Pore and Solid Diffusion Models for Fixed-Bed Adsorbers

Most models for fixed bed adsorbers have used either the homogeneous-solid or pore diffusion model for the pellets. When the adsorption isotherm is linear, the two models can lead to identical breakthrough curves. The conditions for this equivalence are presented here. It is shown that one of the bulk flow factors that was included in the formulation of one pore diffusion model will be significant only for feedstreams containing a relatively high concentration of adsorbate. The porosity factor of the pore model is shown to be very important, especially as the porosity decreases. The importance of the two diffusional models with respect to the predicted breakthrough curves is demonstrated. For comparable beds, it is shown that the breakthrough curve based on the homogeneous model is delayed with respect to that based on the pore model at early times, regardless of the shape of the isotherm. Finally, the various possible solutions for an irreversible isotherm are reviewed for each of the models, and a solution is presented for the general case of a pore model with an outside film resistance.

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SCOPE

In modeling a fixed-bed adsorption column, three equations are required. One describes the concentration of adsorbate in the external voids of the bed as the fluid passes through. The second equation describes the actual diffusion process within the pellets, and the third equation couples the first two equations in terms of a film resistance surrounding the particles. Although some studies have neglected this resistance, the differences between most models have centered around the diffusion model chosen for the adsorbent pellets.

One of these models is the homogeneous-solid diffusion model, according to which the adsorption occurs on the outer surface of a pellet, followed by the diffusion of the adsorbed phase into the pellets. The other model, the so-called "pore diffusion model," pictures the diffusion as occurring in the fluid phase with a distributed adsorption along the pore walls. These models have been used about equally by researchers in this area.

Rosen (1952, 1954) presented an analytical solution for the homogeneous model for the case of a linear isotherm and presented numerical results. Hall et al. (1966) investigated the breakthrough behavior for some cases similar to those considered in this paper but confined their attention to systems displaying constant pattern behavior.

Therefore, only favorable and irreversible isotherms were considered. Furthermore, they neglected the outside film resistance between the bulk fluid and the surface of a pellet except in one special case.

This paper begins with a description of the conditions under which the two models lead to identical breakthrough curves. The main requirement is that the adsorption isotherm be linear. In the formulation of their pore model, Lee and Weber (1969a) incorporated two bulk flow factors that have not been included in previous models. The importance of one of these factors is considered. However, the thrust of the paper is directed toward showing the differences in breakthrough curves that can arise from the two models when the isotherm is nonlinear and when the magnitude of the porosity of the particles is accounted for.

An irreversible isotherm is a limiting case of a favorable isotherm and analytical solutions for this situation are possible. The various cases that can arise are reviewed. The only case that has not been specifically solved for adsorption systems is that for the pore model when there is an outside film resistance. This case was solved by the authors and the results are presented.

CONCLUSIONS AND SIGNIFICANCE

This study indicates that the bulk flow factor in the diffusion equation for the pore model will be significant only for feedstreams containing a relatively high concentration of adsorbate. In most cases, this factor could be ignored. On the other hand, the porosity factor α of the pore model is very important since it relates the portion of the outer surface available for diffusion to the total surface area. This factor becomes increasingly important as this area for diffusion decreases.

If the isotherm is linear, the two diffusional models can result in identical breakthrough curves. Therefore, the choice of models has not been critical in many experimental studies in which the isotherm was approximately linear. However, for a nonlinear isotherm, the results indicate that some care should be exercised in selecting the diffusional model for a fixed-bed system. A series of batch tests might be used for this selection by comparing measured rates of adsorption against those predicted by each of the two diffusional models. Alternatively, an experimental breakthrough curve could be compared with those predicted by each of the two bed models.

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The significance of the results lies in the demonstrated importance of the diffusional models to the locations of the respective breakthrough curves, especially for highly favorable isotherms. In most studies of fixed beds, this choice has apparently not been at issue. These results indicate that the correct model should be determined first, perhaps in a series of batch tests, before the model for a fixed bed is formulated.

DESCRIPTION OF BED MODELS

The goal of most theoretical treatments for adsorption beds has been the prediction of the breakthrough curve that occurs after an initially adsorbate-free bed is subjected to a step input in feed concentration. All models for an adsorption bed must include the following: (1) A description of the diffusional processes within an adsorbent pellet; (2) A mass balance for the adsorbate in the fluid phase in the external voids; and (3) A coupling equation between the fluid and the surface of an adsorbent pellet to account for the mass transfer resistance of the film between the bulk of the fluid and the fluid at the surface of a pellet.

The differences in the models used by various investigators have basically centered around the description of the diffusional process within the pellets. In some studies, kinetic models have been used to approximate this process, but this paper is concerned only with the two diffusional models, namely, the homogeneous solid diffusion model and the pore diffusion model.

Diffusional Processes Within a Pellet

Homogeneous Solid Diffusion Model. This model, which will be referred to as the homogeneous model, pictures the adsorption process as occurring at the outer surface of a pellet, followed by the diffusion of the adsorbate in the adsorbed state. Although the particle is assumed to be homogeneous, this does not preclude the use of this model for particles actually possessing substantial porosity. The main point is, however, that no attempt is made to relate the transport processes to the structure in terms of such properties as surface area and pore size distribution. For spherical geometry, Rosen (1952, 1954) expressed the diffusion equation as follows:

$$\frac{\partial q}{\partial t} = \frac{D}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial q}{\partial r}\right] \quad (1)$$

Pore Diffusion Model. This model pictures the particles as consisting of a solid phase interspersed with very small pores. As indicated in Figure 1, there is a three-way division of the bed volume and the diffusion occurs in the internal void fraction α. Most researchers have assumed that the adsorbate diffuses into the pores in the fluid phase, but with the addition of an extra term surface diffusion in the adsorbed state can also be accounted for. Lee and Weber (1969a) expressed the diffusion equation as follows:

$$\left[\rho + \frac{\rho_a}{\alpha} \frac{dw}{dx} \right] \frac{\partial x}{\partial t}$$
$$= \left[\frac{\rho \mathcal{D}_p}{1-x} + \frac{\rho_a \mathcal{D}_s}{\alpha} \frac{dw}{dx} \right] \frac{1}{r^2} \frac{\partial}{\partial r}\left[r^2 \frac{\partial x}{\partial r}\right] \quad (2)$$

This equation assumes that the adsorption process itself is instantaneous. On the left-hand side, the first term is the accumulation of adsorbate in the fluid phase and the second is that in the adsorbed state. On the right-hand side, the first term is the diffusion of adsorbate in the fluid phase and the second is surface diffusion of the adsorbed species. The factor $1/(1-x)$ accounts for bulk flow and is one of the two bulk flow factors that arise in this model.

The adsorbate loading w refers to the actual mols adsorbed per gram of dry adsorbent and does not include the mols of adsorbate held in the fluid phase in the pores. In the measurement of an adsorption isotherm, the direct result is a determination of the adsorbate in the adsorbed state plus that held in the pores of the particles. The loading w can then be calculated by subtracting out the quantity of the adsorbate in the pores if the porosity of the particles is known.

If the adsorption isotherm is linear, the derivative dw/dx is constant. Hence, the entire coefficient on the right-hand side is a constant and the diffusion can be described in terms of a single pseudo diffusivity.

Mass Balance for the Adsorbate in the External Voids

In all treatments it is assumed that the fluid passes through the bed in plug flow. In his homogeneous model, Rosen (1952, 1954) expressed this equation in the following way:

$$v \frac{\partial c}{\partial z} + \frac{\partial c}{\partial t} = -\frac{3h}{mb}(c - q_s/K) \quad (3)$$

For their pore model, Lee and Weber (1969a) presented the following equation:

$$v \frac{\partial y}{\partial z} + \frac{\partial y}{\partial t} = -\frac{A}{\rho \epsilon}\left(\frac{\alpha}{1-\epsilon} \right) k_f (y - x_s) \quad (4)$$

Although the symbols are different, Equations (3) and (4) are basically the same. There is one important difference, however. In the pore model, the adsorbent presents A cm^2 of external surface area per cc of bed. Assuming that each internal pore has a uniform diameter and that there are no bottlenecks or funnel-type pores, the fraction of this area represented by pore openings is $\alpha/(1-\epsilon)$. This is the only fraction which is effective for diffusion of adsorbate into the pores and therefore this factor appears on the right-hand side of Equation (4).

Coupling Equation Between the Fluid and the Particle Surface

The rate of mass transfer between the bulk of the fluid and the outer surface of the solid is expressed in terms of the driving force between these two regions and the concentration gradient at the surface of the pellet. The equation used by Rosen (1952) is

$$D \left. \frac{\partial q}{\partial r}\right|_{r=b} = h\,(c - q_s/K) \quad (5)$$

For the pore model, the equation is written in the following form of Lee and Weber (1969a)

$$\left[\frac{\mathcal{D}_p \rho}{1-x} + \frac{\rho_a \mathcal{D}_s}{\alpha} \frac{dw}{dx} \right]\Bigg|_{r=r_o \equiv b} = k_f \frac{(y - x_s)}{1-y} \quad (6)$$

The factor $1/(1-y)$ on the right-hand side is the second bulk-flow factor of this model. Neither of these factors was included in Rosen's formulation.

EQUIVALENCE CONDITIONS FOR THE TWO MODELS

From a physical standpoint, the two diffusion models differ considerably. In the homogeneous model, even though the pellets may be rather porous, there are no sinks for the adsorbate since it diffuses into them in the adsorbed state. The entire process might be pictured as an adsorption at the outer surface of the pellets followed by a sponge-like absorption of the adsorbate into them. On the other hand, for the pore diffusion model there is an absorption of the adsorbate into the pores with a concurrent distributed adsorption all along the pore walls. In spite of these very different physical pictures, the two models can result in identical breakthrough curves under certain conditions. The conditions basically fall into two categories as shown in Table 1. One set of conditions comes about from the actual equations used in describing the models and the other set from differences in the geometric parameters and their units.

Turning first to the equations, the first condition in Table 1 relating α and ϵ comes about in the following way. Equation (2) can be reduced to the form of Equation (1) in either of two ways. In the first, the constant α is set equal to zero. However, then the right-hand side of Equation (4) is zero, indicating that there is no mass transfer to the pellets in the pore model. Thus, neither mathematical nor physical equivalence is achieved by this choice. The other way of reducing Equation (2) to Equation (1) is to set $\alpha = 1 - \epsilon$. Equation (4) still retains its mathematical form. From Figure 1, however, it can be seen that now there is no solid fraction. Although there is no longer a physical equivalence between the models, there is the necessary mathematical equivalence. These difficulties could have been avoided if a general fractional term, say f, were used to express the fraction of external surface area available for diffusion. The fraction f could then be approximated by $\alpha/(1 - \epsilon)$. However, the purpose here was to work with the equations

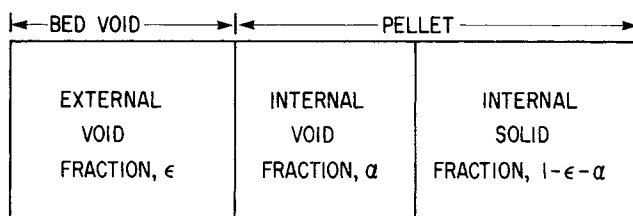| ←—BED VOID—————→|←————————PELLET————————→| |
|---|---|---|
| EXTERNAL VOID FRACTION, ϵ | INTERNAL VOID FRACTION, α | INTERNAL SOLID FRACTION, $1-\epsilon-\alpha$ |

Fig. 1. Fractional breakdown of bed volume for the pore model.

originally presented by Lee and Weber (1969a).

The second condition is that the bulk flow factors must be neglected in the pore model. It should be noted that there is no intrinsic reason for including them in the pore model while excluding them from the homogeneous model. However, Rosen did not include them in his formulation and therefore, for consistency, they must be excluded from the pore model. Furthermore, they will be negligible when the feed concentration is low, and this point will be amplified upon later in this paper.

The third condition indicates the required relationship between the equilibrium curves for the two models. In his analysis, Rosen assumed a linear isotherm, so K is a constant; therefore, it can be seen that the isotherm in terms of w and x will also be linear. The fourth condition comes about from a comparison of the diffusion and coupling equations. Combining the third and fourth conditions, the following relationship is obtained:

$$D = \frac{\mathcal{D}_p + \mathcal{D}_s (K - 1)}{K} \qquad (7)$$

Therefore, if surface diffusion is assumed to be zero, then $D = \mathcal{D}_p/K$, and if pore diffusion is assumed to be zero, $D = \mathcal{D}_s(K - 1)/K$.

The conditions arising from the geometric factors and the differences in the units of the various parameters are easily obtained and require no further comment.

LITERATURE REVIEW

A survey of adsorption studies indicates that the homogeneous model has been used somewhat less often than the pore model. A fairly comprehensive review of these studies is presented in Tables 2 and 3. Batch studies have been included since a first step in a study of a fixed-bed system might be a series of batch tests to determine which of the two models is more suitable for a given system.

Only a few researchers have attempted to correlate experimental data with both models. Dedrick and Beckman (1967) and Hsieh et al. (1971) utilized the two models for some batch studies. Hall et al. (1966) discussed the possibility of discriminating between the two models on the basis of breakthrough curves from a fixed bed. Their analysis assumed constant-pattern behavior that is predicted for systems having a favorable equilibrium curve in relatively deep beds.

Since equivalence conditions do exist when the isotherm is linear, the choice between the two models is not important if the isotherm is of that form. However, as will be demonstrated shortly, the correct choice could be important for a system having a nonlinear isotherm. Before discussing this topic, attention will be first turned to the importance of the bulk-flow factors and then to the significance of particle porosity.

TABLE 1. EQUIVALENCE CONDITIONS FOR THE TWO MODELS

Conditions Based on a Comparison of the Diffusion (D), Fluid-Phase (F), and Coupling (C) Equations

(i)	$\alpha = 1 - \epsilon$	Required by (D), (F), and (C)
(ii)	The bulk-flow factors must be neglected: i.e., $1 - x \cong 1$ and $1 - y \cong 1$	Required by (C)
(iii)	$K = \dfrac{dw}{dx} \dfrac{\rho_a}{\rho} \dfrac{1}{\alpha} + 1$	Required by (F) and (C)
(iv)	$D = \dfrac{\mathcal{D}_p + \dfrac{\rho_a}{\rho} \dfrac{\mathcal{D}_s}{\alpha} \dfrac{dw}{dx}}{\dfrac{\rho_a}{\rho} \dfrac{1}{\alpha} \dfrac{dw}{dx} + 1}$	Required by (D) and and (C)

Conditions Arising from Geometric Factors or from the Different Units of the Parameters Used in the Two Models

(v)	$m = \dfrac{\epsilon}{1 - \epsilon}$
(vi)	$\dfrac{3}{r_o} = \dfrac{A}{\alpha}$
(vii)	$h = \dfrac{k_f}{\rho}$

TABLE 2. HOMOGENEOUS SOLID DIFFUSION MODEL

Investigator	Gas or liquid	Particle shape	Batch or bed	Film resistance	Mathematical treatment
		Linear Isotherm			
Thomas (1951)	Gas	Sphere	Bed	No	Analytical
Rosen (1952, 1954)	Liquid	Sphere	Bed	Yes	Analytical with numerical results
Eagle and Scott (1950)	Liquid	Sphere	Batch	No	Wicke's (1939) analytical solution
Dryden and Kay (1954)	Liquid	Sphere	Batch	No	Modified Paterson's (1947) analytical solution for heat transfer [a]
Smith et al. (1959)	Liquid	Sphere	Batch	No	Modified Dryden and Kay's (1954) solution [a]
Tien and Thodos (1960)	Liquid	Sphere	Bed	Yes	Analytical [b]
Colwell and Dranoff (1966)	Liquid	Sphere	Bed	Yes	Rosen's solution [c] (1952, 1954)
		Nonlinear Isotherm			
Tien and Thodos (1959, 1965)	Liquid	Sphere	Bed	Yes	Numerical
Tien (1960)	Liquid	Sphere	Batch	No	Analytical [d]
Tien (1961)	Liquid	Sphere	Batch	No	Numerical
Miller and Clump (1970)	Liquid	Sphere	Batch	No	Similar solution [e] (Tien, 1961)
Colwell and Dranoff (1969, 1971)	Liquid	Sphere	Bed	Yes	Numerical [f]
Kondis and Dranoff (1971)	Gas	Sphere	Batch	No	Numerical [g]
Morton and Murrill (1967)	Liquid	Sphere	Bed	Yes	Numerical

[a] Experimental isotherm was Freundlich type.
[b] Generalized linear isotherm q (g adsorbed/g adsorbent) $= k_1 + k_2\ c$.
[c] Saturation and Elution runs were conducted.
[d] Liquid phase concentration was approximated by a polynomial function.
[e] Mass transfer coefficient $k_p \left(= \dfrac{15D}{r_0^2} \right)$ calculated from diffusivity data.
[f] Axial dispersion in the bed was considered.
[g] Nonisothermal adsorption; diffusivity was assumed to be a function of temperature and adsorbed gas concentration.

EFFECT OF BULK-FLOW FACTOR, $1/(1-x)$

Equations (2), (4), and (6) were solved numerically in the manner described in the paper of Lee and Weber (1969a). With respect to Equation (6), it is important to note that it was assumed in that solution, and also here, that $1 - x$ is equal to $1 - y$. This assumption is reasonable since x is approximately equal to y at the mouth of a pore. A further assumption in that paper and also here is that $\mathcal{D}_s$ is zero. To assess the effect of the bulk flow factor $1/(1 - x)$ in Equation (2), it was retained in one set of computer solutions and set equal to unity in another. The equivalence conditions of Table 1 were used so that the numerical procedures could be checked against the published solutions of Rosen (1954) for the case in which the factors are unity.

Rosen presents his solutions in terms of the ratios of the following three parameters:

$$X = \frac{3DKz}{mv\ b^2} \qquad \text{Bed length parameter} \qquad (8)$$

$$Y = \frac{2D}{b^2} \left(t - \frac{z}{v} \right) \qquad \text{Contact time parameter} \qquad (9)$$

$$v = \frac{DK}{bh} \qquad \text{Film resistance parameter} \qquad (10)$$

For fixed values of X, the breakthrough concentration is presented as a function of the ratio Y/X with the ratio v/X as a parameter. The ratio Y/X can be looked upon as a dimensionless time, and the ratio v/X can be interpreted as the reciprocal of the mass transfer resistance surrounding a particle.

Among the cases calculated by Rosen, he presents breakthrough curve data for the following set of parameters: $X = 0.2$; $v/X = 0.025$; and seven values of Y/X. Numerical values of the physical parameters in Equations (8) to (10) were arbitrarily selected to yield values of $X = 0.2$ and $v/X = 0.025$. Three values of inlet concentration x_0 were chosen and the concentration at the outlet of the bed was calculated in the dimensionless form $v = x/x_0$ at various values of the dimensionless time, Y/X. Three results are presented in Table 4 and they indicate that the bulk flow factor $1/(1 - x)$ has negligible influence at concentrations as high as 0.1 mole fraction. Even at the unusually high concentration of 0.4, the effect is only about 4 to 5%.

It is important to note that the velocity of the fluid v will change as the adsorbate is removed. This change would be negligible for liquid systems having a low concentration of the adsorbate. In this particular calculation, this change in velocity was completely neglected as the interest here was only in the bulk flow factor $1/(1 - x)$. The influence of concentration on velocity is considered in the aforementioned paper of Lee and Weber (1969a).

The case without the bulk flow factors corresponds to that of Rosen and his values can therefore be used as a check on the numerical solution here. Rosen indicated that the error in his computations was less than 0.002. The values compare very well except for those at $Y/X = 0.1$. A similar discrepancy at the low end of Y/X was noted in several other checks of Rosen's tabulations. A number of other authors have used Rosen's data as a basis for checking their numerical solutions but have not noted any discrepancies. An estimated value of the truncation error for the numerical solution here was 0.0025, which is about the same as that of Rosen. Without further investigation, it is difficult to say whose results are more accurate.

TABLE 3. PORE DIFFUSION MODEL

Investigator	Gas or liquid	Particle shape	Batch or bed	Film resistance	Mathematical treatment
		Linear Isotherm			
Damköhler (1935)	Gas	Sphere	Batch	No	Analytical [a]
Wicke (1939)	Gas	Sphere	Batch	No	Analytical
Wilson (1948)	Liquid	Slab, cylinder [b]	Batch	No	Analytical
Carmen and Haul (1954)	Gas	Slab, sphere	Batch	No	Wilson's (1948) analytical solution
Amundson (1948, 1950)	—	Sphere	Bed	No	Analytical
Edeskuty and Amundson (1952a)	Liquid	Cylinder [c]	Batch	Yes	Analytical
Edeskuty and Amundson (1952b)	Liquid	Sphere	Batch	Yes	Analytical
Kasten et al. (1952)	—	Sphere	Bed	Yes	Analytical
Lapidus and Amundson (1952)	—	Sphere	Bed	No	Analytical [d]
Masamune and Smith (1964a, b; (1965a, b)	Gas	Sphere	Bed	Yes	Analytical
Testin and Stuart (1967)	Gas	Sphere	Batch	No	Modified Wicke's (1939) analytical solution
Chao and Hoelscher (1966)	Gas	Sphere	Bed	Yes	Analytical [d]
Allen (1968)	Gas	Cylinder	Batch	No	Numerical
Nemeth and Stuart (1970)	Gas	Sphere	Batch	No	Modified Damköhler's (1935) analytical solution [e]
		Nonlinear Isotherm			
Weber and Rumer (1965)	Liquid	Cylinder [b]	Batch	No	Numerical
Brecher et al (1967a, b)	Liquid	Sphere	Batch	No	Numerical [a]
Dedrick and Beckmann (1967)	Liquid	Sphere	Batch	No	Analytical [f]
Hsieh et al (1971)	Liquid	Sphere	Batch	No	Numerical [f]
Carter (1966)	Gas	Sphere	Bed	Yes	Numerical [g]
Rimpel (1968)	Gas	Sphere	Bed	Yes	Rosen's (1952, 1954) solution used [h]
Lee and Weber (1969a)	Gas	Sphere	Bed	Yes	Numerical
Lee and Weber (1969b)	Gas	Sphere	Bed	Yes	Numerical [i]
Meyer and Weber (1967)	Gas	Sphere	Bed	Yes	Numerical [j]
Lee and Chi (1971)	Gas	Sphere	Bed	No	Analytical [k]
Marcussen (1970)	Gas	Sphere	Bed [l]	Yes	Numerical
Furusawa and Smith (1973)	Liquid	Sphere	Batch	Yes	Numerical and analytical

[a] Vapor phase and adsorbed phase diffusion were considered.
[b] Cylinder of unit length.
[c] Diffusion was assumed to occur only in the radial direction.
[d] Axial dispersion was considered in an infinite bed.
[e] Experimentally observed isotherm was nonlinear.
[f] Pore and homogeneous models were considered.
[g] Pore and surface diffusion were considered in the adiabatic adsorption system.
[h] Diffusion in Rosen's Model (1952, 1954) was assumed to be composed of pore and surface diffusion, analogous to Masamune and Smith (1964a).
[i] Isothermal and nonisothermal models.
[j] Nonisothermal models.
[k] Acrivos-Vermeulen model (Vermeulen, 1958) for irreversible isotherm was used. However, experimental isotherm was favorable type.
[l] Differential bed.

TABLE 4. EFFECT OF BULK FLOW FACTOR, $1/(1 - x)$
For $X = 0.2$ and $v/X = 0.025$
Numerical solution of this study

Inlet concentration, x_o	with bulk-flow factors			without bulk-flow factors See note below	Rosen's values (1954)
	0.4	0.1	0.05		
	Dimensionless breakthrough concentration, $u = x/x_o = c/c_o$				
Y/X					
0.1	0.238	0.222	0.222	0.221	0.200
0.1475	0.343	0.321	0.319	0.315	0.312
0.2	0.429	0.404	0.400	0.396	0.403
0.3	0.546	0.517	0.512	0.508	0.506
0.5	0.682	0.651	0.646	0.642	0.642
1.0	0.835	0.806	0.801	0.797	0.799
2.0	0.948	0.922	0.919	0.915	0.915

Note: Without the bulk-flow factor, the breakthrough concentration is independent of the feed concentration if the change in fluid velocity with concentration is neglected.

EFFECT OF PARTICLE POROSITY

For the pore model, it can be seen from Figure 1 that the internal void fraction α can take on any value between 0 and $1 - \epsilon$. At the value of 0, the particles are impervious to adsorbate and are therefore inert. At the other extreme, where $\alpha = 1 - \epsilon$, the particle is completely porous—in other words, there is no solid fraction at all.

Two study cases for a linear isotherm were set up. The parameters were the same as those used in the study of the bulk-flow factors and these factors were set equal to unity. In the first case, the void volume ratio m was given a value of 0.4, which in turn gives an external void fraction ϵ of 0.286. To find the maximum possible effect of particle porosity, α was set equal to $1 - \epsilon$ in the first
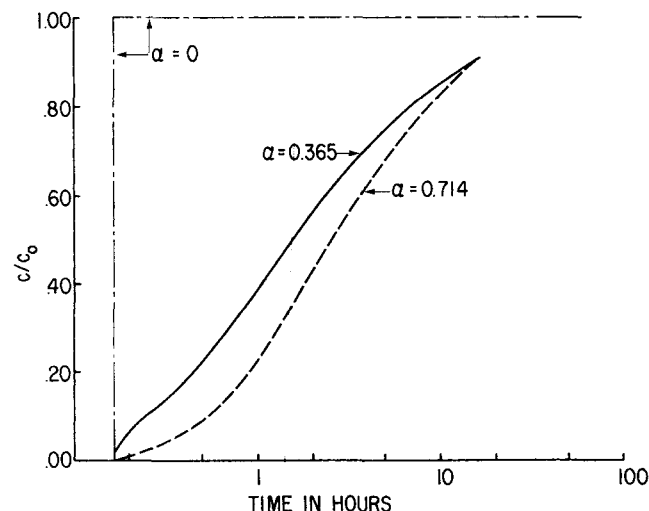
Fig. 2. Effect of porosity on breakthrough curve for the pore model with a linear isotherm.
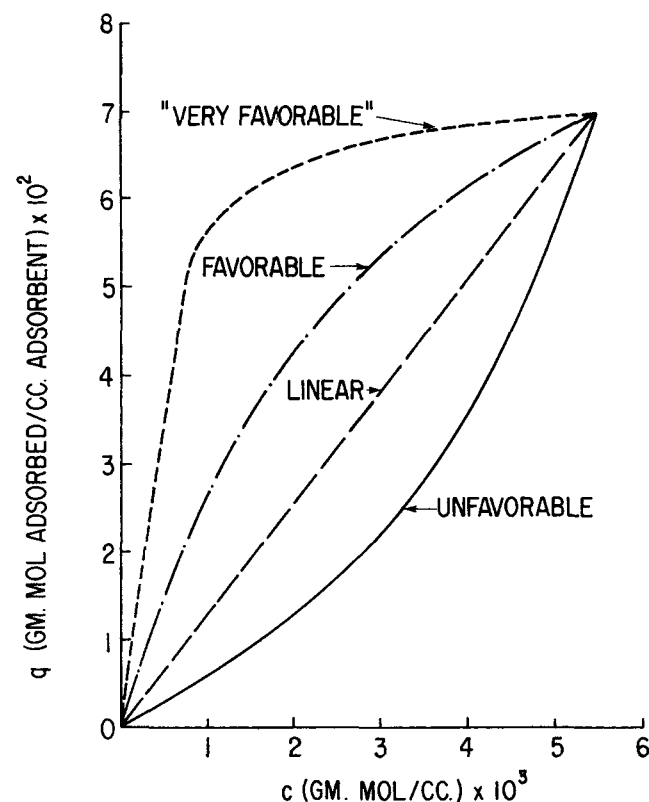
study case, resulting in a value of α of 0.714. In some experimental studies in progress here with activated carbon, the measured value of α was 0.365, and this value was used for the second case, while at the same time keeping ϵ equal to 0.286.

Breakthrough curves for the two cases are presented in Figure 2. Breakthrough commences in both cases at a time of 0.168 hr. since this is the residence time of the fluid in the bed. When α is 0, the breakthrough curve is just a step function of unit magnitude at 0.168 hr. as indicated in the figure. Thus, the effect of α is very considerable, especially at low values of α.

EFFECT OF THE ISOTHERM SHAPE

Linear, Unfavorable, and Favorable Isotherms

As a basis for these computations, the nonlinear isotherm was assumed to be described by the Langmuir equation

$$q = \frac{Q_m dc}{1 + dc} \qquad (11)$$

where Q_m and d are constants. Hall et al. (1966) noted that the essential characteristics of a Langmuir isotherm can be expressed in terms of a dimensionless constant separation factor or equilibrium parameter R which is defined by

$$R = \frac{1}{1 + dc_0} \qquad (12)$$

This parameter indicates the shape of the isotherm as follows:

Values of R	Type of Isotherm
$R > 1$	Unfavorable
$R = 1$	Linear
$0 < R < 1$	Favorable
$R = 0$	Irreversible

Isotherms for four sets of parameters are presented in Figure 3. To facilitate comparisons, it was assumed that the feed concentration in all cases is 0.00562 g-mol of adsorbate/cc which for an aqueous solution is equivalent to a mole fraction x_0 of about 0.1. The linear curve is the same as that used in studying the effect of the bulk flow factors. The constants for the several curves are tabulated below:

| Isotherm shape | K | Q_m | d | R |
	cc external voids / cc pellet	g mol / cc	cc / g mol	
Linear	12.86			1
Unfavorable		−0.0412	−114	2.75
Favorable		0.113	313	0.364
Very favorable		0.076	3130	0.054

In order to compare breakthrough curves for the pore model with those of the homogeneous model, the isotherms in Figure 3 must be converted from the $q - c$ basis to the $w - x$ basis of the pore model. From the definitions and units of q, c, w, and x, it can be shown that

$$q = w\rho_a \left(\frac{1}{1 - \epsilon} \right) + c \qquad (13)$$

and

$$c = \rho x \qquad (14)$$

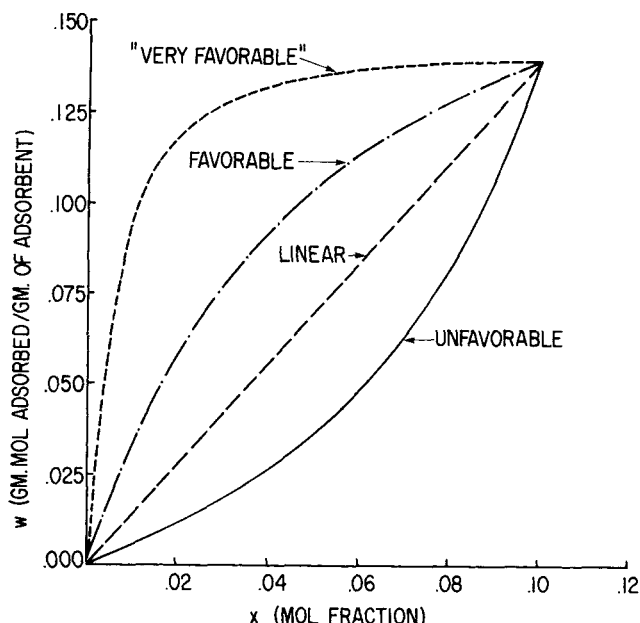For the case of a linear isotherm, since $q = Kc$, Equa-

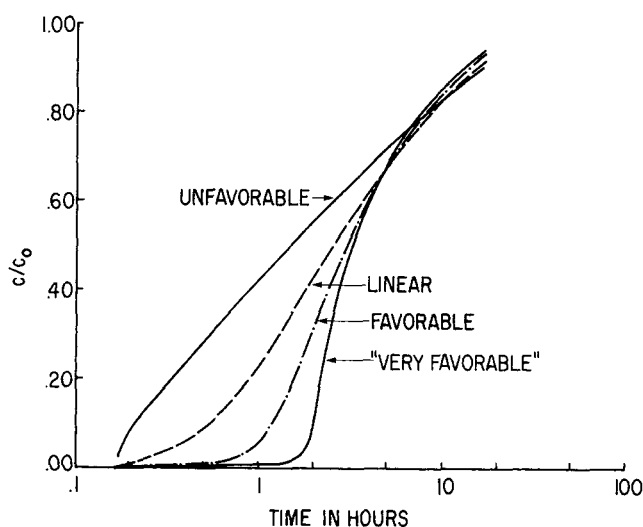Fig. 3. Shapes of isotherms for study cases in terms of q and c.

Fig. 4. Shapes of isotherms for study cases in terms of w and x.

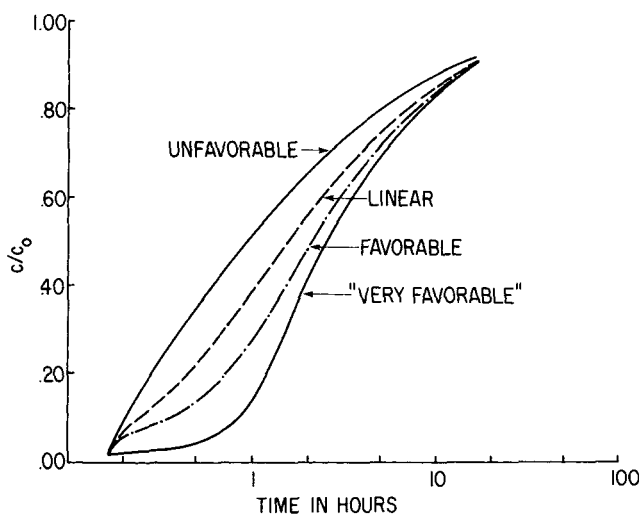Fig. 5. Breakthrough curves for the homogeneous model for the four isotherms.

tions (13) and (14) can be solved simultaneously to give

$$w = \frac{\rho(K-1)(1-\epsilon)}{\rho a} x \qquad (15)$$

This equation, which is linear, is shown in Figure 4. For the nonlinear case, the Langmuir relationship of Equation (11) in combination with Equations (13) and (14) yields

$$w = \frac{1-\epsilon}{\rho a} \left[\frac{(Q_m d - 1)\rho x - d\rho^2 x^2}{1 + d\rho x} \right] \qquad (16)$$

This equation was then used to convert the nonlinear isotherms of Figure 3 to those presented in Figure 4. It can be seen from Equation (16) that if the term $d\rho^2 x^2$ is small in comparison with $(Q_m d - 1)\rho x$, the shape of the $w - x$ isotherm is basically the same as its counterpart in the $q - c$ formulation. This is the situation for the examples presented here, as a comparison of Figures 3 and 4 indicates.

Breakthrough curves were generated for the homogeneous model using the isotherms of Figure 3 and the results are shown in Figure 5. The parameters X and v/X are the same as those used in the study of the bulk-flow factors. In a similar way, a set of breakthrough curves was calculated for the pore model using the isotherms of Figure 4 and is shown in Figure 6. The curves are comparable to those of Figure 5 since the bulk-flow factors were neglected. To account for the porosity of the pellets, the intraparticle void fraction α was set at 0.365, one of the values that was previously used. As expected, for each model, as the isotherm becomes increasingly favorable, the breakthrough curve becomes increasingly sharp.

To assess the effects of the diffusional models, comparable pairs of curves from Figures 5 and 6 are redrawn in Figures 7 to 9. The comparable pair of curves for the linear isotherm already exists in Figure 2. This comes about because the curve for a porosity of 0.714 meets all of the equivalence conditions of Table 1, and therefore this curve applies to the homogeneous model as well. In each of the four figures, the curves must necessarily cross because of material balance considerations.

In each case, at early times, the breakthrough curve based on the homogeneous model is delayed with respect to that based on the pore model. This delay increases substantially as the isotherm becomes increasingly favorable. One contributing factor to this delay is the porosity factor
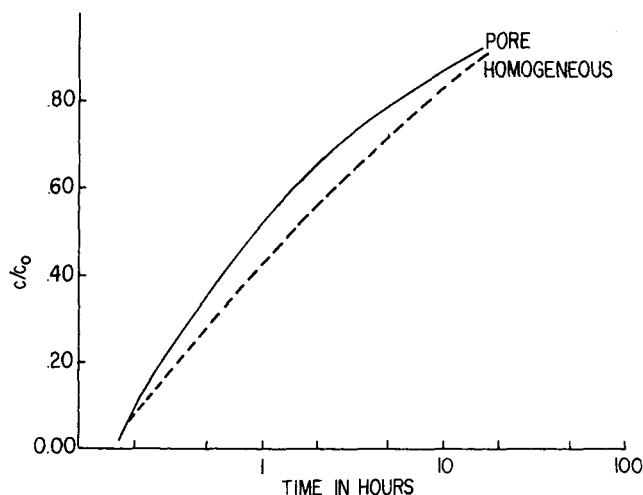

Fig. 6. Breakthrough curves for the pore model for the four isotherms.

Fig. 7. Breakthrough curves for pore and homogeneous models for an unfavorable isotherm.

α. Another factor is that with the homogeneous model, the adsorbate is never immobilized at any stage of the process since diffusion continues after the adsorption reaction. On the other hand, with the pore model, an adsorbate molecule is immobilized at the instant the reaction occurs. Therefore, when the concentration is low, diffusion by the homogeneous model is relatively fast compared with that by the pore model.

Irreversible Isotherm

As the isotherm becomes increasingly favorable, it approaches the limiting situation of an irreversible isotherm. Some physical systems exhibit this behavior, and furthermore analytical solutions for the breakthrough

curves exist for both models. For perspective, a summary of the various cases is presented in Table 5. Since an irreversible isotherm is a limiting form of a favorable isotherm, constant pattern behavior is eventually obtained if the bed is sufficiently long. Because of the mathematical simplicity arising from constant-pattern behavior, this assumption was made in most treatments.

Homogeneous Model. For the homogeneous model, as soon as an adsorbent particle comes into contact with solution containing any of the adsorbate, its surface becomes saturated. The diffusion and adsorption behavior in this pellet are then described by the solutions for the problem of unsteady state heat or mass transfer within single spheres in a batch system of infinite extent so that the outer temperature or concentration can be considered constant. In a sense then, the solution of the problem for
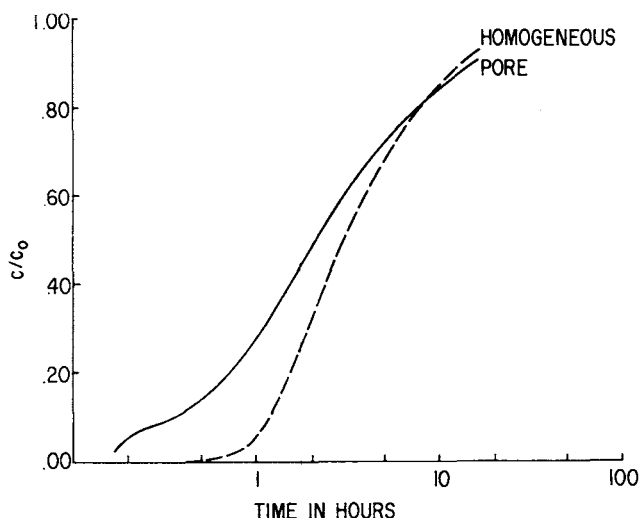

Fig. 8. Breakthrough curves for pore and homogeneous models for a favorable isotherm.
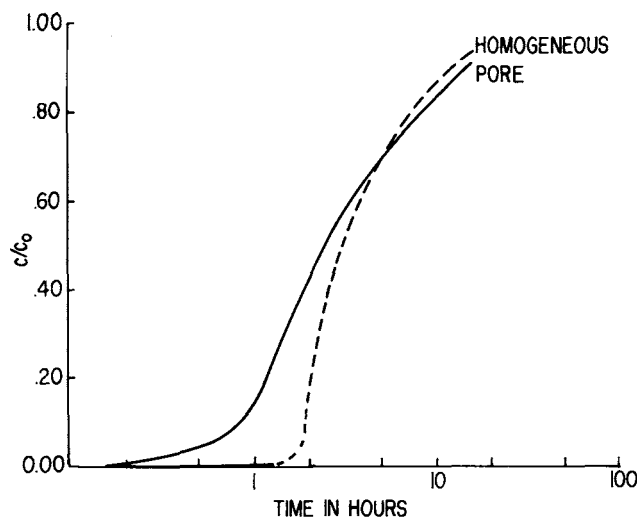

Fig. 9. Breakthrough curves for pore and homogeneous models for a very favorable isotherm.

TABLE 5. SUMMARY OF IRREVERSIBLE CASES

Homogeneous model

General solution		Constant pattern	
With film resistance	Without film resistance	With film resistance	Without film resistance
Impossible	1. Cooper (1965) In addition to the solution for true diffusion in spheres, solutions are also presented for (a) "Early Time" Approximation (b) Linear Driving Force— Glueckauf (1955) (c) Quadratic Driving Force —Vermeulen (1958) 2. Vermeulen (1953) presents an approximate solution for a quadratic driving force.	1. Exact solution is impossible. 2. An approximate solution is given by Vermeulen (1953) based on a quadratic driving force.	1. Vermeulen (1953) In addition to the solution for true diffusion in spheres, solutions are also presented for (a) Linear Driving Force (Glueckauf, 1955) (b) Quadratic Driving Force (Vermeulen, 1958) 2. Special case of Cooper's (1965) solution

Pore model

General solution		Constant pattern	
With film resistance	Without film resistance	With film resistance	Without film resistance
1. The solution of this case is presented here. It is a special case of the treatment of catalyst deactivation in fixed-bed reactors presented by Bischoff (1969).	1. Cooper and Liberman (1970). Bischoff later pointed out that this solution was a special case of his solution for catalyst deactivation in fixed-bed reactors (1969).	1. Hall et al. (1966).	1. Special case of the solution of Cooper and Liberman (1970). 2. Special case of Hall et al. (1966).

TABLE 6. SOLUTION OF PORE MODEL WITH FILM RESISTANCE AND AN IRREVERSIBLE ISOTHERM

See Cooper and Liberman (1970) for Notation

Early times and/or short beds

$$-N_{\text{pore},F} = \left\{ \frac{15}{\sqrt{3}} \tan^{-1} \left[\frac{2(1-Y)^{1/3}+1}{\sqrt{3}} \right] - \frac{15}{2} \ln \left[1 + (1-Y)^{1/3} + (1-Y)^{2/3} \right] \right\}$$

$$+ \frac{N_{\text{pore},F}}{N_{f,F}} \ln Y - 0.82940 \qquad \theta \leq \frac{5}{2} + \frac{N_{\text{pore},F}}{N_{f,F}}$$

Constant pattern

$$\theta - N_{\text{pore},F} = \frac{15}{\sqrt{3}} \tan^{-1} \left[\frac{2(1-Y)^{1/3}+1}{\sqrt{3}} \right] - \frac{15}{2} \left[\ln \left(1 + (1-Y)^{1/3} + (1-Y)^{2/3} \right) - \frac{1}{3} \right]$$

$$+ \frac{N_{\text{pore},F}}{N_{f,F}} (\ln Y + 1) - \frac{5\pi}{2\sqrt{3}} \qquad \theta \geq \frac{5}{2} + \frac{N_{\text{pore},F}}{N_{f,F}}$$

As $N_{f,F} \to \infty$, the film resistance approaches zero and these solutions approach those presented by Cooper and Liberman (1970). Under the same condition, the constant pattern solution also approaches that given by Hall et al. (1966).

a fixed bed consists of patching the mass balance equation for the fluid in the bed to the solution of the equation describing the diffusional behavior of a pellet in a batch system.

If it is assumed that there is an outside film resistance, then the equations are over-determined. This can be seen by referring to Equation (5). For an irreversible isotherm, the surface concentration is constant, so the term q_s/K is replaced by a constant. The gradient within the particle at its surface $(\partial q/\partial r)_{r=r_o}$ on the other hand, is completely independent of concentration c in the fluid, so the coupling equation cannot be satisfied.

Pore Model. Unlike the homogeneous model, solutions are possible for all of the various cases for the pore model. It is important to note, however, that all of these solutions are based on an assumption that greatly simplifies the mathematics. Referring to Equation (2) for the pore model, the first term on the left, namely $\rho(\partial x/\partial t)$, is the accumulation of adsorbate in the fluid phase within a pore, and the second term $(\rho_a/\alpha)(dw/dx)(\partial x/\partial t)$ is the accumulation in the adsorbed state. All treatments of this problem have assumed that the first term is negligible. The second term is zero in the region of the spherical pellet within which adsorption has already occurred, since the concentration w is constant. The process of adsorption within a particle can be visualized as a shrinking core. Since there is assumed to be no accumulation of adsorbate within the region through which it is diffusing, this region can be looked upon as a film resistance for mass transfer in the same way as that surrounding the outside surface. As the core shrinks, the thickness of this inside film increases, and the cross-sectional area for mass transfer is the geometric mean area, which decreases with time. With this assumption, the diffusion equation reduces to that for quasi steady state behavior and the mathematical development is relatively easy compared to that which would result if the assumption were not made.

In contrast, the numerical solution for the pore model used in the studies presented here does not make this assumption. It was originally intended that the very favorable isotherm case treated earlier be even more favorable than that shown so that it would approach an irreversible form more closely. However, it was found that as the isotherm became more and more favorable, the increments in time, axial distance, and radial distance

within a pellet had to be made smaller and smaller. Hence, to keep the computing time reasonable, the very favorable case shown was about the practical limit.

The one case in the table that has not been explicitly treated in the past is the general solution for the pore model with an outside film resistance. This case, like that without film resistance, is a special one of the general solution given by Bischoff (1969) for catalyst deactivation in fixed-bed reactors. However, the derivation used was patterned after that of Cooper and Liberman (1970) and was worked out in terms of the adsorption problem. The results are presented in Table 6. The notation is the same as that used by Cooper and Liberman (1970), and Hall et al. (1969). In particular, the first equation that applies for early times or short beds is analogous to Equation (20) of Cooper and Liberman (1970), and the second equation that applies after a constant pattern has been formed is analogous to Equation (24) of Cooper and Liberman (1970).

NOTATION

A = outside surface area of pellets per unit volume of bed, cm^2/cm^3

b = radius of spherical pellet in Rosen's model = r_o, cm

c = fluid-phase concentration, g-mol adsorbate/cc of fluid phase

c_0 = fluid-phase concentration of adsorbate in feed, g-mol of adsorbate/cc of fluid phase

d = Langmuir equilibrium constant, $\text{cm}^3/\text{g-mol}$

D = effective diffusivity in Rosen's model, cm^2/s

$\mathcal{D}_p$ = fluid-phase diffusivity in pores, cm^2/s

$\mathcal{D}_s$ = surface diffusivity, cm^2/s

h = mass transfer coefficient in Rosen's model, cm/s

k_f = mass transfer coefficient in pore model, g-mol of adsorbate/cm^2, s

K = equilibrium constant for a linear isotherm, cm^3 of external voids/cm^3 of pellet

m = void volume ratio, cm^3 of external voids/cm^3 of pellet

q = concentration of adsorbate, g-mol adsorbed/cm^3 of pellet

q_s = concentration of adsorbate at the surface of a pellet, g-mol adsorbate/g of dry adsorbent

Q_m = ultimate sorptive capacity of particle phase, g-mol adsorbed/cm^3 of pellet

r = radial position in spherical pellet, cm

r_o = radius of spherical pellet in pore model = b, cm

R = equilibrium parameter defined in Equation (12)

t = time, s

u = dimensionless breakthrough concentration, x/x_0

v = interstitial velocity of fluid, cm/s

w = adsorbed-phase concentration, g-mol adsorbed/g of dry adsorbent

x = fluid-phase concentration in a pore, mole fraction

x_0 = fluid-phase concentration in feed, mole fraction

x_s = fluid-phase concentration on the surface of a pellet, mole fraction

X = bed length parameter in Rosen's model given in Equation (8), dimensionless

y = fluid-phase concentration in external voids, mole fraction

Y = contact time parameter in Rosen's model given in Equation (9) dimensionless

z = axial position in bed, cm

α = intraparticle void fraction, cm³ of pore/cm³ of bed

ϵ = external void fraction, cm³ void/cm³ of bed

ν = film resistance parameter in Rosen's model given in Equation (10), dimensionless

ρ = molal density of fluid phase, g-mol/cm³

ρ_a = bulk density of adsorbent particles, g of dry adsorbent/cm³ of bed

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A Calculational Procedure for Design Problems in Multicomponent Distillation

A calculation procedure for multicomponent distillation has been developed that is directly applicable to design problems. It is based on successive approximation methods with adjustment of the number of equilibrium stages in each column section between iterations to meet given reflux flow and feed stage composition conditions while maintaining specified key component recoveries. This procedure has been applied to a number of representative distillation design problems. It converges readily to proper column designs from initial estimates based on a noniterative stage-to-stage calculation. Moreover, the procedure is markedly superior in computational efficiency to solution of design problems by repeated application of operating calculations to assumed column configurations.

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SCOPE

Calculational problems in multicomponent distillation can be divided into two general types: (1) operating problems where the separation that can be obtained with a given column configuration under given conditions is to be found; and (2) design problems where the column configuration and operation to meet desired separation specifications is to be determined.

Quite different approaches are necessary for the solution of these two classes of problems. For the operating problem approximate solutions can be obtained by group methods such as those of Underwood (1946, 1948). When more exact calculations are required the widely used successive approximation methods can be employed, either as a modification of the classical procedure of Thiele and Geddes (1933) or the more recent, and highly effective, matrix approaches as by Napthali and Sandholm (1971).

For the design problem the situation is not so well in hand. Approximate solutions can be derived from calculations of minimum stages (Underwood, 1932; Fenske, 1932) and minimum reflux (Underwood, 1946, 1948), together with an empirical correlation of required stages and reflux (Gilliland, 1940; Erbar and Maddox, 1961). Group methods can also be used. However, where more exact calculations are necessary no really satisfactory techniques have been available. Stage-to-stage methods (Lewis and Matheson, 1932; Waterman and Frazier, 1965) have severe convergence difficulties for many distillation cases

and have not found general acceptance. The successive approximation methods are, unfortunately, not directly applicable, since they are dependent on the number of stages being specified. Very frequently, however, these methods are employed in the solution of design problems by their application to several related operating problems with different numbers of stages. This is repeated until a solution is found that satisfies the design separation requirements. Although this shotgun approach often is successful, it can be a very inefficient and tedious process. There has long existed the need for calculational methods specifically suited to the design of multicomponent distillation columns and capable of results of an accuracy equivalent to those of the better operating calculations.

The aim of this study has been the development of such a computer-oriented design procedure for simple multicomponent distillation columns, that is, for columns with a single feed and only two products. The design specifications are taken to include key component recoveries, optimum feed location, and a set economic multiple of minimum reflux ratio. This work has been based upon the successive approximation matrix methods and the concept of adjustment of numbers of stages above and below the feed between iterations to satisfy design specifications. Moreover, a procedure has been sought that can provide detailed solutions to a design problem at computational expense comparable to that required for equivalent solutions to operating problems rather than at several times operating solution costs as required by shotgun techniques.

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