Analysis of Liquid-Phase Adsorption Fractionation in Fixed Beds.

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by

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DEDICATION

To my late, beloved parents.

Mr. and Mrs. Elmer L. Morton
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ABSTRACT

In those processes involving the separation of solutions, adsorption column design has been one of the latest unit operations to undergo theoretical treatment because of the relative complexity of the mechanisms involved. The purpose of this investigation is to establish an improved method for solving adsorption problems, especially where intraparticle diffusion is a rate controlling mechanism. In particular it is desired to derive a model describing fixed-bed, liquid-phase adsorption fractionation in a column in terms of concentration, bed depth, time and particle radius. The appropriate boundary conditions for liquid-phase adsorption and a general non-linear equilibrium relation are included in deriving a system of partial differential equations describing the process.

The mathematical model consists of a bulk-phase material balance, an intraparticle diffusion equation, and a rate equation for interphase transfer across the surface film; these equations must be solved simultaneously with the boundary conditions and equilibrium function. The equations are expressed in terms of certain dimensionless parameters so that the solution is independent of the physical properties of any particular adsorbent bed. This non-linear set of equations requires a suitable numerical means of solution. A numerical procedure is developed and discussed for use on a high-speed computer. The program used to solve the problem on an IBM 7040 computer is described.
The results obtained in this work are sets of computed curves for four liquid systems, each system requiring a separate computer solution because of changes in concentration or equilibrium relationship. The computed curves are matched with experimental data on these systems to determine mass transfer coefficients, which ultimately are used for design purposes. It is shown that, for three out of four systems tested in this research, experimental data correlate with computed results better than in earlier work. This fact lends support to the validity of the proposed model. Moreover the coefficients calculated from the investigation are within an order of magnitude of values found in an independent determination, again giving some credence to the proposed model. Although the solution of this model has been carried out for particular examples, it should be applicable in the case of other liquid-phase systems following the mechanisms described, as well as the assumptions involved in deriving the model.

A discussion is presented for the purpose of applying the results to an actual column. For purposes of commercial design equations are developed to compute wave formation time and corresponding bed depth, degree of saturation, and length of the ultimate wave in fixed-bed adsorbers.

The results of this project have led to a number of conclusions and recommendations for future consideration. In particular it has been found that a solution can be found for a derived model without the necessity of making oversimplifying assumptions. An improved correlation between experiment and theory has been shown, but at the same time there is need to consider other mechanisms such as longitudinal
diffusion, multi-component systems, effect of concentration on the rate coefficient, and non-isothermal operation. In the future it is possible that numerical methods may be discovered to handle simultaneously some or all of these factors with faster computers than are presently available.
I. INTRODUCTION

This dissertation is the result of research on adsorption fractionation of binary liquids. The primary analysis concerned the effect of intraparticle diffusion on the kinetics of fixed-bed adsorption columns. A theoretical approach was used in which partial differential equations were derived to simulate column operation. Actual equilibrium relations for real systems were incorporated into the numerical solutions which were obtained on a high-speed electronic computer.

Much of the work in this project is an extension of research by numerous investigators as outlined in a survey of papers on adsorption column operation. A large majority of earlier studies were limited to simpler cases, such as linear equilibrium or steady-state operation, which could be solved easily. In this project the particular boundary conditions used, the general equilibrium function, and transient operation all required the solution be obtained numerically. Both film resistance and internal diffusional resistances were incorporated in the mathematical description of the process.

A successful correlation of experimental data obtained in earlier studies with the theoretical model developed herein is considered a useful contribution to the knowledge of adsorption column kinetics. A procedure for solving the model, along with a computer program, is outlined. Also presented were means of applying the
solution to the design of an adsorption column, taking into account the transient phase after startup, and the corresponding length of bed required for formation of the steady-state wave. Equations for calculating the net degree of saturation in an operating fixed-bed column were developed for purposes of economic considerations. The application of fixed-bed data to moving-bed processes was discussed briefly.

It is hoped that this work will serve, at least in part, as the basis of future analysis of adsorption processes.
II. BACKGROUND

The mathematics of a rigorous model of adsorption processes in column operation has until recent times been too complex for exact solution. Simple cases have been treated from a theoretical standpoint, but in such instances actual processes did not generally follow the resulting theory. Some investigators have derived models, primarily for gas-phase operation, in which simplifying assumptions such as linear equilibrium relationships and no internal diffusional resistances within the adsorption bed have been made.

The basic inspiration for this research project evolved from an interest in numerical applications for the solution of engineering problems, where the number of simplifying assumptions is minimized at the expense of more difficult computational techniques. The need for additional work in the subject area of adsorption is summarized by excerpts from Johnson (30):

Since the computed solutions of this work do not yield an exact fit with data of large particle size adsorbent, the next logical improvement in the method of analysis which was used here would be to include in the basic equations a mathematical expression for the intraparticle resistance.

The addition of an extra unknown parameter, D. and an additional independent variable, r, makes the problem a much more difficult one than was solved in this work. It is believed, however, that the techniques demonstrated here will be applied in the future, using faster and larger computers if necessary, to approach more closely the exact solution to adsorption fractionation problems.

With the possibility of further improving the theoretical
approach to adsorption, it was decided to search for a realistic model which involved the additional mechanism of internal particle diffusion, hoping that a more adequate mathematical statement of the behavior of an adsorption column could be developed. A numerical solution to the improved model was anticipated, requiring the use of a very high-speed computer. Since the estimated computing capacity was available at the time this research was begun, it was deemed practical to undertake the project for this dissertation. Initially the computations were to be done at a remote location until similar facilities at L.S.U. were installed.

This research has centered around a model in which four major variables are considered simultaneously: time, bed depth, particle radius, and concentration, along with a general equilibrium function. The liquid-phase was chosen to demonstrate the model because there has been less work in this area, and the boundary conditions are more complicated. No restriction was to be put on the equilibrium relation.
III. LITERATURE SURVEY

In this section, a brief summarization will be given to those previous investigations dealing with the subject of adsorption, especially to papers dealing with column operation. A large storehouse of literature exists for the many separate aspects of adsorption, each of which is involved in the overall operation of a process for the separation of mixtures. Early researchers were concerned with the mechanics of surface processes, equilibrium relationships in the form of isotherms, activation energies, and thermodynamics of adsorption in general. The incorporation of these various mechanisms into the design of a process for the fractionation of mixtures is, however, relatively recent, due to the complexity of the mathematics when these mechanisms are combined. The papers summarized in this section are those primarily involved in the attempt to relate the many known variables into a usable model from which a profitable plant may be designed.

The early attempts to correlate results of adsorption experiments were usually highly empirical. The velocity of adsorption of carbon tetrachloride on charcoal was measured by Hernad in 1920 (20). A resulting empirical, but satisfactory, correlation in which the rate was assumed to be proportional to an expression of the form, $Ae^{-kt}$, was used, but no explanation of the reasons underlying this approach were given. There was some speculation that diffusion possibly affected the rate. Most of the work of this period was still on equilibrium isotherms.
Other papers in line with the work of Hernad were given by Rogensky (42), Schumann, (47) Constable (6), and Taylor (49). The latter author was one of the first to attribute concepts other than activation energies as rate-controlling mechanisms. Important theoretical aspects of adsorption phenomena were described. Not only activation energies, but internal diffusion as a possible rate-determining factor were discussed in Taylor's paper. He obtained data and treated qualitatively the effects of adsorbent material, concentration, surface characteristics, heat of adsorption, and temperature.

An early paper which involved the dynamics of a gas-solid system was written by Furnas (12). Mathematical equations for a heat transfer problem, relating the variables of time and temperature with distance were solved. Experimental data were correlated, using the theoretical results of his model.

The development of more sophisticated theories of adsorption fractionation processes in a column began in the late 1930's and early 1940's largely in the field of chromatography. Some highly complicated mathematical equations were derived, however in many instances they were either overly simplified or not solved for want of a practical means of solution. Wilson (53) applied adsorption to the study of rate processes in chromatographic columns, making the assumption of instantaneous equilibrium between the fluid and adsorbent phases, with negligible diffusion. These assumptions resulted in a straightforward analytical solution for a two-component system. This author recognized the probable, but admittedly complex, effect of intraparticle diffusion.

Devault (7) continued Wilson's work in chromatographic analysis
by deriving partial differential equations which considered multiple components although they were not solved. The characteristic shapes of waves formed in chromatographic columns were discussed qualitatively. Glueckauf and Coates (16,17,18), in a series of papers, described steady-state adsorption for both a single solute and a binary solution as related to chromatography. Thomas (50) developed a kinetic approach to the analysis of chromatography for a single solute. Cases for both initially dry and initially saturated beds are considered using equilibria of linear or Langmuir types. Improved agreement between theory and experiment resulted over that shown where instantaneous equilibrium was assumed.

Other work, carried out during the wartime period, included studies by Gamson, et al. (13) who developed empirical mass transfer rate correlations for various adsorption systems; and by Thomas (51), who applied a second-order rate equation to the surface reaction step which was assumed to control.

In the period following World War II, the study of adsorption processes in a column expanded tremendously. In general most authors recognized at least qualitatively, three rate mechanisms which were thought to influence column operation: surface reaction, intraparticle diffusion, and external diffusion through a film. Most of the work centered on gas-solid systems and with linear isotherms. Some very elegant models were proposed and analytical solutions were found for restricted cases, not only in adsorption, but all of the unit operations, as demonstrated by Marshall and Pigford (37). Theoretical investigations began to explain the phenomena of ion-exchange, which
is allied in many respects to adsorption. Large-scale commercial applications for newly developed adsorption operations began, as exemplified by the Hypersorb and Arosorb processes for separation of petroleum feed-stocks (4,24,27).

Hougen and Marshall (25) developed equations during this period for gas adsorption under both flow and non-flow conditions. Linear equilibrium in an isothermal bed was assumed, for which analytical solutions were found. Graphical methods for the case of non-linear isotherms were given, and also for non-isothermal beds in which chemical reaction occurs. Effects of particle size on the kinetics was not treated quantitatively. A stage-wise approach was made by Mair, et al. (36), for the separation of two components in a fashion analogous to distillation. Lapidus and Rosen (35) proved the existence of the constancy of the ultimate wave-shape in a sufficiently long column, provided the curvature of the equilibrium function is negative. Barrer (3) obtained rate data for batchwise flow of ammonia and other gases and calculated surface diffusion coefficients, using a Henry's Law equilibrium relation. Eagle and Scott (8) published a comprehensive paper giving kinetic and equilibrium data along with other significant measurements, for a number of liquid-phase adsorption systems.

The actual solution of equations in simple cases for which analytical methods were unavailable or overly complicated began in the early 1950's paralleling the introduction of high-speed, stored-program, electronic computing machines, which could often provide accurate numerical results. An early paper dealing with solution of adsorption
kinetics problems on the computer was authored by Rose, Lombardo, and Williams (43), in a simple stagewise approach to fractionation of a binary, liquid mixture. Instantaneous equilibrium at the particle surface was assumed, neglecting pore diffusion resistances. Computed solutions were compared with experimental data obtained from steady-state runs using a mixture of benzene and hexane on fine particles of silica gel. Fairly good agreement was obtained because of the fineness of the absorbent, so that internal diffusion was largely, but not entirely, eliminated. Similar treatment was given to liquid-solid adsorption systems in the steady-state by Schmelzer, et al. (46), who showed qualitatively by a series of interrupted runs that internal diffusion was a significant mechanism. In these tests the feed rate was cut off during the operation of an adsorption experiment. The presence of a vertical, downward displacement of the effluent concentration curves demonstrated the presence of internal diffusion.

Amundson (1,2) was one of the earliest investigators to attack the problem of internal diffusion quantitatively in overall column operation. He considered the process in terms of an irreversible mechanism where the rate of mass transfer is proportional to fluid stream gas concentration and to the quantity of adsorbate contained in the bed. He also found solutions for the rate where a kinetic theory was assumed, and separately for the case of radial diffusion controlling. Kasten and Amundson (32) studied adsorption fractionation from a theoretical standpoint in fluidized beds. Steady-state operation with a linear isotherm and a kinetic rate mechanism was assumed, but with quantitative treatment of internal diffusion. The rate of separation
of the feed into two streams was based on a probability theory. Other papers involved with study of diffusional and other rate processes are those by Edeskuty and Amundson (10), in liquid-phase adsorption and in the field of ion exchange by Lapidus and Amundson (33). In both cases linear equilibrium was assumed. As yet no substantial treatment of the formation time required for the ultimate, or steady-state adsorption wave in fixed beds had been given. Other important papers in this category include work by Jury and Licht (31) in the drying of gases, by Geser and Canjar (14) in adsorption of methane, by Hiester and Vermeulen (22) in ion-exchange, and by Rosen (44).

One of the first papers where the restriction of linear equilibrium could be lifted was by Hiester et al. (21). In this report dealing with ion exchange, methods were presented for correlating experimental results when both external and internal diffusional resistance occur simultaneously. Steady-state operation was assumed as well as a rate of radial diffusion proportional to a concentration driving force. Selke et al. (48) obtained diffusivity data for ion-exchange columns using shallow-bed experiments, and a general equilibrium. They suggested dividing a column into a series of shallow beds for a stepwise solution. No consideration for wave formation time or bed depth was given. Gilliland and Baddour (15) tested a steady-state ion-exchange system, using an overall coefficient of mass transfer for all resistances combined. The variables considered were particle size, bed height and diameter, feed rate and concentration. Column dimensions were found not to affect results over the range of variables investigated. Eberly and Spencer (9), also using a lumped resistance
obtained adsorption rate constants by means of a pulsed-flow experiment. In this research, the shape changes in the pulse were attributed to adsorption effects.

Johnson (30) extended the research into liquid-phase adsorption fractionation in fixed beds by a complete numerical solution to systems which involved simultaneously the variables of bed depth, time, and concentration. The external film was assumed to control, with instantaneous equilibrium at the interface between adsorbed and non-adsorbed phases. Internal diffusion was neglected, although discussed qualitatively. No restrictions were put on the equilibrium, except that it should not cross the operating line. Particularly interesting was a complete re-evaluation of boundary conditions used by past researchers and a resultant modification for use in liquid systems. His work demonstrated that solutions to certain problems for which no known analytical techniques exist may be found by numerical means on a computer, and that the complexity of the problem which could be solved depends largely on the capabilities of the computer itself.

More recently Masamune and Smith (38), recognizing that diffusional resistances within the porous bed are of importance have derived and solved equations relating the variables of concentration, time, level, and particle radius for vapor-phase adsorption. Attention was given to the special cases of surface adsorption controlling, pore diffusion controlling and external diffusion controlling. These investigators assumed linear equilibrium and boundary conditions such that an analytical solution was obtained for each case. Using a nitrogen-helium vapor mixture on vycor particles the results of experimental
tests compared favorably with theory only when the mechanism of pore diffusion was included.
IV. DEVELOPMENT OF A MODEL FOR LIQUID-PHASE ADSORPTION

1. Introduction

In order to define a practical model it is necessary to state the basic assumptions as to the nature of the adsorption process. Since fixed-bed liquid phase binary adsorption is under consideration, all assumptions will be based on this type of process.

a. The flow of liquid through the system is assumed to be plug-like flowing upward from bottom of the system. No concentration or velocity gradients exist in a radial direction from the direction of flow. In deriving the differential equations these terms could be included when the field of fluid dynamics produces more knowledge of radial effects. In addition, longitudinal, or axial, diffusion is considered negligible.

b. A constant feed composition will be assumed, as this is the normal mode of operation, unless changing from one operating level to another.

c. The feed is a binary or pseudo-binary system of components, one of which is preferentially adsorbed, thus effecting a fractionation into two phases, one a non-absorbed, or bulk, phase and the other phase being the liquid solution contained within the adsorbent.

d. An initially dry system is used. In vapor adsorption the
entering vapor stream displaces the gaseous fluid found in the void spaces around the particles of adsorbent, but not the fluid contained within the particles themselves. In liquid processes, it is assumed that as the feed rises through the bed, the entering liquid fills both the void spaces and at the same time enters and fills the pore volume almost instantaneously. Ineffective space containing trapped vapor is not considered a part of the pore volume in which adsorption occurs. As will be pointed out this difference between vapor and liquid phase mechanisms causes a major difficulty in the latter case because of the resulting boundary conditions. This assumption precludes a study of the effect of a step change in feed composition at a later moment of time, without modifying the entire model.

e. The system will be considered to operate isothermally; all heat effects are either negligible or cancel each other out, as is typical of liquid-phase processes.

f. The particles of adsorbent are considered to be spherical and possess an effective radius, constant throughout the bed. Although it is known through microscopic study that the particles are highly irregular, it is impossible to describe them except by means of familiar geometry. The interior pore space, by means of which diffusion occurs in each particle is highly tortuous but will be accounted for by an effective internal overall diffusivity, assuming
only radial diffusion. There are several internal diffusion mechanisms thought to occur, but these are usually lumped together and described by a single effective diffusion constant.

g. The only factor controlling adsorption within the pore space is diffusion itself. Generally this has been shown to be the case, although it is possible that the adsorption step at the interface between fluid and solid may control in some instances. There is no reason why this mechanism could not also be included, provided the rate constants for this step could be found.

h. There is no effect of concentration on the film constant or diffusion constant. This assumption is necessitated by the fact that these effects are very difficult to evaluate.

i. Equimolar counter-diffusion is assumed. There is a net flow of liquid onto the adsorptive surfaces, but this is small compared to the total quantity of liquid in which diffusion occurs.

2. Derivation of Equations

Consider a vertical tower packed with adsorbent material, fed by a binary stream of constant composition entering at the bottom and flowing upward in plug-like flow. Taking a horizontal slice of thickness, \( dz \), one may write an overall bulk-phase material balance on the more adsorbed component, in terms of volumetric flow rates, as follows:
Input stream: \( Q \times ft^3/hr \)

Output stream: \( Q \times + \left( \frac{\partial Q}{\partial z} \right) dz \times ft^3/hr \)

Output from bulk phase to adsorbent: \( W \times ft^3/hr \)

Accumulation in bulk phase: \( f_v \left( \frac{\partial x}{\partial \theta} \right) Sdz \times ft^3/hr \)

where \( x \) = volume fraction of the more adsorbed component

\( Q \) = total feed flow rate, \( ft^3/hr \), assumed constant

\( z \) = bed depth, ft.

\( \theta \) = elapsed time, hr.

\( S \) = cross sectional area, \( ft^2 \)

\( f_v \) = fraction voids in the bed

\( r \) = particle radius, ft

(The above listed dimensions are for illustrative purposes; any other consistent set of units may be used.)

Combining these expressions and holding \( Q \) constant, gives an overall balance:

\[-Q \left( \frac{\partial x}{\partial z} \right) dz + W = f_v \left( \frac{\partial x}{\partial \theta} \right) Sdz \] (4-1)

The quantity, \( W \), is evaluated by means of a term expressing mass transfer from the bulk phase across the outer surface of the adsorbent particles and into the interior of the particles, as follows:

1. The volumetric transfer rate of the more adsorbable component per cubic foot of adsorbent is \( A_s D \left( \frac{\partial Y}{\partial r} \right) \theta, z, r=a \),

where \( A_s \) = surface area across which diffusion occurs on the surface of the spherical particles, \( ft^2/ft^3 \) bed

\( D \) = effective diffusivity, \( ft^2/hr \)

\( \left( \frac{\partial Y}{\partial r} \right) \theta, z, r=a \) = concentration gradient in adsorbed phase at the surface

\( a \) = effective particle radius, ft

2. The surface area, \( A_s \), is computed from the surface area per
sphere times a term expressing the fraction of surface open to the diffusing substance, times the total number of spheres per unit volume of bed:

Surface area per sphere \( = 4\pi a^2 \) \( \text{ft}^2 \)

Number of spheres per \( \text{ft}^3 \) \( = \frac{3(1-f_v)}{4\pi a^3} \)

Pore volume per unit volume of spheres \( = \frac{V_p \rho_b}{1-f_v} \) \( \text{ft}^3/\text{ft}^3 \)

where \( V_p \) = pore volume, \( \text{ft}^3/\text{lb} \) absorbent
\( \rho_b \) = density of absorbent, \( \text{lb}/\text{ft}^3 \) bed

The latter term is a factor which accounts for the solid, non-porous material, and is assumed to be the same on a surface basis as on a volume basis.

Combining these terms gives:

\[
A_s = 4\pi a^2 \cdot \frac{3(1-f_v)}{4\pi a^3} \cdot \frac{V_p \rho_b}{1-f_v} \text{ ft}^2/\text{ft}^3 \text{ bed}
\]

The total diffusion, \( W \), in a volumetric section, \( Sdz \), is thus:

\[
W = \frac{3V_p \rho_b}{a} \cdot Sdz \left( \frac{\partial y}{\partial r} \right) D \theta, z, r = a \text{ ft}^3/\text{hr} \quad (4-2)
\]

Substituting for \( W \) into equation (4-1) gives an overall bulk-phase material balance:

\[
-Q \left( \frac{\partial x}{\partial z} \right) \theta_r dz + \frac{3D(V_p \rho_b)}{a} Sdz \left( \frac{\partial y}{\partial r} \right) \theta, z, r = a \quad = f_v \left( \frac{\partial x}{\partial \theta} \right) z, r \quad (4-3)
\]

or

\[
-Q \left( \frac{\partial x}{\partial z} \right) \theta, r + \frac{3D(V_p \rho_b)}{a} \left( \frac{\partial y}{\partial r} \right) \theta, z, r = a = f_v \left( \frac{\partial x}{\partial \theta} \right) z, r
\]

An adsorbed-phase, or intraparticle material balance may also be derived, using a spherical shell. Making the assumption that
diffusion occurs only in a radial direction one may write the following terms, noting that the direction of diffusion is opposite to the direction of change of radius.

Let the inner radius of a spherical shell be \( r \), then the outer radius is \( r + \Delta r \).

Material entering at \( r + \Delta r \) is thus equal to

\[
4 \pi r^2 D \left( \frac{\partial \gamma}{\partial r} \right)_{\theta,z} \cdot \frac{V_p}{1-f_v} + \left[ \frac{\partial}{\partial r} \left[ r^2 D \left( \frac{\partial \gamma}{\partial r} \right) \right] \right] \cdot \frac{V_p}{1-f_v} \mathrm{dr}
\]

Material leaving at \( r \) is

\[
4 \pi r^2 D \left( \frac{\partial \gamma}{\partial r} \right)_{\theta,z} \cdot \frac{V_p}{1-f_v}
\]

and accumulation is

\[
4 \pi r^2 \frac{V_p}{1-f_v} \left( \frac{\partial \gamma}{\partial \theta} \right)_{r,z} \mathrm{dr}
\]

Equating terms gives the intraparticle material balance:

\[
\left[ \frac{\partial}{\partial r} \left[ r^2 D \left( \frac{\partial \gamma}{\partial r} \right) \right] \right]_{\theta,z} = r^2 \left( \frac{\partial \gamma}{\partial \theta} \right)_{r,z}
\]

or

\[
D \left[ r^2 \left( \frac{\partial^2 \gamma}{\partial r^2} \right)_{\theta,z} + \left( \frac{\partial \gamma}{\partial r} \right)_{\theta,z} \right] 2r = r^2 \left( \frac{\partial \gamma}{\partial \theta} \right)_{r,z}
\]

which leads to:

\[
D \left[ \left( \frac{\partial^2 \gamma}{\partial \theta^2} \right)_{\theta,z} + \frac{2}{r} \left( \frac{\partial \gamma}{\partial r} \right)_{\theta,z} \right] = \left( \frac{\partial \gamma}{\partial \theta} \right)_{r,z} \quad (4-4)
\]

Although the solution of this equation is of academic interest only, it will be necessary to find a particular solution to evaluate the boundary conditions needed to solve equation (4-1).

The conditions at the interface between bulk-phase and adsorbent surface need to be described. It has been shown by several investigators that there exist two resistances, a film resistance
external to the absorbent particles as well as the intraparticle resistance itself. The rate of more adsorbable component flowing across the interface between these resistances is:

\[ K(x-x^*) = D \left( \frac{\partial y}{\partial r} \right)_{\theta,z,r=a} \quad (4-5) \]

where \( K \) = film coefficient of mass transfer, \( \text{ft/sec} \)

\( x-x^* \) = concentration difference proportional to the driving force giving rise to movement of more adsorbable matter across the phase boundaries.

In order to compute the driving force, \( x-x^* \), an equilibrium relationship is required. The simplest, but at the same time most inefficient, method is to assume linear equilibrium, which may in certain cases provide analytical solutions. However it is well known that linear equilibrium relations are good only for dilute gases or a very narrow range of concentration. Since it is typical to cover a wide range, particularly in liquid-phase adsorption, where the equilibrium is usually a complicated or non-linear function a solution to the model will be sought for any type of equilibrium curve. Even if a mathematical relation is unknown it should be possible by a numerical procedure to use an interpolation formula on a table of measured equilibrium data. The equilibrium equation will be given in a most general form: \( y = f(x^*) \)

For purposes of demonstration the equilibrium function may be changed to obtain solutions for a number of systems, without altering the overall method of solution.

Equations (4-3, 4-4, 4-5, and 4-6) simultaneously describe the
model of the adsorption process chosen for this investigation. These equations, along with the boundary conditions to be discussed in a later section, must be solved. Since a general equilibrium is assumed, the equations will require a numerical approach to the solution. As will be shown later, one of the boundary conditions, as far as it is known, also precludes any but a numerical solution. It is hoped that a convergent, stable numerical method may be found to permit an accurate and precise representation of the true process.

Before proceeding directly to a solution of the four equations, it will be highly convenient to find a set of dimensionless parameters whose substitution for the real variables will provide a solution independent of the physical properties of the process. Finding appropriate transformation equations is largely a matter of trial and error. Introduce three new parameters $T$, $H$, and $R$ which are related to the original variables $\theta$, $z$, and $r$ by these equations:

\begin{align*}
R &= r \cdot \frac{K}{D}, \quad \text{or if } r=a, \quad A = a \cdot \frac{K}{D} \quad (4-7) \\
H &= \frac{K V P}{(Q/S)a} \cdot z \\
T &= \frac{K^2}{D} \left( \theta - \frac{f v z}{Q/S} \right) = \frac{\Delta K}{a} \left( \theta - \frac{f v z}{Q/S} \right) \quad (4-9)
\end{align*}

By using the chain rule of differentiation:

\begin{equation}
\left( \frac{\partial y}{\partial r} \right)_{\theta,z} = \left( \frac{\partial y}{\partial R} \right)_{H,T} \left( \frac{\partial R}{\partial r} \right)_{H,T} \quad (4-10)
\end{equation}
From equation (4-7), and since $R$ is a function of $r$,
\[
\left( \frac{\partial R}{\partial r} \right)_{H,T} = \frac{K}{D} \tag{4-11}
\]

Then
\[
\left( \frac{\partial y}{\partial r} \right)_{\theta,z,r=a} = \frac{K}{D} \left( \frac{\partial y}{\partial R} \right)_{H,T,R=A} \tag{4-12}
\]

Substitution of equation (4-12) into equation (4-5) gives the following dimensionless form:
\[
x - x^* = \left( \frac{\partial y}{\partial R} \right)_{H,T,R=A} \tag{4-13}
\]

The intraparticle equation (4-4) may be transformed by the following procedure. The term, $\frac{\partial^2 y}{\partial r^2}$, is first put into dimensionless form:
\[
\left( \frac{\partial^2 y}{\partial r^2} \right)_{\theta,z} = \left[ \frac{\partial}{\partial r} \left( \frac{\partial y}{\partial r} \right) \right]_{\theta,z} = \left[ \frac{\partial}{\partial r} \left( \frac{\partial R}{\partial r} \right) \right]_{\theta,z} \tag{4-14}
\]

Since $\frac{\partial^2 R}{\partial r^2} = 0$ and $\frac{\partial R}{\partial r} = \frac{K}{D}$,
\[
\left( \frac{\partial^2 y}{\partial r^2} \right)_{\theta,z} = \frac{K}{D} \left[ \frac{\partial}{\partial r} \left( \frac{\partial y}{\partial R} \right) \right]_{\theta,z} = \frac{K}{D} \left[ \frac{\partial}{\partial R} \left( \frac{\partial y}{\partial R} \right) \right]_{\theta,z} \tag{4-14}
\]

then
\[
\left( \frac{\partial^2 y}{\partial r^2} \right)_{\theta,z} = \frac{K^2}{D^2} \left( \frac{\partial^2 y}{\partial R^2} \right)_{T,H} \tag{4-14}
\]

The term $\frac{\partial y}{\partial \theta}$ is readily changed to dimensionless form:
\[
\left( \frac{\partial y}{\partial \theta} \right)_{r,z} = \left[ \left( \frac{\partial y}{\partial T} \right) \left( \frac{\partial T}{\partial \theta} \right) + \left( \frac{\partial y}{\partial R} \right) \left( \frac{\partial R}{\partial \theta} \right) + \left( \frac{\partial y}{\partial H} \right) \left( \frac{\partial H}{\partial \theta} \right) \right]_{r,z} \tag{4-14}
\]
The last two terms on the right of this equation are zero and

\[
\left(\frac{\partial T}{\partial \Theta}\right)_{r,z} = \frac{K^2}{D}, \quad \text{so that,} \quad \left(\frac{\partial y}{\partial \Theta}\right)_{r,z} = \frac{K^2}{D} \left(\frac{\partial y}{\partial T}\right)_{r,z} = \frac{K^2}{D} \left(\frac{\partial y}{\partial T}\right)_{R,H}
\] (4-15)

Substituting equations (4-7), (4-14), and (4-15) into equation (4-4) results in

\[
\left[\frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \frac{\partial y}{\partial R}\right]_{H,T} = \left(\frac{\partial y}{\partial T}\right)_{H,R}
\] (4-16)

Equation (4-16) expresses the intraparticle diffusion in terms of the dimensionless parameters, \( R \) and \( T \), thus making its solution completely independent of the physical characteristics of any given process.

The bulk-phase equation is changed by computing the partial derivatives, \( \left(\frac{\partial x}{\partial z}\right)_{r,\Theta}, \left(\frac{\partial x}{\partial \Theta}\right)_{r,z} \), and \( \left(\frac{\partial y}{\partial r}\right)_{\Theta,z,r=a} \) in terms of the dimensionless parameters \( R, T, \) and \( H \):

\[
\left(\frac{\partial x}{\partial z}\right)_{r,\Theta} = \left[\frac{\partial x}{\partial T} \frac{\partial T}{\partial z} + \frac{\partial x}{\partial H} \frac{\partial H}{\partial z} + \frac{\partial x}{\partial R} \frac{\partial R}{\partial z}\right]_{r,\Theta}
\] (4-17)

\[
\left(\frac{\partial x}{\partial \Theta}\right)_{r,z} = \left[\frac{\partial x}{\partial T} \frac{\partial T}{\partial \Theta} + \frac{\partial x}{\partial H} \frac{\partial H}{\partial \Theta} + \frac{\partial x}{\partial R} \frac{\partial R}{\partial \Theta}\right]_{r,z}
\] (4-18)

\[
\left(\frac{\partial y}{\partial r}\right)_{\Theta,z,r=a} = \frac{K}{D} \left(\frac{\partial y}{\partial R}\right)_{H,T,R=A}
\] (4-12)

But since \( R \) is a function of \( r \) only and \( H \) is a function of \( z \) only, equations (4-17) and (4-18) become

\[
\left(\frac{\partial x}{\partial z}\right)_{r,\Theta} = \left[\frac{\partial x}{\partial T} \frac{\partial T}{\partial z} + \frac{\partial x}{\partial H} \frac{\partial H}{\partial z}\right]_{r,\Theta}
\] (4-19)

\[
\left(\frac{\partial x}{\partial \Theta}\right)_{r,z} = \left[\frac{\partial x}{\partial T} \frac{\partial T}{\partial \Theta}\right]_{r,z}
\] (4-20)
The partial derivatives \( \frac{\partial T}{\partial x}, \frac{\partial H}{\partial z}, \text{ and } \frac{\partial T}{\partial \theta} \) are evaluated from equations (4-8) and (4-9):

\[
\left( \frac{\partial T}{\partial z} \right)_{r, \theta} = \frac{K^2}{D} \frac{f_y}{Q/S} \quad (4-21)
\]

\[
\left( \frac{\partial H}{\partial z} \right)_{r, \theta} = \frac{K V_p \rho_b}{(Q/S)a} \quad (4-22)
\]

\[
\left( \frac{\partial T}{\partial \theta} \right)_{r, z} = \frac{K^2}{D} \quad (4-23)
\]

Substitution of equations (4-12), (4-19), (4-20), (4-21), (4-22), and (4-23) into equation (4-3) will result in the following transformed material balance for the bulk-phase:

\[
\left( \frac{\partial x}{\partial H} \right)_{\theta, r} = \left( \frac{\partial x}{\partial H} \right)_{T, R} = 3 \left( \frac{\partial y}{\partial R} \right)_{H, T, R=A} \quad (4-24)
\]

Equations (4-13), (4-16) and (4-24) involve only the dimensionless parameter \( R, T, \) and \( H, \) and with the proper boundary conditions and equilibrium relationship will constitute the mathematical model of the process under study. It is these equations for which a numerical technique must be found, as will be discussed in the next chapter. To summarize, the equations are repeated:

\[
x - x^* = \left( \frac{\partial y}{\partial R} \right)_{H, T, R=A} \quad (4-13)
\]

\[
\left[ \frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \frac{\partial y}{\partial R} \right]_{H, T} = \left( \frac{\partial y}{\partial T} \right)_{H, T} \quad (4-16)
\]

\[
\left( \frac{\partial x}{\partial H} \right)_{T, R} = 3 \left( \frac{\partial y}{\partial R} \right)_{H, T, R=A} \quad (4-24)
\]
3. Boundary Conditions

One of the major areas of difficulty in solving such models as derived in the last section is that of deriving the proper boundary conditions. In vapor-phase work the assumption is generally made that at the start, the bed is filled with fluid having concentration, \( y_0 \), for all levels. As the feed stream enters and displaces this original fluid the pore concentration in contact with feed is always \( y_0 \). Mathematically this condition is given (in terms of the dimensionless parameters) by the following statement:

\[
\text{at } T = 0, \ y = y_0, \text{ for all } \mathcal{H}
\]

In liquid-phase adsorption, it is more reasonable to state that the bed initially contains no fluid, i.e., that the bed is completely dry. Actually there is some gaseous fluid in the bed at the start, but liquid is assumed to fill the pore space as well as the void volume almost instantaneously and therefore the feed stream is now in contact with the pore fluid of the same composition as that of the feed. This condition holds for the front of liquid as it moves up the bed. Therefore at the liquid front, \( x = y \). Johnson, in his study (30), found that the wave front was definable mathematically by the equation \( \mathcal{H} = T \). However when the additional variable, particle radius, is introduced, it can be shown that this boundary equation is no longer applicable and a new one has to be obtained. It may still be assumed that the pores at the liquid front are filled with liquid of bulk composition \( x \), i.e., \( y = x \) at the wave front (for all \( r \)). In order to find the correct equation describing the wave front in terms of the new dimensionless parameters, an equation describing the time elapsed when the
bed is filled to depth $z$ is stated by:

$$
\theta = \frac{z}{Q/S} (f_v + V_p \rho_b) \quad (4-25)
$$

The term, $(f_v + V_p \rho_b)$, gives the total space occupied by liquid per cubic foot of bed depth. Rearrange equation (4-25) as follows:

$$
\theta - \frac{f_v}{Q/S} z = \frac{V_p \rho_b}{Q/S} z
$$

Multiply through by $\frac{K^2}{D}$:

$$
\frac{K^2}{D} \theta - \frac{K^2}{D} \cdot \frac{f_v}{Q/S} z = \frac{V_p \rho_b}{Q/S} \cdot \frac{K^2}{D} z
$$

From equation (4-9), the left hand side is $T$:

$$
T = \frac{V_p \rho_b}{Q/S} \cdot \frac{K^2}{D} z
$$

Since $H = \frac{K V_p \rho_b}{(Q/S)a} x$, the right hand side may be written in terms of $H$:

$$
T = H \cdot \frac{aK}{D}
$$

Let $\frac{aK}{D} = A$, where $A$ is the dimensionless particle radius at the sphere surface. Then

$$
T = HA \quad (4-26)
$$

Equation (4-26) is a statement of the wave front in the dimensionless variables along with the boundary condition: at $T = HA$, $x = y$ for all $R$. An analytical solution using a boundary condition of this type is probably very complex if not impossible. No solutions using this type of boundary conditions have been seen in literature.

The other boundary condition, at the feed inlet is straightforward: at $z = 0$, $x = x_F$ for all $\theta \geq 0$, or in terms of the variables
T and H:

at H = 0, x = x_F for all T ≥ 0

Now the problem may be solved provided a suitable numerical method can be found. The following chapter will illustrate a means of accomplishing a solution through numerical analysis.
V. SOLUTION OF ADSORPTION MODEL BY NUMERICAL METHODS

The numerical solution of a system of non-linear differential equations is often a rather tedious, time-consuming trial-and-error procedure. There has been little success in the numerical analysis of non-linear systems, and the final solution, if one can be found, rests upon considerable computational experimentation (11). In this work the solution, represented by a set of curves relating the dimensionless parameters \( A, H, \) and \( T \), to liquid concentration, was effected by taking advantage, in part, of certain well-established techniques for linear equations. The criteria ensuring convergence and stability for linear equations, cannot usually be guaranteed for a non-linear system such as that encountered in this research project. However, it can be reasonably expected that in those problems representing physical processes a sufficiently accurate solution will have been reached if the variation of increment size and precision over a considerable range results in essentially the same answer (40). Several trial runs were made with different values of the finite dimensionless time increments and with precisions of eight and sixteen digits to check the accuracy of the computer solutions. A comparison of results using four increment sizes and at both precisions is given in Table I of Appendix A. In all cases an attempt was made to yield an approximation of the true solution that was accurate to within one per cent, which is sufficient for the type of process under consideration.
1. **Numerical Analysis**

The typical numerical approximation procedure involves scanning a grid of sufficiently small mesh size and calculating enough single points to cover the range of parameters involved. Many unforeseen problems, not only of a mathematical nature, but practical ones as well, can be expected to arise in the initial attempt to solve any system of differential equations. Even if a convergent, stable numerical method is known, there are also problems of computer storage and speed to be overcome. It is not difficult to tax the capabilities of the largest and fastest machines now in existence. The mathematical problem to be solved in this research is definitely reserved for a fast computer, since several million arithmetic operations are executed in even the simplest case.

In finding a solution to the adsorption model, the following approach was taken. The desired complete solution is a value of \( x \), liquid-phase concentration, for all possible values of the dimensionless variables, \( A, H, \) and \( T \). In this case a three-dimensional grid is necessary. In practice it is necessary to consider only one value of the radius parameter, \( A \), at a time, and for this particular value, compute a complete set of curves for various \( H \) and \( T \). At a given \( A \), the resulting two-dimensional grid can be shown to have a triangular shape, due to the nature of the boundary conditions (30). To illustrate this a sketch of a partial grid at some constant \( A \) is given below:
The position of the line representing the liquid front as it rises through the adsorption column depends upon the value of $A$. All area to the right of the boundary line represents unfilled adsorbent ahead of the liquid front.

To obtain a solution, a systematic method must be derived using all available information. At the outset, when the liquid first enters at the bottom of the bed, the concentration is that of the feed, $x_f$. Thus $x_{1,1} = x_f$. The points corresponding to the bottom of the bed at all later $T$ are positioned along the first column of the sketch ($j = 1$), and thus have a value, $x_{j1} = x_f$, as specified by the boundary condition. The numerical value of all remaining points on the grid, except for column 1, must be determined by numerical means, and as will be seen, the procedure for obtaining these points involves considerable computational effort. Furthermore, certain points require special treatment. A brief discussion of the start of the solution is given in the following section. It would be impossible to include all of the
computational details here, although it should be possible for one who desires to use this approach to obtain all the necessary information from the computer program and flow diagram.

Although the bulk-phase concentration is of primary interest, it is necessary at each stage of computation to compute a solution for the adsorbed-phase concentration. The purpose of the adsorbed-phase solution is to provide a value of \( y \), in equilibrium with \( x \), at the interface. The equilibrium relation gives a value of \( x^* \), which is necessary in the bulk-phase equation.

2. Solution of Adsorbed-Phase (Diffusion) Equation

The most widely-used approach to the numerical solution of the diffusion equation is the selection of a suitable finite-difference equation. The procedure selected for this study is an implicit finite difference method, which as the name implies, involves the solution of a set of simultaneous equations. However, in the case of linear partial differential equations, this method is both convergent and stable (5,11), and the computational aspects are relatively simple. The boundary conditions for this equation require special treatment at the pore opening and at the center of the sphere. The derivation of the finite difference equations is shown in Appendix A.

For an interior point along the pore radius the resulting difference equation is:

\[
y_i = \frac{m(1 - 1/i)y_{i-1} + m(1 +1/i)y_{i+1} + y_i}{(2m + 1)}
\]  

(5-1)

where \( y \) = adsorbed phase concentration at time, \( T + \Delta T \)
\[ y' = \text{adsorbed phase concentration at time, } T \]
\[ i = \text{subscript denoting position along pore radius} \]
\[ m = \text{ratio, } \Delta T/(\Delta R)^2 \]

The corresponding equation for the center of a sphere (at \( R = 0, i = 0 \)) is:

\[
y_o = \frac{6my_1 + y'_1}{1 + 6m} \tag{5-2}
\]

The boundary point involves the concentration gradient at the entrance to the pore and is given by:

\[
y_n = \frac{2my_{i-1} + y'_n + 2(x - x^*)m \cdot (1 + 1/n)\Delta R}{(1 + 2m)} \tag{5-3}
\]

where \( x - x^* = \text{concentration difference in bulk phase proportional to gradient at pore opening} \)

\[ n = \text{number of finite intervals into which pore radius is divided} \]
\[ \Delta R = \text{length of one interval} \]

The maximum error bounds for equations of this type have been shown to be of the order of \((\Delta R)^2\), or less, for any given time level and of \((\Delta T)\), or less, for changes in time \((33)\). No exact limits on the error can be given, although it can be assumed that since the true solution represents a reasonably well-behaved process, the higher order derivatives are small, therefore the actual error is likewise small.

A comparison of computed solutions of the diffusion equation for different values of \(\Delta R\) and \(\Delta T\) in Table I of Appendix A show that the actual error is much less than the limits allowed by numerical analysis. This permits use of larger increment sizes without affecting the overall accuracy of the result, within one per cent.

To solve the diffusion equation it is necessary to obtain a set of values, \(y_0, y_1, \ldots, y_{n-1}, y_n\), along the pore radius. Actually
the only point of interest is the value of $y_n$ at the pore surface, as well as the gradient at the surface, $\left(\frac{\partial y}{\partial R}\right)_{R=A}$. This point is used to obtain $x^*$ from an equilibrium relation, which gives the driving potential $x - x^*$ needed in the solution of the bulk-phase equation. Solution of the set of $n+1$ simultaneous equations (Eq A-16) which were derived for the pore is relatively straightforward, except that a value of $x$ must be assumed. As will be shown later, this procedure involves considerable iteration at every grid point, in which the set of pore equations must be re-solved several times.

3. Solution of Bulk-Phase Equation

The final solution of the problem for a given parameter, $A$, is obtained from the overall bulk-phase material balance equation. A numerical solution may be considered complete when the adsorption wave reaches steady state; however, in order to compare experimental results with computed results does not require the complete solution if the actual experiment does not reach steady state. In the work of Johnson (30) the data were obtained before steady state was reached. Other experimenters cited allowed the system to reach steady state (43,1,2,22,16,17,18).

The procedures for solving the bulk-phase equation will be explained briefly. Points along the diagonal, $AH = T$, and along columns one and two of the triangular grid require a modification of the general methods used for an interior grid point.

In column one, which corresponds to feed entering the adsorption bed, the values of bulk concentration are known: $x_{j,1} = x_f$. 

However it is necessary to have the concentration, $y_n$, at the surface of the particle in order to obtain the solution at the next bed level, i.e., at $i = 2$. The procedure for obtaining $y_n$ at the feed inlet for all later time values can be summarized as follows:

(a) Assume initial estimate of surface concentration, $y_n^{(0)}$

(b) Calculate $x^*$ from equilibrium function: $x^* = f(y_n^{(0)})$

(c) Calculate $x_f - x^*$

(d) Solve diffusion equation using the above estimate of $x_f - x^*$. This gives a new estimate, $y_n^{(1)}$

(e) Compare the assumed $y_n$ with that calculated in solution of diffusion equation. If the two figures are sufficiently close, the solution at this one point is complete.

(f) If the two figures do not balance, adjust the estimate of $y_n$ by a convergence factor, $q$:

$$y_n^{(2)} = y_n^{(0)} + (y_n^{(0)} - y_n^{(1)}) q$$

(5-4)

Repeat the computations from step (b), using $y_n^{(2)}$ as $y_n^{(0)}$.

At the completion of the above approximation for $y_n$ (at point $j,1$), the entire procedure must be repeated for $y_n$ (at point $j+1,1$) which corresponds to the next time level. In order to calculate $y_n$ at any later time step it is necessary to save the entire diffusion curve (as a sequence of points) from the preceding time level, as each of these values is necessary in solving the diffusion equation. As will be seen later, it is also necessary to save the quantities $x$ and $x^*$ for use at higher bed levels. The extent to which the solution steps are carried out along the $T$-axis depends upon the nature of the system being studied. The computer program was so designed to discontinue the above procedure after $y_n$ approached its equilibrium value with $x_f$ at any given dimensionless bed level, $H$, within a pre-determined tolerance.
At this point it can be assumed that the adsorbed phase concentration will remain constant at its equilibrium value.

It is next possible to estimate the bulk phase concentration along column two of the triangular grid. This corresponds to the second dimensionless bed level over a range of time starting with $T = \Delta T$. The procedure for evaluating $x_{2,2}$ is also iterative, but slightly different from the preceding discussion for the first bed level. First an estimate of $x_{2,2}$ is made by fitting a first-order equation over the interval from $H = 0$ to $H = \Delta H$, with error bound of magnitude $(\Delta H)^2$. This estimate is obtained from the bulk-phase material balance:

$$\left(\frac{\partial x}{\partial H}\right)_{T,R} = -3 \left(\frac{\partial y}{\partial R}\right)_{H,T,R=A}$$

(4-24)

The right hand term is equal to $3(x^*-x)$. The first-order approximation is thus:

$$x_{2,2}^{(o)} = x_{2,1} + 3(x - x^*)_{2,1}\Delta H$$

(5-5)

Using $x_{2,2}^{(o)}$ a better estimate, $x_{2,2}^{(1)}$, can be obtained by means of a second-order formula, with error of order $(\Delta H)^3$. This formula can be applied repeatedly until $x_{2,2}$ is determined within a specified tolerance. The second-order equation requires a value of $\frac{\partial x}{\partial H}$ at both grid points (2,1) and (2,2). Using the estimated $x_{2,2}$ from the first order equation, an estimate of $x^*_{2,2}$ is made, since it is known that $x_{2,2} = y_{2,2}$ from the model, and that $x^*_{2,2} = f(y_{2,2})$, from equilibrium data. Now it is possible to get a new estimate of $x_{2,2}$:
\[ x^{(2)}_{2,2} = x_{2,1} - \frac{3}{2} \left[ \left( \frac{\partial y}{\partial R}_{2,1} \right) + \left( \frac{\partial y}{\partial R}_{2,2} \right) \right] \Delta H \]  
\hspace{2cm} (5-6)

or

\[ x^{(2)}_{2,2} = x_{2,1} + 1.5 \left[ (x^* - x)_{2,1} + (x^* - x)_{2,2}^{(1)} \right] \Delta H \]  
\hspace{2cm} (5-7)

The new estimate of \( x_{2,2} \) may be used to refine the term, \((x^* - x)_{2,2}\), and repeat calculations until no further improvement in \( x_{2,2} \) occurs.

During this stage it is not necessary to solve the diffusion equation as the initial distribution of concentration is equal to \( x \) at that point. In order to compute a distribution at the next step (time level 3), the initial distribution within the pore must be defined; i.e.,

\[ y_k = x_{2,2} \quad (k = 0, 1, \ldots, n). \]

The remaining grid points of column two of the triangular grid may be solved by a procedure, which turns out to be double trial-and-error. This happens because two unknowns, both \( x_{j,2} \) and \( y_{j,2} \) must be determined. Basically both \( x_{j,2} \) and \( y_{j,2} \) are estimated. For the estimated \( y_{j,2} \), the corresponding \( x_{j,2} \) is computed by essentially the same means as for point (2,2). This value of \( x_{j,2} \) is then used in solving the diffusion equation to obtain a better estimate of \( y_{j,2} \) as was done for column one, which in turn refines \( x_{j,2} \). After both \( x_{j,2} \) and \( y_{j,2} \) compare favorably with previous estimates, the procedure is repeated for point \((j + 1,2)\), and carried out for successive \( j \)'s until \( y \) is sufficiently close to \( y^* \), in equilibrium with \( x_f \). At each higher time level, the preceding adsorbed-phase distribution must be saved for at least one additional time level. Likewise the term \( x - x^* \) for each point along column one must have been previously saved. As calculations progress column-wise, older terms may be replaced by newer ones as
needed. In terms of computer storage, it is necessary to conserve space, so that only those quantities which must be kept for later use are saved. For instance when the solution for column three has been completed, it is no longer necessary to save the contents of column one. As will be shown it will be necessary to retain only columns two and three to find the solution to column four.

The calculation of remaining grid points, including the diagonal elements, follows a general procedure, described briefly below. The diagonals are obtained by a method similar to that for point \((2,2)\), except that from now on a third-order method is used, with error of order \((\Delta H)^4\). Using a third order integration formula requires that \(x\) and \(x^*\) from two preceding columns must have been retained in computer storage. The third order integration formula used was as follows (where \(3 \leq i\)):

\[
x_{i-1,i}^{(1)} = x_{i-1,i} - 3\Delta H \left[ \frac{5}{12} \left( \frac{\partial y}{\partial R} \right)_{i,i} + \frac{8}{12} \left( \frac{\partial y}{\partial R} \right)_{i-1,i} - \frac{1}{12} \left( \frac{\partial y}{\partial R} \right)_{i-2,i} \right]
\]

which becomes, after substitution of equation (13):

\[
x_{i-1,i}^{(1)} = x_{i-1,i} + \frac{\Delta H}{4} \left[ 5(x^*-x)_{i,i}^{(0)} + 8(x^*-x)_{i-1,i} - (x^*-x)_{i-2,i} \right]
\]

In the above equation it is necessary to guess \(x_{i,i}^{(0)}\), get \((x^*-x)_{i,i}\) from equilibrium relations, then compute \(x_{i,i}^{(1)}\). This value may be employed in turn on the right hand side until the desired balance is reached. As in the case of grid point \((2,2)\) the pore-phase distribution is constant at the diagonal: \(x_{i,i} = y_k\) \((k = 0,1,2,\ldots,N)\).

The remaining points along column three and all higher-numbered
columns are solved by double trial-and-error in a manner similar to that described for column two. The only difference is that a third-order integration formula is applied, requiring the terms, \((x^* - x)\), from two preceding columns. The general procedure is the same: to guess both \(x_{j,i}^{(0)}\) and \(y_{j,i}^{(0)}\), compute a refined value of \(x_{j,i}\), then solve the diffusion equation for a new \(y_{j,i}\). These two new values of \(x\) and \(y\) may be used as initial estimates for further iteration until a balance is achieved.

The overall solution, using the above-described methods is obtained columnwise, that is, the entire history of the bed at a given dimensionless bed level is computed. The bed level is incremented by \(\Delta H\) and the same process repeated. The net result is a family of curves of \(x\) versus \(T\) for various \(H\). A typical solution is shown in Figure 4, in Appendix B. The complete solution to the problem is three-dimensional and would be a family of figures, each one for a value of the parameter \(A\). The results of these calculations will be discussed in the next chapter. Before proceeding with the results, however, a few salient features of the numerical procedure should be described. The practical aspects of this method are of special interest, particularly the computational effort required.

4. Discussion of Computational Problems

The amount of computer time required to solve the problem is of primary concern, and it is almost exactly proportional to the number of iterations; thus every effort needs to be made to keep the total number of iterations at a minimum, yet produce the required accuracy in
the solution. In addition the number of intervals chosen for the
diffusion equation affects overall computing time. At first it might
appear that an increase in step-size in either the H-direction or the
T-direction would reduce the total effort involved. However it has
been observed that if step-size is increased, the number of iterations
in the trial-and-error procedure may also increase, so that very little
net savings in time is realized. One of the most critical values
affecting the rate of convergence, is the damping factor used to adjust
the estimated value of y for iteration purposes. It has been found
that for some values of this factor, an excessive number of iterations
is required, and even in some cases divergence was observed. It is
mostly a matter of trial-and-error to find an optimum factor, which if
too small, could increase the number of iterations, and if too large
cause divergence. Generally a factor between 0.2 and 1.0 was sufficient
to produce relatively rapid convergence. However in the region of most
rapid mass transfer (along the straightest and steepest portions of the
adsorption wave) between ten and thirty iterations was usually required.
In addition to the damping factor, the number of iterations is affected
to some extent by the closeness of estimate required for both x and y
at each grid point. It was concluded that these tolerances should all
be such that the overall solution should be significant to within one
percent.

Even with iteration tolerances small enough to balance the
estimates of x and y to many significant digits, the truncation error
of the numerical integration formulas and finite difference equations
must be considered. Although the maximum bounds for linear systems (11)
are stated, they are assumed to be valid for this particular adsorption model. The process is observed to produce relatively smooth variations in each of the parameters, and hence, follows to some extent the bounds given for a truly linear process. It was found that the actual truncation error was much less than the maximum; this is probably due to a relatively small higher derivative corresponding to the order of the error. Only numerical experimentation can support the validity of the results, and this was done for a fairly wide range of each of the factors affecting accuracy.

That the method is stable and convergent can be presumed, since the results behaved as expected, as well as the fact that the solution converged as the increments $\Delta H$, $\Delta R$, and $\Delta T$ were decreased. The only item found to be critical in producing a stable result is the damping factor described previously. It is conceivable that some very wide variation in parameters or unusual equilibrium could make the process unstable, although such was not the case for any of the runs made in this study, provided a suitable damping factor was used.

The computer time required for the solution of the model for a given $A$ was noted to be roughly proportional to the magnitude of $A$. The shortest times were approximately one hour for values of $A = 1$ or less, and increased to a maximum of 6-8 hours for the largest values of $A$ studied.

5. **Computer Program**

The application of a computer in any situation requires that, once a problem has been defined mathematically, the numerical procedure
be stated in terms of machine operations. The basic computer opera­
tions, known as machine language instructions, may be organized into a
logical arrangement, or program, to solve the numerical problem. In­
stead of coding the machine language program, which is a very arduous
task, an algebraically-oriented language, called FORTRAN, was used (29).
The computer procedures may be stated in FORTRAN and translated into
the basic computer instructions. The major advantage of this method,
is that once the problem is written in FORTRAN, almost any computer
may be used without the necessity of re-programming. Furthermore it is
much simpler for one to scan a FORTRAN-coded program in making any
desired changes or corrections. There are many more persons with a
reasonable knowledge of FORTRAN than of basic machine language, particu­
larly in the sciences. Even though it is relatively simple to code a
numerical procedure in FORTRAN, the complexity of the program used in
this research is considered great enough to be included for reference
purposes, in Appendix C. One of the main features of this program is
the procedure by which the instructions for computing equilibrium rela­
tions are handled. The equilibrium calculations are set apart from the
main numerical procedure in a "subroutine." Any time a change in the
equilibrium function is desired (such as changing adsorbent material) it is a simple matter to replace only those FORTRAN instructions per­
taining to the equilibrium function, without disturbing the main
portion of the program. Many reference books and manuals give basic
instruction in efficient organization of a computer program (28,39,41).

The computer used for solving the numerical procedure de­
scribed in preceding sections was an IBM 7040 data processing system
at the Computer Research Center of Louisiana State University. It was with the anticipated use of a large-scale computer that this research project was undertaken. A brief description of the machine configuration, along with instructions for running the program are included in Appendix C.
VI. DISCUSSION OF RESULTS

1. Presentation of Calculations

Computed solutions for the proposed model for four binary, liquid-phase systems have been obtained. The results are basically a set of tables for each run made, a sample of which is found in Appendix C. However the tabular form is much too bulky to present here, being of the order of a thousand pages; instead the solutions are given as a set of curves in Appendix B, Figures 4 through 32. Table II summarizes the characteristics of each system studied. The main disadvantage of a numerical solution is that no concise algebraic formula relating all variables can be obtained. This means that it is necessary to interpolate or re-run the problem each time a change in one of the variables is made. The problem of handling the large volume of output from a computer has been met in part by the use of modern, highly compact storage devices such as magnetic tapes or disks.

The object of this work is to seek a satisfactory comparison between theoretical and experimental curves without necessarily covering a wide range of parameters. The curves presented in Appendix B reflect a number of trial runs made to search for the optimum solution. As will be discussed later the optimum is reached when an experimental set of data fits closely the computed results. In Figures 4 through 32, the computer solutions are solid lines, while real data, converted to dimensionless form, for the corresponding system are plotted as
points for comparative purposes. In order to clarify the comparisons some discussion of the physical meaning of the dimensionless parameters A, H, and T is needed.

2. **Physical Significance of the Dimensionless Variables A, H, and T**

The use of the dimensionless variables, A, H, and T, should be made with some understanding of their relation to the true variables, particle radius, bed height and time elapsed from startup, as stated in Equations (4-7), (4-8), and (4-9).

The dimensionless parameter A is directly proportional to the real particle radius, a. If a particular system is considered, then A is fixed for all operating conditions, assuming constancy of K and D.

The dimensionless parameter T is related to actual time, as follows. The term, \( \frac{F_y}{Q/S} \), is seen to be the void volume (this does not include pore volume) divided by a flow rate, which is the same as the time required to fill the void volume of bed to depth z. This term, subtracted from total elapsed time, \( \Theta \), gives the time which exceeds that required to fill the void volume to depth z. T is proportional to this excess time, the proportionality factor being \( K^2/D \).

The dimensionless bed depth, H, is directly proportional to bed level, z. The family of curves at constant H thus provide a history of concentration at any bed depth, when the proportionality factor, \( \frac{KV}{a(Q/S)} \), is known. The H-curve corresponding to total bed depth should thus correlate with the experimental measurement of concentration in the effluent over a period of time. A key point to remember is, that if the proposed model holds, the first drop of effluent is also at the liquid front. This means that the initial concentration measurement
should fall on the boundary curve. Hence the minimum possible values of $T$ and $H$ are defined.

3. Behavior of Computed Adsorption Curve

The computed solutions which are shown in Figures 4 through 32 all have a similar appearance, as would be expected from theoretical considerations. The reasons underlying the particular shape of these curves merit some qualitative discussion. Comparison of actual with theoretical curves will be treated in a later section. A sketch, as shown in Figure 1, of the concentration relationships will assist in explaining the dynamic processes involved from initial start-up to steady-state operation.

Figure 1. Equilibrium and Operating Lines for a Typical Case.

The computed curves, as well as the experimental results, are all noted to follow a general pattern in which the first few curves are
strongly concave toward the T-axis, followed by a set of curves showing a slight convexity at low concentrations, and finally, at steady-state a pronounced "S" shape in which the only change is physical displacement of the ultimate curve, or wave, along the T-axis. If the sketch is observed, several implications may be made. It is obvious that the steepness of the curves at any given point is directly related to the rate of mass transfer through the bulk, or unadsorbed, phase. This rate is proportional to the terms, \(x - x^*\), which can be shown on the sketch above as a series of horizontal lines. The line, \(x = y\), is shown, which gives the status of the wave front at any instant. Operating lines, as for example, lines, KA, KC, KE, KI and KL, may be drawn for any depth position within an adsorbent bed. It has been shown for a process of this type that the operating lines are straight (30).

At initial start-up (that is, when feed first contacts the bottom of the adsorbent bed) the maximum driving potential is created at the bed inlet, or \(H = 0\), as shown by the line, AB, between \(x_f\) and \(x^*_1\). This relationship would hold for a point plotted on the upper lefthand corner of the computed curves, at \(x = x_f\) and \(T = 0\).

As time progresses the bulk phase concentration at \(H = 0\) remains at \(x_f\), but the adsorbed phase concentration, \(y\), rises and approaches \(y^*\), the equilibrium value with respect to \(x_f\). The horizontal distance between the vertical operating line for \(H = 0\) and the equilibrium curve (line GH) slowly decreases until the pores are completely saturated with the equilibrium concentration, \(y^*\). Further diffusion will not occur within the adsorbent material at the bed
inlet, and the liquid concentration will remain at $x_f$.

As adsorption proceeds the wave-front concentration diminishes with $T$, as shown by the envelope curve convex toward the origin at all times. The space to the left of this curve represents that portion of the bed not yet reached by the liquid front as it travels up the column. This curve is useful in comparing results at different particle sizes, as will be discussed later. The envelope curve also may be used as an indicator of the approach to steady-state, as it has been observed that by the time this curve reaches a low value of $x$, in every case the adsorption wave is fully developed into its ultimate form.

At slightly higher bed levels, represented by curves at constant $H$, the driving force at the wave front, given by line CD, is large, which results in a very steep adsorption curve. The approach to equilibrium, as transfer of material from bulk to adsorbed phase takes place, is shown as the curve bends over to the right and approaches the line, $x = x_f$, asymptotically. The driving potential, as represented by horizontal lines between the operating lines and equilibrium curve gradually diminishes and become zero when the bulk concentration has reached $x_f$. The adsorbent bed is saturated at this level and fractionation has likewise stopped.

The behavior described above continues for some distance into the bed, but the curves become less and less steep. This is explained by the shorter horizontal distances between the operating line for a particular bed level and the equilibrium line. At some position in the bed an interesting change is noted. The adsorption waves begin to
show as light convexity near the boundary curve. Note that the slope of the equilibrium curve at point J is larger than the operating line corresponding to this bed level. Initially a much smaller driving potential (shown by line IJ) is noted. However, as adsorption occurs, causing higher bulk concentrations, the length of the horizontal lines between the operating line and equilibrium is seen to increase, thus more rapid transfer will occur. This results in a relatively small slope initially, then a steeper slope during the period of high transfer rate, followed by a curvature toward the right as the process nears completion. Eventually the operating line KL, at infinite bed depth, will be reached; this corresponds to steady-state, in which all curves will be the same. In practice the final operating line is reached at some finite distance into the bed, and correspondingly, the adsorption curves have reached an ultimate, or unvarying shape. This final wave shape can be observed to travel down the bed intact, the width of the wave denoting that portion of adsorbent in which mass transfer is actually occurring.

It should be readily apparent from the foregoing discussion that the equilibrium curve is a major factor in controlling the adsorption process. As with any rate process, the closer the equilibrium line to the operating line, the more difficult is the job of separating two components. Previous attempts to study the kinetics of adsorption using straight equilibrium relationships can be seen to give results far different from those presented herein. As shown in Figure 33, computer runs using true equilibrium curves for three different substances were observed to be quite different with respect to the calculated results, for \( A = 1 \) and \( H = 2 \).
If the effect of particle size upon adsorption is to be analyzed, several values of the dimensionless radius parameter, A, must be considered simultaneously. Figure 34 shows how particle size, which is proportional to A, influences the rate of adsorption, hence the relative difficulty of separation. Comparison of slopes shows that the curves are flatter the higher the value of A, which is directly proportional to physical diameter of adsorbent particles. As expected, where intraparticle diffusion is found to affect rate, in other words, at higher particle radii, the longer diffusion path requires more time to come to equilibrium, hence the flattened curves. Note that it requires considerably longer for the wave front curve to fall to a specified level because there is much less tendency for internal diffusion to produce equilibrium. As a result one must anticipate a much wider adsorption zone for large particles. It is realized that there must be an economic balance between the high pressure drop in small particle beds and the extra adsorbent needed for the more difficult separations in beds of large particle size. Whatever particle size is selected for use, it will be seen that the radius variable will be taken into account when experimental data are compared with theoretical results.

If the dimensionless parameter A is decreased, as shown by Figures 23 and 24, it is observed that the adsorption waves approach a constant shape when one plot is compared with another. This phenomenon should be anticipated however, when the qualitative nature of the process is recalled. At lower and lower particle diameters the diffusion mechanism plays a progressively smaller role, and in the limit (at $A = 0$)
there is no diffusion occurring, the entire resistance being due to
the surface film. However the model breaks down mathematically at
$A = 0$, and only the approach to zero radius may be studied. At low
enough radius, the present model should become similar to the one pro­
posed by Johnson. Furthermore one should not expect any improvement
of the new model over that of Johnson at low radii, the latter model
assuming an infinitely rapid intraparticle diffusion rate. Also, the
physical properties of any system under investigation would determine
what actual particle size would be sufficiently small for this effect
to be neglected, so that a model such as that proposed by Johnson,
could be used.

4. The Mass Transfer Coefficient, $K$

One of the principal objectives of this study is the determina­
tion of a suitable mass transfer coefficient so that a practical esti­
mation of operating conditions, and bed height, can be given. The
primary purpose here is to demonstrate an improved method for taking
into account additional factors not previously considered in evaluating
$K$. The ultimate goal of any such work is to reduce or eliminate the
necessity of time-consuming and expensive developmental or pilot-scale
projects. In particular, it is anticipated that a small fixed-bed
plant which is cheaper, easier to build and operate, and capable of
more accurate measurements, can be used to predict design factors for
a moving-bed, countercurrent process. Even for commercial fixed-bed
design, a few tests with bench-scale equipment should suffice to pre­
dict performance of the larger plant. Other factors, such as time to
reach steady-state after start-up, bed depth required to reach steady-state, and percent of unused adsorbent at point of breakthrough, should be determinable from bench-scale tests. Naturally the validity of such procedures depends not only on previously noted assumptions, but on scale-up considerations as well. Problems of feed distribution, wall effects, and channelling, which alter the assumption of a plug-like velocity profile, remain to be considered; these effects generally are more severe in the case of moving beds. The existence of axial diffusion is also a factor which may affect the larger bed.

It has been fairly well established that the mass transfer coefficient is strongly dependent on numerous physical and geometric properties and care must be taken in its use. Even with the inclusion of intraparticle diffusion in the present model, there are many unknowns yet to be found. If the range of conditions covered during bench-scale studies is not too far different from those to be encountered in the large plant, it has frequently been found that actual performance of the large plant is relatively close to predictions. Further theoretical treatment should make these design estimates even more reliable. Fortunately in liquid adsorption the relative velocity of the liquid and solid phases remains constant. The dependency of $K$ on velocity is thus eliminated if the bench-scale and large plant are operated at the same rates. Likewise the effect of particle size and/or geometry can be eliminated if the same material is used for both small and large plants. Any variation of $K$ with concentration will be more difficult to handle. As there has been no satisfactory quantitative analysis of concentration effects on $K$, it should be required that
K either not vary greatly over the ranges of concentration involved or that both the experimental and full-size plants be operated over similar ranges. The actual determination of K from computed and real data will be elaborated upon in the following section.

5. **Comparison of Computed and Experimental Curves**

The theoretical solutions found involve the parameters A, H, and T as defined previously. To convert these results into the terms of actual time, particle radius, and bed depth requires knowledge of the mass transfer coefficient, K, and the effective internal diffusion constant, D. Johnson (30) showed that the value of K may be determined in a trial-and-error procedure of matching experimental with theoretical curves. To do this a value of K was selected so that a curve of T versus X could be converted into \( \Theta \) versus \( x \) by means of the transformation equation. That value of K which produced the closest match of theoretical with experimental curves was selected as the proper mass transfer coefficient for the system under investigation. The criterion of best fit, used by Johnson, was to find a K so that the position of the two curves was the same on a plot of \( x \) versus time (or equivalently, effluent volume). In theory the shape of the theoretical and real curves should have been identical at the same position. In other words there should be some K which gives one curve representing both experimental and theoretical relations. As an example, in Figure 2, \( K_4 \) would be the selected value for the ideal system following Johnson's model. In this illustrative sketch which does not represent any particular system, theoretical curves are solid lines, and experimental data
plotted as circles. The three experimental curves shown in Figure 2 could represent the same system, plotted for different trial values of K.

Figure 2. Method Illustrating Comparison of Computed and Experimental Results (Not Actual Data).

In Figure 2 the lines of constant K are also lines of constant H, because the two are directly proportional to each other. The line matching experimental data with theory is therefore a representation of the adsorption wave at the outlet.

In practice Johnson discovered that no exact match of the actual with theoretical curves could be found. In general, the experimental curves which gave the best fit were somewhat flatter than the theoretical curves. It was because of this fact that Johnson concluded
intraparticle diffusion affected those adsorption systems which he investigated and further recommended that additional theoretical treatment involving this mechanism was necessary.

When intraparticle diffusion is considered, a similar matching procedure can be employed, but it is considerably more involved because of the added parameter, $A$. The following discussion describes briefly how the value of $K$ is determined in the model proposed in this study. Stated briefly, the procedure involves finding the best match, not only on one set of curves but from all curves using any combination of $H$, $T$, and $A$. The problem becomes essentially three-dimensional in scope.

Initially a solution for a selected choice of $A$ is computed. The best match is then formed between theoretical and experimental results. Since the right choice of $A$ is not known, it should not be expected that a very good match will be obtained on the first try. Figure 4 shows the closest match for the value of $A = 1$ for the system, methylcyclohexane-toluene on silica gel at a feed concentration, $x_f = .5$ (Curve A). It is obvious that the fit is unsatisfactory and other values of $A$ should be tried. Whether to increase or decrease $A$ is largely a matter of conjecture. When $A = 5$ was tried, the resulting computer solution was seen to fit the experimental data best at $K = 0.82 \times 10^{-3}$ cm/sec. It was noted that the two curves matched somewhat better than in the previous case. With this information in mind, $A$ was increased and the problem re-run several times. Up to a certain point it was observed that the computer curves matched actual data better with increasing $A$, but after a point, further increase of $A$
yielded poorer comparisons. Hence, the proper choice of $K$ would be from the set of curves for that value of $A$ producing the closest relationship between theory and experiment, provided the model holds. For the case of methylcyclohexane-toluene on silica gel at 0.5 feed concentration, the best match was found to be near $A = 50$, with average $K = 2.54 \times 10^{-3}$ cm/sec, as shown in Figure 9. Other runs at $A = 0.01, 0.1, 10, 20, 40, \text{ and } 60$ were made in attempting to find the best fit. Substantial improvement in matching curves is seen by comparing Figure 9 ($A = 50$) with Figures 35 and 36, obtained from Johnson’s work (30).

Of particular interest is the constancy of $K$ with a change in bed height. An additional experimental run at a different bed level demonstrated that it is possible to obtain approximately the same $K$ through a similar matching procedure (Curve B in Figures 4-11). Figure 9 shows results at the selected optimum fit, for both runs. An experiment of this type tends to support the assumption neglecting longitudinal (axial) diffusion, at least between the two bed heights illustrated, and for the system considered. Over much wider lengths of bed such an assumption may not hold, since it is almost certain axial diffusion can and does occur. One of the systems studied, as will be mentioned later, may have displayed such lengthwise diffusion.

Film coefficients obtained by matching experimental data with computer results for all of the four cases studied are given in Table II, along with the corresponding dimensionless parameter, $A$, giving the best fit for each particular run. Coefficients associated with each plot of experimental data in Figures 4-32 are found on the appropriate drawings.
The film coefficients obtained in this study may be compared with those calculated from rate data given by Eagle and Scott (8). Although direct comparisons for identical systems are not available, it may be seen that the results compare within an order of magnitude. For instance in the adsorption of toluene-octane on 10-14 mesh silica gel values of K are noted to be in the range, $1.27-1.69 \times 10^{-4}$ cm/sec, using the data of Eagle and Scott, which compare with the values of $2.54 \times 10^{-3}$ and $1.12 \times 10^{-3}$ obtained in this study with methylcyclohexane-toluene on silica gel. Although the two figures differ by a factor of about ten, this is not totally unexpected because of the methods used and the difference in systems. Similar comparisons are made for adsorption on alumina. Data obtained from Eagle and Scott yield a value of $K = 0.85 \times 10^{-4}$ for the adsorption of toluene-octane, compared with $0.74 \times 10^{-3}$ in this study for methylcyclohexane-toluene on alumina.

The only system in which a good correlation between experimental data and computed curves is not obtained is that of methylcyclohexane-toluene on alumina (System Number 3 in Table II). A choice of $A = 3$ was made because the actual data fell on both sides of the computed curve, whereas for other values of A the actual data lay well to one or the other side of the computed curve. The lack of perfect agreement is probably attributable to several factors, each one or all contributing to the discrepancy. The nature of the adsorbent is very likely involved, as the liquid solution, methylcyclohexane-toluene was successfully tested in two other cases. The pore volume of alumina is small compared to that of the other systems studied, and hence the
internal diffusional mechanisms are probably involved to a lesser degree, even though a moderately coarse material (8-14 mesh) is used. For all values of A checked, the actual curves are steeper than the computed curves at the lower concentrations, suggesting that the diffusion mechanism within the particle is being overridden by another rate controlling step. The case of external film resistance solely controlling is doubtful, because a good correlation should be found at low A, which is not the case for this system. There is a possibility that the mechanism which does affect rate strongest changes during the course of a change in concentration from high to low. The equilibrium curve also affects the shape of the wave, hence the function expressing equilibrium relationships must be correctly determined. There is some possibility that the equilibrium measured in the laboratory is not the true equilibrium under process conditions.

A major factor is the possible effect of longitudinal diffusion in some cases where it influences the rate of adsorption. If longitudinal diffusion is considered, its effect will be to change the shape of the adsorption wave. The maximum concentration gradient giving rise to axial, or longitudinal, diffusion occurs in the steepest portion of the adsorption wave. At the lower end of the wave small gradients in the axial direction will not produce an extensive transfer of material axially, therefore the shape of the curve should not be changed substantially. However at the upper end of the wave large gradients have occurred during the passage of the wave, tending to reduce the concentration in the bulk phase at a given level. Consequently a flattening of the wave at the upper end should be expected;
this flattening is actually observed for the alumina bed, where a relatively good correlation of data with theory is observed at the lower end. A possible next step in theoretical treatment would be the inclusion of a term in the basic model for axial diffusion. Certain problems would arise, however, which should be considered. An additional parameter, the diffusivity constant in the longitudinal direction would have to be determined. The addition of another term in the model would of course require increased computation.

In the final analysis it must be remembered that the proposed model is not all inclusive of the many known factors in fractionation of any solution. The adsorbent itself is far from being of the geometry proposed. The basic assumptions outlined at the beginning are all approximations to the true system, for mathematical simplicity. It is most encouraging to note, however, that the effect of intraparticle diffusion, the major factor to be considered in this project, has been found quantitatively in three of the four cases studied, and has resulted in an improved correlation over previous models.

6. Design of a Fixed-Bed Adsorber

A complete solution to the equations for fixed-bed adsorption can provide sufficient data for designing an economical adsorption column, provided physical properties and operational data for the system are known. Simpler techniques may be used to find the characteristics of the ultimate adsorption wave, or mass transfer zone, for the steady state alone. However with the latter procedure, nothing can be stated about the formation time of the steady-state wave, or the amount of adsorbent required for this purpose. The usual assumption
is to neglect or guess the height of bed required for formation of the ultimate wave; however this is certainly not always a valid procedure. It is highly possible that for a given throughput, breakthrough may occur before the desired concentration of effluent is reached, or in other words, a column could conceivably be designed in which steady-state is never reached. In this situation the bed would be too shallow to achieve the desired purity of effluent. Where intraparticle diffusion controls, the ultimate wave is more difficult to reach, and in such cases knowledge of the transient state is very important. In beds containing large particles, pore processes may cause a flattening of the adsorption curves, thus increasing time to reach steady-state as well as the amount of adsorbent material required to produce the ultimate wave. This information is of course necessary to predict accurately the total process time required to achieve a given separation at some particular throughput. Moreover, the most economical overall cycle time for both processing and regeneration steps is dependent upon adsorption zone characteristics.

The computed solution for the system, methylcyclohexane-toluene on silica gel, will be used to illustrate how design data for a fixed-bed adsorber may be obtained. The curves of $x$ versus $T$ may be easily converted to a curve of $x$ versus actual time, $\Theta$, by use of the transformation equation

$$T = \frac{AK}{a} (\Theta - \frac{f_z}{Q/S})$$

(4-9)

As described in an earlier section, the values of $A$ and $K$ may be obtained through a comparison of experimental and theoretical curves.
The parameter $H$ is converted to actual bed level, $z$, by Equation (4-8). Figure 35 is a plot of both real and theoretical results for a typical system (Johnson Run F-1)(30). The minimum time to reach steady state is considered to be the point where the envelope curve corresponding to the wave front drops reasonably close to zero. The bed level corresponds to that curve intersecting the boundary curve at just this point. It is conceivable that a column could be designed with a depth just equal to the level at which steady state is reached. However that portion of bed unsaturated with the more adsorbable component is relatively large in comparison to the total bed. The proportion of unspent adsorbent may be reduced by increasing bed height. The limitation upon bed height is an economic one, since operating and fixed costs increase with height.

The amount of unsaturation at any bed level, whether the ultimate wave has been established or not, may be determined as described below. Consider Figure 3, a sketch of effluent concentration as a function of real time. The steady state is considered to occur at $\theta = \theta_s$. At any given level the time required for a wave to pass a particular point is given by

$$\theta_w = \theta_2 - \theta_1$$

(6-1)

This is also the time required for the measurement of a breakthrough wave as it passes out of the adsorption column. The quantity of liquid collected as this wave passes out of the column is expressed volumetrically by the formula

$$V_w = Q\theta_w$$

(6-2)

where $V_w$ is the total volume of effluent liquid, $\text{ft}^3$. 
The maximum quantity of component A, $V'_a$, that could be contained in the length of a wave at saturation is expressed by the following formula:

$$V'_a = Q \theta_w x_f = Q x_f (\theta_2 - \theta_1) \quad (6-3)$$

The amount of unadsorbed component A at breakthrough can be computed by considering a differential section of wave, as shown in the above sketch. At steady state, the quantity of component A in the transfer zone is given by

$$dV_a = Q x d\theta \quad (6-4)$$

The total quantity of component A in the effluent wave, which is the same as the total amount of A not adsorbed, can be obtained by integration between limits, $\theta_1$ and $\theta_2$: 
The volume unadsorbed is the area under the adsorption curve multiplied by overall liquid flow rate. The fraction adsorbed, \( f_a' \), is then given by:

\[
V_a = \int_{\theta_1}^{\theta_2} Q x d\theta = Q \int_{\theta_1}^{\theta_2} x d\theta
\]

The limits of integration, \( \theta_1 \) and \( \theta_2 \), must be selected judiciously, because the theoretical limits are over an infinite range. The actual limits are chosen arbitrarily to include the portion of adsorption zone where, for all practical purposes, the slope of the curve is non-zero, indicating the region of active mass transfer. For the system, methylcyclohexane-toluene on silica gel (at \( x_f = .5 \)), a steady-state value of \( f_a' \) of .372 was obtained. The magnitude of \( f_a' \) depends, of course, on the shape of the adsorption wave.

The net degree of saturation for the entire column should be the total quantity adsorbed, divided by the maximum adsorbable capacity of the bed. The length, \( z \), of the zone between limits, \( \theta_1 \) and \( \theta_2 \), is given by

\[
z = \frac{Q \theta_w}{f_V S + V_p \rho S}
\]

The remainder of the column is saturated, so that the overall degree of saturation, or adsorption, \( f_a \), is expressed by the relation
or in terms of bed weight and density,

\[ f_a = 1 - \frac{Q \theta_w \rho_b}{(V_p \rho_b + f_v)W} (1 - f'_a) \]  

(6-9)

In order to use Equation (6-9) the variable, \( \theta_w \), must be computed.

Rearranging Equation (4-9) gives

\[ \theta = \frac{Ta}{AK} + \frac{f_v z}{Q/S} \]  

(6-10)

Substituting for \( z \) from Equation (4-8) gives

\[ \theta = \frac{Ta}{AK} + \frac{f_v a H}{KV_p \rho_b} \]  

(6-11)

Since \( H = T/A \),

\[ \theta = \frac{Ta}{AK} (1 + \frac{f_v}{V_p \rho_b}) \]  

(6-12)

Since \( \theta_w = \theta_2 - \theta_1 \),

\[ \theta_w = (T_2 - T_1) \frac{a}{AK} (1 + \frac{f_v}{V_p \rho_b}) \]  

(6-13)

At steady state, \( \theta = \theta_s \), and

\[ \theta_s = \frac{T_s a}{AK} (1 + \frac{f_v}{V_p \rho_b}) \]  

(6-14)

According to Equation (6-14) the time of formation of the ultimate wave is independent of operating conditions.

In the event a steady state wave has not been formed, i.e., if \( \theta < \theta_s \),
the effect of the boundary curve must be considered in computing $V_a$.

Equation (6-15) must be modified by subtracting the concentration at the boundary, which corresponds to the wave front:

$$V_a = Q \int_{\theta_1}^{\theta_2} (x - x_b) \, d\theta, \quad \theta < \theta_s \quad (6-15)$$

where $x_b$ is the instantaneous wave front concentration.

The degree of saturation, $f_{as}$, at $\theta_s$ may be obtained by drawing a vertical line from the $\theta$-axis at $\theta_s$. The point at which this line crosses the feed line is the upper limit, $\theta_2$, of the curve representing conditions in the column just as pure effluent appears. The lower limit is the intersection of this curve with the boundary curve.

In Table III are given values of formation time, $\Theta_s$, and corresponding bed length for each system considered, using the most reasonable film coefficient as determined by matching experimental and theoretical curves. Also listed in the table are values of $f_{as}$ and $f_{as}^*$ for each system at the beginning of steady-state; in addition, values of $f_{aw}$, the degree of saturation within a zone of unvarying shape, are listed.

The parameters described above are important to the establishment of the proper operating conditions and sizing of fixed bed equipment. Note that these variables have been determined independently of the position of the actual breakthrough curve with respect to the steady state. In designing fixed bed equipment care must be taken that a bed of sufficient depth for the desired throughput is provided. The
residence time in the bed must be at least equal to $\theta_g$ (corresponding to a length, $z_g$) to remove one component completely from the main stream. The length of bed in excess of the minimum is dependent on economic considerations, and the saturation factor, $f_a$, must be included in an overall economic estimate. For tall columns, $f_a$ approaches 100 percent for an efficient adsorbent utilization, but the cycle time increases, as well as fixed costs. Some economic balance between complete adsorbent utilization and plant cost relative to operation is therefore necessary.

7. Moving Bed Adsorption

Data from small fixed-bed adsorption experiments may be expected to predict performance of moving-bed systems, as will be explained in the following brief description. In fixed-bed adsorbers the steady-state wave is considered as moving through the bed at a fixed velocity, the length and shape of the wave remaining fixed. If however the bed is made to move at a certain velocity, then the adsorption wave may be seen to remain fixed relative to the column. If the column of adsorbent is just the same length as the wave, then the conditions at both ends of the column correspond to the conditions at each end of the wave. That is, if feed is introduced at the bottom of a downward moving bed, the adsorbent emerges from the bottom saturated with the more adsorbable component; at the upper end of the column, corresponding to the wave front in the fixed-bed case, the fluid stream emerges from the column free of the more adsorbable component, while fresh adsorbent is being introduced. The operating line for such a case where the fixed bed
and moving bed processes correspond as just described, is the straight line on the equilibrium diagram connecting points L and K in Figure 1. In reality the height of column (equivalent to the length of the steady-state wave) required for 100 percent separation between points L and K would be infinite, but by accepting a concentration range slightly less than this, say 99.5 percent of the total, a practical length of the column may be determined.

If an operating line other than line L-K is chosen because of process demands, it is still possible to predict the column height required for a moving bed. In this case the transfer unit method may be utilized, although the assumptions relative to the constancy of the mass transfer coefficient must be considered. The rate of transfer from a liquid feed to the adsorbent over a differential section is given by \( Qdx \), and is also equivalent to the rate of interphase transfer as described in an earlier section:

\[
Qdx = Ka(x - x^*) Sdz
\]  

(6-16)

Integration of this equation between appropriate limits gives:

\[
\frac{dx}{x - x^*} = \frac{KaS}{Q} = N_L
\]

(6-17)

This equation defines the number of transfer units, \( N_L \), based on the bulk-phase, liquid-film coefficient, \( K \). The height of a transfer unit based on the same coefficient is defined by

\[
H_L = \frac{Ka}{Q/S}
\]

(6-18)
Assuming that column operation is such that $H_L$ is the same as for the fixed-bed experiment then the height of bed required to fractionate a feed between concentrations of $x_1$ and $x_2$ may be predicted. If column feed rates are known in advance then it is a simple matter to run fixed-bed experiments under similar liquid flow rates. Otherwise the variation of $K_a$ with flow must be predicted by a suitable number of independent tests. The effect of concentration on $K$ is to be considered, although there is little quantitative knowledge on this subject.
VII. CONCLUSIONS AND RECOMMENDATIONS

As a result of research on the subject of liquid-phase, binary adsorption fractionation, the following conclusions can be made:

1. A mathematical description of adsorption fractionation of binary liquids in a column has been developed which considers simultaneously the effect of the variables, time, bed depth, particle radius, and concentration.

2. A sufficiently accurate numerical solution has been found for the system of partial differential equations, derived for the operation of an adsorption column, together with a general equilibrium function and the proper boundary conditions. Otherwise a solution could probably have not been obtainable.

3. A substantial improvement in the correlation between experimental data and theory has been demonstrated for three out of four systems investigated, proving that intraparticle diffusion strongly influences the dynamics of adsorption, at least in those systems studied.

4. The decided effect of equilibrium on the shape of the adsorption has been illustrated, showing that it is important to use the proper equilibrium relation in solving the mathematical model.

5. A computer program in the FORTRAN - 4 language has been prepared, so that the problem may be re-solved on a large number of computers without excessive re-programming effort.
6. The application of the resultant solution to the design of a large fixed-bed adsorber, where the formation time of the ultimate wave, bed depth required for the ultimate wave to form, degree of saturation, and length of the steady-state wave, has been made. Equations relating fixed-bed data to moving-bed adsorbers were developed.

The following procedures or areas of investigation are recommended for future work:

1. The inclusion of longitudinal diffusion as a rate-determining factor may be necessary for certain systems, as possibly evidenced by the methylcyclohexane-toluene-alumina system. The low pore volume of this system possibly results in a greater effect of longitudinal diffusion.

2. A more simplified numerical or analytical approach yielding the same solution is needed, so that additional mechanisms may be included.

3. A similar investigation in the case of more than two components would make this procedure more useful in petroleum processes using adsorption.

4. Non-isothermal operation, in which the heat of adsorption is significant, is of primary concern in gas-phase systems, but may have to be considered in some liquid-phase adsorption processes.

5. Situations involving chemical reaction should be studied, if there is a change in the properties of the system or in the number of components involved.

6. Of particular interest in column operation is the effect of a sudden change in any operating condition. Without making extensive changes the present procedures could possibly be redeveloped to show the effect
of a change in feed composition or rate upon column operation.

7. Variation of the film coefficient and internal diffusion constant
with concentration should be studied.

8. A more adequate description of flow patterns in the void space
between particles is needed.

9. The operation of unit processes, including both fixed and moving
bed adsorbers, under computer control is a relatively new field which
should be of interest in future research projects. Experimentation
in this area is relatively complex because of problems in sensing
and transmitting signals to the computer, and then back to the
process to achieve closed loop control.
LITERATURE CITED


Other References


68. Polanyi, M., _Elektrochem_, 27, 142-50 (1921).


APPENDIX A

NUMERICAL METHODS
TABLE I

ACCURACY CHECK ON INCREMENT SIZE
(At $A = 10$)

<table>
<thead>
<tr>
<th>$\Delta R$</th>
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<th>16-Digit Precision</th>
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Bulk Concentration
At $H = .1$, $T = 10$
DERIVATION OF IMPLICIT FINITE DIFFERENCE EQUATIONS FOR THE INTRAPARTICLE DIFFUSION EQUATION

\[
\left[ \frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \frac{\partial y}{\partial \tau} \right] = \left( \frac{\partial y}{\partial \tau} \right)_R \tag{A-1}
\]

Finite Difference Formulas (Reference 11):

\[
\frac{\partial^2 y}{\partial R^2} = \frac{y_{i+1} - 2y_i + y_{i-1}}{(\Delta R)^2} + 0(\Delta x)^2 \tag{A-2}
\]

\[
\frac{\partial y}{\partial R} = \frac{y_{i+1} - y_{i-1}}{2\Delta R} + 0(\Delta x)^2 \tag{A-3}
\]

\[
\frac{\partial y}{\partial \tau} = \frac{y_i - y_i'}{\Delta \tau} \tag{A-4}
\]

Using \( \frac{\Delta}{R} = \frac{2}{\Delta R} \), the diffusion equation becomes, upon substitution of finite difference formulas, neglecting error terms:

\[
\frac{y_{i-1} - 2y_i + y_{i+1}}{(\Delta R)^2} + \frac{2(y_{i+1} - y_i - y_i)}{\Delta \tau} = \frac{y_i - y_i'}{\Delta \tau} \tag{A-5}
\]

Let \( m = \frac{\Delta \tau}{(\Delta R)^2} \) and solve for \( y_i' \):

\[
- m (1 - \frac{1}{4})y_{i-1} + (2m + 1)y_i - m (1 + \frac{1}{4})y_{i+1} = y_i' \tag{A-6}
\]

This equation expresses the concentration, \( y_i' \), in terms of three neighboring points, as shown in the sketch below:

\[
\begin{array}{c}
\text{T} \\
\hline
y_{i-1} & y_i & y_{i+1} \\
\hline
\end{array}
\]

At the center point of a sphere (at \( R = 0, i = 0 \)) the above finite difference equation becomes undefined, and a modified formula must be derived. This is done by applying La Hopital's rule at the center of the sphere:
Thus the diffusion equation becomes

\[ 3 \cdot \frac{\partial^2 y}{\partial R^2} = \frac{\partial y}{\partial T} \]  

(at \( R = 0 \))  

(A-8)

The corresponding substitution of finite difference formulas gives the following:

\[ 3 \cdot \frac{y_1 - 2y_0 + y_1}{(\Delta R)^2} = \frac{y_0 - y_0}{\Delta T} \]  

(A-9)

Solving for \( y'_o \):

\[ (1 + 6m) y_o - 6my_1 = y'_o \]  

(A-10)

There is one additional formula needed, the finite difference formula stating conditions at the pore surface (at \( R = A, i = n \)).

This formula will provide the linkage to the bulk-phase equation by use of the concentration gradient at the pore opening. A Taylor's series expansion about the point \( y_n \), using the first three terms to estimate \( y_{n-1} \), gives

\[ y_{n-1} = y_n - \left( \frac{\partial y}{\partial R} \right)_{R=A} \Delta R + \left( \frac{\partial^2 y}{\partial R^2} \right)_{R=A} \frac{(\Delta R)^2}{2} \]  

(A-11)

Solve for the term, \( \frac{\partial^2 y}{\partial R^2} \):

\[ \left( \frac{\partial^2 y}{\partial R^2} \right)_{R=A} = (y_{n-1} - y_n) \frac{2}{(\Delta R)^2} + \frac{2}{A} \left( \frac{\partial y}{\partial R} \right)_{R=A} \]  

(A-12)

Substitution of the above expression into the diffusion equation gives

\[ (y_{n-1} - y_n) \frac{2}{(\Delta R)^2} + \left( \frac{\partial y}{\partial R} \right)_{R=A} \frac{2}{A} \left( \frac{\partial y}{\partial R} \right)_{R=A} \left( \frac{\partial y}{\partial T} \right)_A \]  

(A-13)

At the pore opening the gradient, \( (\partial y/\partial R) \), is also given by the term, \( (x - x^*) \). Substitution of this term and the finite difference formula
for \( \frac{\partial^2 y}{\partial T^2} \) results in

\[
\frac{y_{n-1} - y_n}{(\Delta R)^2} + (x - x^*) \frac{1}{\Delta R} + \frac{1}{A} = \frac{y_n - y_n'}{\Delta T}
\]  

(A-14)

Solving for \( y_n' \):

\[
y_n' = -2m y_{n-1} + (1 + 2m)y_n - 2m (x-x^*)(1 + \frac{\Delta R}{A})
\]  

(A-15)

An examination of equations (1), (2), and (3) shows that there can be written \( n + 1 \) equations, and there are \( n+1 \) values of \( y \) to be determined. Assuming that the \( n + 1 \) values of \( y' \) corresponding to the preceding time level are known, as well as an estimate of \( (x - x^*) \), there are thus \( n + 1 \) equations which may be solved simultaneously for a concentration distribution at the next higher time step.

The matrix corresponding to the system of equations as described above may be seen to be tri-diagonal, hence solvable by the Thomas method. The general layout of this system appears as follows:

\[
\begin{align*}
(1 + 6m) y_0 - 6my_1 &= y_0' \\
a y_0 + by_1 + cy_2 &= y_1' \\
ay_1 + by_2 + cy_3 &= y_2' \\
\vdots & \vdots \\
\vdots & \vdots \\
-2my_{n-1} + by_n &= y_n' + w
\end{align*}
\]  

(A-16)

where \( a = -m \left( 1 - \frac{1}{i} \right) \)

\( b = (2m +1) \)

\( c = -m \left( 1 + \frac{1}{i} \right) \)

\( w = 2m (x - x^*) \left( 1 + \frac{\Delta R}{A} \right) \)
A computer subroutine, named TD, was written to provide instructions for solving the above system of equations by elimination during each iteration.
<table>
<thead>
<tr>
<th>System and Reference</th>
<th>Curve Ident.</th>
<th>Feed Fraction, (x_F)</th>
<th>Column Diam. (cm)</th>
<th>Bed Wt. (gm)</th>
<th>Liquid Rate (cc/sec)</th>
<th>Voids Coeff. (K) ((x10^3))</th>
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</tbody>
</table>
### TABLE III

WAVE FORMATION TIMES, BED DEPTH, AND SATURATION

<table>
<thead>
<tr>
<th>System</th>
<th>Curve Ident</th>
<th>$z_s$, cm</th>
<th>$\theta_s$, sec</th>
<th>$f_{as}'$</th>
<th>$f_{as}$</th>
<th>$\theta_w$, sec</th>
<th>$f_{aw}'$</th>
<th>$f_{aw}$</th>
<th>$z_w$, cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. MCH-Toluene-Silica Gel ($x = .5$)</td>
<td>A, B</td>
<td>84.2</td>
<td>2900</td>
<td>0.211</td>
<td>0.26</td>
<td>4830</td>
<td>0.372</td>
<td>140.5</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C, D</td>
<td>53.5</td>
<td>2900</td>
<td>0.211</td>
<td>0.26</td>
<td>4830</td>
<td>0.372</td>
<td>89.4</td>
<td></td>
</tr>
<tr>
<td>2. MCH-Toluene-Silica Gel ($x = .1$)</td>
<td>E, F</td>
<td>95.5</td>
<td>1489</td>
<td>0.183</td>
<td>0.20</td>
<td>3870</td>
<td>0.369</td>
<td>248</td>
<td></td>
</tr>
<tr>
<td>3. MCH-Toluene-Alumina ($x = .5$)</td>
<td>G, H, I</td>
<td>136.0</td>
<td>6170</td>
<td>0.301</td>
<td>0.54</td>
<td>5930</td>
<td>0.434</td>
<td>131.0</td>
<td></td>
</tr>
<tr>
<td>4. Benzene-n-Hexane-Silica Gel ($x = .5$)</td>
<td>J</td>
<td>27.5</td>
<td>2645</td>
<td>0.159</td>
<td>0.24</td>
<td>4020</td>
<td>0.350</td>
<td>41.6</td>
<td></td>
</tr>
</tbody>
</table>
FIGURE 4. METHYLICYCLOHEXANE-TOLUENE ON SILICA GEL, A = 1.0
FIGURE 5. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, A = 5.0

<table>
<thead>
<tr>
<th>Curves</th>
<th>( K \times 10^3 ) cm/sec</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.82</td>
<td>3.8</td>
</tr>
<tr>
<td>B</td>
<td>0.73</td>
<td>1.4</td>
</tr>
<tr>
<td>C</td>
<td>0.89</td>
<td>5.8</td>
</tr>
<tr>
<td>D</td>
<td>0.89</td>
<td>2.9</td>
</tr>
</tbody>
</table>
FIGURE 7. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, A = 20

<table>
<thead>
<tr>
<th>Data Curve</th>
<th>K (x10^3) cm/sec</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>1.30</td>
<td>6.0</td>
</tr>
<tr>
<td>B</td>
<td>1.26</td>
<td>2.6</td>
</tr>
<tr>
<td>D</td>
<td>1.62</td>
<td>5.3</td>
</tr>
</tbody>
</table>
FIGURE 8. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, A = 40
FIGURE 10. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, A = 60

<table>
<thead>
<tr>
<th>Data Curve</th>
<th>K (x10³) cm/sec</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2.75</td>
<td>12.7</td>
</tr>
<tr>
<td>B</td>
<td>3.04</td>
<td>6.2</td>
</tr>
<tr>
<td>C</td>
<td>2.70</td>
<td>17.3</td>
</tr>
<tr>
<td>D</td>
<td>3.22</td>
<td>10.4</td>
</tr>
</tbody>
</table>
Data K Curve \(x10^3\) cm/sec H
A 3.36 15.5
B 3.95 8.1
D 4.01 13.0

FIGURE 11. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, A = 80
Figure 14. Benzene-N-Hexane on Silica Gel, $A = 1.0$
FIGURE 15. BENZENE-N-HEXANE ON SILICA GEL, t = 2.0

Data

K = 1.1 x 10^{-3}
H = 7.5

Curve 1

H = 19.5
17.5
15.5
13.5
11.5
9.5
7.5
5.5
3.5
1.5

H = 1.5
FIGURE 16. BENZENE-N-HEXANE ON SILICA GEL, A = 10

Data
Curve J
H = 15
K = 3.2x10^{-3} cm/sec
FIGURE 18. BENZENE-N-HEXANE ON SILICA GEL, A = 30

Data
Curve J
H = 30
K = 6.3 \times 10^{-3}
\text{cm/sec}
FIGURE 19. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, A = 10
FIGURE 20. METHYL CYCLOHEXANE–TOLUENE ON SILICA GEL, a = 20

<table>
<thead>
<tr>
<th>Curve</th>
<th>K (x10³) cm/sec</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>1.03</td>
<td>0.98</td>
</tr>
<tr>
<td>F</td>
<td>1.17</td>
<td>0.52</td>
</tr>
</tbody>
</table>
FIGURE 22. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, A = 40

Data
Curve  \( K \times 10^3 \)  \( \text{cm/sec} \)  \( H \)
E  1.29  1.22
F  1.32  0.59
FIGURE 24. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, A = .1

<table>
<thead>
<tr>
<th>Data Curve</th>
<th>K (x10^3) cm/sec</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.65</td>
<td>3.00</td>
</tr>
<tr>
<td>H</td>
<td>0.56</td>
<td>1.25</td>
</tr>
<tr>
<td>I</td>
<td>0.47</td>
<td>0.50</td>
</tr>
</tbody>
</table>
FIGURE 25. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, R = 1.0

<table>
<thead>
<tr>
<th>Curve</th>
<th>( K \times 10^3 ) cm/sec</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>0.70</td>
<td>3.2</td>
</tr>
<tr>
<td>H</td>
<td>0.59</td>
<td>1.3</td>
</tr>
<tr>
<td>I</td>
<td>0.56</td>
<td>0.6</td>
</tr>
</tbody>
</table>
FIGURE 27. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, A = 3.0
FIGURE 28. METHYL CYCLOHEXANE-TOLUENE ON ALUMINA, A = 5.0
FIGURE 30. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, A = 20
FIGURE 31. METHYL CYCLOHEXANE-TOLUENE ON ALUMINA, $a = 40$

<table>
<thead>
<tr>
<th>Data Curve</th>
<th>$K \times 10^3$ (cm/sec)</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>G</td>
<td>2.62</td>
<td>11.5</td>
</tr>
<tr>
<td>H</td>
<td>2.70</td>
<td>6.0</td>
</tr>
<tr>
<td>I</td>
<td>2.33</td>
<td>2.5</td>
</tr>
</tbody>
</table>
FIGURE 32, METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, A = 80
Figure 23, Effect of Equilibrium on Computed Results

\[ x, \text{ Concentration of More Adsorbable Component in Effluent} \]

Curve 1: NCH Tolune on Silica Gel
Curve 2: Benzene+hexane on Silica Gel
Curve 3: Benzene+hexane on Alumina

\[ x_f = 0.5, A = 1, R = 2 \]
Figure 34. Effect of Particle Size on the System: MCH-Toluene on Alumina
x, Concentration of More Adsorbable Component in Effluent
Figure 36: Comparison of Johnson's Model (Curves C and D) with the Proposed Model of More Adsorbable Component in Effluent

Concentration of More Adsorbable Component in Effluent

Volume of Effluent, cc

0 20 40 60 80

0.1 0.2 0.3 0.4 0.5

Experimental Data

Johnson Model (30)

New Model: A = 50

System: MCM-Toluene on Silica Gel
APPENDIX C

COMPUTER PROGRAM
SOLUTION OF ADSORPTION MODEL - MAIN PROGRAM

DEFINE ERROR FUNCTION

\[ E(A1, A2, \text{ERROR}) = \text{ABS}((A1 - A2) / A1) - \text{ERROR} \]

DIMENSION AND COMMON DECLARATIONS

\[
\text{DIMENSION X(1001), XS(1001), XB(1001), XSB(1001)}
\]

\[
\text{COMMON YOLD(201), YNEW(201)}
\]

\[
\text{COMMON I,J,K,M,A,XNR, NR, ISW, PTSW, YTOL, NR1, ITPT, ITTOT, ITMAX, INS, KK, HFREQ, TFREQ, RFREQ, YS, DH, DT}
\]

\[
\text{COMMON KDIF, IPCHX, IPCHY, IO, JO, JMAX}
\]

\[
\text{COMMON DELX, DELXO, XFF}
\]

\[
\text{COMMON EW, MAXOUT}
\]

\[
\text{LOGICAL ISW, PTSW}
\]

\[
\text{REAL M}
\]

\[
\text{INTEGER HFREQ, TFREQ, RFREQ}
\]

INPUTS

1 REWIND1
REWIND3
PAUSE1

2 READ3, XF, QQ, DT, A, XNR, P1, P2, P3, P4, P5, P6
READ3, YTOL, EX, EY

3 FORMAT(5E10.0, 6A5)

4 FORMAT(16I5)

PRELIMINARY CALCULATIONS

\[ M = DT \times (XNR / A)^2 \]

NR = XNR
NR1 = NR + 1
DH = DT / A
XFF = XF
L = 1

WRITE DATA IN HEADING

WRITE (L, 5) P1, P2, P3, P4, P5, P6, XF, DH, DT, A, XNR, M
WRITE (L, 6) YTOL, EX, EY
WRITE (L, 7) JMAX, ITMAX
WRITE (L, 1000) QQ

1000 FORMAT (1X, 14, 'DAMPING FACTOR, F4.5)
5 FORMAT (1H1, 7HPROBLEM, 1X, 6A5, /, 1X, 26HINLET FEED COMPOSITION, XF,
1 23X, F11.5 /, 1X, 25HINCREMENTAL BED LEVEL, DH, 24X, F11.5 /
2 1X, 20HINCREMENTAL TIME, DT, 30X, F10.5 /
3 1X, 23HDIMENSIONLESS RADIUS, A, 26X, F11.5 /
4 1X, 34HNUMBER OF INTERVALS OF RADIUS, XNR, 15X, F11.5 /
5 1X, 25HRATIO OF DT TO (A/XNR)**2, F35.5)
6 FORMAT (1X, 10HTOLERANCES, 6X, 21H WAVE FRONT TEST, YTOL, 23X, 1PE15.5 /
7 6X, 38HERROR IN CONCENTRATION - BULK PHASE, EX, 6X, 1PE15.5 /
8 29X19H-ADSORBED PHASE, EY, 1PE17.5)
7 FORMAT (1X, 26HNUMBER OF TIME STEPS, JMAX, 28X, I6 /
9 1X, 43HM A X I M U M ALLOWED ITERATIONS PER POINT, ITMAX, I17)

IF DIFFUSION CURVES ARE TO BE OUTPUT, WRITE HEADING ON LOGICAL
UNIT 3.

L = 3
IF (KDIF .NE. 1) GO TO 17
KDIF = -1
GO TO 14

GO TO FUNCTION EQ TO READ AND WRITE EQUILIBRIUM DATA. SET INSW = 1
TO ENTER EQ INITIALLY.

17 L = 7
IF(IPCHX.NE.1) GO TO 117
IPCHX=-1
GO TO 14
117 INSW=1
IPCHX=IABS(IPCHX)
DUMMY=EQ(.5)
WRITE(1,8)
8 FORMAT(////13X,6HITERA-29X,14HCONCENTRATIONS/4X1HJ4X1HI3X
1 5HTIONS,4X4HTIME,5X5HDEPTH7X2HX,1X4HBULK6X2HY,1X,
2 8HADSORBED//)
IF(KDIF.NE.0) WRITE (3,9)
9 FORMAT(////1X,16HDIFFUSION CURVES //)
ITPT=0
C SET EXCESSIVE ITERATION SWITCH
C 18 KK=1
C SET FREQUENCY OF OUTPUT PARAMETERS
C IO=1
JO=1
C SET TOTAL ITERATION COUNTER
C ITTQT=0
C SET ULTIMATE WAVE SWITCHES
C KULT=1
KULTX=0
KQUIT=JMAX
C SET DIFFUSION CALCULATION SWITCHES
ISW=.FALSE.
PTSW=.FALSE.

C
C INITIALIZE TIME AND BED DEPTH INDEXES
C
I=1
J=1

GRID POINT 1,1 (APEX OF TRIANGLE)

DEFINE YOLD(K) AND INITIAL ESTIMATE OF Y AT SURFACE

DO10K=1,NR1
YNEW(K)=XF
10 YOLD(K)=XF
DO11K=1,JMAX
11 X(K)=XF
CALL OUT(XF,XF)
J=2

GRID POINT J,1 (INCREASE TIME STEP)

20 YEST=YOLD(NR1)
30 XS(J)=EQ(YEST)
DELA=XS(J)-XF
DELX=-DELA
DELXO=XF-XS(J-1)
CALL TD
CALL CK(1,DELA,XS(J),YEST)
IF(KK.NE.1) GO TO 60
40 IF(E(YNEW(NR1),YEST,EY))60,50,50
50 YEST=YEST+QQ*(YNEW(NR1)-YEST)
GOTO30
60 YY=YNEW(NR1)
CALL OUT(XF,YY)
SAVE VALUES OF X AND Y FOR NEXT POINT

DO70 K=1,NR1
70 YOLD(K)=YNEW(K)
72 J=J+1
IF(J.GT.JMAX) GO TO 78
IF(KK.NE.3) GO TO 20
XS(J)=XS(J-1)
GO TO 72

GRID POINT 2,2 (BED LEVEL = DH)

GUESS CONCENTRATION ALONG BOUNDARY A*H=T

I=2
J=1
DELA=XS(J)-X(J)
XB(J)=X(J)+DELA*DH*3.

XSB(J)=EQ(XB(J))
DELB=XSB(J)-XB(J)
XNEW=X(J)+DH*(DELA+DELB)*1.5
CALL CK(2,DELB,XB(J),XSB(J))
IF(KK.NE.1) GO TO 110
90 IF(E(XNEW,XB(J),EX))110,110,100
100 XB(J)=XNEW
GOTO80
110 CALL OUT(XB(J),XB(J))
KK=1

SET YOLD(K) FOR NEXT TIME STEP

DO120 K=1,NR1
120 YOLD(K)=XB(J)
GRID POINT J, 2 (BED LEVEL = DH)

130  J=J+1
     IF(J.GT.JMAX)GOTO230
     IF(KK.NE.3) GO TO 140
     XB(J)=XB(J-1)
     XSB(J)=XSB(J-1)
     GO TO 130

GUESS Y AT SURFACE OF SPHERE - NEXT TIME STEP

140  YEST=YOLD(NR1)

GUESS X AT THE SAME POINT

150  DELA=XS(J)-X(J)
     XB(J)=X(J)+DELA*DH*3.

160  DELB=XSB(J)-XB(J)
     XNEW=X(J)+DH*(DELA+DELB)*1.5
     CALL CK(3,DELB,XB(J),YEST)
     IF(KK.NE.1) GO TO 180

170  IF(E(XNEW,XB(J),EX))180,175,175
175  XB(J)=XNEW
     GOT0160

180  DELX=XNEW-XSB(J)
     DELX0=XB(J-1)-XSB(J-1)
     CALL TD
     CALL CK(4, DELB,XB(J),YEST)
     GOT0(190,210),KK

190  IF(E(YEST,YNEW(NR1),EY))210,210,200
200  YEST=YEST+QQ*(YNEW(NR1)-YEST)
     GOT0150

210  YY=YNEW(NR1)
CALL OUT(XNEW,YY)

SAVE X AND Y FOR NEXT TIME STEP

DO220 K=1, NR1
220 YOLD(K) = YNEW(K)
GO TO 130

GRID POINT I, I (ALONG BOUNDARY A*H=T)

230 I = I + 1
IF (I .GT. JMAX) GO TO 390

TEST IF ULTIMATE WAVE WAS FOUND

IF (I .GT. KQUIT) GO TO 390
IF (KULT .EQ. 0) GO TO 400

TEST SS 4 FOR JOB INTERRUPT

232 CALL SSWTCH(4,II)
IF (II .NE. 1) GO TO 240
REWIND 1
REWIND 3
234 CALL ICKPT
PAUSE2
240 J = I
KULT = 0
DELA = XS(J) - X(J)
DELB = XB(J) - XB(J)

ESTIMATE X AT THIS POINT BY A SECOND DEGREE FIT, THEN THIRD DEGREE

XNEW = XB(J) + DH*(DELB + DELA) + 1.5
XSNEW = EQ(XNEW)
250 DELC=XSNEW-XNEW
XNEW2=XB(J)+DH*(5.*DELC+8.*DELB-DELA)*.25
XSNEW=EQ(XNEW2)
CALL CK(5,XNEW,XNEW2,XSNEW)
IF(KK.NE.1) GO TO 280
260 IF(E(XNEW,XNEW2,EX))280,270,270
270 XNEW=XNEW2
GOTO250
C
C RE-DEFINE Y ALONG BOUNDARY
C
280 DO282K=1,NR1
282 YOLD(K)=XNEW2
CALL OUT(XNEW2,XNEW2)
KK=1
C
C RE-DEFINE X(J),XS(J),XB(J) AND XSB(J) FOR USE AT NEXT BED LEVEL
C
292 X(J)=XB(J)
XS(J)=XSB(J)
XB(J)=XNEW2
XSB(J)=XSNEW
295 J=J+1
IF(J.GT.JMAX)GOTO230
C
C IF AT UPPER END OF WAVE, SKIP INTEGRATION AND
C DEFINE ALL X TERMS EQUAL TO LAST VALUE IN WAVE
C
IF(KK.EQ.3) GO TO 292
C
GRID POINT J,I (TYPICAL POINT)
C
C GUESS Y AT POINT (J,I)
C
YEST=YOLD(NR1)
C ESTIMATE X AT POINT (J,I)

C     XNEW = ((XS(J) - XB(J)) * 4.5 - (XS(J) - X(J)) * 1.5) * DH + XB(J)
300 XSN=EQ(YEST)
      DELA=XS(J)-X(J)
      DELB=XS(J)-XB(J)
310 DELC=XSNEW-XNEW
320 XNEW2=XB(J)+DH*(5.*DELC+8.*DELB-DELA) *.25
      CALL CK(6, XNEW, XNEW2, YEST)

C IF AT LOWER END OF WAVE SKIP INTEGRATION AND
C INCREASE TIME UNTIL WAVE IS ENTERED.
C
C     IF(KK .NE. 1) GO TO 380
330 IF(E(XNEW, XNEW2, EX)) 350, 340, 340
340 XNEW=XNEW2
      GOTO310
350 DELX=XNEW2-XSN=EW
      DELX0=XB(J-1)-XS(J-1)
      CALL TD
      CALL CK(7, XNEW, XNEW2, YEST)
      IF(KK .NE. 1) GO TO 380
360 IF(E(YEST, YNEW(NR1), EY)) 380, 380, 370
370 YEST=YEST+QQ*(YNEW(NR1)-YEST)
      GOTO0300
380 CALL OUT(XNEW2, YNEW(NR1))

C RE-DEFINE Y FOR NEXT TIME STEP
C
381 DO 382 K=1, NR1
382 YOLD(K)=YNEW(K)

C CHECK FOR ULTIMATE WAVE
384 IF(ABS((X(J)-XB(J))-(XB(J)-XNEW2)).GT.YTOL) KULT =1
C
C WAIT UNTIL XNEW2 LESS THAN YTOL BEFORE PERMITTING
C ULTIMATE WAVE TEST TO BE EFFECTIVE
C
C IF(XNEW2.GE.YTOL) KULT=1
GO TO 292
C
C FINAL COMPUTATIONS
C
390 WRITE (1,391) ITTOT
391 FORMAT(//1X16HTOTAL ITERATIONS,110)
GOT01
C
C ULTIMATE WAVE ROUTINE
C TEST IF ULTIMATE WAVE ALREADY FOUND
C
400 IF(KULTX.EQ.1) GO TO 232
   H=DH*FLOAT(1-2)
   IF(IPCHX.EQ.1) WRITE(7,401) H
401 FORMAT(1X,20HULTIMATE WAVE AT H = F10.4)
   WRITE(1,401) H
   KULTX= .
   KQUIT=10+HFREQ*2
GO TO 232
END
SUBROUTINE TD

SOLUTION OF DIFFUSION EQUATION BY THOMAS METHOD

COMMON AND DIMENSION DECLARATIONS

DIMENSION T(101), S(101)
COMMON YOLD(201), YNEW(201)
COMMON I, J, K, M, A, XNR, NR, ISW, PTSW, YTOL, NR1, ITPT, ITTOT, ITMAX, INVX, KK
COMMON HFREQ, TFREQ, RFREQ, YS, DH, DT
COMMON KDF, IPCHV, IPCHY, IO, JO, JMAX
COMMON DELX, DELXO, XFF
COMMON EW, MAXOUT
INTEGER HFREQ, TFREQ, RFREQ
LOGICAL ISW, PTSW
REAL M

REDUCTION

IF (ISW) GOTO 2
ISW = .TRUE.
W = 2.*M*A/XNR*(1.+1./XNR)
XMSQ = M*M
S(1) = 6.*M + 1.
S(2) = B
DO 1 K = 3, NR
1 S(K) = B - XMSQ/S(K-1)
S(NR1) = B - 2.*XMSQ*XNR/(XNR-1.)*S(NR1)
2 YEND = YOLD(NR1) + DELX*W
IF (PTSW) GOTO 4
PTSW = .TRUE.
T(1) = YOLD(1)/S(1)
T(2) = YOLD(2)/S(2)
DO 3 K = 3, NR
Z = K - 1
3  T(K) = (YOLD(K) + (M - M/Z) * T(K - 1)) / S(K)
4  T(NR1) = (YEND + 2 * M * T(NR)) / S(NR1)
C
  BACK SOLUTION
C
YNEW(NR + 1) = T(NR + 1)
K = NR
5  Z = K - 1
YNEW(K) = T(K) + (M + M/Z) * YNEW(K + 1) / S(K)
K = K - 1
IF(K.GT.1) GOTO 5
YNEW(1) = T(1) + 6 * M * YNEW(2) / S(1)
RETURN
END
SUBROUTINE OUT (XX, YY)

IF INSIDE WAVE OUTPUT SUBROUTINE WRITES RESULTS AT SELECTED INTERVALS

DIMENSION AND COMMON DECLARATIONS

COMMON YOLD(201), YNEW(201)
COMMON I, J, K, M, A, XNR, NR, ISW, PTSW, YTOL, NR1, ITPT, ITTOT, ITMAX, NWH, KK
COMMON HFREQ, TFREQ, RFREQ, YS, DH, DT
COMMON KDIF, IPCHX, IPCHY, IO, JO, JMAX
COMMON DELX, DELXO, XFF
COMMON EW, MAXOUT
LOGICAL ISW, PTSW
REAL M
INTEGER HFREQ, TFREQ, RFREQ

KWRITE = 0
IF(I.EQ.1 .AND. J.EQ.1) GO TO 21

TEST WHETHER Y IS CHANGING WITH T
IF NOT, SET KK=3 TO SKIP REMAINDER OF POINTS IN THIS LEVEL

IF(ABS(YNEW(NR1)-YOLD(NR1)).LT.EW) KK=3

IF AT UPPER END OF WAVE SET KK = 3 TO SKIP REMAINDER
OF POINTS IN THIS BED LEVEL.

IF(ABS(YS-YY).LE.YTOL) KK=3
IF(I.NE.IO) GO TO 12
IF(J.LT.JMAX) IF(KK=3) 7, 20, 7
20 IO=IO+HFREQ
    JD=IO
    GO TO 3
7 IF(J.NE.JO) GO TO 12
21 JO = JO + TFREQ
3 H = DH * FLOAT(I - 1)
 T = DT * FLOAT(J - 1)
 IF (IABS(IPCHX) .EQ. 1) WRITE (7, 1) J, I, ITPT, I, H, XX, YY
 WRITE (1, 1) J, I, ITPT, T, H, XX, YY
1 FORMAT (1X, 2I5, 16, F11.4, F10.4, 2F14.8)
 IF (KDIF) 4, 2, 4
4 IF (I .NE. J) GO TO 9
 DO 8 K = 1, NR, RFREQ
8 YNEW(K) = XX
 YNEW(NR1) = XX
9 WRITE (3, 6) J, I
6 FORMAT (/1X5HP0INT I4V1H ,,I4)
 IF (IPCHY .EQ. 1) WRITE (7, 6) J, I
 IF (IPCHY .EQ. 1) WRITE (7, 5) (K, YNEW(K), K = 1, NR, RFREQ), NR1, YNEW(NR1)
 WRITE (3, 5) (K, YNEW(K), K = 1, NR, RFREQ), NR1, YNEW(NR1)
5 FORMAT (4(1X, I7, F12.8))
2 ITPT = 0
 PTSW = .FALSE.
11 RETURN
12 IF (I .LT. MAXOUT) GO TO 3
 GO TO 2
END
SUBROUTINE CK(L,D,XX,YY)

C THIS SUBROUTINE CHECKS FOR EXCESS ITERATIONS AND CONTROLS OUTPUT
C OUTPUT OF INTERMEDIATE RESULTS

C DIMENSION AND COMMON DECLARATIONS

COMMON YOLD(201),YNEW(201)
COMMON I,J,K,M,A,XNR,NR,ISW,PTSW,YTOL,VR1,ITPT,ITTOT,ITMAX,ITSW,KK
COMMON HFREQ,TFREQ,RFREQ,YS,DH,DT
COMMON KDIF,IPCHX,IPCHY,IO,JO,JMAX
COMMON DELX,DELXO,XFF
COMMON EW,MAXOUT
INTEGER HFREQ,TFREQ,RFREQ
LOGICAL ISW,PTSW
REAL M

CALL SSWTCH(6,MM)
GO TO (11,12),MM
11 WRITE (?,2) J,I
MM=I-1
REWIND 2
12 KK=1
ITPT=ITPT+1

WRITE OUTPUT IF SS2 IS ON

CALL SSWTCH(2,MM)
GOTO (1,4),MM
1 WRITE(1,2) J,I,ITPT,D,XX,YY,L
2 FORMAT(1X,215,16, 7X, 3F14.8,2X3HCK=12)
4 CONTINUE

TEST FOR EXCESSIVE ITERATIONS
IF(ITPT-ITMAX)3,3,5
C
C WRITE LOCATION OF EXCESSIVE ITERATIONS AND SET KK TO EXIT LOOP
C
5 WRITE(1,6)J,I,ITPT
7 KK=2
3 RETURN
GO TO 3
6 FORMAT(IX,215,16,50X,11H(EXC LOOPS))
END
FUNCTION EQMCHA(Y)
C
C METHYL CYCLOHEXANE - TOLUENE EQUILIBRIUM ON ALUMINA (JOHNSON)
C
C DIMENSION AND COMMON DECLARATIONS
COMMON YOLD(201), YNEW(201)
COMMON I, J, K, M, A, XNR, NR, ISW, PTSW, YTOL, NR1, ITPT, ITTOT, ITMAX, INSW, KK
COMMON HFREQ, TFREQ, RFREQ, YS, DH, DT
COMMON KDIF, IPCHX, IPCHY, IO, JD, JMAX
COMMON DLX, DELXO, XFF
COMMON EW, MAXOUT
LOGICAL ISW, PTSW
REAL M
INTEGER HFREQ, TFREQ, RFREQ
IF(INSW)7,7,1
1 INSW=0
C
1 GET Y* IN EQUILIBRIUM WITH FEED CONCENTRATION
C
YS = 2.718*(XFF/(1.-XFF))**.76
YS = YS/(1.+YS)
WRITE(1,5) YS
5 FORMAT(1X,42HADSORBED PHASE CONC IN EQUILIBRIUM WITH XF, F18.5)
WRITE(1,6)
6 FORMAT(15X,28H(METHYL CYCLOHEXANE-ALUMINA))
C
C GET X IN EQUILIBRIUM WITH Y
C
7 ITTOT=ITTOT +1
EQMCHA = (Y/(1.-Y)**.368)**1.316
EQMCHA = EQMCHA/(1.+EQMCHA)
RETURN
END
C BENZENE N-HEXANE EQUILIBRIUM
C
FUNCTION EQBZHXY(Y)
C
DIMENSION AND COMMON DECLARATIONS
C
COMMON YOLD(201),YNEW(201)
COMMON I,J,K,M,A,XNR,NR,ISW,PTSW,YTOL,NR1,ITPT,ITTOT,ITMAX,INSW,KK
COMMON HFREQ,TFREQ,RFREQ,YS,DH,DT
COMMON KDIF,IPCHX,IPCHY,ID,JO,JMAX
COMMON DELX,DELXO,XFF
COMMON EW,MAXOUT
LOGICAL ISW,PTSW
REAL M
INTEGER HFREQ,TFREQ,RFREQ
C
IF(INSW)6,6,1
C
GET Y* IN EQN WITH XF
C 1 INSW=0
  IF(XFF-.22612,2,3
  2 YS=XFF/(1.1354*XFF+.1032)
  GO TO 4
  3 YS=XFF/(.9398*XFF+.1475)
  4 WRITE(1,5) YS
  5 FORMAT(1X,42HADSORBED PHASE CONC IN EQUILIBRIUM WITH XF,F18.5)
  WRITE(1,10)
  10 FORMAT(15X,18H(BENZENE N-HEXANE))
C
GET X IN EQUILIBRIUM WITH Y
C 6 ITTOT=ITTOT+1
  IF(Y-.629)7,7,8
  7 EQ=.1032*Y/(1.-1.1354*Y)
GO TO 9

8   EQ=.1475*Y/(1-.9398*Y)

9   EQBZHX=EQ
    RETURN
    END
SAMPLE LISTING OF COMPUTED RESULTS
(METHYLCYCLOHEXANE-TOluene-ALUMINA, $a = 40$, $x = .5$)

PROBLEM MCH-TOL-AL, $a=40..$, $x=.5$, 11/2

| INLET FEED COMPOSITION, $x_F$ | 0.50000 |
| INCREMENTAL BED LEVEL, $d_H$ | 0.05000 |
| INCREMENTAL TIME, $d_T$ | 2.00000 |
| DIMENSIONLESS RADIUS, $a$ | 40.00000 |
| NUMBER OF INTERVALS OF RADIUS, $XNR$ | 25.00000 |
| RATIO OF $d_T$ TO $(a/XNR)^{**2}$ | 0.78125 |

TOLERANCES

| WAVE FRONT TEST, $Y_{TOL}$ | 1.00000e-05 |
| ERROR IN CONCENTRATION -BULK PHASE, $E_X$ | 1.00000e-05 |
| -ADSORBED PHASE, $E_Y$ | 1.00000e-05 |

| NUMBER OF TIME STEPS, $J_{MAX}$ | 401 |
| MAXIMUM ALLOWED ITERATIONS PER POINT, $I_{MAX}$ | 200 |

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<th>T</th>
<th>H</th>
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GENERAL BLOCK DIAGRAM FOR SOLUTION OF ADSORPTION MODEL

START

Rewind 1,3

Pause 1

Read Data

Preliminary Calculations: M, ΔH

Write Identification on Output Units

Set INSW = 1 to enter EQ

A

Initialize Problem Parameters:
KK = 1
IO = 1
JO = 1
ITTOT = 1
KULTX = 1
KULT = 1
KQUIT = JMAX
PTSW = .FALSE.
ISW = .FALSE.
I = 1
J = 1
ITPT = 0

Define:
YOLD(K), YNEW(K), (K = 1, N + 1)
Define:
X(K), (K = 1, JMAX)

Write Output for Pt. (1,1)

B

Grid Pt. (J,1):
Set YEST at surface = YOLD(N + 1)

Calc. X* from Function EQ

Call TD

Call CK

C

13

KK = 1 ?

13

YEST - YNEW at surface ?

Y

N

Adjust YEST by Eq (5-4) for another iteration
Grid Pt. (2,2): Set I = 2  
J = 2

Guess $x_{2,2}^{*}$:  
$X B_j = 3(x_j^* - x_j) \Delta H$

Calculate $x^*$ from EQ

Calc XNEW By Quadratic Fit

Call CK

Is $KK = 1$?  
Y  
N

Is $X B_j \approx X N E W$?  
Y  
N

Set $X B_j = X N E W$

Call OUT Pt. (2,2)

Set $K K = 1$

Grid Pt. (J,2): Re-define:  
$Y O L D_k = Y N E W_k$  
$(k = 1, \ldots, n+1)$

Increase $J$ by 1

End of Column 2?  
N  
Y

End of Wave?  
Y  
N

Set $X B_j = X B_{j-1}$  
$X S B_j = X S B_{j-1}$

Guess $y_{n+1}$:  
$y_{est} = Y O L D_{n+1}$

Guess $x_{j,2}^{*}$:  
$X B_j = x_j^* + 3(x_j^* - x_j) \Delta H$

Set $X B_j = X B_j$  
$X S B_j = X S B_j$

End of Wave?  
Y  
N

Is $KK = 1$?  
Y  
N

Set $X B_j = X N E W$

Call OUT Pt. (1,1)
Calc XNEW₂ by Cubic Fit

Re-calc. XNEW* by Function EQ

Call CK

Is KK = 1 ?

Y N

Is XNEW ≠ XNEW₂ ?

N Y

Set XNEW = XNEW₂

Re-define y at Boundary:
YOLDₖ = XNEW₂
(k = 1,...,n+1)

Guess xₖ,i

Guess xₖ,i(XNEW)

Grid Pt. (J,I)
(Typical Point):

Yest = YOLDₙ+1

Calc XNEW₂ by Cubic Fit

Calc XNEW* from Function EQ

Increase J by 1

End of Column I ?

N Y

End of Wave ?

N Y

In Wave ?

N Y

Is XNEW ≠ XNEW₂ ?

N Y

Set XNEW = XNEW₂

Call TD

Call CK
Adjust \textit{yest} by Eq. (5-4)

Is \( Y_{\text{est}} \geq Y_{\text{NEW}}_{n+1} \) ?

Yes \( Y \), No \( N \)

Call \textit{OUT} Pt. \((J, L)\)

Re-define \( y \) for next time step:

\[ Y_{\text{OLD}}_k = Y_{\text{NEW}}_k \]

\((k = 1, \ldots, n+1)\)

Is This an \textit{Ultimate Wave} ?

Yes \( Y \), No \( N \)

Set \( \text{KULT} = 1 \)

Ultimate Wave Routine:
Test \( \text{KULT} \)

Is \( \text{KULT} = 1 \) ?

Yes \( Y \), No \( N \)

Calc \( H \)

Write \( H \) on 1 and/or 3

Set \( \text{KULT} = 1 \)

Calc \( K_{\text{QUIT}} \)

Write Total Iterations on 3 (\text{ITTOT})

To \text{START}
SUBROUTINE TD

Initial Entry

Set ISW=.TRUE.

Calc B by Eq(A18)
Calc W by Eq(A20)

Calc S1=6m + 1
S2 = B

Calc Sk = B - x2/Sk-1
(k = 3,...,n)

Calc S_{n+1} = R - \frac{2x^n}{(n-1)S_n}

Calc YEND = YOLD_{n+1} + WΔx

First Use of TD at this Pt

Y N

N

Set PTSW=.TRUE.

SUBROUTINE CK

Set KK = 1

Accumulate Iteration Count (ITPT)

Is S. S. 2 ON

Yes

Write output on 1 (for tracing use)

Too Many Iterations

No

Write Location of this Point (I, J)

Set KK = 2

RETURN
SUBROUTINE OUT

Is y Changing?

Set KK = 3

End of Wave?

Set KK = 3

Is I = IO?

Is J < JMAX?

Is KK = 3?

Increase IO by HFREQ
Set JO = IO

Calc H and T

Write Results on 1 and/or 7

Increase JO by TFREQ

Is J = JO?

Is I = J?

Is I < MAXOUT?

Set ITPT = 0
PTSW = .FALSE.

Set KK = 3

Re-define YNEW_k = x_{i,j} (k=1,...,n)

Write y_k on 3 and/or 7 (k = 1,...,n+1)

RETURN
Operating Instructions

Although the program as written is in the FORTRAN language, some modifications may be required before it is used on another computer, particularly the input/output operations. The operating procedure outlined herein will involve primarily the preparation of input data, along with certain options that are available for results. Details of machine operation may be found in the appropriate reference manuals (28).

Data Cards

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<td>I5</td>
<td>31-35</td>
<td>KDIF,</td>
<td>code for output of diffusion curves: zero for no output; one for output on logical unit one and/or three</td>
</tr>
</tbody>
</table>
Card Format Columns Variable

3 I5 36-40 IPCHX, code for output of bulk-phase solutions: one for both printed output on logical unit one and punched output on logical unit seven; zero for printed output only

I5 41-45 IPCHY, code for output of diffusion curves: one for punched output on logical unit 7, and printed output on logical unit three; zero for printed output (only effective for KDIF = 1)

I5 46-50 MAXOUT, column number up to which output for every grid point is given overriding HFREQ and TFREQ. Same logical units as for IPCHX and IPCHY

Equilibrium Function

Before the program can be used with any system other than those included in this work, an appropriate subroutine for equilibrium relationships must be prepared. The requirements of this subroutine are as follows. The name of the subroutine must be given by the FORTRAN statement, FUNCTION EQ (argument). The FORTRAN COMMON statements listed in the main program must be reproduced and included with the subroutine. In the first use of the subroutine, the argument is the feed concentration, for which \( y^* \) (YS in the program) must be computed. Whatever instructions are necessary, including input or output, may be included to obtain \( y^* \). There must be a statement to test a parameter INSW, which initially is set to 1 by the main program, then to zero after \( y^* \) is computed. Thereafter the calculation for \( y^* \) will be skipped and the subsequent use of EQ will be to compute \( x^* \) in terms of the given
argument $y$. Any appropriate instructions may be given, the last executed statement calling for a return to the main program. A flow diagram illustrating the general requirements for this subroutine is given below.

Each time the function is used one is to be added to a variable, ITTOT, to record the total number of iterations executed.

**General Comments on Use of the Program**

If all options are called for, a total of four output devices are necessary, exclusive of whatever devices are required by the computer system itself. The normal mode of operation is to obtain both printed and punched output for only the bulk phase concentration, as it is this output which is compared with experimental data to determine the mass transfer coefficient.

The input data, except for feed concentration and identification, is to some extent a matter of experimentation. Once a feasible operating set of parameters is found, slight variations may be made to optimize computer usage. For instance the damping factor, QQ, must be determined, as there is usually some value above which divergence will
occur. If QQ is made too low, the number of iterations increases. The optimum value may be obtained by making a few false starts at various QQ values to get the number of iterations made at some selected point, then plotting QQ versus number of iterations. Similar tests may be run to get optimum values of the error tolerances, which if too high, cause inaccurate results, or if too low increase the number of iterations, with a waste of accuracy.

For each system checked in the present study, a convergent process, no matter how time-consuming, could always be found. There is no guarantee, however, that any system will behave so well. One must expect to spend considerable effort before obtaining the first successful run.

Since some problems require much time on the computer a built-in interrupt procedure has been included. If, in the middle of a run, it is desired to suspend calculations temporarily, a console switch may be depressed to cause output of all intermediate results. This output may be used to restart from the point of interruption. The present program, as used on the 7040, permits a dump of computer storage, and registers on a magnetic tape (B-1) by depressing console switch 4; later restart from this point may be accomplished by mounting the dumped output on the same tape unit from which the dump was taken, and then using the installation restart procedure.

The program also provides a means for tracing the progress of intermediate calculations by use of console switch number 2. If trouble is encountered more detail may be obtained by depressing this switch, with the results of each iteration being printed on logical unit 1.
This switch should not be used except for debugging purposes due to the high volume of output.

A built-in check for excessive iterations is provided. If the maximum number (called ITMAX in the program) is exceeded a message will be written on the main output unit (logical unit 1), along with the grid point location. Also provided are checks to prevent computing grid points outside of the adsorption wave. If the difference between \( y \) and \( y^* \) is less than the variable YTOL, then calculations are stopped for that particular bed level. All remaining points are then set to the equilibrium values corresponding to the upper end of the wave.

The maximum mesh size permitted in the present version of the program allows one thousand intervals in both the H- and T-directions. This number may be altered according to storage limitations of the computer. Approximately 20,000 words of storage are required with the present program and machine configuration.

**Machine Configuration Used**

**Computer:** IBM 7040 Data Processing System  
Data channels  
A: 1622 Card Read Punch (BCD only)  
B: 4 magnetic tape units (7330)  
C: 4 magnetic tape units (7330)  
Memory Size: 32,768 binary words  
Extended Instruction set

**Monitor System:** IBM 7040/7044 Operating System (16/32K)  
Version 6
NOMENCLATURE

a  Effective particle radius, ft
A  Dimensionless particle radius, defined by Eq. (4-7)
As  Surface area across which diffusion occurs on the surface of the spherical particles, ft$^2$/ft$^3$ bed
D  Effective intraparticle diffusivity, ft$^2$/hr
fa  Fraction of saturation, or degree of adsorption in a column of length, z
fa'  Fraction of saturation in a length of column equivalent to the length of a wave
fag  Fractional saturation of column at beginning of steady state
fas  Fractional saturation of adsorption zone at beginning of steady state
fasw  Fractional saturation of adsorption zone at any point within the column
fv  Fraction voids within adsorbent bed
H  Dimensionless bed level parameter, defined by Eq. (4-8)
HL  Height of transfer unit based on liquid film coefficient, K, ft
i,j  Subscripts denoting column number of triangular grid
K  Mass transfer coefficient for external surface film, ft/sec
m  Ratio of $\Delta T$ to $(\Delta R)^2$ in finite difference equation for internal diffusion
n  Number of increments used in finite difference equation for internal diffusion
NL  Number of transfer units, based on liquid-film coefficient, K
Q  Total liquid feed flow rate, ft$^3$/hr
r  Particle radius variable, ft
R  Dimensionless particle radius variable, defined by Eq. (4-7)
S  Cross-sectional area of adsorbent column, ft²
T  Dimensionless time variable, defined by Eq. (4-9)
Tₛ  Dimensionless time corresponding to beginning of steady state
Vₐ  Total quantity of more adsorbable component in effluent stream, ft³
Vₐ'  Maximum quantity of more adsorbable component that could be contained in a length of bed equal to the length of a wave, ft³
Vₚ  Pore volume, ft³/lb adsorbent
Vₐₖ  Total volume of liquid in effluent liquid, ft³
W  Rate of transfer of more adsorbable component from bulk phase to adsorbed phase in differential section, dz, ft³/hr
x  Volumetric concentration of more adsorbable component in non-adsorbed phase ft³/ft³
xₘ  Instantaneous volumetric concentration of more adsorbable component at wave front, ft³/ft³
xₕ  Volumetric feed concentration of more adsorbable component, ft³/ft³
x*  Volumetric concentration of more adsorbable component on bulk-phase side of interface in equilibrium with the adsorbed phase interfacial concentration, ft³/ft³
y  Volumetric concentration of more adsorbable component in adsorbed phase, ft³/ft³
y*  Volumetric concentration of more adsorbable component in adsorbed phase in equilibrium with feed, ft³/ft³
z  Bed height variable, ft
zₛ  Length of adsorbent bed required for formation of ultimate wave, hr
zₘ  Length of an adsorption zone, ft
θ  Real time elapsed since initial contact of feed with adsorbent, hr
$\theta_s$  Real time elapsed from initial startup until beginning of steady-state, hr

$\theta_w$  Real time required for adsorption zone to pass a given point, hr

$\rho_b$  Bed density, lb/ft$^3$
AUTobiography

The author was born July 18, 1934, in West Palm Beach, Florida, attended public schools in that city, and graduated from Palm Beach High School in June, 1951. He attended the University of Chicago, Chicago, Illinois, during 1951-1952; attended the Georgia Institute of Technology, Atlanta, Georgia, from 1952 to 1955, majoring in chemical engineering, and graduated with the bachelor's degree in June, 1956; worked for Esso Research Laboratories, Baton Rouge, Louisiana, as an engineer from 1955 to 1958; enrolled in Louisiana State University, Baton Rouge, Louisiana in 1959, majoring in chemical engineering and minoring in business administration, worked as a graduate assistant in the Department of Chemical Engineering and the Computer Research Center and as an instructor in the Department of Mechanical Engineering, and graduated with the master's degree in chemical engineering in August, 1960; enrolled in L.S.U. in 1960 on the doctoral program, majoring in chemical engineering, and is presently a candidate for the degree of doctor of philosophy. He is presently employed full-time by the Computer Research Center as Assistant Director. He is a member of Tau Beta Pi, Phi Lambda Upsilon, Phi Kappa Phi, the American Institute of Chemical Engineers, and the Association for Computing Machinery; and is a registered professional engineer, State of Louisiana. He is married to the former Marilyn Joyce Griffin of Jonesboro, Arkansas.
EXAMINATION AND THESIS REPORT

Candidate: Elmer Lawrence Morton, Jr.

Major Field: Chemical Engineering

Title of Thesis: Analysis of Liquid-Phase Adsorption Fractionation in Fixed Beds

Approved:

[Signatures]

Major Professor and Chairman

Dean of the Graduate School

EXAMINING COMMITTEE:

[Signatures]

Date of Examination: January 11, 1965