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Analysis of Liquid-Phase Adsorption Fractionation in Fixed Beds.

Elmer Lawrence Morton Jr

Louisiana State University and Agricultural & Mechanical College

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ANALYSIS OF LIQUID-PHASE ADSORPTION FRACTIONATION
IN FIXED BEDS

A Dissertation

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requirements for the degree of
Doctor of Philosophy

in

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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:	Qx	ft^3/hr
Output stream:	$Qx + \left(\frac{\partial Qx}{\partial z} \right)_{\theta, r} dz$	ft^3/hr
Output from bulk phase to adsorbent: W		ft^3/hr
Accumulation in bulk phase:	$f_v \left(\frac{\partial x}{\partial \theta} \right)_{z, r} S dz$	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.

θ = 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:

$$-Q \left(\frac{\partial x}{\partial z} \right)_{\theta, r} dz + W = f_v \left(\frac{\partial x}{\partial \theta} \right)_{z, r} S dz \quad (4-1)$$

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;

$$\text{Surface area per sphere} = 4 \pi a^2 \quad \text{ft}^2$$

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

$$\begin{aligned} \text{Pore volume per unit} \\ \text{volume of spheres} \end{aligned} = \frac{V_p \rho_b}{1-f_v} \quad \text{ft}^3/\text{ft}^3$$

where	V_p	= pore volume, ft ³ /lb absorbent
	ρ_b	= density of absorbent, lb/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:

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

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

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

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

$$\begin{aligned} -Q \left(\frac{\partial x}{\partial z} \right)_{\theta, r} dz + \frac{3D(V_p \rho_b)}{a} Sdz \left(\frac{\partial y}{\partial r} \right)_{\theta, z, r=a} &= f_v \left(\frac{\partial x}{\partial \theta} \right)_{z, r} Sdz \\ \text{or } -\frac{Q}{S} \left(\frac{\partial x}{\partial z} \right)_{\theta, r} + \frac{3D(V_p \rho_b)}{a} \left(\frac{\partial y}{\partial r} \right)_{\theta, z, r=a} &= f_v \left(\frac{\partial x}{\partial \theta} \right)_{z, r} \end{aligned} \quad (4-3)$$

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

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

Material leaving at r is $4 \pi r^2 D \left(\frac{\partial y}{\partial r} \right)_{\theta, z} \cdot \frac{V_p}{1-f_v}$

and accumulation is $4 \pi r^2 \frac{V_p}{1-f_v} \left(\frac{\partial y}{\partial \theta} \right)_{r, z} d\theta$

Equating terms gives the intraparticle material balance:

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

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

which leads to:

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

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, 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 θ , z , and r by these equations:

$$R = r \cdot \frac{K}{D}, \text{ or if } r=a, A = a \cdot \frac{K}{D} \quad (4-7)$$

$$H = \frac{KV_p \rho_b}{(Q/S)a} \cdot z \quad (4-8)$$

$$T = \frac{K^2}{D} \left(\theta - \frac{f_v z}{Q/S} \right) = \frac{AK}{a} \left(\theta - \frac{f_v z}{Q/S} \right) \quad (4-9)$$

By using the chain rule of differentiation:

$$\left(\frac{\partial y}{\partial r} \right)_{\theta, z} = \left(\frac{\partial y}{\partial R} \right)_{H, T} \left(\frac{\partial R}{\partial r} \right)_{H, T} \quad (4-10)$$

From equation (4-7), and since R is a function of r ,

$$\left(\frac{\partial R}{\partial r}\right)_{H,T} = \frac{K}{D} \quad (4-11)$$

Then

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

Substitution of equation (4-12) into equation (4-5) gives the following dimensionless form:

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

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:

$$\begin{aligned} \left(\frac{\partial^2 y}{\partial r^2}\right)_{\theta,z} &= \left[\frac{\partial \left(\frac{\partial y}{\partial r}\right)}{\partial r} \right]_{\theta,z} = \left[\frac{\partial \left(\frac{\partial y}{\partial R}\right) \left(\frac{\partial R}{\partial r}\right)}{\partial r} \right]_{\theta,z} \\ &= \left[\left(\frac{\partial y}{\partial R}\right) \left(\frac{\partial^2 R}{\partial r^2}\right) + \left(\frac{\partial R}{\partial r}\right) \frac{\partial \left(\frac{\partial y}{\partial R}\right)}{\partial r} \right]_{\theta,z} \end{aligned}$$

Since $\frac{\partial^2 R}{\partial r^2} = 0$ and $\frac{\partial R}{\partial r} = \frac{K}{D}$,

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

then

$$\left(\frac{\partial^2 y}{\partial r^2}\right)_{\theta,z} = \frac{K^2}{D^2} \left(\frac{\partial^2 y}{\partial R^2}\right)_{T,H}$$

The term $\frac{\partial y}{\partial \theta}$ is readily changed to dimensionless form:

$$\left(\frac{\partial y}{\partial \theta}\right)_{r,z} = \left[\left(\frac{\partial y}{\partial T}\right) \left(\frac{\partial T}{\partial \theta}\right) + \left(\frac{\partial y}{\partial R}\right) \left(\frac{\partial R}{\partial \theta}\right) + \left(\frac{\partial y}{\partial H}\right) \left(\frac{\partial H}{\partial \theta}\right) \right]_{r,z}$$

The last two terms on the right of this equation are zero and

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

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

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

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 :

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

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

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

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

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

$$\left(\frac{\partial x}{\partial \theta}\right)_{r,z} = \left[\frac{\partial x}{\partial T} \frac{\partial T}{\partial \theta} \right]_{r,z} \quad (4-20)$$

The partial derivatives $\left(\frac{\partial T}{\partial x}\right)_{r,\theta}$, $\left(\frac{\partial H}{\partial z}\right)_{r,\theta}$, and $\left(\frac{\partial T}{\partial \theta}\right)_{r,z}$ are evaluated

from equations (4-8) and (4-9):

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

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

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

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:

$$\text{at } T = 0, y = y_0, \text{ for all } H$$

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 $H = T$. 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 $T \geq 0$

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:

$$y_i = \frac{m(1 - 1/i)y_{i-1} + m(1 + 1/i)y_{i+1} + y_i}{(2m + 1)} \quad (5-1)$$

where y = adsorbed phase concentration at time, $T + \Delta T$

y^i = adsorbed phase concentration at time, T
 i = subscript denoting position along pore radius
 m = ratio, $\Delta T / (\Delta R)^2$

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

$$y_0 = \frac{6my_1 + y_0^i}{1 + 6m} \quad (5-2)$$

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

$$y_n = \frac{2my_{i-1} + y_n^i + 2(x - x^*)m \cdot (1 + 1/n)\Delta R}{(1 + 2m)} \quad (5-3)$$

where $x - x^*$ = concentration difference in bulk phase proportional to gradient at pore opening

n = number of finite intervals into which pore radius is divided

ΔR = 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 (ΔT) , 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 ΔR and ΔT 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, $y_0, y_1, \dots, y_{n-1}, y_n$, 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, $(\partial y / \partial R)_{R=A}$. 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 :

$$y_n^{(2)} = y_n^{(0)} + (y_n^{(0)} - y_n^{(1)})q \quad (5-4)$$

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:

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

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

$$x_{2,2}^{(0)} = x_{2,1} + 3(x - x^*)_{2,1}\Delta H \quad (5-5)$$

Using $x_{2,2}^{(0)}$ 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 $x_{2,2}$:

$$x_{2,2}^{(2)} = x_{2,1} - \frac{3}{2} \left[\left(\frac{\partial y}{\partial R} \right)_{2,1} + \left(\frac{\partial y}{\partial R} \right)_{2,2} \right] \Delta H \quad (5-6)$$

or

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

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., $y_k = x_{2,2}$ ($k = 0, 1, \dots, n$).

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 $3 \leq i$):

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

which becomes, after substitution of equation (13):

$$x_{i,i}^{(1)} = x_{i-1,i} + \frac{\Delta H}{4} \left[5(x^*-x)_{i,i}^{(0)} + 8(x^*-x)_{i-1,i} - (x^*-x)_{i-2,i} \right] \quad (5-9)$$

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: $x_{i,i} = y_k$ ($k = 0, 1, 2, \dots, n$).

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 ΔH 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 ΔH , ΔR , and ΔT 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 operations, known as machine language instructions, may be organized into a logical arrangement, or program, to solve the numerical problem. Instead 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, particularly 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 relations 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 pertaining 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 described 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, $\frac{f_v z}{Q/S}$, 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, θ , 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, $\frac{KV_p \rho_b}{a(Q/S)}$, 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 proposed 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 determination of a suitable mass transfer coefficient so that a practical estimation 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 predict 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 θ 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, 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 2.54×10^{-3} and 1.12×10^{-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 $K = .85 \times 10^{-4}$ for the adsorption of toluene-octane, compared with 0.74×10^{-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, θ , by use of the transformation equation

$$T = \frac{AK}{a} \left(\theta - \frac{f_v z}{Q/S} \right) \quad (4-9)$$

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

$$\theta_w = \theta_2 - \theta_1 \quad (6-1)$$

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

$$V_w = Q\theta_w \quad (6-2)$$

where V_w is the total volume of effluent liquid, ft^3 .

Figure 3. Formation of the Ultimate Wave

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, θ_1 and θ_2 :

$$V_a = \int_{\theta_1}^{\theta_2} Qx d\theta = Q \int_{\theta_1}^{\theta_2} x d\theta \quad (6-5)$$

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:

$$f_a' = \frac{V_a' - V_a}{V_a'} = 1 - \frac{\int_{\theta_1}^{\theta_2} x d\theta}{(\theta_2 - \theta_1)x_f} \quad (6-6)$$

The limits of integration, θ_1 and θ_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, θ_1 and θ_2 , is given by

$$z_w = \frac{Q\theta_w}{f_v S + V_p \rho_b S} \quad (6-7)$$

The remainder of the column is saturated, so that the overall degree of saturation, or adsorption, f_a , is expressed by the relation

$$\begin{aligned}
 f_a &= \frac{z - z_w}{z} + \frac{f_a' z_w}{z} \\
 &= 1 - \frac{Q\theta_w}{(V_p \rho_b + f_v) S z} (1 - f_a')
 \end{aligned} \tag{6-8}$$

or in terms of bed weight and density,

$$f_a = 1 - \frac{Q\theta_w \rho_b}{(V_p \rho_b + f_v) W} (1 - f_a') \tag{6-9}$$

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

Rearranging Equation (4-9) gives

$$\theta = \frac{Ta}{AK} + \frac{f_v z}{Q/S} \tag{6-10}$$

Substituting for z from Equation (4-8) gives

$$\theta = \frac{Ta}{AK} + \frac{f_v a H}{KV_p \rho_b} \tag{6-11}$$

Since $H = T/A$,

$$\theta = \frac{Ta}{AK} \left(1 + \frac{f_v}{V_p \rho_b} \right) \tag{6-12}$$

Since $\theta_w = \theta_2 - \theta_1$,

$$\theta_w = (T_2 - T_1) \frac{a}{AK} \left(1 + \frac{f_v}{V_p \rho_b} \right) \tag{6-13}$$

At steady state, $\theta = \theta_s$, and

$$\theta_s = \frac{T_s a}{AK} \left(1 + \frac{f_v}{V_p \rho_b} \right) \tag{6-14}$$

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_{a_s} , at θ_s may be obtained by drawing a vertical line from the θ - axis at θ_s . The point at which this line crosses the feed line is the upper limit, θ_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, θ_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_{a_s} and $f_{a_s}^*$ 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 θ_s (corresponding to a length, z_s) 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:

$$Qdx = Ka (x - x^*) Sdz \quad (6-16)$$

Integration of this equation between appropriate limits gives:

$$\int_{x_1}^{x_2} \frac{dx}{x - x^*} = \frac{KaSz}{Q} = N_L \quad (6-17)$$

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

$$H_L = \frac{Ka}{Q/S} \quad (6-18)$$

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.

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APPENDIX A
NUMERICAL METHODS

TABLE I
 ACCURACY CHECK ON INCREMENT SIZE
 (At A = 10)

Bulk Concentration At H = .1, T = 10			
<u>ΔR</u>	<u>ΔT</u>	<u>8-Digit Precision</u>	<u>16-Digit Precision</u>
.4	.10	.49094	.49094
	.25	.49052	.49084
	.50	.49055	
	1.00	.49016	
.2	.10	.49044	
	.25	.49079	.49084
	.50	.49055	
	1.00	.49015	
.1	.10	.49044	
	.25	.49079	.49084
	.50	.49055	
	1.00	.49015	

DERIVATION OF IMPLICIT FINITE DIFFERENCE EQUATIONS FOR THE
INTRAPARTICLE DIFFUSION EQUATION

$$\left[\frac{\partial^2 y}{\partial R^2} + \frac{2}{R} \frac{\partial y}{\partial R} \right]_T = \left(\frac{\partial y}{\partial T} \right)_R \quad (\text{A-1})$$

Finite Difference Formulas (Reference 11):

$$\frac{\partial^2 y}{\partial R^2} = \frac{y_{i-1} - 2y_i + y_{i+1}}{(\Delta R)^2} + O(\Delta x)^2 \quad (\text{A-2})$$

$$\frac{\partial y}{\partial R} = \frac{y_{i+1} - y_{i-1}}{2\Delta R} + O(\Delta x)^2 \quad (\text{A-3})$$

$$\frac{\partial y}{\partial T} = \frac{y_i' - y_i}{\Delta T} + O(\Delta t) \quad (\text{A-4})$$

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

$$\frac{y_{i-1} - 2y_i + y_{i+1}}{(\Delta R)^2} + \frac{2(y_{i+1} - y_{i-1})}{i(\Delta R)^2} = \frac{y_i' - y_i}{\Delta T} \quad (\text{A-5})$$

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

$$-m \left(1 - \frac{1}{i}\right) y_{i-1} + (2m + 1) y_i - m \left(1 + \frac{1}{i}\right) y_{i+1} = y_i' \quad (\text{A-6})$$

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

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:

$$\lim_{R \rightarrow 0} \frac{2}{R} \frac{\partial y}{\partial R} = 2 \frac{\partial^2 y}{\partial R^2} \quad (\text{A-7})$$

$$R \rightarrow 0$$

Thus the diffusion equation becomes

$$3 \cdot \frac{\partial^2 y}{\partial R^2} = \frac{\partial y}{\partial T} \quad (\text{at } R = 0) \quad (\text{A-8})$$

The corresponding substitution of finite difference formulas gives the following:

$$3 \cdot \frac{y_1 - 2y_0 + y_1'}{(\Delta R)^2} = \frac{y_0 - y_0'}{\Delta T} \quad (\text{A-9})$$

Solving for y_0' :

$$(1 + 6m) y_0 - 6my_1 = y_0' \quad (\text{A-10})$$

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

$$y_{n-1} = y_n - \left(\frac{\partial y}{\partial R} \right)_{R=A} \Delta R + \left(\frac{\partial^2 y}{\partial R^2} \right)_{R=A} \cdot \frac{(\Delta R)^2}{2} \quad (\text{A-11})$$

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

$$\left(\frac{\partial^2 y}{\partial R^2} \right)_{R=A} = (y_{n-1} - y_n) \frac{2}{(\Delta R)^2} + \left(\frac{\partial y}{\partial R} \right)_{R=A} \quad (\text{A-12})$$

Substitution of the above expression into the diffusion equation gives

$$(y_{n-1} - y_n) \frac{2}{(\Delta R)^2} + \left(\frac{\partial y}{\partial R} \right)_{R=A} \cdot \frac{2}{\Delta R} + \frac{2}{A} \left(\frac{\partial y}{\partial R} \right)_{R=A} = \left(\frac{\partial y}{\partial T} \right)_A \quad (\text{A-13})$$

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 $\left(\frac{\partial y}{\partial T}\right)_A$ results in

$$\frac{y_{n-1} - y_n}{(\Delta R)^2} + (x - x^*) \frac{1}{\Delta R} + \frac{1}{A} = \frac{y_n - y_n'}{\Delta T} \quad (A-14)$$

Solving for y_n' :

$$y_n' = -2m y_{n-1} + (1 + 2m)y_n - 2m (x - x^*) \left(1 + \frac{\Delta R}{A}\right) \quad (A-15)$$

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:

$$\begin{array}{rcl} (1 + 6m) y_0 - 6m y_1 & & = y_0' \\ a y_0 + b y_1 + c y_2 & & = y_1' \\ \quad a y_1 + b y_2 + c y_3 & & = y_2' \\ \quad \quad \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & & \cdot \\ \quad \quad \quad \cdot \quad \cdot \quad \cdot \quad \cdot \quad \cdot & & \cdot \\ \quad \quad \quad \quad \quad \quad -2m y_{n-1} + b y_n & & = y_n' + w \end{array} \quad (A-16)$$

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.

APPENDIX B

RESULTS

TABLE II

SUMMARY OF ADSORPTION SYSTEMS INVESTIGATED

System and Reference	Curve Ident.	Feed Fraction, x_f	Column Diam.	Bed Wt.	Liquid Rate	Bed Density	Pore Vol.	Fraction Voids	M. T. Coeff. $K(x10^3)$	Dimensionless Parameter, A (Best for System)	K_{av} ($x10^3$)
	(Figs. 4-32)		(cm)	(gm)	(cc/sec)	(g/cc)	(cc/g)		(cm/sec)		(cm/sec)
1. MCH-Toluene on 6-12 Mesh Silica Gel (30)	A	0.5	2.47	195	0.0786	0.679	0.402	0.293	2.42		
	B	0.5	2.47	95	0.0786	0.679	0.402	0.293	2.43	50	2.54
	C	0.5	2.47	191	0.050	0.679	0.402	0.293	2.61		
	D	0.5	2.47	95	0.050	0.679	0.402	0.293	2.70		
2. MCH-Toluene on 6-12 Mesh Silica Gel (30)	E	0.1	2.47	96	0.174	0.679	0.402	0.293	1.07	30	1.12
	F	0.1	2.47	45	0.174	0.679	0.402	0.293	1.17		
3. MCH-Toluene on 8-14 Mesh Alumina (30)	G	0.5	2.47	268	0.0625	0.883	0.189	0.425	0.816		
	H	0.5	2.47	130	0.0625	0.883	0.189	0.425	0.711	3	0.741
	I	0.5	2.47	63	0.0625	0.883	0.189	0.425	0.697		
4. Benzene-n-Hexane on Thru-200-Mesh Silica Gel (43)	J	0.5	1.9	20	0.00406	0.712	0.357	0.528	0.0442	20	0.0442

TABLE III

WAVE FORMATION TIMES, BED DEPTH, AND SATURATION

<u>System</u>	<u>Curve Ident</u>	<u>z_s, cm</u>	<u>θ_s, sec</u>	<u>f_{as}'</u>	<u>f_{as}</u>	<u>Constant wave data</u>		
				<u>Eq (6-6)</u>	<u>Eq (6-9)</u>	<u>θ_w, sec</u>	<u>f_{aw}'</u>	<u>z_w, cm</u>
1. MCH-Toluene- Silica Gel ($x = .5$)	A,B	84.2	2900	0.211	0.26	4830	0.372	140.5
	C,D	53.5	2900	0.211	0.26	4830	0.372	89.4
2. MCH-Toluene- Silica Gel ($x = .1$)	E,F	95.5	1489	0.183	0.20	3870	0.369	248
3. MCH-Toluene- Alumina ($x = .5$)	G,H,I	136.0	6170	0.301	0.54	5930	0.434	131.0
4. Benzene-n-Hexane- Silica Gel ($x = .5$)	J	27.5	2645	0.159	0.24	4020	0.350	41.6

FIGURE 4. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 1.0$

FIGURE 5. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 5.0$

FIGURE 6. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 10$

FIGURE 7. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 20$

FIGURE 8. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 40$

FIGURE 9. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 50$

FIGURE 10. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 60$

FIGURE 11. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 80$

FIGURE 12. BENZENE-N-HEXANE ON SILICA GEL, $A = .01$

FIGURE 13. BENZENE-N-HEXANE ON SILICA GEL, $A = .1$

FIGURE 14. BENZENE-N-HEXANE ON SILICA GEL, $\alpha = 1.0$

FIGURE 15. BENZENE-N-HEXANE ON SILICA GEL, $\mu = 2.0$

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

FIGURE 17. BENZENE-N-HEXANE ON SILICA GEL, $A = 20$

FIGURE 18. BENZENE-N-HEXANE ON SILICA GEL, $A = 30$

FIGURE 19. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 10$

FIGURE 20. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 20$

FIGURE 22. METHYLCYCLOHEXANE-TOLUENE ON SILICA GEL, $A = 40$

FIGURE 23. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, $P = .01$

FIGURE 24. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, $A = .1$

FIGURE 25. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, $A = 1.0$

FIGURE 26. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, $A = 2.0$

FIGURE 27. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, $A = 3.0$

FIGURE 28. METHYL CYCLOHEXANE-TOLUENE ON ALUMINA, $A = 5.0$

FIGURE 29. METHYL CYCLOHEXENE-TOLUENE

FIGURE 30. METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, $A = 20$

FIGURE 31. METHYL CYCLOHEXANE-TOLUENE ON ALUMINA, $A = 40$

FIGURE 32, METHYLCYCLOHEXANE-TOLUENE ON ALUMINA, A = 80

Figure 33. Effect of Equilibrium on Computed Results

Figure 34. Effect of Particle Size on the System: MCH-Toluene on Alumina

Figure 35. Comparison of Johnson's Model with the Proposed Model (Curves A and B)

APPENDIX C
COMPUTER PROGRAM

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C      SOLUTION OF ADSORPTION MODEL - MAIN PROGRAM
C
C
C      DEFINE ERROR FUNCTION
C
C      E(A1,A2,ERROR)=ABS((A1-A2)/A1)-ERROR
C
C      DIMENSION AND COMMON DECLARATIONS
C      DIMENSION X(1001),XS(1001),XB(1001),XSB(1001)
C      COMMON YOLD(201),YNEW(201)
C      COMMON I,J,K,M,A,XNR,NR,ISW,PTSW,YTOL,NR1,ITPT,ITTOT,ITMAX,INSW,KK
C      COMMON HFREQ,TFREQ,RFREQ,YS,DH,DT
C      COMMON KDIF,IPCHX,IPCHY,IO,JO,JMAX
C      COMMON DELX,DELXD,XFF
C      COMMON EW,MAXOUT
C      LOGICAL ISW,PTSW
C      REAL M
C      INTEGER HFREQ,TFREQ,RFREQ
C
C      INPUTS
C
C      1      REWIND1
C      REWIND3
C      PAUSE1
C      2      READ3,XF,QQ,DT,A,XNR,P1,P2,P3,P4,P5,P6
C      READ3,YTOL,EX,EY
C      3      FORMAT(5E10.0,6A5)
C      READ4,JMAX,ITMAX,HFREQ,TFREQ,RFREQ,KDIF,IPCHX,IPCHY,MAXOUT
C      4      FORMAT(16I5)
C
C      PRELIMINARY CALCULATIONS
C
C      M=DT*(XNR/A)**2
C      NR=XNR
C      NR1=NR+1

```

```

      DH=DT/A
      XFF=XF
      L=1
C
C      WRITE DATA IN HEADING
C
14  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,14HDAMPING FACTOR,F46.5)
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(1X10HTOLERANCES/6X,21HWAVE 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(1X26HNUMBER OF TIME STEPS, JMAX,28X,I6/
9      1X,43HMAXIMUM ALLOWED ITERATIONS PER POINT, ITMAX,I17)
C
C      IF DIFFUSION CURVES ARE TO BE OUTPUT, WRITE HEADING ON LOGICAL
C      UNIT 3.
C
      L=3
      IF(KDIF.NE.1) GO TO 17
      KDIF=-1
      GO TO 14
C
C      GO TO FUNCTION EQ TO READ AND WRITE EQUILIBRIUM DATA.  SET INSW = 1
C      TO ENTER EQ INITIALLY.
C
17  L=7

```

```

        IF(IPCHX.NE.1) GO TO 117
        IPCHX=-1
        GO TO 14
117     INSW=1
        IPCHX=1ABS(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
C       SET EXCESSIVE ITERATION SWITCH
C
18      KK=1
C
C       SET FREQUENCY OF OUTPUT PARAMETERS
C
        IO=1
        JO=1
C
C       SET TOTAL ITERATION COUNTER
C
        ITTOT=0
C
C       SET ULTIMATE WAVE SWITCHES
C
        KULT=1
        KULTX=0
        KQUIT=JMAX
C
C       SET DIFFUSION CALCULATION SWITCHES
C

```

```

        ISW=.FALSE.
        PTSW=.FALSE.
C
C      INITIALIZE TIME AND BED DEPTH INDEXES
C
        I=1
        J=1
C
C
C      GRID POINT 1,1 (APEX OF TRIANGLE)
C
C      DEFINE YOLD(K) AND INITIAL ESTIMATE OF Y AT SURFACE
C
        DO10K=1,NR1
        YNEW(K)=XF
10      YOLD(K)=XF
        DO11K=1,JMAX
11      X(K)=XF
        CALL OUT(XF,XF)
        J=2
C
C
C      GRID POINT J,1 (INCREASE TIME STEP)
C
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)

```

```

C
C      SAVE VALUES OF X AND Y FOR NEXT POINT
C
      DO70K=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
78     I=2
C
C                                     GRID POINT 2,2 (BED LEVEL = DH)
C
C      GUESS CONCENTRATION ALONG BOUNDARY A*H=T
C
      I=2
      J=1
      DELA=XS(J)-X(J)
      XB(J)=X(J)+DELA*DH*3.
80     XSB(J)=EQ(XB(J))
      DELB=XSB(J)-XB(J)
      XNEW=X(J)+ DH*(DELA+DELB)*1.5
      CALL CK(2,DELB,X B(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
C
C      SET YOLD(K) FOR NEXT TIME STEP
C
      DO120K=1,NR1
120    YOLD(K)=XB(J)

```



```

        CALL OUT(XNEW,YY)
C
C      SAVE X AND Y FOR NEXT TIME STEP
C
        DO220K=1,NR1
220     YOLD(K)=YNEW(K)
        GO TO 130
C
C
C                                     GRID POINT I,I (ALONG BOUNDARY A*H=T)
C
230     I=I+1
        IF(I.GT.JMAX)GOTO390
C
C      TEST IF ULTIMATE WAVE WAS FOUND
C
        IF(I.GT.KQUIT) GO TO 390
        IF(KULT.EQ.0) GO TO 400
C
C      TEST SS 4 FOR JOB INTERRUPT
C
232     CALL SSWTCH(4,I1)
        IF(I1.NE.1) GO TO 240
        REWIND 1
        REWIND 3
234     CALL ICKPT
        PAUSE2
240     J=I
        KULT=0
        DELA=XS(J)-X(J)
        DELB=XSBJ(J)-XB(J)
C
C      ESTIMATE X AT THIS POINT BY A SECOND DEGREE FIT, THEN THIRD DEGREE
C
        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
C
C      GRID POINT J,I (TYPICAL POINT)
C
C      GUESS Y AT POINT (J,I)
C
      YEST=YOLD(NR1)

```

```

C
C     ESTIMATE X AT POINT (J,I)
C
      XNEW = ((XSB(J)-XB(J))*4.5-(XS(J)-X(J))*1.5)*DH+XB(J)
300  XSNEW=EQ(YEST)
      DELA=XS(J)-X(J)
      DELB=XSB(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
C     IF AT LOWER END OF WAVE SKIP INTEGRATION AND
C     INCREASE TIME UNTIL WAVE IS ENTERED.
C
      IF(KK.NE.1) GO TO 380
330  IF(E(XNEW,XNEW2,EX))350,340,340
340  XNEW=XNEW2
      GOTO310
350  DELX=XNEW2-XSNEW
      DELXO=XB(J-1)-XSB(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)
      GOTO300
380  CALL OUT(XNEW2,YNEW(NR1))
C
C     RE-DEFINE Y FOR NEXT TIME STEP
C
381  DO 382 K=1,NR1
382  YOLD(K)=YNEW(K)
C
C     CHECK FOR ULTIMATE WAVE
C

```

```

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
      IF(XNEW2.GE.YTOL) KULT=1
      GO TO 292
C
C    FINAL COMPUTATIONS
C
390  WRITE (1,391) ITTOT
391  FORMAT(//1X16HTOTAL ITERATIONS,I10)
      GOTO1
C
C    ULTIMATE WAVE ROUTINE
C    TEST IF ULTIMATE WAVE ALREADY FOUND
C
400  IF(KULTX.EQ.1) GO TO 232
      H=DH*FLOAT(I-2)
      IF(IPCHX.EQ.1) WRITE(7,401) H
401  FORMAT(1X,20HULTIMATE WAVE AT H = F10.4)
      WRITE(1,401) H
      KULTX=1
      KQUIT=10+HFREQ*2
      GO TO 232
      END

```

```

SUBROUTINE TD
C
C SOLUTION OF DIFFUSION EQUATION BY THOMAS METHOD
C
C COMMON AND DIMENSION DECLARATIONS
C
  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,INVSX,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
C
C REDUCTION
C
  IF(ISW)GOTO2
  ISW=.TRUE.
  B=2.*M+1.
  W=2.*M*A/XNR*(1.+1./XNR)
  XMSQ=M*M
  S(1)=6.*M+1.
  S(2)=B
  DO1K=3,NR
1  S(K)=B-XMSQ/S(K-1)
  S(NR1)=B-2.*XMSQ*XNR/((XNR-1.)*S(NR))
2  YEND=YOLD(NR1)+DELX*W
  IF(PTSW)GOTO4
  PTSW=.TRUE.
  T(1)=YOLD(1)/S(1)
  T(2)=YOLD(2)/S(2)
  DO3K=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
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)GOTO5
      YNEW(1)=T(1)+6.*M*YNEW(2)/S(1)
      RETURN
      END

```

```

SUBROUTINE OUT (XX,YY)
C
C IF INSIDE WAVE OUTPUT SUBROUTINE WRITES RESULTS AT SELECTED INTERVALS
C
C
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,IO,JO,JMAX
COMMON DELX,DELXO,XFF
COMMON EW,MAXOUT
LOGICAL ISW,PTSW
REAL M
INTEGER HFREQ,TFREQ,RFREQ
C
KWRITE=0
IF(I.EQ.1.AND.J.EQ.1) GO TO 21
C
C TEST WHETHER Y IS CHANGING WITH T
C IF NOT, SET KK=3 TO SKIP REMAINDER OF POINTS IN THIS LEVEL
C
IF(ABS(YNEW(NR1)-YOLD(NR1)).LT.EW) KK=3
C
C IF AT UPPER END OF WAVE SET KK = 3 TO SKIP REMAINDER
C OF POINTS IN THIS BED LEVEL.
C
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
JO=IO
GO TO 3
7 IF(J.NE.JO) GO TO 12

```

```

21  JD = 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,I6,F11.4,F10.4,2F14.8)
    IF(KDIF)4,2,4
4   IF(I.NE.J) GO TO 9
    DOBK=1,NR,RFREQ
8   YNEW(K)=XX
    YNEW(NR1)=XX
9   WRITE(3,6) J,I
6   FORMAT(/1X5HPOINT I4,IH,,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
C      THIS SUBROUTINE CHECKS FOR EXCESS ITERATIONS AND CONTROLS OUTPUT
C      OUTPUT OF INTERMEDIATE RESULTS
C
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,IO,JO,JMAX
      COMMON DELX,DELXD,XFF
      COMMON EW,MAXOUT
      INTEGER HFREQ,TFREQ,RFREQ
      LOGICAL ISW,PTSW
      REAL M
C
      CALL SSWTCH(6,MM)
      GO TO (11,12),MM
11     WRITE (7,2) J,I
      MM=I-1
      REWIND 2
12     KK=1
      ITPT=ITPT+1
C
C      WRITE OUTPUT IF SS2 IS ON
C
      CALL SSWTCH(2,MM)
      GOTO (1,4),MM
1     WRITE(1,2) J,I,ITPT,D,XX,YY,L
2     FORMAT(1X,2I5,16, 7X, 3F14.8,2X3HCK=12)
4     CONTINUE
C
C      TEST FOR EXCESSIVE ITERATIONS
C

```



```
      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(1X,2I5,16,50X,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,JO,JMAX
      COMMON DELX,DELXO,XFF
      COMMON EW,MAXOUT
      LOGICAL ISW,PTSW
      REAL M
      INTEGER HFREQ,TFREQ,RFREQ
      IF(INSW)7,7,1
1      INSW=0
C
C      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)**.316
      EQMCHA = EQMCHA/(1.+EQMCHA)
      RETURN
      END

```

```

C      BENZENE N-HEXANE EQUILIBRIUM
C
      FUNCTION EQBZHX(Y)
C
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,IO,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
C      GET Y* IN EQM WITH XF
C
      1  INSW=0
          IF(XFF-.226)2,2,3
      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
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, XF	0.50000
INCREMENTAL BED LEVEL, DH	0.05000
INCREMENTAL TIME, DT	2.00000
DIMENSIONLESS RADIUS, A	40.00000
NUMBER OF INTERVALS OF RADIUS, XNR	25.00000
RATIO OF DT TO (A/XNR)**2	0.78125
TOLERANCES	
WAVE FRONT TEST, YTOL	1.00000E-05
ERROR IN CONCENTRATION -BULK PHASE, EX	1.00000E-05
-ADSORBED PHASE, EY	1.00000E-05
NUMBER OF TIME STEPS, JMAX	401
MAXIMUM ALLOWED ITERATIONS PER POINT, ITMAX	200

J	I	LOOPS	T	H	X(J,I)	Y(J,I)
1	1	0	0.	0.	0.50000000	0.50000000
11	11	4	20.0000	0.5000	0.39861267	0.39861267
16	11	27	30.0000	0.5000	0.44982319	0.66467742
21	11	21	40.0000	0.5000	0.46216760	0.68496262
26	11	20	50.0000	0.5000	0.46906116	0.69463018
31	11	17	60.0000	0.5000	0.47365807	0.70063554
36	11	15	70.0000	0.5000	0.47700959	0.70463501
41	11	15	80.0000	0.5000	0.47959932	0.70798935
46	11	13	90.0000	0.5000	0.48167903	0.71047626
51	11	13	100.0000	0.5000	0.48339721	0.71249633
56	11	13	110.0000	0.5000	0.48484820	0.71418148
61	11	13	120.0000	0.5000	0.48609461	0.71561532
66	11	12	130.0000	0.5000	0.48718073	0.71685466

71	11	12	140.0000	0.5000	0.48813755	0.71793959
76	11	12	150.0000	0.5000	0.48899003	0.71889997
81	11	12	160.0000	0.5000	0.48975432	0.71975744
86	11	12	170.0000	0.5000	0.49044504	0.72052886
91	11	10	180.0000	0.5000	0.49107355	0.72123223
96	11	10	190.0000	0.5000	0.49164785	0.72186884
101	11	10	200.0000	0.5000	0.49217524	0.72245163
106	11	10	210.0000	0.5000	0.49266134	0.72298749
111	11	10	220.0000	0.5000	0.49311070	0.72348186
116	11	10	230.0000	0.5000	0.49352778	0.72393966
121	11	10	240.0000	0.5000	0.49391536	0.72436453
126	11	10	250.0000	0.5000	0.49427715	0.72476018
131	11	10	260.0000	0.5000	0.49461439	0.72512685
136	11	10	270.0000	0.5000	0.49492633	0.72547143
141	11	10	280.0000	0.5000	0.49522148	0.72579332
146	11	10	290.0000	0.5000	0.49549814	0.72609484
151	11	10	300.0000	0.5000	0.49575842	0.72637795
156	11	10	310.0000	0.5000	0.49600251	0.72664355
161	11	8	320.0000	0.5000	0.49623210	0.72689322
166	11	8	330.0000	0.5000	0.49644775	0.72712769
171	11	8	340.0000	0.5000	0.49665070	0.72734825
176	11	6	350.0000	0.5000	0.49684173	0.72755951
181	11	6	360.0000	0.5000	0.49702187	0.72775546
186	11	6	370.0000	0.5000	0.49719141	0.72793943
191	11	6	380.0000	0.5000	0.49735112	0.72811260
196	11	6	390.0000	0.5000	0.49750151	0.72827575
201	11	6	400.0000	0.5000	0.49764398	0.72842983
206	11	6	410.0000	0.5000	0.49777770	0.72857480
211	11	6	420.0000	0.5000	0.49790362	0.72871139
216	11	6	430.0000	0.5000	0.49802251	0.72884025
221	11	6	440.0000	0.5000	0.49813458	0.72896176
226	11	6	450.0000	0.5000	0.49824017	0.72907631
231	11	6	460.0000	0.5000	0.49833986	0.72918443
236	11	6	470.0000	0.5000	0.49843377	0.72928634
241	11	6	480.0000	0.5000	0.49852247	0.72938256

246	11	6	490.0000	0.5000	0.49860602	0.72947325
251	11	6	500.0000	0.5000	0.49868496	0.72955889
256	11	6	510.0000	0.5000	0.49875928	0.72963963
261	11	6	520.0000	0.5000	0.49882954	0.72971587
266	11	6	530.0000	0.5000	0.49889570	0.72978778
271	11	6	540.0000	0.5000	0.49895871	0.72985566
276	11	6	550.0000	0.5000	0.49901712	0.72991968
281	11	6	560.0000	0.5000	0.49907419	0.72998093
286	11	4	570.0000	0.5000	0.49912192	0.73003872
291	11	4	580.0000	0.5000	0.49916584	0.73008937
296	11	4	590.0000	0.5000	0.49920737	0.73013708
301	11	4	600.0000	0.5000	0.49924266	0.73017995
306	11	4	610.0000	0.5000	0.49927254	0.73021845
311	11	4	620.0000	0.5000	0.49929694	0.73025262
316	11	4	630.0000	0.5000	0.49931614	0.73028267
321	11	4	640.0000	0.5000	0.49933044	0.73030882
326	11	2	650.0000	0.5000	0.49933794	0.73032906
21	21	4	40.0000	1.0000	0.35392200	0.35392200
26	21	29	50.0000	1.0000	0.41143354	0.63342936
31	21	24	60.0000	1.0000	0.42938936	0.65965568
36	21	21	70.0000	1.0000	0.44038668	0.67329055
41	21	20	80.0000	1.0000	0.44815937	0.68198659
46	21	18	90.0000	1.0000	0.45407055	0.68826271
51	21	17	100.0000	1.0000	0.45877693	0.69308115
56	21	16	110.0000	1.0000	0.46264582	0.69693863
61	21	15	120.0000	1.0000	0.46590211	0.70012125
66	21	15	130.0000	1.0000	0.46869389	0.70280622
71	21	13	140.0000	1.0000	0.47112328	0.70511553
76	21	13	150.0000	1.0000	0.47326381	0.70712513
81	21	13	160.0000	1.0000	0.47516743	0.70889535
86	21	13	170.0000	1.0000	0.47687513	0.71047050
91	21	13	180.0000	1.0000	0.47841828	0.71188424
96	21	13	190.0000	1.0000	0.47982177	0.71316184
101	21	12	200.0000	1.0000	0.48110453	0.71432397
106	21	12	210.0000	1.0000	0.48228227	0.71538581

111	21	12	220.0000	1.0000	0.48336793	0.71636067
116	21	12	230.0000	1.0000	0.48437258	0.71725942
121	21	12	240.0000	1.0000	0.48530423	0.71809041
126	21	12	250.0000	1.0000	0.48617195	0.71866172
131	21	10	260.0000	1.0000	0.48698068	0.71958324
136	21	10	270.0000	1.0000	0.48773342	0.72025034
141	21	10	280.0000	1.0000	0.48843973	0.72087394
146	21	10	290.0000	1.0000	0.48910181	0.72145744
151	21	10	300.0000	1.0000	0.48972329	0.72200413
156	21	10	310.0000	1.0000	0.49030673	0.72251675
161	21	10	320.0000	1.0000	0.49085531	0.72299810
166	21	10	330.0000	1.0000	0.49137107	0.72345027
171	21	10	340.0000	1.0000	0.49185653	0.72387545
176	21	10	350.0000	1.0000	0.49231360	0.72427549
181	21	10	360.0000	1.0000	0.49274460	0.72465230
186	21	10	370.0000	1.0000	0.49315055	0.72500709
191	21	10	380.0000	1.0000	0.49353330	0.72534142
196	21	10	390.0000	1.0000	0.49389422	0.72565661
201	21	10	400.0000	1.0000	0.49423505	0.72595388
206	21	10	410.0000	1.0000	0.49455640	0.72623426
211	21	10	420.0000	1.0000	0.49485986	0.72649883
216	21	8	430.0000	1.0000	0.49514608	0.72674850
221	21	8	440.0000	1.0000	0.49541622	0.72698404
226	21	8	450.0000	1.0000	0.49567112	0.72720630
231	21	8	460.0000	1.0000	0.49591188	0.72741617
236	21	6	470.0000	1.0000	0.49613913	0.72761847
241	21	6	480.0000	1.0000	0.49635386	0.72780553
246	21	6	490.0000	1.0000	0.49655646	0.72798199
251	21	6	500.0000	1.0000	0.49674791	0.72814868
256	21	6	510.0000	1.0000	0.49692854	0.72830601
261	21	6	520.0000	1.0000	0.49709926	0.72845466
266	21	6	530.0000	1.0000	0.49726036	0.72859499
271	21	6	540.0000	1.0000	0.49741259	0.72872759
276	21	6	550.0000	1.0000	0.49755628	0.72885279
281	21	6	560.0000	1.0000	0.49769343	0.72897183

286	21	6	570.0000	1.0000	0.49761791	0.72908169
291	21	6	580.0000	1.0000	0.49793414	0.72918460
296	21	6	590.0000	1.0000	0.49804353	0.72928153
301	21	6	600.0000	1.0000	0.49814394	0.72937157
306	21	6	610.0000	1.0000	0.49823586	0.72945493
311	21	6	620.0000	1.0000	0.49831903	0.72953167
316	21	6	630.0000	1.0000	0.49839363	0.72960192
321	21	6	640.0000	1.0000	0.49846084	0.72966637
326	21	4	650.0000	1.0000	0.49851928	0.72972822
331	21	4	660.0000	1.0000	0.49856640	0.72977784
336	21	4	670.0000	1.0000	0.49860654	0.72982252
341	21	4	680.0000	1.0000	0.49863905	0.72986142
346	21	4	690.0000	1.0000	0.49866067	0.72989320
351	21	4	700.0000	1.0000	0.49867693	0.72992063
356	21	4	710.0000	1.0000	0.49868874	0.72994446
358	21	2	714.0000	1.0000	0.49868961	0.72995034
31	31	4	60.0000	1.5000	0.31854293	0.31854293
36	31	31	70.0000	1.5000	0.37853168	0.60503529
41	31	27	80.0000	1.5000	0.40003780	0.63638628
46	31	23	90.0000	1.5000	0.41391728	0.65293057
51	31	21	100.0000	1.5000	0.42408321	0.66392522
56	31	20	110.0000	1.5000	0.43202191	0.67200945
61	31	20	120.0000	1.5000	0.43847483	0.67831420
66	31	17	130.0000	1.5000	0.44386932	0.68342902
71	31	17	140.0000	1.5000	0.44847396	0.68768857
76	31	16	150.0000	1.5000	0.45246844	0.69131299
81	31	15	160.0000	1.5000	0.45597883	0.69444874
86	31	15	170.0000	1.5000	0.45909590	0.69719630
91	31	15	180.0000	1.5000	0.46188939	0.69963081
96	31	15	190.0000	1.5000	0.46441193	0.70180761
101	31	13	200.0000	1.5000	0.46670453	0.70377313
106	31	13	210.0000	1.5000	0.46879967	0.70555192
111	31	13	220.0000	1.5000	0.47072314	0.70717410
116	31	13	230.0000	1.5000	0.47249698	0.70866121
121	31	13	240.0000	1.5000	0.47413783	0.71002985

126	31	13	250.0000	1.5000	0.47566111	0.71129416
131	31	12	260.0000	1.5000	0.47707870	0.71246625
136	31	12	270.0000	1.5000	0.47839794	0.71355387
141	31	12	280.0000	1.5000	0.47963237	0.71456739
146	31	12	290.0000	1.5000	0.48078843	0.71551372
151	31	12	300.0000	1.5000	0.48187217	0.71639855
156	31	12	310.0000	1.5000	0.48288988	0.71722734
161	31	12	320.0000	1.5000	0.48384632	0.71800460
166	31	10	330.0000	1.5000	0.48474557	0.71873765
171	31	10	340.0000	1.5000	0.48559247	0.71942415
176	31	10	350.0000	1.5000	0.48639003	0.72006883
181	31	10	360.0000	1.5000	0.48714189	0.72067562
186	31	10	370.0000	1.5000	0.48785068	0.72124697
191	31	10	380.0000	1.5000	0.48851930	0.72178532
196	31	10	390.0000	1.5000	0.48915027	0.72229289
201	31	10	400.0000	1.5000	0.48974615	0.72277172
206	31	10	410.0000	1.5000	0.49030854	0.72322336
211	31	10	420.0000	1.5000	0.49083968	0.72364957
216	31	10	430.0000	1.5000	0.49134132	0.72405189
221	31	10	440.0000	1.5000	0.49181519	0.72443173
226	31	10	450.0000	1.5000	0.49226284	0.72479042
231	31	10	460.0000	1.5000	0.49268591	0.72512925
236	31	10	470.0000	1.5000	0.49308557	0.72544928
241	31	10	480.0000	1.5000	0.49346313	0.72575148
246	31	10	490.0000	1.5000	0.49382035	0.72603727
251	31	10	500.0000	1.5000	0.49415802	0.72630736
256	31	10	510.0000	1.5000	0.49447712	0.72656262
261	31	8	520.0000	1.5000	0.49477884	0.72680399
266	31	8	530.0000	1.5000	0.49506398	0.72703201
271	31	8	540.0000	1.5000	0.49533316	0.72724742
276	31	6	550.0000	1.5000	0.49558832	0.72745549
281	31	6	560.0000	1.5000	0.49583057	0.72764885
286	31	6	570.0000	1.5000	0.49605566	0.72782954
291	31	6	580.0000	1.5000	0.49626688	0.72799935
296	31	6	590.0000	1.5000	0.49646605	0.72815953

301	31	6	600.0000	1.5000	0.49665196	0.72830968
306	31	6	610.0000	1.5000	0.49682496	0.72845009
311	31	6	620.0000	1.5000	0.49698528	0.72858102
316	31	6	630.0000	1.5000	0.49713327	0.72870281
321	31	6	640.0000	1.5000	0.49727001	0.72881611
326	31	6	650.0000	1.5000	0.49739466	0.72892068
331	31	6	660.0000	1.5000	0.49750532	0.72901551
336	31	6	670.0000	1.5000	0.49760535	0.72910244
341	31	6	680.0000	1.5000	0.49769501	0.72918184
346	31	6	690.0000	1.5000	0.49777162	0.72925237
351	31	6	700.0000	1.5000	0.49783984	0.72931635
356	31	6	710.0000	1.5000	0.49790008	0.72937433
361	31	4	720.0000	1.5000	0.49794808	0.72942710
366	31	4	730.0000	1.5000	0.49798818	0.72947077
371	31	4	740.0000	1.5000	0.49801879	0.72950757
376	31	4	750.0000	1.5000	0.49804042	0.72953857
381	31	4	760.0000	1.5000	0.49805319	0.72956301
384	31	2	766.0000	1.5000	0.49805710	0.72957401
41	41	4	80.0000	2.0000	0.28818507	0.28818507
46	41	35	90.0000	2.0000	0.34900831	0.57791845
51	41	27	100.0000	2.0000	0.37305456	0.61368362
56	41	23	110.0000	2.0000	0.38913804	0.63304233
61	41	23	120.0000	2.0000	0.40121784	0.64613426
66	41	21	130.0000	2.0000	0.41083593	0.65589839
71	41	20	140.0000	2.0000	0.41877670	0.66359571
76	41	20	150.0000	2.0000	0.42549992	0.66989124
81	41	19	160.0000	2.0000	0.43130154	0.67517823
86	41	17	170.0000	2.0000	0.43637998	0.67970942
91	41	16	180.0000	2.0000	0.44087918	0.68364753
96	41	16	190.0000	2.0000	0.44490301	0.68711526
101	41	15	200.0000	2.0000	0.44853072	0.69020097
106	41	15	210.0000	2.0000	0.45182377	0.69296966
111	41	15	220.0000	2.0000	0.45483055	0.69547229
116	41	15	230.0000	2.0000	0.45759000	0.69774863
121	41	15	240.0000	2.0000	0.46013297	0.69982995

126	41	13	250.0000	2.0000	0.46248593	0.70174615
131	41	13	260.0000	2.0000	0.46466961	0.70350939
136	41	13	270.0000	2.0000	0.46670010	0.70514007
141	41	13	280.0000	2.0000	0.46859507	0.70665392
146	41	13	290.0000	2.0000	0.47036728	0.70806316
151	41	13	300.0000	2.0000	0.47202692	0.70937749
156	41	13	310.0000	2.0000	0.47358359	0.71060549
161	41	12	320.0000	2.0000	0.47504599	0.71175568
166	41	12	330.0000	2.0000	0.47642005	0.71283318
171	41	12	340.0000	2.0000	0.47771361	0.71384457
176	41	12	350.0000	2.0000	0.47893173	0.71479478
181	41	12	360.0000	2.0000	0.48008046	0.71568862
186	41	12	370.0000	2.0000	0.48116339	0.71652979
191	41	12	380.0000	2.0000	0.48218581	0.71732226
196	41	12	390.0000	2.0000	0.48315074	0.71806903
201	41	10	400.0000	2.0000	0.48406267	0.71877798
206	41	10	410.0000	2.0000	0.48492398	0.71944251
211	41	10	420.0000	2.0000	0.48573785	0.72006954
216	41	10	430.0000	2.0000	0.48650707	0.72066148
221	41	10	440.0000	2.0000	0.48723425	0.72122047
226	41	10	450.0000	2.0000	0.48792176	0.72174843
231	41	10	460.0000	2.0000	0.48857198	0.72224744
236	41	10	470.0000	2.0000	0.48918685	0.72271892
241	41	10	480.0000	2.0000	0.48976834	0.72316457
246	41	10	490.0000	2.0000	0.49031854	0.72358588
251	41	10	500.0000	2.0000	0.49083906	0.72398428
256	41	10	510.0000	2.0000	0.49133148	0.72436099
261	41	10	520.0000	2.0000	0.49179740	0.72471729
266	41	10	530.0000	2.0000	0.49223820	0.72505424
271	41	10	540.0000	2.0000	0.49265506	0.72537289
276	41	10	550.0000	2.0000	0.49304980	0.72567432
281	41	10	560.0000	2.0000	0.49342432	0.72596008
286	41	10	570.0000	2.0000	0.49377570	0.72622900
291	41	8	580.0000	2.0000	0.49410677	0.72648262
296	41	8	590.0000	2.0000	0.49441921	0.72672200

301	41	8	600.0000	2.0000	0.49471312	0.72694755
306	41	8	610.0000	2.0000	0.49498851	0.72715344
311	41	6	620.0000	2.0000	0.49524651	0.72736263
316	41	6	630.0000	2.0000	0.49548737	0.72754905
321	41	6	640.0000	2.0000	0.49571219	0.72772355
326	41	6	650.0000	2.0000	0.49592084	0.72788636
331	41	6	660.0000	2.0000	0.49611176	0.72803675
336	41	6	670.0000	2.0000	0.49628782	0.72817635
341	41	6	680.0000	2.0000	0.49644998	0.72830589
346	41	6	690.0000	2.0000	0.49659606	0.72842433
351	41	6	700.0000	2.0000	0.49672956	0.72853354
356	41	6	710.0000	2.0000	0.49685170	0.72863438
361	41	6	720.0000	2.0000	0.49695921	0.72872536
366	41	6	730.0000	2.0000	0.49705590	0.72880635
371	41	6	740.0000	2.0000	0.49713993	0.72888264
376	41	6	750.0000	2.0000	0.49721318	0.72894924
381	41	6	760.0000	2.0000	0.49727553	0.72900629
386	41	4	770.0000	2.0000	0.49732588	0.72906210
391	41	4	780.0000	2.0000	0.49736479	0.72910489
396	41	4	790.0000	2.0000	0.49739586	0.72914167
401	41	4	800.0000	2.0000	0.49741655	0.72917170
51	51	4	100.0000	2.5000	0.26122727	0.26122727
56	51	37	110.0000	2.5000	0.32190111	0.55141412
61	51	30	120.0000	2.5000	0.34785337	0.59130754
66	51	27	130.0000	2.5000	0.36570021	0.61333340
71	51	23	140.0000	2.5000	0.37936971	0.62843145
76	51	23	150.0000	2.5000	0.39041921	0.63980100
81	51	23	160.0000	2.5000	0.39965631	0.64884011
86	51	20	170.0000	2.5000	0.40755811	0.65628735
91	51	20	180.0000	2.5000	0.41443566	0.66257380
96	51	19	190.0000	2.5000	0.42050231	0.66798422
101	51	19	200.0000	2.5000	0.42591173	0.67271025
106	51	17	210.0000	2.5000	0.43077899	0.67689182
111	51	16	220.0000	2.5000	0.43518974	0.68062097
116	51	16	230.0000	2.5000	0.43921233	0.68397693

121	51	15	240.0000	2.5000	0.44289966	0.68701836
126	51	15	250.0000	2.5000	0.44629558	0.68979046
131	51	15	260.0000	2.5000	0.44943532	0.69233016
136	51	15	270.0000	2.5000	0.45234742	0.69466674
141	51	15	280.0000	2.5000	0.45505727	0.69682493
146	51	13	290.0000	2.5000	0.45758616	0.69882675
151	51	13	300.0000	2.5000	0.45995070	0.70068888
156	51	13	310.0000	2.5000	0.46216547	0.70242090
161	51	13	320.0000	2.5000	0.46424365	0.70403793
166	51	13	330.0000	2.5000	0.46619621	0.70555055
171	51	13	340.0000	2.5000	0.46803309	0.70696776
176	51	13	350.0000	2.5000	0.46976270	0.70829736
181	51	13	360.0000	2.5000	0.47139285	0.70954628
186	51	13	370.0000	2.5000	0.47293036	0.71072041
191	51	12	380.0000	2.5000	0.47438149	0.71182600
196	51	12	390.0000	2.5000	0.47575136	0.71286682
201	51	12	400.0000	2.5000	0.47704570	0.71384794
206	51	12	410.0000	2.5000	0.47826925	0.71477332
211	51	12	420.0000	2.5000	0.47942577	0.71564636
216	51	12	430.0000	2.5000	0.48051941	0.71647052
221	51	12	440.0000	2.5000	0.48155405	0.71724889
226	51	12	450.0000	2.5000	0.48253336	0.71798439
231	51	10	460.0000	2.5000	0.48346008	0.71868391
236	51	10	470.0000	2.5000	0.48433711	0.71934084
241	51	10	480.0000	2.5000	0.48516718	0.71996180
246	51	10	490.0000	2.5000	0.48595304	0.72054904
251	51	10	500.0000	2.5000	0.48669709	0.72110447
256	51	10	510.0000	2.5000	0.48740155	0.72162990
261	51	10	520.0000	2.5000	0.48806864	0.72212704
266	51	10	530.0000	2.5000	0.48870029	0.72259743
271	51	10	540.0000	2.5000	0.48929833	0.72304255
276	51	10	550.0000	2.5000	0.48986482	0.72346387
281	51	10	560.0000	2.5000	0.49040201	0.72386303
286	51	10	570.0000	2.5000	0.49090866	0.72423989
291	51	10	580.0000	2.5000	0.49138697	0.72459574

296	51	10	590.0000	2.5000	0.49183906	0.72493209
301	51	10	600.0000	2.5000	0.49226581	0.72524974
306	51	10	610.0000	2.5000	0.49266757	0.72554908
311	51	10	620.0000	2.5000	0.49304548	0.72583116
316	51	10	630.0000	2.5000	0.49340083	0.72609676
321	51	8	640.0000	2.5000	0.49373423	0.72634653
326	51	8	650.0000	2.5000	0.49404635	0.72658695
331	51	8	660.0000	2.5000	0.49433618	0.72679973
336	51	6	670.0000	2.5000	0.49460625	0.72700834
341	51	6	680.0000	2.5000	0.49485805	0.72719983
346	51	6	690.0000	2.5000	0.49508984	0.72737718
351	51	6	700.0000	2.5000	0.49530436	0.72754207
356	51	6	710.0000	2.5000	0.49550333	0.72769570
361	51	6	720.0000	2.5000	0.49568480	0.72783733
366	51	6	730.0000	2.5000	0.49585127	0.72796819
371	51	6	740.0000	2.5000	0.49600215	0.72808827
376	51	6	750.0000	2.5000	0.49613877	0.72819828
381	51	6	760.0000	2.5000	0.49626179	0.72829880
386	51	6	770.0000	2.5000	0.49637004	0.72838926
391	51	6	780.0000	2.5000	0.49646407	0.72846998
396	51	6	790.0000	2.5000	0.49654723	0.72854292
401	51	6	900.0000	2.5000	0.49661806	0.72860735
61	61	4	120.0000	3.0000	0.23684900	0.23684900
66	61	41	130.0000	3.0000	0.29668261	0.52517207
71	61	32	140.0000	3.0000	0.32408241	0.56900238
76	61	29	150.0000	3.0000	0.34337255	0.59362071
81	61	26	160.0000	3.0000	0.35839079	0.61067739
86	61	23	170.0000	3.0000	0.37068442	0.62362821
91	61	23	180.0000	3.0000	0.38106716	0.63398726
96	61	23	190.0000	3.0000	0.39002699	0.64256375
101	61	20	200.0000	3.0000	0.39788443	0.64984313
106	61	20	210.0000	3.0000	0.40485980	0.65612899
111	61	19	220.0000	3.0000	0.41111433	0.66163770
116	61	19	230.0000	3.0000	0.41676912	0.66652146
121	61	19	240.0000	3.0000	0.42191669	0.67089222

126	61	17	250.0000	3.0000	0.42662997	0.67483657
131	61	16	260.0000	3.0000	0.43096606	0.67841831
136	61	16	270.0000	3.0000	0.43497174	0.68168674
141	61	15	280.0000	3.0000	0.43868546	0.68468602
146	61	15	290.0000	3.0000	0.44214016	0.68744971
151	61	15	300.0000	3.0000	0.44536239	0.69000573
156	61	15	310.0000	3.0000	0.44837495	0.69237719
161	61	15	320.0000	3.0000	0.45119715	0.69458346
166	61	15	330.0000	3.0000	0.45384540	0.69664081
171	61	13	340.0000	3.0000	0.45633442	0.69856741
176	61	13	350.0000	3.0000	0.45867672	0.70036715
181	61	13	360.0000	3.0000	0.46088317	0.70205427
186	61	13	370.0000	3.0000	0.46296369	0.70363808
191	61	13	380.0000	3.0000	0.46492741	0.70512696
196	61	13	390.0000	3.0000	0.46678181	0.70652784
201	61	13	400.0000	3.0000	0.46853420	0.70784719
206	61	13	410.0000	3.0000	0.47019098	0.70909069
211	61	13	420.0000	3.0000	0.47175778	0.71026309
216	61	12	430.0000	3.0000	0.47323988	0.71136988
221	61	12	440.0000	3.0000	0.47464228	0.71241432
226	61	12	450.0000	3.0000	0.47597015	0.71340097
231	61	12	460.0000	3.0000	0.47722726	0.71433320
236	61	12	470.0000	3.0000	0.47841782	0.71521439
241	61	12	480.0000	3.0000	0.47954540	0.71604760
246	61	12	490.0000	3.0000	0.48061371	0.71683567
251	61	12	500.0000	3.0000	0.48162586	0.71758121
256	61	10	510.0000	3.0000	0.48258551	0.71829123
261	61	10	520.0000	3.0000	0.48349468	0.71895914
266	61	10	530.0000	3.0000	0.48435616	0.71959109
271	61	10	540.0000	3.0000	0.48517252	0.72018929
276	61	10	550.0000	3.0000	0.48594626	0.72075565
281	61	10	560.0000	3.0000	0.48668016	0.72129224
286	61	10	570.0000	3.0000	0.48737429	0.72179972
291	61	10	580.0000	3.0000	0.48803075	0.72227953
296	61	10	590.0000	3.0000	0.48865205	0.72273344

301	61	10	600.0000	3.0000	0.48923973	0.72316273
306	61	10	610.0000	3.0000	0.48979464	0.72356822
311	61	10	620.0000	3.0000	0.49031821	0.72395102
316	61	10	630.0000	3.0000	0.49081200	0.72431227
321	61	10	640.0000	3.0000	0.49127716	0.72465289
326	61	10	650.0000	3.0000	0.49171481	0.72497378
331	61	10	660.0000	3.0000	0.49212451	0.72527492
336	61	10	670.0000	3.0000	0.49250860	0.72555783
341	61	10	680.0000	3.0000	0.49286870	0.72582360
346	61	8	690.0000	3.0000	0.49320418	0.72607228
351	61	8	700.0000	3.0000	0.49351716	0.72630489
356	61	8	710.0000	3.0000	0.49380963	0.72652281
361	61	6	720.0000	3.0000	0.49408085	0.72673090
366	61	6	730.0000	3.0000	0.49433257	0.72691944
371	61	6	740.0000	3.0000	0.49456487	0.72709513
376	61	6	750.0000	3.0000	0.49477683	0.72725791
381	61	6	760.0000	3.0000	0.49497563	0.72740871
386	61	6	770.0000	3.0000	0.49515445	0.72754718
391	61	6	780.0000	3.0000	0.49531580	0.72767370
396	61	6	790.0000	3.0000	0.49546285	0.72779906
401	61	6	800.0000	3.0000	0.49559456	0.72789591

GENERAL BLOCK DIAGRAM FOR SOLUTION OF ADSORPTION MODEL

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

<u>Card</u>	<u>Format</u>	<u>Columns</u>	<u>Variable</u>	
1	E10.0	1-10	XF,	feed concentration, fraction of more adsorbable component
	E10.0	11-20	QQ,	damping factor
	E10.0	21-30	DT,	dimensionless time increment
	E10.0	31-40	A,	dimensionless particle size
	E10.0	41-50	XNR,	number of radius increments
	6A5	51-80	P1-P6,	problem identification
2	E10.0	1-10	YTOL,	tolerance for end of wave
	E10.0	11-20	EX,	tolerance for fitting polynomials in x by trial and error
	E10.0	21-30	EY,	tolerance for fitting surface concentration
3	I5	1-5	JMAX,	number of grid points in J-, or T-direction
	I5	6-10	ITMAX,	maximum number of iterations allowed per point
	I5	11-15	HFREQ,	frequency of output along J-axis, at given H
	I5	16-20	TFREQ,	frequency of output along I-axis, at given T
	I5	21-30	RFREQ,	frequency of output of internal diffusion curve (only effective when KDIF = 1)
	I5	31-35	KDIF,	code for output of diffusion curves: zero for no output; one for output on logical unit one and/or three

<u>Card</u>	<u>Format</u>	<u>Columns</u>	<u>Variable</u>
3 (cont)	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)
A_s	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
f_a	Fraction of saturation, or degree of adsorption in a column of length, z
f'_a	Fraction of saturation in a length of column equivalent to the length of a wave
f_{a_s}	Fractional saturation of column at beginning of steady state
f'_{a_s}	Fractional saturation of adsorption zone at beginning of steady state
f_{a_w}	Fractional saturation of adsorption zone at any point within the column
f_v	Fraction voids within adsorbent bed
H	Dimensionless bed level parameter, defined by Eq. (4-8)
H_L	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 ΔT to $(\Delta R)^2$ in finite difference equation for internal diffusion.
n	Number of increments used in finite difference equation for internal diffusion
N_L	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, ft^2
T	Dimensionless time variable, defined by Eq. (4-9)
T_s	Dimensionless time corresponding to beginning of steady state
V_a	Total quantity of more adsorbable component in effluent stream, ft^3
V'_a	Maximum quantity of more adsorbable component that could be contained in a length of bed equal to the length of a wave, ft^3
V_p	Pore volume, ft^3/lb adsorbent
V_w	Total volume of liquid in effluent liquid, ft^3
W	Rate of transfer of more adsorbable component from bulk phase to adsorbed phase in differential section, dz , ft^3/hr
x	Volumetric concentration of more adsorbable component in non-adsorbed phase ft^3/ft^3
x_b	Instantaneous volumetric concentration of more adsorbable component at wave front, ft^3/ft^3
x_f	Volumetric feed concentration of more adsorbable component, ft^3/ft^3
x^*	Volumetric concentration of more adsorbable component on bulk-phase side of interface in equilibrium with the adsorbed phase interfacial concentration, ft^3/ft^3
y	Volumetric concentration of more adsorbable component in adsorbed phase, ft^3/ft^3
y^*	Volumetric concentration of more adsorbable component in adsorbed phase in equilibrium with feed, ft^3/ft^3
z	Bed height variable, ft
z_s	Length of adsorbent bed required for formation of ultimate wave, hr
z_w	Length of an adsorption zone, ft
θ	Real time elapsed since initial contact of feed with adsorbent, hr

θ_s	Real time elapsed from initial startup until beginning of steady-state, hr
θ_w	Real time required for adsorption zone to pass a given point, hr
ρ_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:

Paul W. Merrill
Major Professor and Chairman

Wm Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Fritz O. McCarson

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Benjamin E. Mitchell

James B. Cordner

Date of Examination: January 11, 1965