Fixed-Bed Adsorption of Gases: Effect of Velocity Variations on Transition Types

In fixed-bed adsorption or desorption of gases, velocity variations accompany changes in gas composition, and these variations affect the transition types (spreading waves or shocks). A general criterion is developed for determining the transition type for isothermal monovariant systems (one adsorbable component in inert gas or two adsorbable components with no inert gas). Several examples are given to illustrate the determination of transition types for simple waves, contact discontinuities, shocks, and combined waves.

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Introduction

Adsorption isotherms are classified as favorable or unfavorable depending on whether a propagating concentration wave approaches an asymptotic breadth or spreads without bound in a deep bed. Based on local equilibrium theory, in the absence of dispersion a favorable isotherm gives a shock (abrupt transition) while an unfavorable isotherm gives a simple wave (gradual transition, dispersive front). With mass transfer resistances and dispersion the shock approaches the asymptotic constant-pattern shape and the simple wave gives proportionate pattern spreading.

Favorable and unfavorable isotherms are separated by an intermediate type which, based on local equilibrium theory, gives a contact discontinuity (indifferent front; a transition for which all concentration velocities are equal and thus which tends neither to spread nor to sharpen) but gives so-called square root spreading with mass transfer resistances or dispersion. For trace gases this intermediate type is the linear isotherm.

Previous work on the determination of transition types and shapes for the isothermal adsorption of gases has been concerned largely with trace systems, for which the fluid velocity is approximately constant throughout the bed. Solutions for this case, based on both local equilibrium theory and rate models, have been reviewed by Vermeulen et al. (1984) and Ruthven (1984).

Comparatively little attention has been given to transition types for nontrace systems, for which changes in fluid velocity *resulting* from adsorption or desorption may be large. The problem has been discussed by Helfferich and Klein (1970) and Aris and Amundson (1973). Effects on peak shapes and separations in chromatograph columns have been considered by Bosanquet and Morgan (1957), Bosanquet (1958), Golay (1964), Guiochon et al. (1969), Guiochon and Jacob (1970), and Ruthven (1984). The adsorption of two- and three-component mixtures in a fixed bed has been considered by Tsabek (1981a, b; 1982a, b). Each of these treatments is restricted to an isotherm of a certain form, either linear or of the Langmuir type, which is assumed at the beginning of the analysis.

As part of a comprehensive study on the effects of high solute concentrations on migration rates in isothermal chromatography, Peterson and Helfferich (1965) have considered the limiting criterion for the existence of a contact discontinuity. Both concentration velocities and transition types are treated in their paper and constant void and stationary-phase volumes are assumed throughout (i.e., the authors neglect any changes in the local volume fraction of the bed that is occupied by adsorbate). They show that for one adsorbable component in inert gas a transition would be a contact discontinuity, provided that the adsorption isotherm is of a certain form. In referring to their treatment of concentration velocities, they indicate that the assumption of the constant volumes is not necessary, with the reason given that they are readily obtainable experimental quantities. They also mention briefly but do not treat in any detail the criterion for a contact discontinuity for the case of more than one adsorbable component.

In this paper, we consider transition types for high solute concentrations with an analysis restricted only to isothermal behavior and constant gas-phase molar density (or, equivalently, isobaric behavior for an ideal gas). Void and stationary-phase volumes are allowed to vary arbitrarily with adsorbed-phase

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concentration. A general criterion is derived from which transition types for monovariant systems can easily be determined. In examples we consider the two possible cases of monovariance: one-component adsorption from inert gas and two-component adsorption in the absence of inert gas. These are the only cases consistent with the existence of a single transition (possibly combining simple wave and shock parts) for arbitrary initial and feed states.

Only effects on transition types caused by changes in gas velocity under isothermal conditions are treated. The assumption of isothermality is easily justified provided that adequate time is allowed for exchange of energy with the surroundings and also for systems with little adsorption, such as those encountered in some pressure-swing adsorption processes. For nonisothermal adsorption, transition types are affected also by changes in velocity due to heating and physical property variations with temperature (Pan and Basmadjian, 1967; Jacob and Tondeur, 1983; Roizard and Tondeur, 1986).

Theory

Material balances for two adsorbable components (one of which may actually be nonadsorbing inert gas) can be written

$$\rho_b \frac{\partial q_A}{\partial t} + \frac{\partial(\epsilon c_A)}{\partial t} + \frac{\partial(v c_A)}{\partial z} = 0 \tag{1}$$

$$\rho_b \frac{\partial q_B}{\partial t} + \frac{\partial(\epsilon c_B)}{\partial t} + \frac{\partial(v c_B)}{\partial z} = 0 \tag{2}$$

where v is the superficial fluid velocity and ϵ is the local volume fraction of the bed occupied by gas, including that within the pore space of the absorbent. We allow ϵ to depend on the adsorbed-phase concentration. Since no other components are present and pressure and temperature are assumed to be constant, we have

$$c = c_A + c_B \tag{3}$$

Below, we consider separately the existence of simple waves, contact discontinuities, shocks, and combined waves.

Simple wave

Concentration velocity (the velocity of a given concentration) is defined by

$$w \equiv \left.\frac{\partial z}{\partial t}\right|_{c_A} = -\frac{\partial c_A/\partial t}{\partial c_A/\partial z} = \frac{d(v c_A)}{d(\rho_b q_A + \epsilon c_A)} \tag{4}$$

Equation 4 has been written for component A; a similar equation exists for component B. The rightmost equality in Eq. 4 is obtained from Eq. 1. Using Eq. 4, concentration velocities can be determined from a plot of total volumetric concentration of A ($\rho_b q_A + \epsilon c_A$; ordinate) vs. flux ($v c_A$; abscissa). The reciprocal of the slope in this plane is the concentration velocity. This procedure can indeed be followed and will give correct results. However, a second method (Bossy, 1987) is also possible, one that simplifies significantly the determination of combined transition shapes for one-component adsorption and transition shapes in general for two-component adsorption. This second method will be followed here.

Assuming that the system is monovariant (or equivalently, that c_A fixes q_A, q_B, and ϵ), Eqs. 1 and 2 can be written

$$\left[\rho_b \frac{dq_A}{dc_A} + \frac{d(\epsilon c_A)}{dc_A}\right] \frac{\partial c_A}{\partial t} + v \frac{\partial c_A}{\partial z} + c_A \frac{\partial v}{\partial z} = 0 \tag{5}$$

$$\left[\rho_b \frac{dq_B}{dc_A} + \frac{d[\epsilon(c - c_A)]}{dc_A}\right] \frac{\partial c_A}{\partial t} - v \frac{\partial c_A}{\partial z} + (c - c_A) \frac{\partial v}{\partial z} = 0 \tag{6}$$

Equations 5 and 6 will be combined in two different ways to obtain two equations which when combined will yield the transition-type criterion.

First, an equation is developed for concentration velocity. Combining Eqs. 5 and 6 by eliminating $\partial v/\partial z$ between them gives, after rearrangement according to Eq. 4,

$$w = \frac{vc}{\rho_b[(c - c_A)dq_A/dc_A - c_A dq_B/dc_A] + \epsilon c} \tag{7}$$

Second, an equation is developed for the local fluid velocity v. Eliminating $\partial c_A/\partial t$ between Eqs. 5 and 6 gives

$$\frac{1}{v}\frac{dv}{dc_A} = \frac{\rho_b(dq_A/dc_A + dq_B/dc_A) + c\,d\epsilon/dc_A}{\rho_b[(c - c_A)dq_A/dc_A - c_A dq_B/dc_A] + \epsilon c} \tag{8}$$

Integration of Eq. 8 from the bed inlet, where $v = v''$ and $c_A = c''_A$, gives

$$v = v'' \exp \int_{c''_A}^{c_A} \frac{\rho_b(dq_A/dc_A + dq_B/dc_A) + c\,d\epsilon/dc_A}{\rho_b[(c - c_A)dq_A/dc_A - c_A dq_B/dc_A] + \epsilon c}\, dc_A \tag{9}$$

The criterion for the stability of a simple wave is determined by differentiating the logarithm of Eq. 7 with respect to c_A. Using Eq. 8 or 9, this gives

$$\frac{d \ln w}{dc_A} = \frac{-\,d^2 f/dc_A^2}{[(c - c_A)dq_A/dc_A - c_A dq_B/dc_A] + \epsilon c/\rho_b} \tag{10}$$

where

$$f \equiv f(c_A) \equiv q_A c - (q_A + q_B)c_A \tag{11}$$

Using Eq. 3, f can be written in the form

$$f \equiv q_A c_B - q_B c_A \tag{12}$$

We note that for a given temperature and pressure, f depends only on the adsorption equilibrium relation. It is equal to zero at both $c_A = 0$ and $c_A = c$ (or $c_B = 0$); also, f is positive if component A is the more strongly adsorbed component (as measured by the ratio of mole fraction in the adsorbed phase to that in the gas phase). The relationship between f and selectivity α is given by

$$\frac{f}{q_A c_B} = 1 - \alpha \tag{13}$$

where

$$\alpha \equiv \frac{y_B x_A}{y_A x_B} = \frac{q_B c_A}{q_A c_B} \tag{14}$$

Equation 10 is used to determine if a transition is a simple wave as follows. The denominator of the righthand side of Eq. 10 is positive (since $dq_A/dc_A > 0$ and, for two-component adsorption, $dq_B/dc_A < 0$). Thus, the sign of d^2f/dc_A^2 determines whether the concentration velocity w will increase or decrease as c_A increases.

Without loss of generality, we will classify steps as they pertain to component *A*. Furthermore, the following discussion applies to Riemann's problem (constant initial condition and step change in feed concentration), although the results pertain as well to the general case if the long-term stability of the transition is considered.

In order for a simple wave to exist, concentration velocities must be greater for concentrations well down the bed than for concentrations near the bed inlet. Let primes and double primes denote presaturation and feed values, respectively. For a desorption step ($c''_A < c'_A$) the concentration velocities must increase with increasing c_A ($dw/dc_A > 0$; also $d(\ln w)/dc_A > 0$); then, from Eq. 10 we find that $d^2f/dc_A^2 < 0$. This case is depicted in Figure 1 (top), where the curve is concave downward. By similar reasoning, if a simple wave exists for an adsorption step ($c''_A > c'_A$) we have $d^2f/dc_A^2 > 0$. This is shown by the concave upward curve in Figure 1 (bottom).

Contact discontinuity

The contact discontinuity separates simple waves and shocks, and along it all concentration velocities are equal. Thus, the derivative on the righthand side of Eq. 4 is constant and may be written in difference form between any two points along the contact discontinuity. Using both end points and one end point and an arbitrary point, Eq. 4 gives

$$
\begin{aligned}
w &= \frac{v''c''_A - v'c'_A}{(\rho_b q''_A + \epsilon''c''_A) - (\rho_b q'_A + \epsilon'c'_A)} \\
&= \frac{v''c''_A - vc_A}{(\rho_b q''_A + \epsilon''c''_A) - (\rho_b q_A + \epsilon c_A)} \\
&= \frac{v''c''_B - v'c'_B}{(\rho_b q''_B + \epsilon''c''_B) - (\rho_b q'_B + \epsilon'c'_B)} \\
&= \frac{v''c''_B - vc_B}{(\rho_b q''_B + \epsilon''c''_B) - (\rho_b q_B + \epsilon c_B)}
\end{aligned}
\tag{15}
$$

The local fluid velocity is obtained from the second and fourth of the four major terms of Eq. 15. Simple rearrangement gives

$$
v = v'' \frac{\rho_b[(q''_A - q_A)(c - c''_A) + (q_B - q''_B)c''_A] + \epsilon c(c''_A - c_A)}{\rho_b[(q''_A - q_A)(c - c_A) + (q_B - q''_B)c_A] + \epsilon''c(c''_A - c_A)}
\tag{16}
$$

Substituting Eq. 16 into Eq. 15 gives

$$
w = \frac{v''c}{\rho_b[(c - c'_A)(q''_A - q'_A)/(c''_A - c'_A) - c'_A(q''_B - q'_B)/(c''_A - c'_A)] + \epsilon''c}
\tag{17}
$$

which resembles Eq. 8 for a simple wave. Equation 17 has been written in terms of end-point concentrations. Many variations on this equation are possible since Eq. 15 can be written between any two points; these involve replacing primes with double primes and vice versa, or removing all primes or double primes.

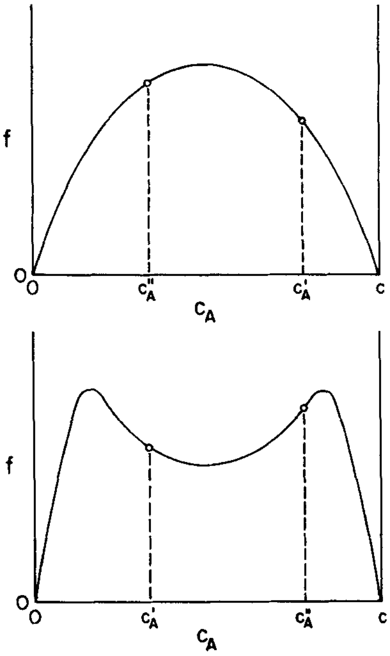

Figure 1. Conditions for existence of pure simple waves.
(Top) Desorption; (bottom) adsorption of component *A*

Further algebraic manipulation of Eq. 15 gives

$$
\frac{q_A - q'_A}{q''_A - q'_A} = \frac{(c - c''_A)(c_A - c'_A)}{(c - c_A)(c''_A - c'_A)} - \frac{(q'_B - q_B)(c''_A - c'_A)c_A - (q'_B - q''_B)c''_A(c_A - c'_A)}{(q''_A - q'_A)(c - c_A)(c''_A - c'_A)}
\tag{18}
$$

Equation 18 is the equation of a surface in three dimensions (c_A, q_A, q_B). It is symmetric for components *A* and *B* and contains no dependence on ϵ. Any path connecting the presaturation and feed end points and lying fully on this surface is a contact discontinuity. There is an infinite number of such paths.

In terms of the function f, Eq. 18 can be written in two dimensions (c_A, f) simply as

$$
\frac{f(c_A) - f(c'_A)}{c_A - c'_A} = \frac{f(c''_A) - f(c'_A)}{c''_A - c'_A}
\tag{19}
$$

Equation 19 can also be obtained from Eq. 10. Since all concentration velocities are the same for a contact discontinuity, Eq. 10 gives $d^2f/dc_A^2 = 0$; then, we obtain by integration

$$
f = k_1 c_A + k_2
\tag{20}
$$

which, like Eq. 19, is the equation of a straight line in the plane of Figure 1.

Shock

If the relationships described above for d^2f/dc_A^2 for simple waves and contact discontinuities are not satisfied, then the transition will be a shock. That is, if $d^2f/dc_A^2 > 0$ for a desorption step or $d^2f/dc_A^2 < 0$ for an adsorption step, then an analysis based on a simple wave would predict the impossible condition of the simultaneous coexistence of three or more concentrations at points in the bed. Thus, the only physically conceivable solution is the shock.

For a shock the derivative on the righthand side of Eq. 4 must be replaced by the ratio of the differences between variables at the end points of the transition giving the shock velocity

$$w_s \equiv \frac{\Delta(vc_A)}{\Delta(\rho_b q_A + \epsilon c_A)} \tag{21}$$

A similar equation pertains to component B. Thus, for the two components we may use the end points to write

$$w_s = \frac{v''c_A'' - v'c_A'}{(\rho_b q_A'' + \epsilon''c_A'') - (\rho_b q_A' + \epsilon'c_A')} = \frac{v''c_B'' - v'c_B'}{(\rho_b q_B'' + \epsilon''c_B'') - (\rho_b q_B' + \epsilon'c_B')} \tag{22}$$

Solving Eq. 22 for the downstream velocity gives

$$v' = v'' \frac{\rho_b[(q_A'' - q_A')(c - c_A'') + (q_B' - q_B'')c_A''] + \epsilon'c(c_A'' - c_A')}{\rho_b[(q_A'' - q_A')(c - c_A') + (q_B' - q_B'')c_A'] + \epsilon''c(c_A'' - c_A')} \tag{23}$$

Substituting Eq. 23 into the term for component A in Eq. 22 gives

$$w_s = \frac{v''c}{\rho_b[(c - c_A')(q_A'' - q_A')/(c_A'' - c_A') - c_A'(q_B'' - q_B')/(c_A'' - c_A')] + \epsilon''c} \tag{24}$$

which is identical to Eq. 17 except that it can only be written in a form involving end-point concentrations (an alternate form can be written with primes and double primes reversed) and it is a shock velocity rather than a local concentration velocity.

The conditions for the existence of a pure shock are depicted in Figure 2. The end points of a shock must lie on the curve of f vs. c_A, since this curve depends only on the fixed temperature and pressure and the adsorption equilibrium relation and is therefore entirely independent of transition type.

Combined wave

A combined wave with both simple wave and shock (or contact discontinuity) parts is shown in Figure 3. For the shock portion, the variables are subscripted s and primes and double primes are used to denote values at ends connected to downstream and upstream regions, respectively. Where simple wave and shock parts meet, concentration/shock velocities, concentrations, gas velocities, and local volume fractions must be equal. Thus, for the case depicted in Figure 3, we have at the point of intersection: $w = w_s$, $c_A = c_{As}''$, and so on.

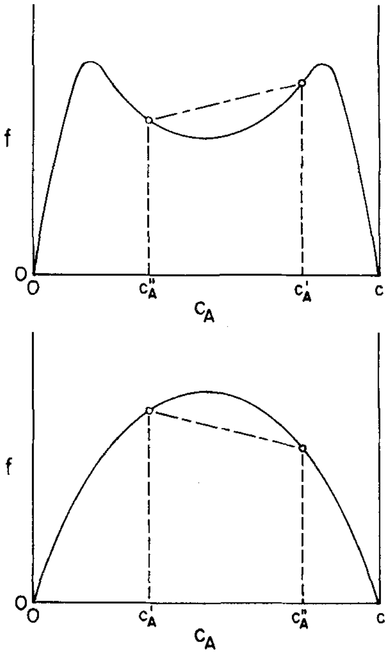

Figure 2. Conditions for existence of pure shocks.
(Top) Desorption; (bottom) adsorption of component A

Concentration and shock velocities are given by Eqs. 7 and 24, respectively. Equating them gives the following relation among terms contained in the denominators

$$c_B \frac{dq_A}{dc_A} - c_A \frac{dq_B}{dc_A} = c_B' \frac{q_{As}'' - q_{As}'}{c_{As}'' - c_{As}'} - c_A' \frac{q_{Bs}'' - q_{Bs}'}{c_{As}'' - c_{As}'} \tag{25}$$

Subtracting $q_A + q_B$ from both sides of Eq. 25 gives, after rearrangement,

$$\frac{df}{dc_A} = \frac{f(c_{As}'') - f(c_{As}')}{c_{As}'' - c_{As}'} \tag{26}$$

Figure 4 shows examples of the f vs. c_A plane for the existence of combined waves. For both desorption (top) and adsorption (bottom) cases, the dependence of f on c_A is shown to be the same. From Eq. 26, the shock parts join the gradual wave parts at points of tangency. For both cases, the simple wave parts will exist near the bed inlet, with the shock parts further downstream. The bed profile for the adsorption case will be like that shown in Figure 3.

Examples

One adsorbable component and inert gas

To simplify the discussion in numerical examples below, we will use a dimensionless fluid velocity defined by

$$v^* = \frac{v}{v''} \tag{27}$$

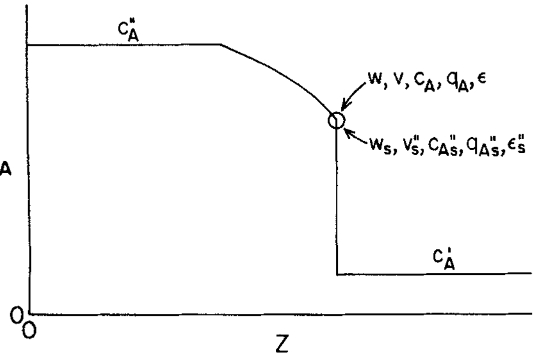

Figure 3. Depiction of a combined wave with simple wave part near bed inlet and shock part downstream.
Properties are equal at point of intersection

where v'' is the fluid velocity at the bed inlet and a dimensionless axial coordinate (or normalized concentration velocity) given by

$$\zeta = \frac{z}{v''t} = \frac{w}{v''} \tag{28}$$

Example 1. Isotherm for Contact Discontinuities. For the adsorption or desorption of one component present in an inert gas, Eq. 11 becomes

$$f = q_A (c - c_A) \tag{29}$$

For a contact discontinuity, Eq. 20 is

$$f = k_1 c_A \tag{30}$$

where we have set k_2 equal to zero to satisfy $f = 0$ at $c_A = 0$. Eliminating f between Eqs. 29 and 30 and rearranging gives

$$q_A = k_1 c_A/(c - c_A) \tag{31}$$

which is a result first obtained by Peterson and Helfferich (1965) based on an analysis restricted to constant void and stationary-phase volumes.

Here we cast Eq. 31 into a simple recognizable form in terms of the dimensionless transition concentrations (Vermeulen et al., 1984)

$$Y = \frac{q_A - q'_A}{q''_A - q'_A} \tag{32}$$

$$X = \frac{c_A - c'_A}{c''_A - c'_A} \tag{33}$$

Substituting Eq. 31 into Eq. 32 (or substituting Eq. 29 into Eq. 19) gives

$$Y = \frac{(c - c''_A)(c_A - c'_A)}{(c - c_A)(c''_A - c'_A)} \tag{34}$$

Equation 34 can be written in the form of the constant separation factor isotherm (Vermeulen et al., 1984)

$$Y = \frac{X}{R + (1 - R)X} \tag{35}$$

where R is the separation factor defined by (rearranging Eq. 35)

$$R \equiv \frac{X(1 - Y)}{Y(1 - X)} \tag{36}$$

The numerical value of the separation factor to make Eqs. 34 and 35 equivalent is given by

$$R = \frac{c - c'_A}{c - c''_A} = \frac{1 - x'_A}{1 - x''_A} \tag{37}$$

where x_A is gas-phase mole fraction. Equation 37 gives the separation factor for the contact discontinuity in terms of the presaturation and feed mole fractions of the solute in the gas phase. Equation 35 is plotted for several values of the separation factor in Figure 5.

To consider specific examples, let $c = 60$ mol/m³. First, consider an adsorption step beginning with a solute-free bed, i.e., $c'_A = 0$ mol/m³, and a feed of $c''_A = 40$ mol/m³. Equations 37 then gives that the isotherm corresponding to the contact discontinuity is the constant separation factor isotherm with $R = 3$. Second, consider a desorption step with a presaturation condition of $c'_A = 40$ mol/m³ and solute-free feed, i.e., $c''_A = 0$ mol/m³. Equation 37 gives that if $R = 0.33$ for the actual isotherm, then the transition will be a contact discontinuity.

Example 2. Adsorption Step with Linear Isotherm. Examples 2, 3, and 4 are numerical examples and use the following

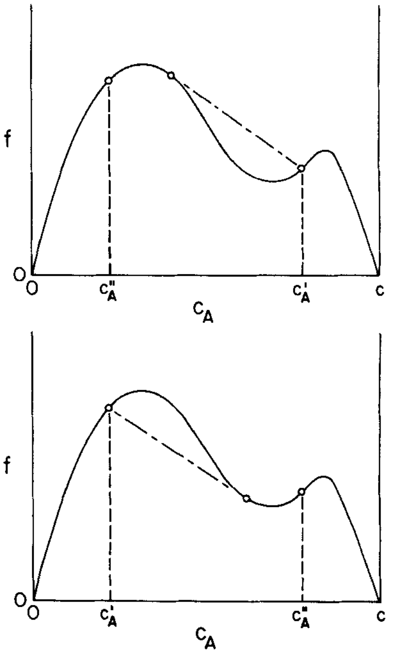

Figure 4. Conditions for existence of combined waves.
(Top) Desorption; (bottom) adsorption of component *A*
Shock chords shown as dashed lines

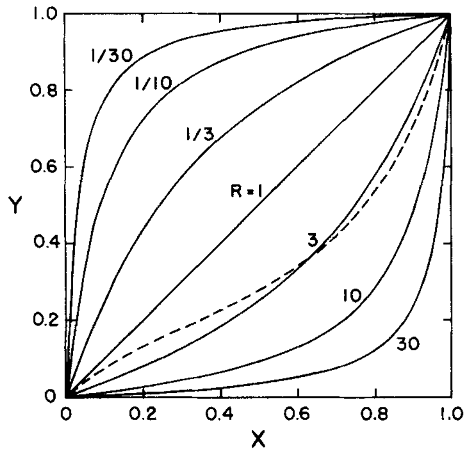

Figure 5. Constant separation factor isotherms.
---- BET isotherm of example 4

common parameters

$$\rho_b = 500 \text{ kg/m}^3$$

$$\epsilon = 0.7 - (0.04 \text{ kg/mol})\, q_A$$

$$c = 60 \text{ mol/m}^3$$

Here, we consider an adsorption step beginning with a solute-free bed

$$c'_A = 0 \text{ mol/m}^3$$

$$q'_A = 0 \text{ mol/kg}$$

and feed of

$$c''_A = 40 \text{ mol/m}^3$$

Adsorbed and fluid-phase concentrations are related by the linear isotherm

$$q_A = (0.1 \text{ m}^3/\text{kg})\, c_A \tag{38}$$

The transition type can be determined immediately by plotting Eq. 29. The resulting curve, shown in Figure 6, is concave downward, indicating that the transition is a shock (Figure 2).

Bed profiles for this example are shown in Figure 7. The solid curves show the solution resulting from an analysis for a simple wave. For this case, the gas velocity is obtained from Eq. 9 and the concentration profile from Eq. 7. Clearly, the profiles overhang, giving the nonphysical condition of the coexistence of three distinct concentrations at points in the bed.

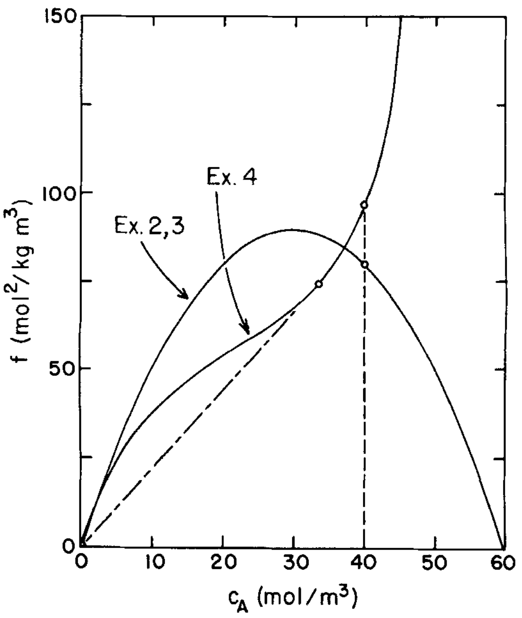

Figure 6. Determination of transition types for examples 2, 3, 4.

	Ex. 2, 4	Ex. 3
c'_A, mol/m³	0	40
c''_A, mol/m³	40	0

The shock between presaturation and feed states is determined directly from Eqs. 23 and 24. This solution is shown as straight dashed lines in Figure 7. The shock is located at $\zeta = 0.0198$. The initial dimensionless fluid velocity from the bed, v^*, is only 0.3436. (This is somewhat greater than the value 0.3431 obtained by integration of Eq. 9. This difference is due to the inclusion of a variable ϵ in the analysis; with a linear isotherm and constant ϵ, Eq. 9 is easily integrated to obtain Eq. 16.) Based on these results, the ratio of the flux of inert gas from the bed prior to breakthrough to the flux of inert gas at the bed inlet, $v^* c'_I / c''_I$, is 1.031, consistent with net removal of inert gas from the bed. (An assumption frequently made in the analysis of adsorption processes is that the flux of inert gas is constant throughout the bed. It is easily seen from Eq. 16 that this can be strictly true only if ϵ is equal to zero everywhere, which prevents the accumulation of inert gas in the bed but is not physically realistic.)

Example 3. Desorption Step with Linear Isotherm. As a third example we consider a desorption step with a presaturation condition of

$$c'_A = 40 \text{ mol/m}^3$$

$$q'_A = 4 \text{ mol/kg}$$

and the solute-free feed

$$c''_A = 0 \text{ mol/m}^3$$

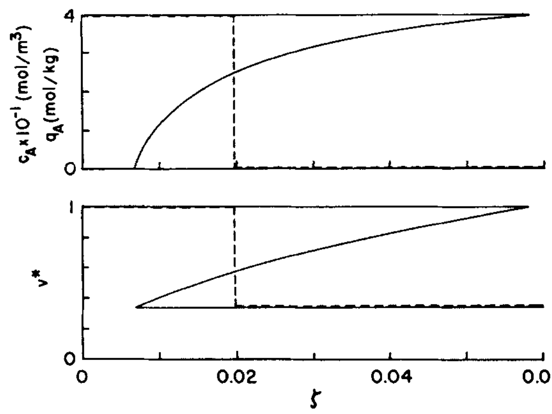

Figure 7. Bed profiles for example 2.

The isotherm is linear and given by Eq. 38.

Equation 29, applied to determine the transition type, again generates the concave downward curve shown in Figure 6. Comparing this curve with those in Figure 1 indicates that the transition is indeed a simple wave.

Bed profiles, determined from Eqs. 7 and 9, are shown in Figure 8. The adsorbate has been completely removed from the bed between $\zeta = 0$ and 0.0198. (Note that the shock in example 2 was also located at $\zeta = 0.0198$.) The initial velocity from the bed is $v^* = 2.918$, which is caused by the large expansion in volumetric flow rate due to desorption.

Example 4. Adsorption Step with BET Isotherm. As a fourth and more complicated example, we consider the transition type for an adsorption step with a BET isotherm. Parameters and initial conditions are those of example 2; only the isotherm is different. The BET isotherm is given by

$$q = \frac{Q K c_A}{[1 + K c_A - (c_A/c_s)][1 - (c_A/c_s)]} \qquad (39)$$

where c_s is the vapor-phase saturation concentration for adsorbate A. Parameters appearing in the isotherm were set as follows:

$$Q = 1 \text{ mol/kg}$$

$$K = 0.12 \text{ m}^3\text{/mol}$$

$$c_s = 50 \text{ mol/m}^3$$

This isotherm is shown as a dashed curve in Figure 5 in terms of the dimensionless concentrations defined by Eqs. 32 and 33.

Equation 29 is plotted in Figure 6 for this case. By comparison with Figure 4 (bottom) the transition is found to be of combined form. In Figure 6, the shock chord exists between $c_A = 0$ and 33 mol/m^3 and the simple wave part between $c_A = 33$ and 40 mol/m^3.

Bed profiles are shown in Figure 9. Solid curves for a pure simple wave solution are clearly unsatisfactory. Equation 9 gives a velocity of $v^* = 0.755$ at the point of intersection of the simple wave and shock parts. Shock parts of the concentration and velocity profiles are shown in Figure 9 as dashed straight lines. They are located at $\zeta = 0.0179$. The initial velocity from the bed, obtained from Eq. 23, is $v^* = 0.343$.

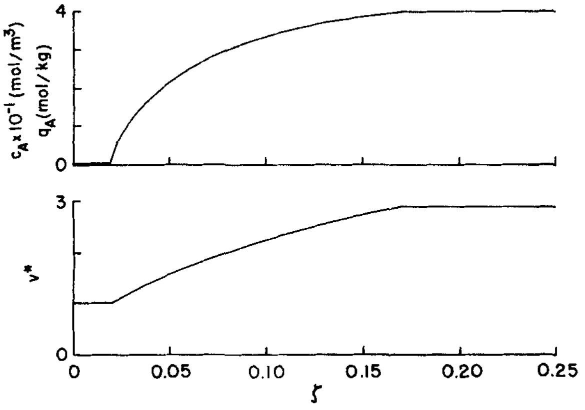

Figure 8. Bed profiles for example 3.

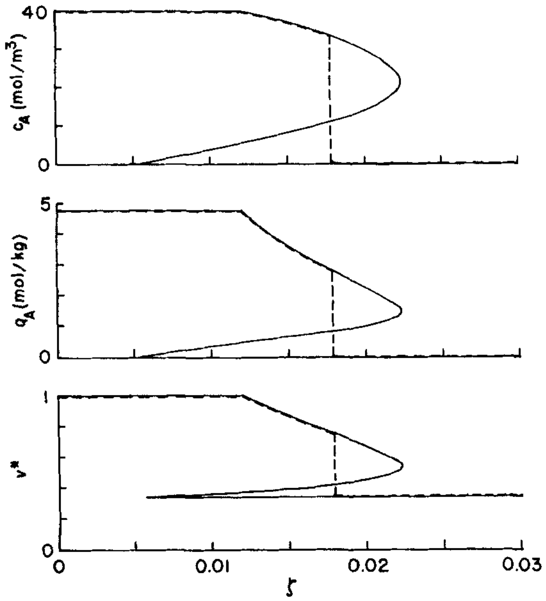

Figure 9. Bed profiles for example 4.

Two adsorbable components

Example 5. Contact Discontinuities for Constant Separation Factor. We first determine adsorption equilibrium relations of the constant separation factor type that satisfy Eq. 18 for the contact discontinuty. If we solve Eq. 14 for q_B and substitute it into Eq. 18, the resulting equation is satisfied only by $\alpha = 0$, 1, and ∞. Since $\alpha = 0$ and ∞ pertain to one adsorbable component in inert gas, the solution of interest is $\alpha = 1$. This condition is met by any isotherm of the form

$$q_i = g(c_A, c_B)\, c_i \quad i = A, B \qquad (40)$$

where g is the same function for both components, and indicates that $y_A = x_A$ along the path.

The result $\alpha = 1$ is also required for the existence of a contact discontinuity any time that a pure adsorbable component (no inert gas) is eluted by a second pure adsorbable component. For example, let A elute B. We then have $c''_A = c'_B = c$, $q'_A = c'_A = 0$, and $q''_B = c''_B = 0$. Equation 18 becomes simply

$$(q_B/c_B)/(q_A/c_A) = 1 \qquad (41)$$

Example 6. Displacement Step with Linear Isotherms. Consider the isotherm

$$q_i = K_i\, c_i \quad i = A, B \qquad (42)$$

Taking the second derivative of Eq. 11, for this case, gives

$$\frac{d^2 f}{dc_A^2} = -2\,(K_A - K_B) \qquad (43)$$

If $K_A > K_B$, then d^2f/dc_A^2 is negative. If $c''_A < c'_A$, then the transition is a simple wave; if $c''_A > c'_A$, it is a shock. Similar reasoning can be applied for $K_A < K_B$. Treatments of specific cases here would resemble those of the next example.

Example 7. Displacement Step with Binary Langmuir

Isotherm. This numerical example for two-component adsorption considers three cases using the following parameters and variables throughout

$$\rho_b = 500\ \mathrm{kg/m^3}$$

$$\epsilon = 0.7 - (0.04\ \mathrm{kg/mol})\ q_A - (0.02\ \mathrm{kg/mol})\ q_B$$

$$c = 40\ \mathrm{mol/m^3}$$

$$c'_A = 0\ \mathrm{mol/m^3}$$

$$q'_A = 0\ \mathrm{mol/kg}$$

$$q'_B = 2\ \mathrm{mol/kg}$$

$$c''_A = 40\ \mathrm{mol/m^3}$$

$$q''_A = 4\ \mathrm{mol/kg}$$

$$q''_B = 0\ \mathrm{mol/kg}$$

Component A is displacing component B. Furthermore, the presaturation and final states for all cases are identical.

As an empirical description of adsorption equilibria, we adopt the binary Langmuir isotherm, which is

$$q_i = \frac{Q_i K_i c_i}{1 + K_A c_A + K_B c_B} \qquad i = A, B \tag{44}$$

(With unequal monolayer capacities Q_i, Eq. 44 does not satisfy a thermodynamic consistency test based on the Gibbs adsorption isotherm; for the extent of the deviation and correction terms, see LeVan and Vermeulen, 1981.) As is well known, this isotherm is of the constant separation factor type; i.e., when substituted into Eq. 14, it gives

$$\alpha = \frac{Q_B K_B}{Q_A K_A} \tag{45}$$

where α is constant.

Transition types can be determined at once for this isotherm by finding d^2f/dc_A^2, with f defined by Eq. 11. We obtain

$$\frac{d^2f}{dc_A^2} = -2\,\frac{(Q_A K_A - Q_B K_B)\,(1 + K_A c)\,(1 + K_B c)}{[1 + K_A c_A + K_B(c - c_A)]^3} \tag{46}$$

Thus, the sign of d^2f/dc_A^2 is opposite that of the group $(Q_A K_A - Q_B K_B)$. Based on Figures 1 and 2 and the attendant discussion, the transition is a simple wave if $(Q_A K_A - Q_B K_B)$ is negative, a contact discontinuity if zero, and a shock if positive. The different cases below are distinguished by different values of the constants appearing in the isotherm.

Case A. We first let

$$Q_A = 6\ \mathrm{mol/kg} \qquad K_A = 0.05\ \mathrm{m^3/mol}$$

$$Q_B = 2.4\ \mathrm{mol/kg} \qquad K_B = 0.125\ \mathrm{m^3/mol}$$

Thus, α is unity and $(Q_A K_A - Q_B K_B)$ is zero, indicating a contact discontinuity. Furthermore, f plotted in Figure 10 is zero everywhere, confirming this predicted behavior. Concentration velocities calculated from Eqs. 7 are all equal. From Eq. 7 or 17, the transitions (not shown) all occur at $\zeta = 0.0198$. End points of the contact discontinuities in concentrations have been given above. The initial velocity at which gas leaves the bed is $v^* = 0.508$.

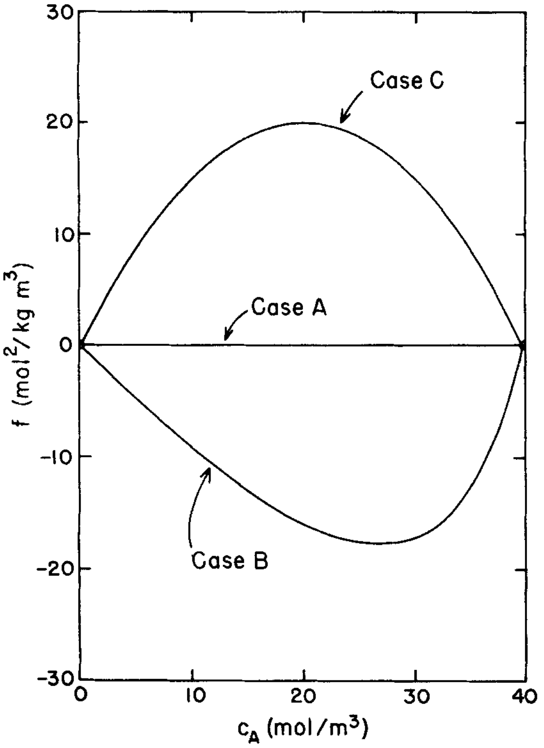

Figure 10. Determination of transition types for example 7.

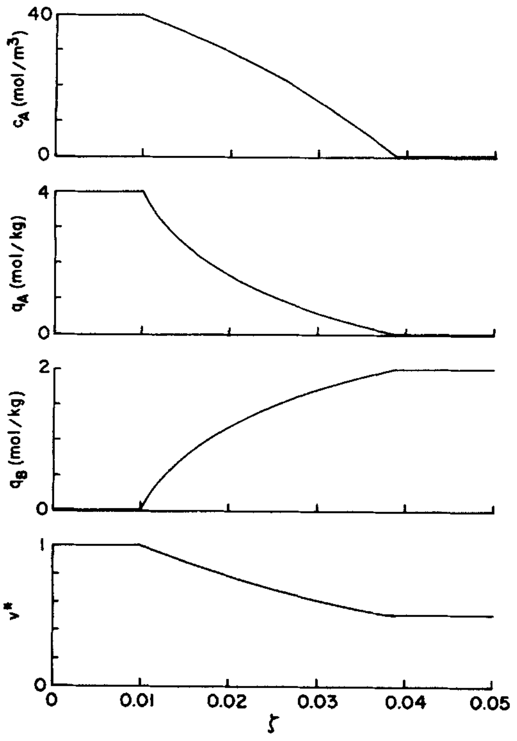

Figure 11. Bed profiles for example 7, case B.

Case B. As a second case, we let

$$Q_A = 12 \text{ mol/kg} \quad K_A = 0.0125 \text{ m}^3/\text{mol}$$

$$Q_B = 2.4 \text{ mol/kg} \quad K_B = 0.125 \text{ m}^3/\text{mol}$$

We have $\alpha = 2$ and $(Q_A K_A - Q_B K_B) = -0.15$, indicating a simple wave. The plot of f, shown in Figure 10, is concave upward. Equations 7 and 9 are used to construct concentration and velocity profiles, which are shown in Figure 11. The transition lies between $\zeta = 0.0098$ and 0.0387. The initial fluid velocity at the bed outlet is $v^* = 0.510$.

Case C. Finally, we consider

$$Q_A = 6 \text{ mol/kg} \quad K_A = 0.05 \text{ m}^3/\text{mol}$$

$$Q_B = 3 \text{ mol/kg} \quad K_B = 0.05 \text{ m}^3/\text{mol}$$

For this case, we have $\alpha = 0.5$ and $(Q_A K_A - Q_B K_B) = 0.15$, corresponding to a shock. The curve for f, shown in Figure 10, is concave downward. Equations 23 and 24 are solved to obtain the bed profiles, which are shown as straight dashed lines in Figure 12. They occur again at $\zeta = 0.0198$. Prior to the appearance of the transition at the bed outlet the fluid velocity there is $v^* = 0.508$. The solid curves shown in Figure 12 indicate the solution for a simple wave, which is clearly inappropriate.

Conclusions

In gas adsorption, when a nonnegligible proportion of adsorbable components is present, the adsorption or desorption causes appreciable variations of velocity inside the bed. These variations may have a strong nonlinear influence on the adsorption/desorption fronts, causing shocks or spreading waves where otherwise a plain linear behavior would be observed. It is of course of interest for design of gas-adsorption processes to understand and predict these effects.

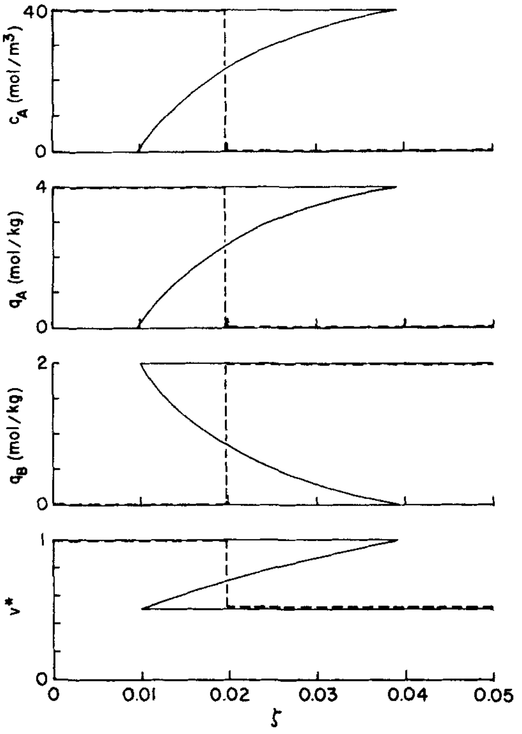

Figure 12. Bed profiles for example 7, case C.

A straightforward and simple method based on the function f, defined by Eq. 11, has been developed to determine the transition type. The method pertains to the two cases in which the existence of a single transition for arbitrary initial and feed states can be guaranteed: the adsorption of one component from inert gas and the adsorption of two components in the absence of inert gas.

Transition type is not affected by changes in void and stationary-phase volumes. However, actual transition shapes as well as concentration and fluid velocities do depend to some extent on these changes.

Examples have shown the existence of simple waves and shocks for linear isotherms where contact discontinuities would have been expected based on well-known methods (Vermeulen et al., 1984). For the adsorption of a single component, we have considered the variation of $q_A(c - c_A)$ with c_A rather than simply the variation of q_A with c_A.

Adsorption isotherms consistent with the existence of contact discontinuities have been derived. For the adsorption of one component, we have obtained the result of Peterson and Helfferich (1965), allowing for variations in void and stationary-phase volumes. We have shown that this relation can be written in the form of the constant separation factor isotherm with the separation factor depending only on the presaturation and feed mole fractions of the solute in the gas phase. For two-component adsorption, we have shown that an infinite number of isotherms exist for contact discontinuities; for transitions covering the full concentration range (mole fractions varying from zero to unity), these isotherms all have separation factors (or selectivities) of unity.

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Notation

c = fluid-phase concentration, mol/m^3
f = function defined by Eq. 11, mol^2/kg · m^3
k = integration constant, Eq. 20
q = adsorbed-phase concentration, mol/kg
R = separation factor, Eq. 36
t = time, s
v = fluid superficial velocity, m/s
v^* = dimensionless velocity, Eq. 27
w = concentration velocity, m/s
x = gas-phase mole fraction
X = dimensionless gas-phase concentration, Eq. 33
y = adsorbed-phase mole fraction
Y = dimensionless adsorbed-phase concentration, Eq. 32
z = axial coordinate, m

Greek letters

α = selectivity, Eq. 14
ϵ = local volume fraction of bed occupied by gas
ρ_b = bulk density of packing, kg/m^3
ζ = dimensionless axial coordinate, Eq. 28

Subscripts

A, B = adsorbable components
s = shock

Superscripts

′ = presaturation value or downstream end of shock part of combined wave

″ = feed value or upstream end of shock part of combined wave

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