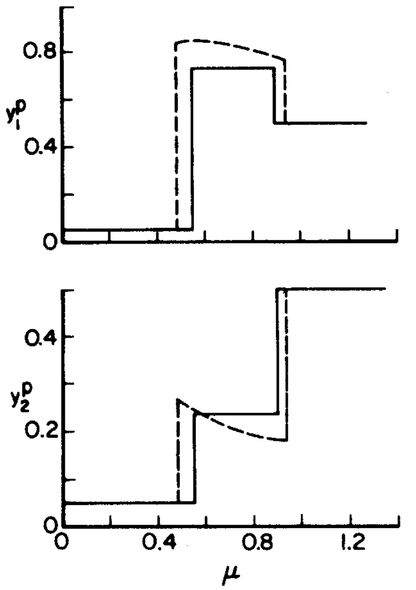

Figure 2. Composition of pinch state as a function of dimensionless flow ratio μ for example 1.

—Equilibrium theory approach as well as direct method for $\alpha_1/\alpha_2 = 1.0$
---Direct method for $\alpha_1/\alpha_2 = 3.0$

Example 2: Exchange adsorption of two species

$$y_1^o = 0.05, \quad y_2^o = 0.50, \quad y_1^{eq} = 0.50, \quad y_2^{eq} = 0.05$$

It was found that the direct calculation with $\alpha_1/\alpha_2 = 1.0$ and the equilibrium theory approach yielded identical results for the pinch state composition, just as in the previous example, but the effect of the α_1/α_2 ratio on the pinch state composition is more dramatic. Figure 5 shows the pinch state composition as a function of μ for $\alpha_1/\alpha_2 = 1.0$ and $\alpha_1/\alpha_2 = 3.0$.

According to the equilibrium theory, the pinch state is the same as the state of the entering solid for $\mu < 0.41$, and it is the same as the state of the entering fluid for $\mu > 1.34$. In the region $0.57 < \mu < 1.34$, a pinch state having a composition independent of μ is obtained. The change in the pinch state composition at $\mu = 1.34$ is discontinuous. In the region $0.41 < \mu < 0.57$, the pinch state composition varies smoothly with μ and no discontinuous change in the pinch state composition occurs in the vicinity of $\mu = 0.41$ or $\mu = 0.57$. (This is referred to as a simple wave transition in the equilibrium theory. In this region, according to the equilibrium theory, an infinite length of time will be required to attain the final steady state.)

For $\alpha_1/\alpha_2 = 3.0$, the pinch state composition corresponds to that of the entering solid for $\mu < 0.26$, and it is the same as the state of the entering fluid for $\mu > 1.33$. Furthermore, the changes in the pinch state composition are discontinuous both at $\mu = 0.26$ and $\mu = 1.33$. In the region $0.26 < \mu < 1.33$ the pinch state composition changes smoothly with μ. Thus even the qualitative features of the equilibrium theory predictions are not correct in this example if $\alpha_1/\alpha_2 \neq 1.0$.

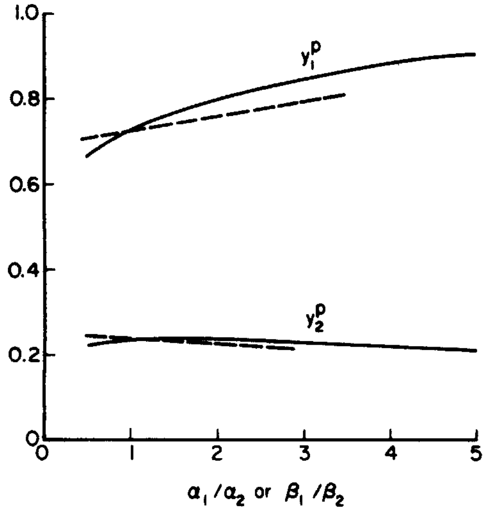

Figure 3. Composition of pinch state for example 1.

—As a function of solid-side mass transfer ratio (α_1/α_2)
---As a function of fluid-side mass transfer ratio β_1/β_2
$\mu = 0.60$

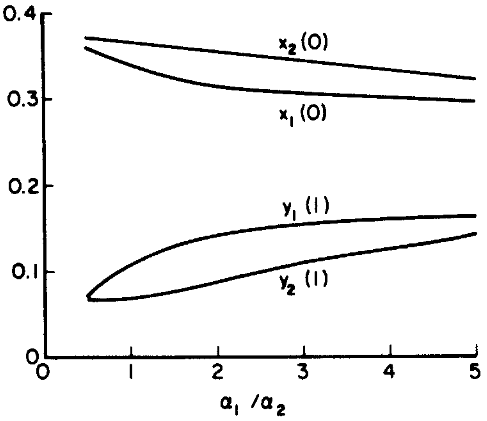

Figure 4. Composition of pinch effluent solid and fluid streams for example 1.

Composition as a function of solid-side mass transfer ratio α_1/α_2
$\mu = 0.60$

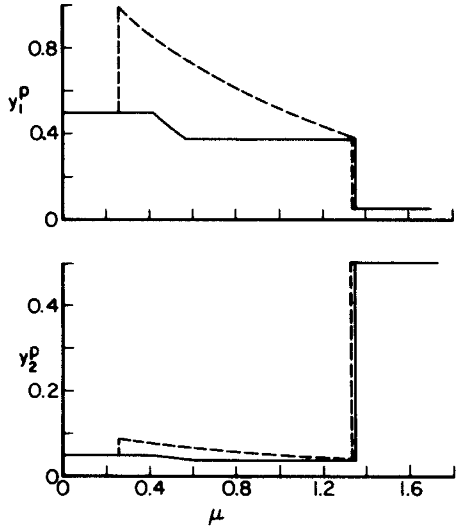

Figure 5. Composition of pinch state as a function of dimensionless flow ratio μ for example 2.

—Equilibrium theory approach as well as direct method for $\alpha_1/\alpha_2 = 1.0$
---Direct method for $\alpha_1/\alpha_2 = 3.0$

We repeated the type of calculation described for the above two examples for a number of different feed compositions. In every case it was found that the pinch state composition computed by the direct approach for $\alpha_1/\alpha_2 = 1.0$ was exactly the same as that predicted by the equilibrium theory. This appears intuitively reasonable, as the equilibrium theory does not assume anywhere that any one particular species approaches equilibrium any faster than the other species present. We speculate that even in the case where $M > 2$ the equilibrium theory approach will predict the pinch state composition correctly if all the mass transfer ratios (α_j/α_i) are unity. However, it would be a rare situation in practice for which $\alpha_i = \alpha_j, \forall\, i, j$.

Model for Interphase Transfer

In the analysis presented above it was assumed that the dominant resistance for interphase mass transfer was on the solid side of the fluid-solid interface. In what follows, we shall refer to this case as model I. Let us consider two other models.

Model II. The dominant resistance for interphase mass transfer is on the fluid side. Then, for a two-component system, Eq. 1 is replaced by

$$\frac{\partial y_i}{\partial \tau} + \frac{\partial y_i}{\partial \xi} + \beta_i(y_i - y_i^e) = 0, \quad i = 1, 2 \qquad (14)$$

where

$$y_i^e = x_i/\tilde{K}_i(1 - x_1 - x_2), \quad i = 1, 2 \qquad (15)$$

and a similar equation replaces Eq. 2. Here y_i^e is the dimensionless fluid phase concentration of species i that would be in equilibrium with the solid phase, and β_i is a dimensionless mass transfer coefficient for species i. In the direct approach, Eq. 12 is still valid, while instead of Eq. 13 we shall have

$$\frac{dy_j}{dy_i} = \frac{\beta_j}{\beta_i}\left(\frac{y_j - y_j^e}{y_i - y_i^e}\right) \qquad (16)$$

Model III. Not mass transfer, but the absorption/desorption process is rate limiting. For Langmuir adsorption/desorption kinetics, we then have instead of Eq. 1,

$$\frac{\partial y_j}{\partial \tau} + \frac{\partial y_i}{\partial \xi} + \Upsilon_i[y_i(1 - x_1 - x_2) - x_i/\tilde{K}_i] = 0, \quad i = 1, 2 \qquad (17)$$

where Υ_i is a dimensionless rate constant for the absorption of species i. It can easily be shown that Eq. 12 is still valid, while Eq. 13 is replaced by

$$\frac{dy_j}{dy_i} = \frac{\Upsilon_j}{\Upsilon_i}\left[\frac{y_j(1 - x_1 - x_2) - x_j/\tilde{K}_j}{y_i(1 - x_1 - x_2) - x_i/\tilde{K}_i}\right]$$

which can be rewritten [by dividing the numerator and denominator on the righthand side by $(1 - x_1 - x_2)$] as

$$\frac{dy_j}{dy_i} = \frac{\Upsilon_j}{\Upsilon_i}\left(\frac{y_j - y_j}{y_i - y_i^e}\right) \qquad (18)$$

where y_i^e, $i = 1, 2$ are given by Eq. 15.

Comparing Eqs. 16 and 18, we see that the role played by the ratio (β_1/β_2) of model II in relation to the pinch state composition is identical to that of the ratio (Υ_1/Υ_2) of model III. Thus, for the purpose of calculating the pinch state composition, these two models need not be considered separately.

The equilibrium theory approach does not take into consideration the details of the interphase transfer processes, and the pinch state composition obtained from this approach is independent of whether we are considering model I, II, or III. Numerical computations of the pinch compositions were carried out by the direct approach, using models II and III, for a variety of operating conditions. It was found that in all the examples studied, the results of the direct approach agreed with the predictions of the equilibrium theory approach if $\beta_1/\beta_2 = 1$ for model II (and, equivalently, if $\Upsilon_1/\Upsilon_2 = 1$ for model III). Comparing these observations for all three models, one might conjecture that the equilibrium theory works if the approaches to local equilibrium for all the species are driven in an unbiased way.

In an earlier section describing results obtained by the direct-approach solution of model I, we presented the effect of the α_1/α_2 ratio on the pinch state composition (the solid line in Figure 3). These calculations were repeated for model II, and the variation of the pinch state composition with the (β_1/β_2) ratio is also presented in Figure 3, as a broken line. The purpose of this comparison is to bring out an important feature, namely, that the pinch composition depends not only on the ratio of the rate constants but also on the functional form used for the driving force. This is of course not surprising, as the equation describing the equilibrium curve (compare Eqs. 13 and 16) depends on both the ratio of the rate constants and the functional form used for the driving force.

The computational results presented in this paper demonstrate unequivocally the limitations of the equilibrium theory approach. In the limit of a very long column, the size of the boundary layer regions at one or both ends of the column, where the compositions in the entering phases change from the feed conditions to those of the pinch state, become a vanishingly small fraction of the total column length. The equilibrium theory avoids having to deal with these regions by viewing them as boundary discontinuities, and this is responsible for the failure of the theory. Our work shows that the details of the interphase mass transfer processes in these boundary layers and, in particular, the relative ease with which interphase mass transfer occurs for the various species, are of paramount importance in accurate modeling of such mass transfer processes, even in the limit of a very long column.

Validity of Equilibrium Theory in Other Contexts

The local equilibrium assumption is often invoked in the analysis of the performance of absorption, extraction, and distillation processes; for example, multicomponent distillation in a tray tower. In the design of such a distillation process, the minimum reflux required to achieve the desired separation is an important consideration. Under minimum reflux conditions, infinite numbers of trays are required in both the rectifying and stripping sections. For the purpose of computing the minimum reflux ratio, it is common to presume ideal trays, so that in each tray the effluent liquid and vapor streams are assumed to be in equilibrium. It is then straightforward to show that the unsteady tray-by-tray conservation equations can be reduced to a set of first-order partial differential equations under the conditions of minimum reflux (Nandakumar and Andres, 1981a, b). The equations for the stripping and rectifying sections resemble the equilibrium theory equations discussed here for the countercurrent adsorption process. Nandakumar and Andres describe how the equilibrium theory can be employed to compute efficiently the minimum reflux ratio in multicomponent distillation processes and note that this scheme predicts the same minimum reflux ratio as obtained from tray-by-tray calculations using ideal trays.

In practice, however, the trays are not ideal, and the concept of tray efficiency has been introduced to account for this. When a tray's efficiency is not unity, local equilibrium has not been established between liquid and vapor leaving that tray. This can arise if the characteristic times for the interphase mass and energy transfer are not very much smaller than the residence times of the fluids in that tray. Strictly speaking, the efficiency of a tray is never unity although it can be made to approach unity (arbitrarily closely) by proper design. Most of the studies that treat the trays as nonideal tend to associate a single tray efficiency parameter with each tray. However, a recent experimental study of tray efficiency for a multicomponent system shows that the tray efficiencies of the various species are appreciably different (Biddulph et al., 1986). The physical implication of this observation is that the approach to local equilibrium in a tray does not happen with the same ease for the various species present (and temperature). This is not surprising, as the bulk of the resistance for interphase transport will be concentrated on the liquid side of the gas-liquid interface and the effective mass transfer coefficient here for the various species will, in general, be different. Thus, even if the tray efficiencies for the various species are arbitrarily close to unity in a tray, the departure from unity will not in general be the same for all the species. In light of the analysis presented here, a reexamination of the classical procedures for minimum reflux calculation such as the Underwood (1948) method, relaxing the assumption of equilibrium trays and retaining the finite interphase mass transfer rates in the trays, appears warranted.

Summary

Separation devices in which mass transfer between a flowing fluid phase and another mobile phase facilitates the desired separation are widely used in the chemical process industry. An equilibrium theory, in which local equilibrium between the two phases is postulated, has been studied extensively as a limit of performance for such devices. In this theory, when applied to a countercurrent adsorption process, the only operating parameter that affects the composition of the pinch state prevailing over most of the length of the column is the flow ratio between the two phases. It is shown that this equilibrium theory is deficient and that there are other parameters, which are lost in the procedure by which the model equations for the equilibrium theory are formulated, that can have a profound effect on the composition of the pinch state. These parameters, namely the ratios of the mass transfer coefficients between the various adsorbing species, determine the composition profiles in the boundary layers regions at one or both ends of the column and through them the composition of the pinch state itself.

Notation

a_v = external surface area of particles per unit volume of bed
A_x = cross-sectional area of bed
C_o = a reference concentration
C_i = concentration of species i in fluid phase
C_i^o = concentration of species i in feed fluid
k_i = mass transfer coefficient for species i
K_i = equilibrium constant for species i in Langmuir adsorption isotherm
$\tilde{K}_i$ = dimensionless equilibrium constant for adsorption of species i
L = length of adsorption column
M = total number of adsorbing species
n_i = concentration of species i in adsorbed phase
n_i^e = concentration of species i in adsorbed phase that would be in equilibrium with local gas phase composition
n_i^L = concentration of species i in entering solid stream
N = maximum adsorption capacity of solid adsorbent
q_f = volumetric flow rate of the fluid
q_s = volumetric flow rate of the solid
t = time
x_i = dimensionless concentration of species i in adsorbed phase
x_i^e = dimensionless concentration of species i in adsorbed phase that would be in equilibrium with local gas phase
x_i^1 = dimensionless concentration of species i in entering solid
x_i^p = dimensionless concentration of species i in solid phase corresponding to pinch state
$x_i(0)$ = dimensionless concentration of species i in exiting solid
y_i = dimensionless concentration of species i in fluid phase
y_i^o = dimensionless concentration of species i in entering fluid
y_i^e = dimensionless concentration of species i in fluid phase that would be in equilibrium with local solid phase
y_i^{eq} = dimensionless concentration of species i in fluid phase that would be in equilibrium with entering solid
$y_i(1)$ = dimensionless concentration of species i in exiting fluid
y_i^p = dimensionless fluid phase concentration of species i corresponding to pinch state
z = spatial coordinate along length of adsorption column

Greek letters

α_i = dimensionless solid-side mass transfer coefficient for species i
β_i = dimensionless fluid-side mass transfer coefficient for species i
Υ_i = dimensionless adsorption rate constant for species i
ϵ = bed voidage
ξ = dimensionless spatial coordinate
τ = dimensionless time
μ = dimensionless flow ratio between fluid and solid
μ_* = critical flow ratio below which pinch state is the same as the state of the entering solid
μ^* = critical flow ratio above which pinch state is the same as the state of the entering fluid
ν = dimensionless capacity ratio between solid and fluid phases

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