Determination of Multicomponent Sorption Equilibria Using Perturbation Gas Chromatography

Perturbation chromatography previously has been used experimentally as an efficient method for obtaining sorption equilibria for systems with up to two vapor phase components at finite concentration. The objective of this work was to obtain a theoretical result that could be used for experimental determinations of sorption of multiple interfering species at finite concentration. Results obtained are applicable for both non-stoichiometric and stoichiometric situations for systems that may have flowing phase velocity and volume changes associated with interphase transport and also may have interactions among the sorbed components. The dependence of each effluent peak characteristic velocity upon all of the component equilibrium isotherms requires that the equilibria be considered as a whole by simultaneously fitting a set of composition grid perturbation response data to appropriate isotherm surface equations.

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SCOPE

Perturbation chromatography has been used for a number of single component and two-component finite concentration experimental studies of vapor-liquid or vapor-solid equilibrium sorption. Theoretical approaches designed for these specific circumstances have appeared in the literature but are not readily adaptable to more general systems. Generalized theories for systems of multiple interfering species have been outlined by Stalkup and Deans (1963), Helfferich and Klein (1970), and by Deans et al. (1970), but the variety of end-use equations that have been determined for specific experimental situations is very limited.

Isotopic tracers have been used for some determinations at finite concentration (Stalkup and Deans, 1963; Gilmer and Kobayashi, 1964; Koonce et al., 1965) and can be used for multicomponent systems with any number of species but the method is not always feasible for lack of the needed tracers. The objective of this work was to develop perturbation gas chromatography equations for sorption in multicomponent, finite concentration systems that are not limited to stoichiometric exchange. Such results can be used for supplementation of isotopic tracer measurements or for independent experimental determinations.

CONCLUSIONS AND SIGNIFICANCE

Considerable simplification of perturbation chromatography derivations is realized if a dry mass basis is used for defining sorbed phase concentrations. This has been pointed out in a number of treatments but has not been universally used to best advantage. Using these definitions a perturbation chromatography result has been obtained for multicomponent sorption that includes sorption effects on gas phase velocity and phase volumes and can be used to determine component interactions in the sorbed phase.

From this result it is seen that for an n-component vapor-phase chromatographic system the $(n - 1)$ effluent response peak velocities that are observed if coherence exists at a given set of experimental conditions will be related to the $(n - 1)^2$ sorbed phase concentration partial derivatives through $(n - 1)$ polynomial equations. Retention data obtained for a sufficient number of composition grid points along with an independently determined or known sorption isotherm for the nth component can be used to determine the isotherms of the remaining $(n - 1)$ components.

Equations obtained for some specific experimental conditions of non-stoichiometric exchange are consistent with results previously reported in the literature as is the result for stoichiometric exchange. Aside from demonstrating agreement of the more general results with previously reported special cases, the inclusion of these cases in this paper also serves to provide a unified approach to the analysis of these various situations for future ease of reference.

INTRODUCTION

A number of papers have dealt with the theoretical understanding of the separation of components in a chromatographic column and the elegant and relatively simple use of column responses to determine thermodynamic data. An interesting historical summary, given by Laub and Pecksok (1978), traces the use of chromatography for physicochemical determinations from the original work of Martin and Synge (1941) that models chromatographic columns as a series of "theoretical plates" to the work of Conder and Purnell (1968a,b, 1969a,b) concerning sorption of a single component which is at finite concentration in a mobile phase that also contains an inert carrier component.

DeVault (1943) formulated a theoretical treatment for multicomponent systems neglecting diffusion and assuming instanta-

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neous equilibrium and obtained a solution for sorption of a single component. His work assumed constant mobile phase flow rate and constant mobile phase and stationary phase volumes and so is not generally applicable to gas chromatography. Discussion of the differential equation characteristics and implications was given by Gleuckauf (1949). Mangelsdorf (1966) discussed the application of DeVault's treatment to perturbation chromatography and obtained the necessary matrix for relating isotherm derivatives to the characteristic peak velocities. Again, this work is limited to appropriate liquid systems or very specific gas systems where there is no sorption effect on gas phase velocity or phase volumes.

Zhukhovitskii et al. (1963) discussed the movement of concentration boundaries through a chromatographic column with multiple components at finite concentration and later reported the necessary equations for evaluating equilibrium (Zhukhovitskii et al., 1965; Zhukhovitskii et al., 1967). These results take into account sorption effects on vapor phase flow rate but are restricted to noninterfering components whose isotherms depend only on their own concentration. Additionally, the results are presented in terms of linear isotherms although the same results hold for nonlinear isotherms, if the isotherm derivatives are substituted for the Henry's constants. Peterson and Helfferich (1965) also point out the importance of including sorption effects and discuss a number of finite concentration situations. A more recent paper by Deans et al. (1970) explains a very general linearized analysis for multicomponent systems that includes any number of components at finite concentration and allows for chemical and mass transfer reactions as well as axial dispersion. This treatment is so very general, however, that its application to desired experimental situations is quite cumbersome.

Helfferich and Klein (1970) have discussed multicomponent chromatography and interference and introduced the concept of coherence in the movement of components through a column. Their treatment is exceptional in its completeness of discussion of fundamental physical phenomena and in its thorough review and discussion of the chromatography literature, but lacks specific applications to experimental situations, especially to gas chromatography.

Most recently, Valentin and Guiochon (1976) have presented a theory for perturbation chromatography with three components in the mobile phase at finite concentration, two of which are sorbed by the stationary phase. Their results allow for both sorption effects and nonlinear isotherms. Stalkup and Deans (1963) and Helfferich and Peterson (1963) point out that experimental determinations for components at finite concentration are simplified considerably if isotopic tracers are used but this method is restricted to those applications for which the desired tracers are available.

The objective of this work was to provide a theoretical analysis for multicomponent non-stoichiometric sorption during perturbation gas chromatography (also known as concentration pulse, step and pulse, elution on a plateau, or minor disturbance chromatography) that would provide the end-use equations necessary for application to experimental determinations. The treatment that follows applies to small perturbations of a gas chromatography column operating at constant temperature and pressure. The flowing vapor phase contains n components which may be sorbed by a non-volatile stationary phase species. Requirements for the experimental determination of equilibrium isotherms for $(n-1)$ of the volatile components given the nth component sorption are discussed below and the specific case of two-component sorption from a mobile phase that also contains an inert carrier component is given as an example. The method for determination of these $(n-1)$ component isotherms is independent of any isotopic tracer determinations.

BASIC CONCEPTS AND DEFINITIONS

In perturbation chromatography, the chromatographic column is perturbed from an initial steady state by the injection of a small amount of a component (or components) into the mobile phase. The initial operating steady state is achieved by flowing the desired constant composition mobile phase through the column for a sufficiently long period of time for the stationary phase to become equilibrated with the flowing phase. The injection introduces a composition perturbation into the flowing phase which, upon entering the column, induces a perturbation in the stationary phase due to the mass transfer which occurs to achieve local equilibrium. This combined mobile and stationary phase perturbation will separate in passing through the column into several composition perturbations which emerge from the column and are detected in the mobile phase as pulses or peaks in some appropriate composition-dependent property such as thermal conductivity.

The number and composition of the perturbation response peaks depend upon the components in the mobile phase, their equilibria and mass transfer with the stationary phase, and the composition of the perturbation sample injected. The column residence time for each peak (measured to the center of mass for the peak) in general will depend upon both phase equilibrium and mass transfer resistance. Under the experimental condition of sufficiently low mobile phase flow rate, however, the effect of the mass transfer rate on peak retention times can be eliminated (Deans et al., 1970) and this condition is an assumption of perturbation chromatography theories, including that presented here.

With this assumption of local equilibrium, experimental results (elution times) obtained from multicomponent perturbation chromatography are dependent upon the values of sorption isotherm derivatives at the steady-state operating composition. For the special case of one-component non-stoichiometric sorption from a two-component mobile phase (one non-sorbing species plus one sorbing species), perturbation at a single steady-state composition allows calculation of the derivative of this component's sorption isotherm at this operating composition. A number of determinations over a range of compositions then allows calculation of the actual isotherm (Conder and Purnell, 1969a, e.g.). As shown from the development that follows, in the case of multicomponent non-stoichiometric sorption of interfering species a determination at a single composition is not sufficient to allow any isotherm partial derivatives to be calculated. In this case isotherms must be determined by simultaneously fitting the isotherm surface equation's partial derivatives with respect to each component's concentration using data obtained over a grid of compositions. Both non-stoichiometric and stoichiometric sorption are considered below.

NON-STOICHIOMETRIC SORPTION

Chromatographic Relations

In the development that follows, we will consider systems with n gaseous components in the flowing phase and $(n+1)$ components in the stationary phase (the n vapor-phase species plus one non-volatile component). Vapor-phase compositions will be described in terms of component concentrations expressed either as moles per vapor phase volume or as mole fraction. Stationary-phase compositions will be defined in terms of moles per mass or per mole or (for sorbents with constant volume such as zeolites) per volume of dry sorbent. (This dry basis definition for concentration has considerable advantage over conventional concentrations by simplifying the manipulations required and therefore the form of the results obtained. This is a consequence of the fact that changes in this concentration occur only due to component transport between flowing and stationary phases and not due to accompanying secondary effects such as changes in the stationary phase volume.)

Sorption is assumed to be non-stoichiometric (there is no constraint on the amount of sorption of any of the components individually, other than equilibrium, or on the total amount), local equilibrium is assumed to hold everywhere in the column, and axial dispersive effects (from diffusion in both phases along with flow dispersion in the mobile phase) are neglected on the grounds that they result in peak broadening but do not alter the peak propagation velocity (Peterson and Helfferich, 1965; Deans et al., 1970). Additionally, the column pressure, temperature, and vapor-phase total concentration (moles/volume) are assumed constant, flow is assumed to be one-dimensional, and the column packing is assumed to be uniformly distributed. The conditions of local equilibrium and negligible pressure drop both require that the flowing-phase velocity be "low." For local equilibrium to be achieved, mass transfer between phases must occur very fast relative to axial flow. While heats of sorption can create local temperature perturbations accompanying the concentration perturbations and hence errors to the isotherm determination, the restriction by this technique to small perturbations from steady state should minimize this effect.

Transport Equations

Considering a differential section of a chromatographic column the one-dimensional transport equations can be written for each component in both the flowing and stationary phases. For the flowing phase,

$$\frac{\partial}{\partial t}(y_i ca) = -\frac{\partial}{\partial z}(y_i caV) - r_i, \qquad i = 1,2,\ldots,n \tag{1}$$

and for the stationary phase

$$m_s \frac{\partial X_i}{\partial t} = r_i, \qquad i = 1,2,\ldots,n \tag{2}$$

where m_s, the (constant) amount of stationary phase sorbent is mass, moles, or volume (per unit length), whichever is appropriate for the definition of the X_i used.

Addition of the n Eqs. 1 gives

$$\frac{\partial}{\partial t}(ca) = -\frac{\partial}{\partial z}(caV) - \sum_{j=1}^{n} r_j. \tag{3}$$

This result allows substitution in Eqs. 1 for changes in vapor-phase cross-sectional area and local flow velocity which are caused by transport between the two phases to give

$$ca\frac{\partial y_i}{\partial t} = -caV\frac{\partial y_i}{\partial z} - r_i + y_i\sum_{j=1}^{n} r_j, \qquad i = 1,2,\ldots,(n-1). \tag{4}$$

Note that the magnitude of the effect of these changes on each component's transport is proportional to its mobile-phase concentration; the effect is larger for components higher in concentration and is zero for components at infinite dilution. This phenomenon has been termed the "sorption" effect. Substitution now for the n transport rates using the stationary-phase equations gives $(n-1)$ partial differential equations for the $(n-1)$ vapor-phase compositions and the n stationary-phase compositions:

$$ca\frac{\partial y_i}{\partial t} = -caV\frac{\partial y_i}{\partial z} - m_s\left[\frac{\partial X_i}{\partial t} - y_i\sum_{j=1}^{n}\frac{\partial X_j}{\partial t}\right], \qquad i = 1,2,\ldots,(n-1). \tag{5}$$

These equations allow for non-stoichiometric exchange of the sorbing species in that there is no constraint on the amount of sorption present.

Linearized Transport Equations

The $(n-1)$ partial differential equations above describe changes in vapor-phase and stationary-phase concentrations of the sorbing components. They hold under the assumptions of one-dimensional flow in a uniformly packed column with negligible axial dispersion.

In perturbation chromatography composition deviations from the steady-state values are small and in the limit of infinitesimal perturbations the linearized forms of these equations hold:

$$c^*a^*\frac{\partial \Delta y_i}{\partial t} = -c^*a^*V^*\frac{\partial \Delta y_i}{\partial z} - m_s\left[\frac{\partial \Delta X_i}{\partial t} - y_i^*\sum_{j=1}^{n}\frac{\partial \Delta X_j}{\partial t}\right], \qquad i = 1,2,\ldots,(n-1). \tag{6}$$

Asterisks indicate unperturbed, steady-state values of the experimental parameters.

Linearized Sorption Isotherms

If the mobile phase flow rate is sufficiently slow, then local equilibrium will be achieved as the perturbation proceeds through the column. Under this assumption stationary-phase concentrations will be related to the mobile phase concentrations through the appropriate sorption isotherms. For this $(n+1)$ component system with two phases there are $(n+1)$ degrees of freedom, say temperature, pressure, and $(n-1)$ mobile phase mole fractions, so that

$$X_i = g_i(y_1, y_2, \ldots, y_{n-1}, T, P), \qquad i = 1,2,\ldots,n. \tag{7}$$

If we assume constant temperature and pressure, differential perturbations in the stationary-phase concentrations can be written as

$$dX_i = \left(\frac{\partial g_i}{\partial y_1}\right)_{T,P,y_j} dy_1 + \left(\frac{\partial g_i}{\partial y_2}\right)_{T,P,y_j} dy_2 + \ldots + \left(\frac{\partial g_i}{\partial y_{n-1}}\right)_{T,P,y_j} dy_{n-1}, \qquad i = 1,2,\ldots,n, \tag{8}$$

which can be linearized about the unperturbed steady state for sufficiently small perturbations to give

$$\Delta X_i = \left(\frac{\partial g_i}{\partial y_1}\right)^*_{T,P,y_j} \Delta y_1 + \left(\frac{\partial g_i}{\partial y_2}\right)^*_{T,P,y_j} \Delta y_2 + \ldots + \left(\frac{\partial g_i}{\partial y_{n-1}}\right)^*_{T,P,y_j} \Delta y_{n-1}, \qquad i = 1,2,\ldots,n. \tag{9}$$

Linearized Chromatographic Relations

It is especially convenient to express Eqs. 6 and 9 in matrix form. For convenience we write $\Delta\underline{X}$ and $\Delta\underline{y}$ to represent the column vectors made up of the stationary and vapor phase concentration perturbations for components 1 through $(n-1)$. We need not be concerned with the vapor phase perturbation, Δy_n, but will need the quality ΔX_n, which is best written separately from the other terms. Equations 6 then become

$$c^*a^*\frac{\partial \Delta\underline{y}}{\partial t} = -c^*a^*V^*\frac{\partial \Delta\underline{y}}{\partial z} - m_s\left[\frac{\partial \Delta\underline{X}}{\partial t} - \underline{Y}^*\cdot\frac{\partial \Delta\underline{X}}{\partial t} - \underline{y}^*\frac{\partial \Delta X_n}{\partial t}\right]. \tag{10}$$

In this equation $\underline{Y}^*$ is an $(n-1)\times(n-1)$ square matrix created from the known steady-state vapor-phase composition vector, $\underline{y}^*$,

$$\underline{Y}^* = \begin{bmatrix} y_1^* & y_1^* & \cdots & y_1^* \\ y_2^* & y_2^* & \cdots & y_2^* \\ \vdots & \vdots & \cdots & \vdots \\ y_{n-1}^* & y_{n-1}^* & & y_{n-1}^* \end{bmatrix}. \tag{11}$$

Equations 9 can be written

$$\Delta\underline{X} = \underline{\beta}^*\cdot\Delta\underline{y}$$

and (12)

$$\Delta X_n = \underline{b}_n^*\cdot\Delta\underline{y}$$

where $\underline{\beta}^*$ is an $(n-1)\times(n-1)$ matrix made up of the appropriate partial derivatives and $\underline{b}_n^*$ is a $1\times(n-1)$ row vector composed of the $(n-1)$ partial derivatives of g_n. All of the partial derivatives are evaluated at the steady-state composition.

Characteristic Velocity

If an equilibrium composition perturbation is moving through the chromatographic column with constant velocity V^c, then to an observer moving with this perturbation the $(n-1)$ concentrations do not change so that the substantial derivative is zero or

$$\frac{\partial \Delta \underset{\sim}{y}}{\partial t} = -V^c \frac{\partial \Delta \underset{\sim}{y}}{\partial z}. \tag{13}$$

Experimentally, this characteristic velocity can be determined from composition peak retention times and column length in the same way that V^* is determined from an inert peak retention time and column length. The question of the existence of a constant characteristic velocity is discussed by Helfferich and Klein (1970) in their concept of coherence and has been assumed in many previous treatments.

Equations 12 and 13 can be substituted into Eq. 10 to obtain a compact equation involving only the spatial derivative of the vapor-phase concentrations:

$$\left[\frac{c^*a^*}{m_s}\left(\frac{V^*}{V^c}-1\right)\underset{\sim}{I} + (\underset{\sim}{Y}^* - \underset{\sim}{I})\cdot\underset{\sim}{\beta}^* + \underset{\sim}{y}^*\underset{\sim}{b}_n^*\right]\cdot\frac{\partial \Delta \underset{\sim}{y}}{\partial z} = 0. \tag{14}$$

The term $\underset{\sim}{y}^*\underset{\sim}{b}_n^*$ is a dyad whose ijth component is $y_i^*b_{nj}^*$. In this linearized matrix equation, the coefficient matrix involves the steady-state values of the various experimental parameters (total vapor-phase concentration, vapor-phase cross-sectional area, sorbent mass per unit length of column, vapor-phase molar average velocity, and vapor-phase component concentrations), the characteristic peak velocity (an experimentally determined value), the sorption isotherm partial derivatives for component n, and the sorption isotherm partial derivatives for the other $(n-1)$ components (evaluated at the steady-state composition). These values are all constants for any given experimental condition and response peak. Experimentally, it is more convenient to write this equation in terms of the total vapor-phase steady-state molar flow rate and the total sorbent mass (or moles or volume, as appropriate) contained in the column. Additionally, the vapor phase velocity and the peak velocity can be expressed in terms of column length and column residence times for an inert (nonsorbing) tracer component at infinite dilution (air is frequently used) and the residence time for the sorbing peak respectively.

$$\left[\left(\frac{Nt_r}{M_s}\right)\underset{\sim}{I} + (\underset{\sim}{Y}^* - \underset{\sim}{I})\cdot\underset{\sim}{\beta}^* + \underset{\sim}{y}^*\underset{\sim}{b}_n^*\right]\cdot\frac{\partial \Delta \underset{\sim}{y}}{\partial z} = 0. \tag{15}$$

It should be emphasized that this result holds only when the flowing-phase velocity can be determined by perturbation with an inert component. Otherwise, Eq. 14 must be used.

This last equation (or Eq. 14 when appropriate) is the required relation that is the key to evaluating sorption equilibria from constant pressure gas chromatographic determinations of peak retention times or characteristic velocities. It is quite general in that it accounts for flowing phase velocity and volume changes associated with interphase transport (the sorption effect which occurs in gas chromatography) and makes possible the determination of stationary phase interactions among multiple sorbing components.

Equation 14 or 15 is satisfied for nontrivial cases of composition perturbations which have retention times for which the determinant of the coefficient matrix in this equation is zero. Equating this determinant to zero, then, gives an $(n-1)$th degree polynomial equation in the peak retention time or characteristic velocity with experimental parameters and the sorption isotherm partial derivatives as terms in the coefficients. Composition perturbations which have retention times which are roots of this polynomial are the perturbations which move with the characteristic velocity described above. For sorption from an n component flowing phase there will be $(n-1)$ equilibrium perturbations for which there will be $(n-1)$ retention times. These times will be known from experimental determinations so that the polynomial equation obtained from the coefficient matrix determinant can be written equivalently as $(n-1)$ simultaneous equations, each one relating the unknown isotherm partial derivatives to one of the peak retention times.

Applications

It should be noted that if all vapor phase components are sorbed, then the results above are insufficient to allow determination of the sorption isotherms of all of the components. Since the coefficient matrix above has only $(n-1)$ roots (characteristic times) we can only determine $(n-1)$ sorption values or sorption isotherms. Consequently, the isotherm for the nth component must be known from an independent source or experimental determination.

If one of the flowing phase components is nonsorbing, then we can call it component n and its sorption term in the coefficient matrix is zero. The polynomial equation obtained from the coefficient matrix then involves only the $(n-1)$ retention times and the $(n-1)$ remaining sorption isotherms.

The actual determination of the sorption isotherms from experimental data is seen to be a complex process in general. At each condition of experimental steady-state composition, there are $(n-1)$ unknowns to be determined, the $(n-1)$ values of stationary phase sorption, for which we have $(n-1)$ equations in terms of the $(n-1)$ equilibrium peak retention times. The problem is that the equations are not explicit in the actual sorption values but rather are in terms of the $(n-1)^2$ partial derivatives taken with respect to the various component concentrations.

Consequently, isotherm information cannot be obtained, in general, from experimental determinations made at a single composition. Instead, data must be obtained at a number of steady-state compositions that is sufficient to allow fitting the appropriate sorption surface equations (Eq. 7) through their partial derivatives by using the $(n-1)$ equations that hold at each composition.

Physically, this means that each composition perturbation that is an equilibrium perturbation (satisfies the required polynomial equation) in general is composed of concentration perturbations in each component. Consequently, we cannot associate each column effluent peak with a single component. This phenomenon has been referred to as coupling (Deans et al.) or component interference (Helfferich and Klein, 1970).

A special case holds for a component at infinite dilution. In this case the cross-partial derivatives of the sorption isotherms are zero for that component (its sorption depends only upon its own concentration) and the contribution from the nth component is zero as a result of multiplication by the mole fraction. In this case the row that corresponds to this component in the sorption matrix is zero except for the diagonal term and expansion of the determinant by cofactors gives decoupling of this component. For component i at infinite dilution ($y_i^* = 0$),

$$\left[\frac{N}{M_s}t_r - \beta_{ii}^*\right]\det(\alpha_{ii}) = 0. \tag{16}$$

The other components remain coupled through the cofactor, α_{ii}.

If component i is not at infinite dilution, it will not decouple, even if its sorption isotherm is independent of the other components. Even if sorption for all of the components depends only on their own concentration, decoupling does not occur. This is seen for the example that follows in Eq. 17 and has been pointed out by Helfferich and Klein (1970).

Sorption of Two components for $n = 3$

As a specific example of multicomponent sorption from a flowing phase that contains one nonsorbing component, consider a flowing phase with three components, two of which are sorbing. This situation previously was reported by Valentin and Guiochon (1976) and is obtained easily from Eq. 15 above. Equation 15 for this case has a coefficient matrix which is 2 × 2 and the vapor phase concentration vector is 2 × 1. The condition obtained from the coefficient matrix then is

$$\begin{vmatrix} \frac{N}{M_s}t_r + (y_1^* - 1)\beta_{11}^* + y_1^*\beta_{21}^* & (y_1^* - 1)\,\beta_{12}^* + y_1^*\beta_{22}^* \\ y_2^*\beta_{11}^* + (y_2^* - 1)\beta_{21}^* & \frac{N}{Ms}t_r + y_2^*\beta_{12}^* + (y_2^* - 1)\beta_{22}^* \end{vmatrix} = 0. \quad (17)$$

This equation is second degree in t_r so that there are two equilibrium perturbation retention times (any upstream perturbation separates in passing through the column into two equilibrium perturbations which move with the appropriate characteristic velocities to give net retention times which are roots of this equation). Both of these retention times will be known from experimental determinations and so we can view Eq. 15 as two independent equations in terms of the two unknown values of sorption but expressed in terms of the four sorption isotherm partial derivatives. These two equations can be written either as two equations that are both quadratic in one of the known values of retention time (by direct substitution of each experimental t_r into Eq. 17) or equivalently as one equation in terms of the sum of the two retention times and another in terms of their product (from consideration of the relations between the sum and product of the roots of a polynomial and the polynomial coefficients). This latter form is useful for comparison with simpler single component sorption cases previously reported in the literature:

$$\left(\frac{\partial g_1}{\partial y_1}\right)^* \left(\frac{\partial g_2}{\partial y_2}\right)^* - \left(\frac{\partial g_1}{\partial y_2}\right)^* \left(\frac{\partial g_2}{\partial y_1}\right)^* = \left(\frac{N}{M_s}\right)^2 \frac{t_{ra}t_{rb}}{(1 - y_1^* - y_2^*)}$$

and (18)

$$(1 - y_1^*) \left(\frac{\partial g_1}{\partial y_1}\right)^* + (1 - y_2^*) \left(\frac{\partial g_2}{\partial y_2}\right)^* - y_1^* \left(\frac{\partial g_2}{\partial y_1}\right)^* - y_2^* \left(\frac{\partial g_1}{\partial y_2}\right)^* = \frac{N}{M_s}(t_{ra} + t_{rb})$$

where each partial derivative $(\partial g_i/\partial y_j)$ is at constant temperature, pressure and mole fraction y_k. Whichever form is used, the two equations may be used to fit perturbation peak retention time data taken over a composition grid. Again, it should be emphasized that the two peak retention times depend upon both component's sorption and cannot be associated with any one of the individual components, hence the subscripts a and b instead of 1 and 2.

This result can be used for gas chromatographic determinations of phase equilibrium in systems such as the solvent(1)/polymer/solvent(2) ternary systems described by Dincer et al. (1979) where the interactions that occur may be of prime importance in the evaluation of the processing of polymers with solvents and their subsequent drying.

Comparisons with Previous Work

The discussion above can be used to obtain the results previously given in the literature for several special cases.

The first and simplest case is for a component at infinite dilution. Equation 16 gives the result immediately that for component (1) at infinite dilution

$$\left(\frac{\partial g_1}{\partial y_1}\right)^*_{T,P,y_2} = \frac{N}{M_s}t_{r1}. \quad (19)$$

In this case, the residence time of one of the response peaks produced depends only upon the sorption isotherm of component (1), allowing explicit determination of this component's isotherm derivative at infinite dilution (related to its Henry's law constant) directly from a single retention time determination. This result is obtained even though additional sorbing components may be present and even though they may be at finite concentration. Equation 18, of course, reduces to this same result since for component (1) at infinite dilution $y_1^* = 0$ and $(\partial g_1/\partial y_2)^* = 0$.

A second case is for a single finite concentration sorbing component in an inert carrier. Equation 18 with component (1) at infinite dilution gives that for component (2)

$$\left(\frac{\partial g_2}{\partial y_2}\right)^*_{T,P,y_1} = \frac{N}{M_s}\frac{t_{r2}}{(1 - y_2^*)}. \quad (20)$$

In this case with one sorbing component at finite concentration and another at infinite dilution in the carrier gas the two residence time equations decouple completely and it is appropriate to associate each peak retention time with a particular component by using the corresponding subscript. These last two equations have appeared frequently in the literature for sorption determinations involving components at either infinite or finite dilution. In the finite dilution case experimental determinations must still be made over a range of concentrations to allow a fit or integration of the sorption isotherm. This result holds only for a flowing phase that contains an inert component in addition to the one (and only one) sorbing component at finite concentration.

As a third case, if the flowing phase steady-state composition contains two sorbing components without an inert component, then a perturbation with one of these components (or both) produces a single response peak, always at the same time, regardless of the composition of the perturbation. The coefficient in Eq. 15 is a scalar which gives

$$(1 - y_1^*) \left(\frac{\partial g_1}{\partial y_1}\right)^*_{T,P} + (1 - y_2^*) \left(\frac{\partial g_2}{\partial y_2}\right)^*_{T,P} = \frac{N}{M_s}t_r. \quad (21)$$

In this equation, we must know independently the sorption of one of the components in order to evaluate the other using this equation. This result has been presented by Stalkup and Deans (1963) in terms of K-values. Their Eq. 16 can be shown (with considerable algebraic manipulation) to be equivalent to this equation by using the relations that (for X with units of moles/mole of "dry" stationary phase) $g_i/(1 + \Sigma_{k=1}^{2} g_k) = y_i/K_i$ and $g_i/g_j = y_iK_j/y_jK_i$. In comparing these two forms of the equation, the simplicity of the result using the dry mass basis definition for the stationary phase concentrations is clear. It is much easier to determine the dry mass sorption isotherms using the above equations and then convert them to the desired concentrations (conventional concentrations, K-values, etc.) than to determine conventional concentrations, etc. directly. Equation 21 has also been derived by Peterson and Helfferich (1965) and again by Ruthven and Kumar (1980) who applied the result to binary sorption by a zeolite catalyst. Their concentration definitions and hence their results are exactly analogous to Eq. 21. It should be noted, however, that for zeolites, determination of the vapor phase flow rate and hence t_r must be carefully considered. The vapor-phase velocity that appears in Eq. 14 must be the velocity of the gas phase that has the steady-state gas-phase composition. In the case of zeolites a component like helium, air, etc., which might be used in a direct experimental determination of the flowing-phase velocity or residence time will partition into the cages where composition may be different from the bulk flowing phase and consequently will not give the correct value. The approach that has been used in this case is to calculate from the total column volume and the total zeolite packing volume a net column void volume. This along with the measured volumetric flow rate can be used to obtain the residence time, t_a, used to determine the net retention time.

The problem of having independent data for the sorption of component n when there is no inert component in the flowing phase steady-state composition has been handled by Stalkup and Deans (1963), Gilmer and Kobayashi (1964), Helfferich and Peterson (1963), and others by using isotopic tracers. As was shown by Stalkup and Deans (1963), a perturbation with an isotopic tracer produces a response peak that behaves as a component at infinite dilution since the molecules of this tracer can be detected separately from other molecules of the same chemical species. This allows direct measurement of the actual sorption (not the concentration partial derivative) for that species. When suitable isotopic tracers are available, this method provides considerable simplification of the determination of the sorption of all components in a multicomponent system, since each single measurement gives directly a point on the isotherm for that component without surface fits.

STOICHIOMETRIC EXCHANGE

With stoichiometric exchange there is a fixed (constant) amount of sorption so that the X_i are not all independent, $\Sigma_{i=1}^{n} X_i$ = constant, or $y_i^* \Sigma_{j=1}^{n} \partial \Delta X_j/\partial t = 0$ so that Eq. 6 becomes

$$c^*a^* \frac{\partial \Delta y_i}{\partial t} = -c^*a^*V^* \frac{\partial \Delta y_i}{\partial z} - m_s \frac{\partial \Delta X_i}{\partial t}, \qquad i = 1, \ldots, (n-1) \tag{22}$$

and Eq. 14 becomes

$$\left[\frac{c^*a^*}{m_s}\left(\frac{V^*}{V^c} - 1\right)\underset{\sim}{I} - \underset{\sim}{\beta}^*\right] \cdot \frac{\partial \Delta \underset{\sim}{y}}{\partial z} = 0. \tag{23}$$

In this situation, the sorption effect is absent, just as it would be for non-stoichiometric sorption at finite dilution. The results are different, however, in that the components do not necessarily decouple since they may still interfere at finite concentration ($\underset{\sim}{\beta}^*$ is not diagonal as it is if all sorbing components are at infinite dilution). Equation 23 previously has been given by Mangelsdorf (1966).

The above result was obtained assuming that all n vapor-phase components may exchange. If one vapor component does not exchange, then the same result is obtained but the coefficient matrix is $(n-2)$ by $(n-2)$. In this case, there are $(n-1)$ sorbed components in the stationary phase for which $(n-2)$ compositions are independent. Also the nth component in the flowing phase, which does not exchange, stays at constant concentration so that the sum of the other $(n-1)$ vapor-phase concentrations is constant, resulting in $(n-2)$ vapor-phase concentrations which are independent. If exchange is to occur under these circumstances, then there must be at least three components in the flowing phase and two in the stationary phase for which there will be one perturbation peak observed.

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NOTATION

a = flowing phase cross-sectional area

$\underset{\sim}{b}_n$ = $1 \times (n-1)$ vector of sorption derivatives for component n

c = total vapor-phase molar concentration, a constant

g_i = sorption isotherm for component i (Eq. 7), $i = 1, \ldots, n$

$\underset{\sim}{I}$ = identity matrix, $(n-1) \times (n-1)$

K_i = component i K-value equal to y_i/x_i, $i = 1, \ldots, n$

L = column length

M_s = total amount of inert stationary phase in the column

m_s = amount of inert stationary phase per unit column length

N = vapor-phase molar flow rate

n = total number of components in the flowing phase

P = total pressure

r_i = net rate of transfer of component i from the flowing phase to the stationary phase, $i = 1, \ldots, n$

t = time or response peak residence time

t_r = net retention time for a peak, $t_r = (t_{\text{peak}} - t_a)$

t_a = residence time for an inert tracer component

t_{peak} = residence time for a delayed response peak

t_{ra} or t_{rb} = net retention time for peak a or b

V = vapor-phase molar average velocity

V^c = response peak characteristic velocity

x_i = conventional mole fraction of component i in the stationary phase, $i = 1, \ldots, (n+1)$

X_i = sorption of component i, (moles sorbed)/M_s, $i = 1, \ldots, n$

ΔX_i = deviation from steady-state of X_i

$\Delta \underset{\sim}{X}$ = $(n-1) \times 1$ column vector of the ΔX_i, $i = 1, \ldots, (n-1)$

y_i = vapor phase mole fraction of component i, $i = 1, \ldots, n$

Δy_i = deviation from steady-state of y_i

$\Delta \underset{\sim}{y}$ = $(n-1) \times 1$ column vector of the Δy_i, $i = 1, \ldots, (n-1)$

$\underset{\sim}{Y}^*$ = $(n-1) \times (n-1)$ matrix of vapor phase mole fractions (Eq. 11)

z = distance in the direction of flow through the column

Superscripts

$*$ = steady-state value

Greek Letters

α_{ii} = cofactor (matrix) of β_{ii}^*

$\underset{\sim}{\beta}$ = matrix of sorption derivatives for components 1 through $(n-1)$, $\beta_{ij} = (\partial g_i/\partial y_j)_{T,P,y_k}; k \neq j$

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Effect of the Product Layer on the Kinetics of the CO_2-Lime Reaction

The kinetics of reaction between CO_2 and lime is investigated in the range of 673 to 998 K with a view to examining the effects of product layer deposition and variations in the limestone calcination atmosphere. The reaction is initially rapid and chemically controlled and goes through a sudden transition to a much slower regime controlled by diffusion in the product $CaCO_3$ layer. The magnitude of the estimated product layer diffusivity is in the range of 10^{-18} to 10^{-21} m^2/s, the corresponding activation energy is 88.9 ± 3.7 kJ/mol below 688 K and 179.2 ± 7.0 kJ/mol above that temperature, suggestive of solid state diffusion. Plausible mechanisms are discussed.

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SCOPE

The effect of pore structure and the influence of product layer diffusion on the CO_2-lime reaction has been examined in the temperature range of 673 to 998 K under CO_2 levels varying from 10 to 42% in nitrogen. The data is analyzed by means of the random pore model (Bhatia and Perlmutter, 1980, 1981a), and intrinsic rate constants as well as product layer diffusion coefficients are determined. Product layer diffusion coefficients for calcines prepared under varying levels of CO_2 in nitrogen are compared, and the role of solid state processes in the product layer diffusion process is examined.

CONCLUSIONS AND SIGNIFICANCE

Analysis of kinetics data indicates that after nucleation is complete at about 12% conversion the CaO-CO_2 reaction proceeds by a rapid surface reaction-controlled step, followed by a slower second stage product layer diffusion-controlled process. The high activation energy for product layer diffusion (88.9 kJ/mol below 688 K and 179 kJ/mol above 688 K) and the low values of the effective diffusitivity (10^{-18} to $10^{-22} m^2/s$) are suggestive of a solid state diffusion. Calcines with different surface areas prepared under CO_2-containing atmospheres show agreement in the estimated product layer diffusivity. The values for the calcines prepared under nitrogen are however different, indicating variations in defect structure.

The bulk of the pores in all the calcines lie in a narrow size range with a small amount of porosity distributed among larger pores. Over most of the conversion range the smaller pores dominate reaction, but at about 60% conversion the pores in this narrow size range appear to close because the molar volume of $CaCO_3$ far exceeds that of CaO. Further conversion is thus restricted to the much larger pores which react only slowly. The incomplete conversions obtained for this reaction in this study and those of Nitsch (1962), Dedman and Owen (1962), and Barker (1973, 1974) may be attributed to this phenomenon.

The literature reports many studies of the kinetics of the decomposition of calcium carbonate (Zawadzki and Betsznajder, 1935; Hyatt et al., 1958; Cremer and Nitsch, 1962; Beruto and Searcy, 1974; Searcy and Beruto, 1976), but less attention has been paid to the reverse reaction:

$$CaO\ (s) + CO_2\ (g) \rightleftharpoons CaCO_3\ (s)$$

This reaction is of practical significance in the CO_2 acceptor process for coal gasification, and in the synthesis of calcium cyanamide (Dedman and Owens, 1962). Further, it has recently been suggested as an attractive candidate reaction for consideration in energy storage (Barker, 1973, 1974). This paper reports experimental kinetics for this reaction and applies the random pore model (Bhatia and Perlmutter, 1980, 1981a) to interpret the data.

The prior studies of Nitsch (1962), Dedman and Owen (1962), and Barker (1973, 1974) on the recarbonation of lime indicate a relatively rapid initial reaction followed by a much slower second stage. Nitsch (1962) found that the initial growth stage reaction rate in the temperature range of 1073 to 1123 K could be correlated by

$$\frac{dX}{dt} = k_x\,(1 - X)^{2/3}\,(C - C_e) \qquad (1)$$

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