
Cecil Paul Loechelt

Louisiana State University and Agricultural & Mechanical College

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THE DYNAMIC BEHAVIOR OF NON-ISOTHERMAL, FIXED-BED ADSORPTION SYSTEMS

A Dissertation

Submitted to the Graduate Faculty of the Louisiana State University and Agricultural and Mechanical College in partial fulfillment of the requirements for the degree of Doctor of Philosophy

in

The Department of Chemical Engineering

by

Cecil Paul Loechelt
B.E., Vanderbilt University, 1956
M.S., Louisiana State University, 1962
August, 1964
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ABSTRACT

Gas-solid adsorption is a method of separating mixtures of gases which has received considerable attention in more recent years. Due to the complexity of the various models which may be derived for these systems, the majority of the studies of this phenomena have been concerned with mechanism of the phenomena itself, the qualitative behavior of more complicated systems or the quantitative behavior of simplified systems. This particular study is intended to determine the significant variables in a particular dynamic regime and to investigate the difficulties involved in specifying the quantitative behavior of a system of considerable complexity.

The system studied is the fixed bed, binary gas system. One purpose of this study was to determine the significance of variations of temperatures on the dynamic behavior of the system. Concentrated gas mixtures were required in order to obtain a significant temperature rise. As a result, the theory developed in this study is not limited to dilute gas mixtures. The theory is limited to low flow regimes in order to justify the use of overall heat and mass transfer coefficients for expressing the transfer processes of the system. The theory is initially developed for an adiabatic system in order to facilitate the solution of the resulting mathematical model of the theoretical model generated.

The experimental phase of the study was designed to operate under approximately the same restrictions of those of the theoretical
model. The system consisted of an insulated, galvanized pipe (two inches in nominal diameter) packed to a depth of 68 inches with activated carbon and a gas metering system. The system utilized a multipoint recorder and regularly spaced thermocouples to determine the dynamic behavior of the system temperature and frequent samples of the gas phase were obtained at the same bed positions as above to determine the dynamic behavior of the gas phase concentration.

Twelve experimental runs were performed for three significantly different carrier gas flow rates. Each set of three runs was for the same significantly different inlet gas phase concentrations. The second set was for an initial solid concentration significantly different from that of the first set. The qualitative results were as one would predict for isothermal operation.

The initial second order correct solution technique was found to be unstable for all but low flow rates and was replaced by a third-order correct technique which was stable for all flow rates studied provided that two criteria are maintained. The assumption of an adiabatic system was not achieved experimentally as determined by comparison of experimental and theoretical results. A non-rigorous expression for the rate of heat loss at the wall was included in the model in order to simulate the behavior of the experimental system.

The effects of the mass transfer parameter, heat loss parameter and small variations in the equilibrium data were studied and presented. It was determined that even in this low flow regime the gas and solid temperatures were not significantly different. It was also determined that small (2-3°F) temperature variations could cause a significant change in the shape of the concentration wave.
Comparison of experimental and theoretical data indicated that the calculated overall mass transfer coefficient could be used to predict the dynamics and the shape of the concentration wave very well (20-30%). The estimated rate of heat loss obtained by comparing experimental and theoretical results after 90 minutes of operation was about 10% of the total entering enthalpy.
CHAPTER I

INTRODUCTION\(^\text{9,12}\)

Adsorption is the loss of mobility experienced by some of the molecules of a fluid relative to a solid surface which has been brought into close proximity of the surface. The actual mechanism of adsorption can not be explicitly defined in that the mechanism itself varies with the component identity and the physical configuration of the system. A comprehensive treatment of the mechanism of the adsorption phenomenon is outside the scope of this study. Where specific information in this area of adsorption is required, conventional thermodynamic equilibrium relations are used herein to guide an empirical specification of the required equilibrium relations.\(^\text{13}\) Supplementary references, of value for general information but not necessary to this study, are listed in the Selected Bibliography.\(^\text{1,4,8}\)

The dynamics of an adsorption system are of special interest to the engineer in that the sizing and controlling of such processes is directly related to the rates of transport involved. The purpose of this study is to investigate one specific aspect of the dynamics of a particular adsorption system in terms of the most conventionally used transport theories. The remainder of this chapter lists and explains several adsorption processes and the variables and mechanisms involved in specifying the dynamic behavior of such processes.

Various types of physical configurations might be used for the
adsorption process, \(^{(9,12)}\) The requirement of the fluid being in close proximity to the surface implies that there must exist some means for movement of the fluid or solid or both. The shape and various characteristic dimensions of the solid are also significant in the overall physical configuration.

The usual systems configurations are the fixed and moving bed contactors. The moving bed contactors have been well defined for conditions of constant feed and operating conditions and behave essentially as any other countercurrent two phase separation process.\(^{(12)}\) Restrictions on solutions for this configuration are only slightly greater than other processes of this type.

The fixed bed systems, however, are not as well defined. Analytic solutions are available for binary systems of dilute gases which exhibit linear equilibrium behavior provided that isothermal conditions are maintained.\(^{(6,7)}\) The additional restrictions of constant feed conditions and initial bed composition are also inherent in the solution. Graphical solutions are also available for non-dilute systems exhibiting complex equilibrium relations but these solutions maintain the other restrictions of the analytic solution.\(^{(6)}\)

Thus the fixed bed system represents an area where there is a gap in engineering knowledge as far as solution techniques are concerned for simplified models. In order to properly evaluate the effects of the internal solid transport and surface rate phenomena which are usually neglected in order to obtain solutions for the overall system, solution techniques must be developed which justify the presently used transport models. Given a solution technique for
the simpler cases which has been experimentally justified, the technique may possibly be generalized to include the effects of the neglected phenomena. A schematic diagram of a typical fixed bed system is included on the next page (Figure 1).

The dynamics of an adsorption process are defined by the three transport processes. These are the rates of transfer of momentum, mass and energy. The momentum transport has been well defined in terms of an empirical friction factor for fixed bed systems. The solutions to the momentum transport equations are thus available for defining mean values for the solid dimensions.

The solid is available in a range of shapes and sizes with a variety of distributions of each variable. Some solids lend themselves to mechanical forming and thus are available in a uniform shape of essentially constant size. The remainder of the solids are not ductile enough to be formed which results in batches of irregular shapes and sizes. This group is usually referred to as granular solids. The granular solids may be screened to give a narrow distribution of sizes. Usually a mean size dimension is sufficient to represent the narrow distribution of sizes especially if a sufficient number of particles are available per unit depth to insure a probable size distribution equal to that of the entire batch.

Energy transport in fixed granular beds has also been studied in some detail for gas systems in which no mass transfer is taking place. The theoretical equations have been used to define the rates in terms of a dimensionless "j" factor as a function of the physical shape and dimensions of the system, physical properties, and
FIGURE 1. FIXED BED ADSORBER

Rich Gas

Packed Solid

Column Wall

Solid Support

Screen

Lean Gas
flow rate. Numerical solutions are also available for those systems in which a heat source is present in the bed but no experimental verification of the model is presented.\(10\)

The types of energy transport present in a fixed bed system are numerous and of varying importance depending on the operating conditions and physical configuration. These include:

(a). Bulk transport with the flow.

(b). Longitudinal and radial conduction and convection in the fluid phase.

(c). Longitudinal and radial conduction in the bulk solid phase.

(d). Radial conduction within the solid particles.

(e). Bulk transport in conjunction with the mass transport between the fluid and solid phases.

(f). Convective transport between the fluid and solid phases.

(g). Radial conduction and convection in the vicinity of the system boundaries.

(h). Longitudinal conduction within the boundary itself.

Items (a), (d), (e) and (f) predominate in flow systems especially for situations in which the thermal conductivity of the solid is low. The effects of item (b) are small compared to item (a) as a result of the flow; the study of von Rosenberg; et al,\(10\) indicates that item (c) might also be neglected. Further, one might eliminate the effects of items (c) and (g) entirely by properly insulating the boundaries. Item (h) is not as easily eliminated, but resulting errors might be minimized by minimizing the cross-sectional area for
transport in the longitudinal direction. The four predominant transport items will be considered in detail in Chapter II.

The heat transport mechanisms indicate a dependence on the mass transfer rates in that the molecules of the fluid have an associated energy level which may vary with position. Thus the molecular displacement, irregardless of the mechanism has an effect on the energy level at each position affected. The types of mass transport mechanisms which might be expected in a fixed bed system are:

(a). Bulk flow in conjunction with a longitudinal pressure gradient.

(b). Transport between the bulk gas phase and the gas phase in close proximity of the external solid surface in conjunction with a concentration gradient.

(c). Transport inside the solid in conjunction with an internal concentration gradient.

(d). Transport between the gas phase in close proximity of the solid surface and the solid surface.

(e). Longitudinal and radial transport in the bulk gas phase as a result of diffusion and turbulence.

All of the transport mechanisms listed could be significant in the overall model with the possible exception of item (e); this diffusional transport should be negligible even if the flow is only moderate while the scale of turbulence in a packed bed should be sufficiently small to eliminate most turbulent transport. The remainder of the items should be significant in some flow regime and possibly in all as indicated by investigations made to date.\(^6,^{12}\)
This study will be primarily concerned with items (a) and (b) above in that these mechanisms are common to all flow adsorption processes to some extent and the theoretical models are substantially invariant as far as changes in configuration and structure of the solid are concerned. At low flow rates these two items might predominate and essentially control the rate of mass transfer in the system. If items (c) and (d) are of some significance even at low flow rates then perhaps some method of indicating the significance of the individual mechanisms might be obtained from this study in this flow regime.

A discussion of flow adsorption processes would not be complete without mention of the variables concerned and the operational technique one might utilize to study each. The significant independent variables are:

(a). Time relative to some reference (usually the time at which the most significant external change is made).

(b). Longitudinal bed position.

(c). Radial bed position.

(d). Radial position within the solid particle.

The principal dependent variables as functions of time and position are:

(e). Gas phase concentration.

(f). Solid phase concentration.

(g). Gas phase temperature.

(h). Solid phase temperature.

(i). Total pressure in the bed.

The following variables might best be separately listed in that they are the controllable parameters which may be used to vary the system.
(j). Component identity and associated physical properties.
(k). Inlet feed rate, temperature and concentration.
(l). Initial solid temperature and concentration.
(m). Inlet pressure.
(n). External temperature adjacent to the system.

This list of variables appears to be quite formidable; however, by operating in a particular flow regime perhaps items (d) and (i) might be neglected. There is a sufficient amount of information available which would eliminate item (c) from consideration especially if the system is isolated from the surroundings. This would also eliminate item (n) from consideration. Item (m) might also be neglected if the pressure drop through the system is low enough to be neglected. Items (k) and (l) are boundary conditions of the system and except for the inlet feed rate will be incorporated into the transformed independent variables.

This is then the scope of the study to be undertaken. A theoretical model, developed in Chapter II, and an experimental study, described in Chapter III, will be compared in order to evaluate the validity of the model. This information will be used as a basis for recommendations for further work in this field.
1. Conservation Equations

The theoretical approach to the study of the dynamics of a fixed bed absorption system may be based on two commonly used distinct techniques with approximately the same results. One technique involves the specification of all significant variables, the formation of dimensionless groups by dimensional analysis, and the correlating of experimental data in terms of some devised function of the dimensionless groups obtained previously. The other technique is to develop a model for the various mechanisms involved and to derive and solve the equations describing the model. This study will utilize the latter technique as a basis of approaching the theoretical study.

In order to guide the development of the model for this study, various equations will be derived and a model will be formed based on the equations, the assumptions required for the derivation and an intuitive understanding of the model to be developed. The equations for the conservation of mass and energy in the system are of primary importance in the development of the model. The mass conservation equations (material balances) about a differential section of the bed are:
for the overall fluid phase:

\[- \frac{\partial G}{\partial z} - Na = Fe \frac{\partial \rho_G}{\partial t}\]  \hspace{1cm} (II-1)

for the solute in the fluid phase:

\[- \frac{\partial}{\partial z} (G_y) - Na = Fe \frac{\partial}{\partial t} (\rho_G y),\]  \hspace{1cm} (II-2)

and for the solute in the solid phase:

\[Na = \rho_B \frac{\partial \omega}{\partial t}\]  \hspace{1cm} (II-3)

The assumptions required are:

(a). The magnitude of the velocity components in the axial and radial directions is approximately zero.

(b). Longitudinal diffusion is negligible.

(c). The mass transfer rate and specific surface are independent of axial and radial position.

(d). The specific surface is independent of longitudinal position.

(e). The fractional void volume is independent of time and position.
(f). The bulk density of the packed solid is independent of time and position.

The energy conservation equations are:

\[
\text{GH}_G \quad y, T_G
\]

for the gas phase:

\[
- \frac{\partial}{\partial z} (\text{GH}_G) + qa - \text{NaHA} = \frac{\partial}{\partial t} (\text{Fe}_{\rho G} \text{H}_G),
\]

(II-4)

and for the solid phase:

\[
\text{Na H}_A - qa = \rho_B \frac{\partial}{\partial t} H_s.
\]

(II-5)

The reference conditions for enthalpy are:

(a). The solute in the absorbed phase at \( T_R \), \( P \) and \( w_0 \)

(b). The carrier gas as a gas at \( T_R \) and \( P \).

(c). The solid phase at \( T_R \) and \( w_0 \).

The assumptions required for these equations in addition to the previous assumptions are:

(a). Radial heat transfer through the boundary is negligible.

(b). Longitudinal conduction in the gas and solid phases is negligible.

(c). Longitudinal conduction in the boundary is negligible.
Equations (II-2) and (II-4) may be simplified by substitution. The following equations may be used for the simplification provided that the specific heats are assumed to be constant over the range of interest.

\[ H_A = C_{PA} (T_G - T_R) + H^0_{AD} \quad (II-6) \]

\[ H_G = [(1-y) C_{PB} + y C_{PA}] (T_G - T_R) + y H^0_{AD} \quad (II-7) \]

The enthalpies and their derivatives may be used in conjunction with the derivative of the gas density from equation (II-1) to yield the following forms of equations (II-2) and (II-4):

\[ - G \frac{\partial y}{\partial z} - (1-y) Na = \rho e_{PG} \frac{\partial y}{\partial t} \quad (II-8) \]

and

\[ - G \frac{\partial T_G}{\partial z} + \frac{\partial \rho}{\partial C_{PG}} = \rho e_{PG} \frac{\partial T_G}{\partial t} \quad (II-9) \]

Equation (II-5) may also be expressed in terms of temperature through the use of the definition of the solid phase enthalpy:

\[ H_s = (C + w C_{PA}) (T_s - T_o) + W (H^0_{AD} - H_{AD}) \quad (II-10) \]

and the definition for the enthalpy of the adsorbate in the gas phase, equation (II-6). The derivative of the solid phase enthalpy may be expressed as follows:

\[ \frac{\partial H_s}{\partial t} = (C + w C_{PA}) \frac{\partial T_s}{\partial t} + \left[ C_{PA} (T_s - T_o) + (H^0_{AD} - H_{AD}) \right] \frac{\partial W}{\partial t} \]

\[ -W \frac{\partial H_{AD}}{\partial t} \quad (II-11) \]

Equation (II-5) may now be expressed as follows by means of equation (II-3):
\[
Na [H_{AD}- C_{PA}(T_s - T_g)] - qa = \rho_B(C + \omega_{C_{PA}}) \frac{\partial T_s}{\partial t} - \rho_B^{V} \frac{\partial H_{AD}}{\partial t}
\]  

(II-12)

The last term above may be expanded by means of the equilibrium relations to be derived.

The development has now basically defined the model of the system and has yielded four equations; (II-3), (II-8), (II-9), and (II-12) which are the basic equations of the system. These equations will be expanded by means of the expressions for the rates of transfer and the equilibrium relation which are derived in the following sections.

2. Transfer Rate Model

The conventional method of specifying the mass transfer rate is by means of the product of the difference between the average gas concentration and the gas concentration in equilibrium with the average solid concentration and some empirically determined transfer rate constant. (5,12) This method will also be used in this study. With this model, the rate equation is:

\[
N = M_g K'_y (y - y_E). \tag{II-14}
\]

Substitution of this expression directly into equation (II-8) results in an expression which is non-linear in \( y \) and eventually an implicit expression for \( y \). This solution complication may be eliminated by use of mass ratios for concentration. The rate equation for this system of concentration units is:

\[
N = M_B K'_y (Y - Y_E). \tag{II-15}
\]

and

\[
N = M_g K'_y (1-y)(1-y_E)(Y - Y_E), \tag{II-16}
\]
where:

\[ Y = \frac{y}{1-y} \]  \hspace{1cm} (II-17)

Substituting for \( N \) and \( y \) and the derivatives of \( y \) in (II-8) yields the following solute balance for the gas phase:

\[ -G \frac{\partial Y}{\partial z} - M_g K' y a (1-y_E)(Y-Y_E) = \frac{F_{pG}}{\partial t} \frac{\partial Y}{\partial t} \]  \hspace{1cm} (II-18)

The above equation may be further simplified by substitution of a term known as the height of a gas phase mass transfer unit as defined below:

\[ H_{DG} = \frac{G}{K' y a M_g} = \frac{G}{K_y Y_{BM} a M_g} \]  \hspace{1cm} (II-19)

Since \( K' y \) is directly related to \( G \) it can be seen that \( H_{DG} \) would be more constant than \( K' y \) alone. (12) It can also be shown that:

\[ 1 - y_E = \frac{1}{1 + Y_E} \]  \hspace{1cm} (II-20)

With the substitutions indicated above, equation (II-18) becomes:

\[ -\frac{\partial Y}{\partial z} = \frac{1}{H_{DG}} \left[ \frac{Y - Y_E}{1 + Y_E} \right] = \frac{F_{pG}}{G} \frac{\partial Y}{\partial t} \]  \hspace{1cm} (II-21)

Equation (II-3) can now be revised to:

\[ \frac{G}{H_{DG}} \frac{(Y - Y_E)}{(1 + Y)(1 + Y_E)} = \frac{\partial}{\partial t} \frac{\partial \omega}{\partial t} \]  \hspace{1cm} (II-22)

The rate of heat transfer can also be defined in a conventional manner:

\[ q = h (T_s - T_G) \]  \hspace{1cm} (II-23)

A height of a gas phase heat transfer unit may be defined as:

\[ H_{HG} = \frac{G C_{PG}}{h a} \]  \hspace{1cm} (II-24)
Substituting for \( h \) and rearranging equation (11-23) gives:

\[
qa = \frac{GC_{PG}(T_s - T_G)}{H_{HG}}.
\]  
(II-25)

Equation (II-9) can now be rewritten in terms of \( H_{HG} \) as:

\[
-\frac{\partial T_G}{\partial z} + \frac{1}{H_{HG}}(T_s - T_G) = \frac{\rho \partial H_A}{G \partial t}.
\]  
(II-26)

Equation (II-12) may also be written in terms of \( H_{HG} \) and \( H_{DG} \):

\[
\frac{G_s}{H_{DG}} \left[ \frac{Y - Y_E}{1 + Y_E} \right] \left[ H_{AD} - C_{PA}(T_s - T_G) \right] - \frac{GC_{PG}(T_s - T_G)}{H_{HG}} = \frac{\rho_B(C + \omega C_{PA}) \partial T_A}{\partial t} - \frac{\rho_B \omega \partial H_{AD}}{\partial t}.
\]  
(II-27)

The next section will complete the description of the adsorption model by defining a relation expressing the gas-solid equilibrium and indirectly the enthalpy change associated with the change of phase.

3. Thermodynamic Relations

This section will develop the necessary thermodynamic relations for expressing the gas phase concentration in equilibrium with the adsorbed solute as a function of solid concentration and solid temperature. Other thermodynamic relations will be used to evaluate the heat of adsorption associated with the adsorption of the gas. These relations will then be used as a basis for empirically specifying the equilibrium relations and the heat of adsorption relations for a particular system.

The approach to the determination of the equilibrium relations might be based on a purely theoretical treatment if the
potential field involved were known or could be determined. It is anticipated, however, that not only would the parameters involved in the relations for the potential field vary but in addition the form of the relation itself might vary from one system of components to another. Another approach available is one similar to that used in binary vapor-liquid equilibria studies. This approach, although it is partially empirical, is firmly based on theoretical principles and, because of the empirical determination of the parameters, can be expected to yield fairly accurate results.

Consider a vapor-liquid system that has been in contact for a sufficient length of time so that the two phases have reached thermodynamic equilibrium. For a defined reference state the following relations may be written:

$$f^e_{v_1} = \gamma_{v_1} y^e_{L_1} f^e_{v_1} = \gamma_{L_1} x^e_{L_1} f^e_{L_1} = f^e_{L_1}. \quad (II-28)$$

A similar set of relations may be written for a system of solutes in equilibrium with a solid:

$$f^e_{G_1} = \gamma_{G_1} y^e_{A_1} f^e_{G_1} = \gamma_{A_1} x^e_{A_1} f^e_{A_1} = f^e_{A_1}. \quad (II-29)$$

Let us assume that the adsorbed solute exists as a liquid on the surface of the solid. Then for this assumption the following expression is valid:

$$f^e_{s_1} = f^e_{L_1} = f^e_{A_1} \quad (II-30)$$

and hence,

$$\gamma_{A_1} = \frac{f^e_{G_1}}{x^e_{A_1} f^e_{s_1}} = \frac{\gamma_{G_1} y^e_{A_1} f^e_{G_1}}{x^e_{A_1} f^e_{s_1}}. \quad (II-31)$$
A standard derivation in most thermodynamic text books gives the variation of fugacity with temperature at constant pressure as follows:

\[
\left( \frac{\partial \ln f}{\partial T} \right)_p = \frac{H^* - H}{RT^2} \quad \text{(II-32)}
\]

Consider a pure liquid system at temperature, \( T_L \), and pressure, \( p_s \). Under these conditions, the fugacity of the liquid is the saturation fugacity of the liquid and equation (II-32) may be written:

\[
\left[ \frac{d \ln f_{s}^L}{dT} \right]_{p_s} = \left[ \frac{H^* - H_L}{RT_L^2} \right]_{T_L} \quad \text{(II-33)}
\]

Similarly if one considers a system which consists of a solute adsorbed on a solid at \( T_A \), \( p_A^e \) and concentration, \( x_A^e \); then the fugacity is the equilibrium fugacity of the solute and equation (II-32) may be written as:

\[
\left[ \frac{d \ln f_{s}^G}{dT} \right]_{p_A^e, x_A^e} = \left[ \frac{H^* - H_A}{RT_A^2} \right]_{T_A} \quad \text{(II-34)}
\]

Finally, for \( T_L \) equal to \( T_A \) equal to \( T \) the quotient of equations (II-33) and (II-34) may be written:

\[
\left\{ \frac{\ln f_{s}^G}{\ln f_{s}^L} \right\}_{p_A^e, x_A^e} = \frac{(H^* - H_L)}{(H^* - H_A)} \quad \text{with} \quad \frac{1}{m} \quad \text{(II-35)}
\]

Equation (II-35) indicates that a log-log plot of \( f_{s}^G \) versus \( f_{s}^L \) may be used to obtain a ratio of enthalpy differences, provided that the fugacities are evaluated under the specified conditions. The enthalpy difference between the vapor as an ideal gas and the
liquid may be obtained from tabulated heats of vaporization after applying a correction, usually referred to as an enthalpy departure, evaluated at T and P. Values for the heat of adsorption may then be obtained at conditions T, P, and x by applying the enthalpy correction for these conditions to the product of m and the corrected heat of vaporization.

Equation (II-35) is of the same form as the expression used as a basis for reference substance plots, of vapor-liquid equilibrium data. If, as in the vapor-liquid case, one assumes that the ratio of the enthalpy differences is fairly constant, this implies that the isoteres of a log-log plot of gas-solid equilibrium data would be straight lines. The error involved in this assumption will be proportional to the magnitude of the temperature differences in the system and will be reduced, for a well behaved function, by utilizing a tangent to the curve taken at some point within the temperature range encountered.

For the assumption that the isoteres are straight line, the following relation may be written:

\[ \ln f_G^\infty = m \ln f_S^\infty + \ln C, \]  

(II-36)

where it can be seen that m is identical to the m of equation (II-35). Now utilizing the definition:

\[ f_0 = f_S^\infty \bigg|_{f_G^\infty} = 1.0 \]  

(II-37)
equation (II-36) can be rewritten as:

\[ f_G^\infty = \left( \frac{f_S^\infty}{f_0} \right)^m. \]  

(II-38)
It can be seen that $f_Q$ and $m$ are functions of the solute concentration on the solid, only, and that $f_s^o$ is required to be a function of temperature, only, in that it must be evaluated at the saturation pressure corresponding to the temperature.

Equation (II-29) may be expressed in terms of a fugacity coefficient:

$$f_{G_1}^e = \gamma_{G_1} y_{A_1}^{e} \frac{v_{T,P}}{P} = f_G^e. \quad (II-39)$$

Equation (II-39) may be solved for the gas phase concentration in terms of Equation (II-38):

$$y_{A_1}^e = \frac{1}{\gamma_{G_1}^{e} \frac{v_{T,P}}{P}} \left( \frac{f_s^o}{f_o^e} \right)^m. \quad (II-40)$$

In the case in which the fluid is a perfect gas this expression simplifies to:

$$y_{A_1}^e = \frac{1}{P} \left( \frac{f_s^o}{f_o^e} \right)^m. \quad (II-41)$$

Empirical expressions were formulated for determining $f_o$ and $m$ for normal, aliphatic hydrocarbons as functions of the mass ratio of adsorbate to adsorbent. The data used for these correlations were obtained from three isotherms for type BPLP Pittsburgh Activated Carbon. The forms of the correlations were:

$$m = a w^b \quad (II-42)$$

and

$$f_o = c w^d \quad (II-43)$$

The saturation fugacity $f_s^o$ was also correlated for the function:

$$\log f_s^o = A + B/(C + T). \quad (II-44)$$
Values for the coefficients obtained and the square of the correlation coefficients are listed in Table I.

This, then, completes the specification of the physical model to be studied. The model can now be described as a conventional fixed bed adsorber, operating under adiabatic plug flow conditions. The transfer model is that of an external gas film controlled mass and heat transfer rate based on average concentrations and temperatures in the respective phases. Equations (II-21), (II-22), (II-26), (II-27), (II-35) and (II-40) describe the physical model which in conjunction with the various physical properties and equations (II-42), (II-43) and (II-44) will be used to attempt a solution of the system.

Equation (II-27) may now be expanded by means of the derived expressions for the heat of adsorption.

\[ H_{AD} = m(w) \lambda_s(T_s) \]

\[ m = a w^b \]

\[ \lambda_s = A + B T_s \]

The result of the substitution is:

\[
\frac{G_s}{H_{DG}} \left( \frac{Y - Y_E}{1 + Y_E} \right) \left[ (1 + b) H_{AD} - C_{PA} (T_s - T_G) \right] - \frac{G C_{PG}}{H_{HG}} (T_s - T_G)
\]

\[ = \rho_B \left[ C + w (C_{PA} - mB) \right] \frac{\partial T_s}{\partial t} \]
### TABLE I

**ADSORPTION EQUILIBRIUM COEFFICIENTS FOR THE ADSORPTION OF THREE NORMAL ALIPHATIC HYDROCARBONS ON TYPE BPL(6x16) PITTSBURGH ACTIVATED CARBON**

<table>
<thead>
<tr>
<th>Coefficient</th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>-0.19717</td>
<td>-0.11647</td>
<td>-0.21700</td>
</tr>
<tr>
<td>b</td>
<td>0.93318</td>
<td>1.5753</td>
<td>0.94752</td>
</tr>
<tr>
<td>c</td>
<td>-0.91455</td>
<td>-0.54025</td>
<td>-1.50904</td>
</tr>
<tr>
<td>d</td>
<td>11.810</td>
<td>59.141</td>
<td>2.5727</td>
</tr>
<tr>
<td>A</td>
<td>4.2376</td>
<td>4.1037</td>
<td>4.0098</td>
</tr>
<tr>
<td>B</td>
<td>-411.6</td>
<td>-600.8</td>
<td>-720.5</td>
</tr>
<tr>
<td>C</td>
<td>386.4</td>
<td>330.2</td>
<td>301.0</td>
</tr>
</tbody>
</table>

**Correlation Coefficient (Squared)**

<table>
<thead>
<tr>
<th></th>
<th>Methane</th>
<th>Ethane</th>
<th>Propane</th>
</tr>
</thead>
<tbody>
<tr>
<td>m</td>
<td>.9909</td>
<td>.9925</td>
<td>.9642</td>
</tr>
<tr>
<td>f₀</td>
<td>.9857</td>
<td>.9928</td>
<td>.9392</td>
</tr>
<tr>
<td>fₐ</td>
<td>.9986</td>
<td>.9998</td>
<td>.9988</td>
</tr>
</tbody>
</table>

4. **Mathematical Model**

The basic equations and the physical model of the fixed bed adsorber have been specified in the previous sections. This section will be concerned with the transformation of the equations and the boundary conditions to give a general system of equations applicable to any physical system of the same model. The final transformed equations
will then be referred to as the mathematical model of the system.

The basic equations of the system are:

\[
-\frac{\partial Y}{\partial z} - \frac{1}{H_{DG}} \left( \frac{Y - Y_E}{1 + Y_E} \right) = \frac{D_P}{G} \frac{\partial Y}{\partial t},
\]

\[
\frac{1}{H_{DG}} \left( \frac{Y - Y_E}{1 + Y_E} \right) = \frac{\rho_B}{G_s} \frac{\partial w}{\partial t},
\]

\[
-\frac{\partial T_G}{\partial z} + \frac{1}{H_{HG}} (T_s - T_G) = \frac{D_P}{G} \frac{\partial T_G}{\partial t},
\]

and

\[
\frac{1}{H_{DG}} \left( \frac{Y - Y_E}{1 + Y_E} \right) \left[ (1+b) H_{AD} - C_{PA} (T_s - T_G) \right]
- \frac{(1 + Y) C_{PG}}{H_{HG}} (T_s - T_G) = \frac{\rho_B}{G_s} \left[ C + w(C_{PA} - m_B) \right] \frac{\partial T_s}{\partial t}.
\]

(II-45)

The following boundary conditions specify a particular solution to equations (II-45):

1. At \( t = 0 \); \( Y = Y_{0e} \) for \( 0 < z < L \).
2. At \( z = 0 \); \( Y = Y_0 \) for \( t > 0 \).
3. At \( t = 0 \); \( w = w_0 \) for \( 0 < z < L \).
4. At \( t = 0 \); \( T_G = T_{Go} \) for \( 0 < z < L \).
5. At \( z = 0 \); \( T_G = T_0 \) for \( t > 0 \).
6. At \( t = 0 \); \( T_s = T_{So} \) for \( 0 < z < L \).

The usual transformations initially performed are the transformations of the independent variables. The following transformations are defined in order to make the independent variables dimensionless:

\[
\xi = \frac{z}{L}, \quad (II-46)
\]

\[
\theta = \frac{G_s t}{\nu_B L}, \quad (II-47)
\]
In General, where $X$ represents any dependent variable one may write:

$$\left(\frac{\partial X}{\partial z}\right)_t = \left(\frac{\partial X}{\partial z}\right)_t \left(\frac{\partial \xi}{\partial z}\right)_t \left(\frac{\partial \theta}{\partial z}\right)_t \frac{\partial \xi}{\partial z} + \left(\frac{\partial \theta}{\partial z}\right)_t \frac{\partial \xi}{\partial z} \frac{\partial \theta}{\partial z}, \right) \tag{II-48}$$

where:

$$\left(\frac{\partial \xi}{\partial z}\right)_t = \frac{1}{L} \tag{II-49}$$

and

$$\left(\frac{\partial \theta}{\partial z}\right)_t = 0 \tag{II-50}$$

The derivative in terms of $t$ may be written:

$$\left(\frac{\partial X}{\partial t}\right)_z = \left(\frac{\partial X}{\partial t}\right)_z \left(\frac{\partial \xi}{\partial z}\right)_z \left(\frac{\partial \theta}{\partial z}\right)_z \frac{\partial \xi}{\partial z} + \left(\frac{\partial \theta}{\partial z}\right)_z \frac{\partial \xi}{\partial z} \frac{\partial \theta}{\partial z}, \right) \tag{II-51}$$

where:

$$\left(\frac{\partial \xi}{\partial t}\right)_z = 0 \tag{II-52}$$

$$\left(\frac{\partial \theta}{\partial t}\right)_z = \frac{G_s}{\rho_B L} \tag{II-53}$$

Let:

$$\varphi = \frac{G}{\rho_G F_e} ,$$

and

$$\psi = \frac{dz}{dt} X = -\left(\frac{\partial X}{\partial t}\right)_t \frac{\partial \xi}{\partial z} \frac{\partial \theta}{\partial z} \tag{II-48}$$

where $\varphi$ is the actual average gas flow and $\psi$ is the velocity of the adsorption wave. Now it can be seen that:

$$\frac{\partial X}{\partial t} = -\psi \frac{\partial X}{\partial z}$$
and
\[
\frac{1}{\varphi} \frac{\partial x}{\partial t} = - \frac{\psi}{\varphi} \frac{\partial x}{\partial z} .
\]

For \( \psi \ll \varphi \) then:
\[
- \frac{1}{\varphi} \frac{\partial x}{\partial t} = + \frac{\psi}{\varphi} \frac{\partial x}{\partial z} \ll \frac{\partial x}{\partial z} .
\]

This permits the elimination of the derivatives with respect to time in the first and third equations of equations (II-45).

Equations (II-48) and (II-51) may now be written as:
\[
\left. \frac{\partial x}{\partial z} \right|_t = \frac{1}{L} \left. \frac{\partial x}{\partial \xi} \right|_\theta \quad (II-55)
\]

and
\[
\left. \frac{\partial x}{\partial t} \right|_z = \frac{G_s}{\rho_B L} \left. \frac{\partial x}{\partial \xi} \right|_\xi . \tag{II-56}
\]

Equations (II-45) may now be revised by means of equations (II-54), (II-55) and (II-56) to the following form:
\[
\frac{\partial Y}{\partial \xi} = - \frac{L}{H_{DG}} \left( \frac{Y - Y_E}{1 + Y_E} \right) \tag{II-57}
\]
\[
\frac{\partial W}{\partial \vartheta} = \frac{L}{H_{DG}} \left( \frac{Y - Y_E}{1 + Y_E} \right) \tag{II-58}
\]
\[
\frac{\partial T_G}{\partial \xi} = \frac{L}{H_{HG}} (T_s - T_G) \tag{II-59}
\]
\[
\frac{\partial T_s}{\partial \vartheta} = \left\{ \frac{L}{H_{HG}} \left( \frac{Y - Y_E}{1 + Y_E} \right) \right\} \left[ (1 + b) H_{AD} - C_{PA} (T_s - T_G) \right] \\
- (1 + Y) (C_{PG}) \left\{ \frac{L}{H_{HG}} \right\} (T_s - T_G) \left/ \left[ C + w(C_{PA} - mB) \right] \right. \tag{II-60}
\]

The boundary conditions in this system of coordinates are
essentially the same as for the untransformed system. This can be seen by investigation of the transformation. First consider the boundary values specified at \( z = 0 \) for \( t > 0 \):

\[
\xi = \frac{z}{L} = 0,
\]

and

\[
\theta = \frac{G_{st}}{\rho_{BL}} > 0.
\]

Now consider the condition at \( \theta \) equal to zero. Then:

\[
\frac{G_{st}}{\rho_{BL}} = 0,
\]

and \( t = 0 \).

It can also be seen that, \( 0 < z < L \), implies from the definition of \( \xi \) that, \( 0 < \xi < 1 \).

The boundary conditions for the system in terms of the transformed variables becomes:

1. At \( \xi = 0 \); \( Y = Y_0 \) for \( \theta > 0 \).
2. At \( \theta = 0 \); \( w = w_0 \) for \( 0 < \xi < 1 \).
3. At \( \xi = 0 \); \( T_g = T_0 \) for \( \theta > 0 \).
4. At \( \theta = 0 \); \( T_s = T_{so} \) for \( 0 < \xi < 1 \).

The final equations which describe the mathematical model may be written in terms of the following definitions:

\[
\lambda = (1 + b)H_{AD} - C_{PA} (T_s - T_g) \quad (II-61)
\]

\[
C_s = C + W [C_{PA} - mB] \quad (II-62)
\]

\[
N_1 = \frac{L}{HA_DG}, \quad (II-63)
\]

and
5. Solution Technique

The final system, as described by the equations (11-65) through (11-69) appear to have no analytic solution for the complex equilibrium relation to be used. Consequently a numerical difference technique will be used. This section will fully develop the equations to be used.

The basic equations for the solution are obtained from a Taylor series written in terms of any dependent variable $M$ as follows:

$$M(\xi + \Delta \xi, \theta) = M(\xi, \theta) + \sum_{n=1}^{\infty} \frac{(\Delta \xi)^n}{n!} \left( \frac{\partial M}{\partial \xi^n} \right)_{\xi, \theta}$$

Define:

$$I = \xi / (\Delta \xi)$$

and

$$J = \theta / (\Delta \theta)$$

Equation (II-70) may now be written as:

$$M_{I+1, J} = M_{I, J} + (\Delta \xi) \frac{\partial M}{\partial \xi} \bigg|_{I, J} + \frac{(\Delta \xi)^2}{2} \frac{\partial^2 M}{\partial \xi^2} \bigg|_{I, J} +$$

$$\sum_{n=3}^{\infty} \frac{(\Delta \xi)^n}{n!} \frac{\partial^n M}{\partial \xi^n} \bigg|_{I, J}$$
or for $\Delta \xi < 0$ as:

\[
M_{I-1,J} = M_{I,J} - (\Delta \xi) \frac{\partial M}{\partial \xi} \bigg|_{I,J} + \frac{(\Delta \xi)^2}{2} \frac{\partial^2 M}{\partial \xi^2} \bigg|_{I,J} + \sum_{n=3}^{\infty} \frac{(\Delta \xi)^n}{n!} \frac{\partial^n M}{\partial \xi^n} \bigg|_{I,J},
\]

(II-73)

The first derivative of the dependent variable may now be defined in terms of $\Delta M$ and higher derivatives of $M$.

\[
\frac{\partial M}{\partial \xi} \bigg|_{I,J} = \frac{M_{I+1,J} - M_{I,J}}{\Delta \xi} - \frac{(\Delta \xi)^2}{2} \frac{\partial^2 M}{\partial \xi^2} \bigg|_{I,J} - \sum_{n=3}^{\infty} \frac{(\Delta \xi)^n}{n!} \frac{\partial^n M}{\partial \xi^n} \bigg|_{I,J}.
\]

A first order correct approximation for the derivative may be obtained by truncating all derivatives of order two and above.

\[
\frac{\partial M}{\partial \xi} \bigg|_{I,J} = \frac{M_{I+1,J} - M_{I,J}}{\Delta \xi}.
\]

(II-74)

A second order correct approximation may be obtained by first subtracting equation (II-73) from (II-72).

\[
M_{I+1,J} - M_{I-1,J} = 2(\Delta \xi) \frac{\partial M}{\partial \xi} \bigg|_{I,J} + 2 \sum_{k=3}^{\infty} \frac{(\Delta \xi)^k}{k!} \frac{\partial^k M}{\partial \xi^k} \bigg|_{I,J}
\]

where $k$ is an odd number only.

(II-75)

The final expression is obtained by truncating all derivatives of order three and above.

\[
\frac{\partial M}{\partial \xi} \bigg|_{I,J} = \frac{M_{I+1,J} - M_{I-1,J}}{2(\Delta \xi)}.
\]

(II-76)

A similar derivation may be used to obtain approximations for the derivations with respect to $\theta$. The expressions for the first
order correct and second order correct approximations are respectively:

\[
\frac{\partial M}{\partial \theta} \bigg|_{I,J} = \frac{M_{I,J+1} - M_{I,J}}{\Delta \theta} \quad \text{(II-77)}
\]

and

\[
\frac{\partial M}{\partial \theta} \bigg|_{I,J} = \frac{M_{I,J+1} - M_{I,J-1}}{2(\Delta \theta)} \quad \text{(II-78)}
\]

These four approximations for the derivatives of equations (II-66) through (II-69) will be used to solve the equations simultaneously.

The solution of the equations will be obtained by the following procedure.

(1). Calculate \( Y_E \) at \( \theta \) for \( 0 \leq \xi \leq 1 \) by means of the equilibrium relation and known values of \( w \) and \( T_g \) at \( \theta \) for \( 0 \leq \xi \leq 1 \).

(At \( \theta = 0 \), the values of \( w \) and \( T_g \) are given by the initial conditions.)

(2). Calculate \( Y \) and \( T_g \) at \( \theta \) for \( \Delta \xi \leq \xi \leq 1 \) by means of equations (II-74) and (II-76) and the boundary conditions for \( Y \) and \( T_g \).

(3). Calculate values of \( W \) and \( T_s \) at \( \theta + \Delta \theta \) by means of equation (II-77), if \( \theta = 0 \), or by equation (II-78) for \( \theta > 0 \).

(4). Recalculate values of \( w \) and \( T_s \) at \( \theta + \Delta \theta \) by means of as many Euler improvement cycles as required for a stable solution.

(5). Repeat steps (1) through (4) as many times as necessary in order to solve the system.

The first step in the procedure is fully explained in section
three. The equations of section three may be solved directly to obtain $Y_\xi$ and $\lambda$ for $0 \leq \xi \leq 1$ and a particular value of $\theta$.

The second step in the procedure must be developed. The derivative of equation (II-66) may be replaced by use of either of equations (II-74) or (II-76). It has been previously determined that the first order correct expression does not yield stable solutions for a fixed bed system with a linear equilibrium relation. It is intuitively apparent that at least a second order correct expression must be used for a more complicated equilibrium relation. The first order correct approximation must be used at $\xi = 1$ since the domain of $Y(\xi)$ lies in the closed interval of $0 \leq \xi \leq 1$.

Substitution for the derivative of equation (II-66) yields a system of $N$ equations in $N$ unknowns provided that $Y_\xi$ and $Y_{\xi,0}$ (the boundary condition) are specified. This system of nonhomogeneous linear equations is consistent since the rank of the coefficient matrix is equal to the rank of the augmented matrix. Having proved the existence of the solution, the solution itself may be obtained for this augmented tri-diagonal matrix by the Thomas method. (11)

The equations are listed in terms of any dependent variable $M$ for a particular value of $\theta$ in Table II. The expressions for the coefficients and the non-homogeneous terms are obtained from the substituted form of equations (II-66) and (II-68) and are listed in Table III. The solution for $M$ at $\theta$ is obtained by solving the following equations:

$$f_i = a_{i,1} - \frac{a_{i,i-1} a_{i-1,i+1}}{f_{i-1}}$$

and
TABLE II
THE GENERAL NON-HOMOGENEOUS SYSTEM OF EQUATIONS

<table>
<thead>
<tr>
<th>i</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>( A_{1,1} M_1 + A_{1,2} M_2 + 0 + \cdots + 0 = CD_1 )</td>
</tr>
<tr>
<td>2</td>
<td>( A_{2,1} M_1 + A_{2,2} M_2 + A_{2,3} M_3 + 0 + \cdots + 0 = CD_2 )</td>
</tr>
<tr>
<td>i</td>
<td>( 0 + 0 + A_{i,i-1} M_{i-1} + A_{i,i} M_i + A_{i,i+1} M_{i+1} + 0^+ = CD_i )</td>
</tr>
<tr>
<td>n-1</td>
<td>( 0 + \cdots + 0 + A_{n-1,n-2} M_{n-2} + A_{n-1,n-1} M_{n-1} + A_{n-1,n} M_n = CD_{n-1} )</td>
</tr>
<tr>
<td>n</td>
<td>( 0 + \cdots + 0 + A_{n,n-1} M_{n-1} + A_{n,n} M_n = CD_n )</td>
</tr>
</tbody>
</table>
### TABLE III

**EXPRESSIONS FOR THE SCALERS OF TABLE II**

<table>
<thead>
<tr>
<th>Scaler</th>
<th>Expression</th>
<th>$i = 1$</th>
<th>$1 &lt; i &lt; N$</th>
<th>$i = N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y = M$</td>
<td>$A_{i,i-1}$</td>
<td>0</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_{i,i}$</td>
<td>$\frac{2(\Delta \xi)N_1}{1 + Y_{E_1}}$</td>
<td>$\frac{2(\Delta \xi)N_1}{1 + Y_{E_1}}$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$A_{i,i+1}$</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$C_{D,i}$</td>
<td>$Y_0 + A_{i,1}Y_{E_1}$</td>
<td>$A_{i,i}Y_{E_1}$</td>
<td>$\frac{(\Delta \xi)N_1 Y_{E_n-1}}{1 + Y_{E_n-1}}$</td>
</tr>
<tr>
<td>$T_G = M$</td>
<td>$A_{i,i-1}$</td>
<td>0</td>
<td>-1</td>
<td></td>
</tr>
<tr>
<td></td>
<td>$A_{i,i}$</td>
<td>$2(\Delta \xi)N_3$</td>
<td>$2(\Delta \xi)N_3$</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>$A_{i,i+1}$</td>
<td>1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td></td>
<td>$C_{D,i}$</td>
<td>$T_{G_0} + A_{i,1}T_{s_{1,j}}$</td>
<td>$A_{i,i}T_{s_{1,j}}$</td>
<td>$\frac{(\Delta \xi)N_3 T_{s_{n-1,j}}}{1 + T_{s_{n-1,j}}}$</td>
</tr>
</tbody>
</table>
\[ s_i = \frac{CD_i - a_{i,i-1} g_{i-1}}{f_i} \]

where \( i \) varies from 1 to \( n \). Then the values for \( M \) are obtained by the following expression:

\[ M_{i,j} = s_i \left( a_{i,i+1} \right) M_{i+1,j} \]

The calculations for step (3) are performed through the use of equation (II-77), if \( \theta = 0 \), or equation (II-78), for \( \theta > 0 \). The procedure for making the calculations are listed below.

(a) Calculate \( D_{2i,j} \) and \( D_{4i,j} \), for all \( i \), by means of equations (II-67) and (II-69) using the final values of \( D_{1i,j} \) and \( D_{3i,j} \) obtained in the previous step.

(b) Calculate \( w_{i,j+1} \) and \( T_{s_{i,j+1}} \) by the equations and restrictions above.

The calculations of step (4) are the Euler Improvement Cycle. The procedure is as follows:

(a) Calculate \( D_{2i,j+1} \) and \( D_{4i,j+1} \) by means of the procedures specified in steps (1) through (2) and part (a) of step (3).

(b) Recalculate \( w_{i,j+1} \) and \( T_{s_{i,j+1}} \) by means of the equations and restrictions as specified in step (3) using the arithmetic mean of \( D_{k_{i,j+1}} \) and \( D_{k_{i,j}} \) for the derivative term.

(c) Repeat (a) and (b) above as many times as required for a
stable solution.

Step (5) completes the solution procedure for the mathematical model proposed. The solution is then defined in terms of the equilibrium relation, the boundary conditions, and the parameters as specified in equations (II-62) through (II-65). A computer program for the solution of this system is listed in Appendix F.

The output from the computer program is also obtained in terms of the following transformed variables:

\[
R \equiv \frac{Y - Y_{oe}}{Y_o - Y_{oe}}
\]

\[
S \equiv \frac{w - w_o}{w_{oe} - w_o}
\]

\[
U \equiv \frac{T_G - T_o}{T_o - T_R}
\]

\[
V \equiv \frac{T_S - T_{so}}{T_{so} - T_R}
\]

This output will allow the comparison of runs for the same parameter values but with different boundary conditions in order to determine the influence, if any, of the boundary conditions on a general solution of the equation. The transformations above do not eliminate the boundary conditions from equations (II-66) through (II-69) and thus do not permit a general solution as such. Additional derivations are also obtained if the transformation is performed and the boundary conditions are allowed to vary thus complicating the solution. In order to obtain this convenient output of results and still maintain a general calculation method with a minimum of complexity; the previous calculation technique was devised.
CHAPTER III

EXPERIMENTAL APPARATUS AND TECHNIQUES

1. Design bases

The experimental study was conducted in order to evaluate the ability of the mathematical solution for the postulated theoretical model to predict the behavior of a fixed bed, adiabatic, adsorption system. This study also investigated the existence of a general solution for several values of boundary conditions and flow rates. Several design bases must be established to accomplish these objectives.

The theoretical aspects of this study were based on the use of overall gas phase transfer coefficients to predict the heat and mass transfer rates in the system. The Two-Film Theory Concept indicates that the decrease in individual gas phase transfer coefficients resulting from a decrease in gas phase flow, causes the overall coefficient to approach the individual gas phase coefficient. In order to study the degree of this approach, it was decided to operate at flow rates an order of magnitude lower than normally used for these systems.

Another factor which was considered was the components to be used in the system. An experimental determination of equilibrium data is a study of some magnitude in itself, hence it was decided to use a system for which data and materials were readily available. Since the data obtained were for the specific brand of activated carbon to be
used, it is expected that the data is as accurate as one might obtain by experimental methods.

The sampling technique is still another important factor. It was decided that samples taken near the center of the bed would exhibit the most correct values in that wall effects would be minimized at this point. Sampling at several longitudinal positions should be equivalent to sampling the outlet stream for several bed depths, hence one run for this system would yield as much data as several runs from the exit sampled system.

The assumption of adiabatic operating conditions must be considered in the design of the apparatus. It is anticipated that the heat loss through the walls may be made negligible by proper insulation. This assumption will be studied in more detail by comparison of the experimental and theoretical results.

The final factor considered in the design of the equipment is the physical size of the equipment. The two geometric variables of interest are the column diameter and the length of the packed bed. The diameter is of interest in that the superficial mass velocity is a function of the empty cross sectional area. The magnitude of any wall effects is also reduced by an increase in column diameter.

The length of the bed determines the time interval during which the wave front may be measured. Given a particular sampling rate then the duration of the sampling period determines the number of samples that may be obtained. It would also be of interest to investigate the influence of time on the actual shape of the adsorption wave itself.
2. **General description of the apparatus.**

The primary piece of equipment in the system is the column. A length of galvanized steel, schedule number 40, two inch pipe was selected as the basic column structure. It was decided that this pipe could be drilled and tapped to accommodate sampling ports with a minimum of leakage. The necessary fittings and supporting members could also be combined easily with a unit of this material.

The pipe was cut to a length of 76 inches and threaded at each end. Three rows of sample ports were drilled at intervals of eight inches starting from the top of the column. The drilled holes were then tapped to accommodate one-eighth inch pipe thread. A packing support was cut from a multilayered, fine-mesh, stainless steel screen and silver-soldered to the bottom of the column. Unions were attached at both ends to facilitate filling and emptying the column and plugs were attached to the unions after being drilled and tapped.

The column was then mounted in a portable stand by means of a plate bolted to the bottom of the stand and two notched, steel strips bolted to the top of the stand. The bottom plate had a hexagonal hole cut in it to accommodate and immobilize the bottom half of the lower union. A panel was then attached to the side of the stand by two lengths of angle iron for mounting the flow control system.

The carrier gas was routed from a gas cylinder through a pressure regulator to the metering system as was the adsorbate gas. The carrier gas was directed via a Whitey needle valve (1RS4) to a Fisher and Porter rotameter (V3-1530/2) for measurement of the flow. The adsorbate was controlled by a Nupro, fine-metering valve (4M) and
measured by a Fisher and Porter rotameter (T3-1562/3). The gases were then mixed and directed to the top of the column via a cooling bath in order to maintain a constant inlet temperature.

Two Whitey, on-off, toggle valves were mounted at the top of the column in order to permit by-passing the column. A Nupro, safety-relief valve was mounted immediately above the column as a safety precaution. The various pieces of equipment were connected, primarily by one-fourth inch poly-ethylene tubing, but also by one-fourth inch copper tubing where flexibility was not essential.

The basic system was then placed in front of a hood equipped with an exhaust fan in order to prevent any accumulation of adsorbate gas in the vicinity of the equipment. The room in which the experimentation took place was maintained at a fairly constant temperature. A photograph of the system, in place, is displayed as Figure 2; and a schematic diagram of the system is displayed as Figure 3.

The sampling devices were then attached and the column was insulated with one inch molded pipe covering. Glass wool and tape were used to patch the molded pipe covering. Asbestos tape was used to insulate the fittings and valves above the molded pipe covering.

3. Sampling Techniques

It was decided that sampling would be performed by measurement of the temperature in the bed and by taking samples of the gas in the bed. It was anticipated that there would be little difference between the gas phase temperature and the solid temperature; therefore, special precautions insuring the measurements of either of the two temperatures would not be necessary. In order to prevent any noticeable effect as a
FIGURE 2. PHOTOGRAPH OF THE SYSTEM FROM FRONT
Pressure Regulator

Rotameter

Pressure Regulator

Needle Valve

Rotameter

Nitrogen Cylinder

Ethane Cylinder

Needle Valve

Safety Relief Valve

FIXED-BED ADSORPTION COLUMN

To Vent

On-Off Valve

On-Off Valve

V-Jet Test Meter

Wet Test Meter

(SP-Sample Port)

FIGURE 3. SCHEMATIC DIAGRAM OF THE SYSTEM
result of removing gas samples from the column, only very small quantities (25-50 \( \mu \)l) were used.

The temperature in the bed was sensed by means of fine thermocouples and measured by a Minneapolis-Honeywell Universal Electronik, type 153, multipoint recorder. Twelve points were recorded at intervals of five seconds per point. The chart speed was thirty inches per hour. The temperature range of the instrument was 0-250\( ^\circ \) F.

The thermocouples were welded from 24 gauge, solid wire, copper constantan thermocouple wire. Each wire was individually insulated with nylon and the two wires were insulated by a polyethylene coating which yielded a wire of circular cross-section, 0.1 inches in outside diameter. Each wire was then slipped through a one inch length of one-eighth inch stainless steel tubing. The tubing and wire were slipped into a one-eighth inch pipe to one-eighth inch tubing, union of brass construction. The fitting with ferrules installed were tightened in position so that the thermocouple bead protruded one inch from the end of the fitting.

The thermocouples and recorder were calibrated by immersing the thermocouples in an ice-bath, boiling methyl-alcohol, and boiling water. The recorder was adjusted to read 32\( ^\circ \) F with the thermocouples immersed in the ice bath. The maximum deviation observed in the readings was 0.2\( ^\circ \) F with a mean deviation of less than 0.1\( ^\circ \) F. The deviation of the readings with the thermocouples in boiling water was essentially the same as in the ice bath as was the case when tested in boiling methyl-alcohol. The thermocouples to be used in the bed had a deviation of about 0.1\( ^\circ \) F which is as accurate as the chart can be read.
During the calibration of the thermocouples it was observed that the potentiometer would occasionally drift up to 2-3° F. In order to eliminate errors as a result of this drift a thermocouple was placed in an ice bath and monitored in sequence with the other thermocouples in order to correct all readings obtained. The drift was observed to be the same at 32° F as at 212° F and so was assumed to be the same over the entire range.

The gas sampling system was composed of three primary units: the sampling ports, the sampling device and the measuring device. The sample ports were devised and assembled locally. Several syringes of 50 micro-liter capacity were used to extract samples from the column and a MicroTek (GC-2500R) gas chromatograph was utilized to measure the concentrations of the samples.

Several different types of sample ports were tested, but proved to be unsatisfactory because of leakage. The system which was found to be satisfactory was assembled as a basic unit, a one-eighth inch pipe to one-fourth inch tubing, brass, Swagelok union. The union was attached to the column with the tubing side extending to the edge of the column insulation.

A teflon sealant gland was used instead of the usual brass front ferrule. A one inch length of one-eighth inch brass tubing was forced into the hole in the center of the sealant gland to prevent the gland from collapsing, to direct the syringe needle into the proper position of the bed and to prevent the packing from spilling into the fitting. A three-eighth inch silicone rubber septum was placed between two brass washers of the same outside diameter and with a one-eighth inch hole diameter and the three pieces were placed inside the
nut of the union. The nut was tightened until the septum began to protrude through the washer yielding a gas tight, self-sealing sample port.

The sampling devices used were several Hamilton (705 series) syringes. The syringes were affixed with 24 gauge, sheathed needles with $17^\circ$ bent points. These syringes were found to be satisfactory if frequently lubricated with water. This also prevented an accumulation of plugs in the needle which resulted from septum penetration. A plugged needle during operation required about three minutes to clear, which during an actual run might be critical.

The measuring system consisted of a column for separating the two components, the thermal conductivity detector for sensing the components, the electronic amplifier and master control section and the recorder. This report will discuss the system only in terms of those subjects peculiar to this study.

The column was made by packing a 5.5 feet long section of one-fourth inch copper tubing with fine-grained silica gel to a depth of five feet. The packing was held in place by glass wool. The system has dual columns but the second column was not used for sampling. The detector is in the lines beyond the two columns. The detector unit consists of four filaments, with two filaments in each of the parallel lines. The unit is heated by means of a temperature controlled external heater. The filaments are supplied by a 22 volt, D.C. power supply with a current of up to 725 milliamperes; if used with helium as a carrier gas.

The heater control, power supply, cell current control and the output attenuator are contained in the T.C. detector panel. The oven
temperature control is mounted in the same unit, in addition to the master power supply unit, blower control and the temperature indicator and selector switch. The inlet and outlet block heater controls and the carrier flow controls are mounted on still another unit.

The recorder utilized with the system was a Minneapolis-Honeywell, Electronik 15 Chromatography Recorder. The indicating range of the recorder is from -0.05 to +1.05 milli-volts. Charts speed were selectable from 15 inches per hour to 720 inches per hour.

The concentration measurement system was calibrated for a binary gas mixture consisting of Nitrogen and Ethane. It was determined that a helium carrier flow through the silica-gel column of 24.8 standard cc/min with a column temperature of 35°C would give sufficient resolution of a fifty micro-liter sample. The outlet block and the T.C. detector were maintained at 100°C. The detector current was set at 600 milli-amperes.

Twelve 50µl samples of pure ethane were analysed using a chart speed of 720 inches per minute with the attenuation at 32. The areas were then measured and analyzed statistically. The sample estimate of the population variance was found to be 1.73% in the case of ethane and 1.0% for seven samples of pure nitrogen. The variance of the sample mean for ethane is 0.5% and for nitrogen, 0.3%. This implies that there exists only a 5% probability of the true means lying outside of the 1% range of the sample means calculated. This variance can probably be attributed to the variation in sample size and to a smaller extent to the error in measuring the areas with a polar planimeter.
These mean areas were then used to calculate the conversion factors for obtaining the pounds of each component per unit area measured under the curve. The factors were calculated for ethane and nitrogen respectively as $5.91 \times 10^{-10}$ and $6.99 \times 10^{-10}$ lbs/in$^2$. This would have been sufficient to calculate the concentrations of the samples but since a large number of samples were to be analyzed it was decided to correlate the ethane peak height to a per-cent of the sum of the two peak heights as a function of concentration (mole per-cent and weight per-cent) as determined by measurement of the areas utilizing a polar planimeter and the factor just determined. The square of the correlation coefficient for the following equation was 0.99996.

$$Y = 1.29609x - .42266x^2 - .03005x^3$$

where:

- $Y$ - weight per-cent ethane in the sample
- $X$ - ethane per-cent peak-height.

4. **Specific Operating Procedure**

The number of individual steps in the operating procedure is quite large. In order to simplify the procedure, the individual steps are grouped under various categories. The groups of steps are listed below and a detailed explanation follows.

(a). Fill the column.

(b). Perform pressure drop measurements.

(c). Purge the impurities from the column.

(d). Prepare the chromatograph for operation.

(e). Set the flow rates required to establish initial conditions.
(f). Set the flow rates required to establish inlet conditions and set time equal to zero.

(g). Sample as required to determine the rate of movement of the absorption wave through the column.

The experimental adsorption column was initially filled and packed with 2511 grams of BPL (6x16) Pittsburgh Activated Carbon. This quantity of packing gave a bed depth of 68 inches which is the depth from number three sample level to the packing support. The packing procedure consisted of alternately pouring small amounts of carbon into the column and rapping on the side for several minutes. This insured that a dense packed bed was obtained.

Step (b) was performed in order to obtain an average particle diameter \(D_p\) which could be used in calculating the height of a gas phase heat and mass transfer group from standard correlations. The specific surface calculated from the pressure drop study may also be used as an estimate for mass and heat transfer specific surfaces.

Step (c) is for the purpose of removing any impurities from the carbon. This step was performed by flowing a hot stream of nitrogen through the bed for a period of several hours. Step (d) may be initiated while purging the column since it was found that approximately six hours were required for the chromatograph to reach a stable state. After this "warm-up" period the base line drift was small enough such that corrections were made only about once per hour with no significant error resulting.

The next step (e) was for the purpose of setting up the initial bed conditions for the run. This step was performed by first establishing the carrier flow desired. This is accomplished by opening the
shut-off valves between the pressurized source and the metering valve and adjusting the pressure regulator to obtain a pressure for which the rotameter was calibrated. The line beyond the rotameter was set to direct the flow through the column and into the hood vent. The carrier flow was then established by adjusting the metering valve until the desired flow was obtained as indicated by the rotameter. The carrier flow was then checked by measurement of the existing flow with a wet test meter and by an analysis of the stream.

The desired initial solid concentration was then established by metering the proper flow of ethane to the column utilizing the same procedure as for the carrier gas. This feed rate was continued until the outlet gas phase concentration reached the inlet concentration. It was assumed at that time that the gas and the solid were at equilibrium and the actual run could be started. The solid temperatures were then determined from the temperature recorder and the solid concentration from equilibrium curves.

Now that the initial conditions were established, the boundary conditions (or inlet conditions) could be set. Step (f) was then accomplished by increasing the ethane flow rate to give the desired inlet feed concentration as measured by the rotameter in the ethane line. The chart drives on the chromatograph and temperature recorders were started simultaneously with the flow change and were marked to establish time zero.

The sampling phase, step (g), was then commenced. The temperature recorder required very little observation during the runs and was used primarily to determine the proper place to sample gas
phase concentration. The gas phase concentration sampling required most of the time. The samples were obtained and immediately analyzed during all runs.

Immediately after completing step (f), a sample was taken from sample port three. The sample was injected into the inlet block of the right column of the chromatograph. While the sample was preceding through the column, the output attenuation was set as required by the sample size, and the chart was marked to indicate the time and the point from which the sample was taken. Approximately 50 seconds after the sample was injected, the nitrogen peak was observed. During this period the base line and other variables of the chromatograph were adjusted as necessary. Also during this period the syringe was flushed and the point to be sampled next was selected.

The ethane peak required approximately 85 seconds after injection to reach the T.C. detector and to be recorded. During the 35 second interval between the nitrogen peak and the ethane peak the attenuation was reset to obtain a larger ethane peak. The attenuations used for the various samples were also recorded on the chart. The ethane required about 110 seconds to be swept from the column.

Two sampling frequencies were used. At the slower rate, the next sample was taken after the ethane was removed from the system or at the rate of 30 samples per hour. The higher rate was 45 samples per hour. This was achieved by taking a sample at the maximum of the nitrogen peak. This rate was the maximum rate possible which gave resolution between successive samples.

The sampling continued until the adsorption wave reached the
end of the column. At this time the carrier flow was checked as described previously. The flow rates were adjusted at this point to re-establish the initial conditions for the next run.
CHAPTER IV

PRESENTATION OF RESULTS

1. Description of Runs Performed

The experimental data was obtained utilizing a system that consisted of the adsorbate, ethane, the carrier gas, nitrogen, and the adsorbent which was BPL (6x16) type, Pittsburgh Activated Carbon. A total of twelve runs were made to study the influence of flow rate, the initial conditions, and the inlet conditions. In addition, seven other runs were made to develop experimental techniques and to determine the range of the variables to be presented in this report.

There are two primary reasons for utilizing only one tertiary system. The first reason is that using another system for the investigation of the variables to be studied would introduce additional variation into the mathematical solution. Since the equations themselves are not dependent on any specific property of any of the components it is felt that the generality of the solution technique is established and need not be proven experimentally. On the basis of the above facts, it was decided that a single system investigation would be of more significance in terms of the variables to be studied.

The second reason for utilizing a single system is the time requirements for the calibration of the auxiliary systems if a change of adsorbate is made or the additional experimentation required to determine the properties of the bed for each different size of adsorbent.
A study of three adsorbates was made to check the generality of the equilibrium relation used. The consistency of the relation in representing the physical data indicated that the time required to change systems would not be justified.

A summary of the runs performed is listed in Table IV. The runs are classified first according to the flow rate. The first number in the designation of each run is the same for all runs with approximately the same flow rate. The second number indicates the order in which the runs were performed. Run 2-2 is not presented in that it was the desorption of run 2-1 and was observed primarily for the purpose of obtaining initial information for future studies.

Two sets of three runs each are presented in the two series. The first three runs (2-1, 2-3, 2-4) have a similar initial condition \((Y_{OE})\) and may be compared with runs 4-1, 4-3, and 4-2 respectively to observe the effects of an increase in flow rate on the dynamic behavior of the system. In addition runs 2-5, 2-6, and 2-7 may be compared with runs 3-1, 3-2, and 3-3 respectively to observe the effects resulting from a decrease in flow rate.

In addition, runs 2-1, 2-3 and 2-4 may be compared with runs 2-5, 2-6, and 2-7 respectively to observe the effects of the initial value where other conditions are approximately constant. Finally, each run in the sets of three runs may be compared to observe the effects of the inlet concentration on the system behavior.
<table>
<thead>
<tr>
<th>Run No.</th>
<th>$G_s$</th>
<th>$\bar{G}$</th>
<th>$Y_0$</th>
<th>$Y_{OE}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-1</td>
<td>12.45</td>
<td>13.25</td>
<td>0.138</td>
<td>0.0058</td>
</tr>
<tr>
<td>2-3</td>
<td>12.90</td>
<td>14.18</td>
<td>0.207</td>
<td>0.0059</td>
</tr>
<tr>
<td>2-4</td>
<td>12.22</td>
<td>13.90</td>
<td>0.280</td>
<td>0.0056</td>
</tr>
<tr>
<td>2-5</td>
<td>11.78</td>
<td>12.70</td>
<td>0.144</td>
<td>0.0220</td>
</tr>
<tr>
<td>2-6</td>
<td>11.33</td>
<td>12.48</td>
<td>0.200</td>
<td>0.0200</td>
</tr>
<tr>
<td>2-7</td>
<td>10.95</td>
<td>12.48</td>
<td>0.274</td>
<td>0.0232</td>
</tr>
<tr>
<td>3-1</td>
<td>7.64</td>
<td>8.14</td>
<td>0.138</td>
<td>0.0196</td>
</tr>
<tr>
<td>3-2</td>
<td>7.73</td>
<td>8.51</td>
<td>0.200</td>
<td>0.0182</td>
</tr>
<tr>
<td>3-3</td>
<td>7.56</td>
<td>8.36</td>
<td>0.265</td>
<td>0.0182</td>
</tr>
<tr>
<td>4-1</td>
<td>21.4</td>
<td>22.7</td>
<td>0.1295</td>
<td>0.0045</td>
</tr>
<tr>
<td>4-2</td>
<td>21.5</td>
<td>23.8</td>
<td>0.236</td>
<td>0.0050</td>
</tr>
<tr>
<td>4-3</td>
<td>21.7</td>
<td>23.4</td>
<td>0.180</td>
<td>0.0050</td>
</tr>
</tbody>
</table>
FIGURE 4. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 2-1

\[
\begin{align*}
Y_{oe} &= 0.0058 \\
Y_{oo} &= 0.138 \\
G_s &= 12.45
\end{align*}
\]
FIGURE 5. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 2-3

Yoe = 0.0059
Yoo = 0.207
Gs = 12.90
FIGURE 6. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 2-4

\[ \text{Yoe} = 0.0056 \]
\[ \text{Yoo} = 0.280 \]
\[ \text{Gs} = 12.22 \]
FIGURE 7. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 2-5

$Y_{ee} = 0.0220$

$Y_{oo} = 0.144$

$G_s = 11.78$
FIGURE 8. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 2-6

Yoe = 0.0200
Yoo = 0.200
Gs = 11.33
FIGURE 9. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 2-7

\[ Y_{oe} = 0.0232 \]
\[ Y_{oo} = 0.274 \]
\[ G_s = 10.95 \]
FIGURE 10. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 3-1

\[ \text{Yoe} = 0.0196 \]
\[ \text{Yoo} = 0.138 \]
\[ G_s = 7.64 \]
FIGURE 11. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 3-2

Yoe = 0.0182
Yoo = 0.200
Gs = 7.73
FIGURE 12. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 3-3

Yoe = 0.0182
Yoo = 0.265
Gs = 7.56
FIGURE 13. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 4-1

\[ Y_{oe} = 0.0045 \]

\[ Y_{oo} = 0.1295 \]

\[ G_s = 21.4 \]
FIGURE 14. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 4-2

Yoe = 0.0050
Yoo = 0.236
Gs = 21.5
FIGURE 15. EXPERIMENTAL GAS PHASE CONCENTRATION DATA, RUN 4-3

- Yoe = 0.0050
- Yoo = 0.180
- Gs = 21.7
FIGURE 16. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 2-1

$Y_{oe} = 0.0058$

$Y_{oo} = 0.138$

$G_s = 12.45$
FIGURE 17. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 2-3

Yoe = 0.0059
Yoo = 0.207
Gs = 12.90
FIGURE 18. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 2-4

Yoe = 0.0056
Yoo = 0.280
Gs = 12.22
FIGURE 19. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 2-5

Yoe = 0.0220
Yoo = 0.144
Gs = 11.78
FIGURE 20. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 2-6

Yoe = 0.0200
Yoo = 0.200
Gs = 11.33
FIGURE 21. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 2-7

\[ Y_{oe} = 0.0232 \]
\[ Y_{oo} = 0.274 \]
\[ G_s = 10.95 \]
FIGURE 22. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 3-1

\[ Y_{oe} = 0.0196 \]
\[ Y_{oo} = 0.138 \]
\[ G_s = 7.64 \]
FIGURE 23. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 3-2

\[ Y_{oe} = 0.0182 \]

\[ Y_{oo} = 0.200 \]

\[ G_s = 7.73 \]
FIGURE 24. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 3-3

Yoe = 0.0182
Yoo = 0.265
Gs = 7.56
FIGURE 26. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 4-2

Yoe = 0.0050
Yoo = 0.236
Gs = 21.5
FIGURE 27. EXPERIMENTAL GAS TEMPERATURE DATA, RUN 4-3

Yoe = 0.0050
Yoo = 0.180
Gs = 21.7
2. **Results of Experimental Runs**

The experimental data are presented as figures 4 through 27. In a dynamic system of this type a presentation of individual points in tabular form does not lend itself to analysis. The graphical presentation, on the other hand, lends itself to an immediate interpretation of the functional behavior of the system. The cross-ruled paper facilitates interpretation of the data to obtain individual points if desired.

The experimental concentration data is presented in mass ratio units (mass of adsorbate per unit mass of carrier gas) as a function of time for various positions in the bed. The data point is represented by the intersection of the "+" sign and identified as to bed position by the Arabic numeral immediately adjacent to the right side of the "+" sign. Position three (3) is the inlet end of the bed and each succeeding position is eight (8) inches deeper in the bed than the preceding position.

The numerical value of the data points was obtained from the chromatograph chart paper by the following procedure. The time, position, peak heights and attenuations were read from the chart and recorded on a rough data sheet. These numbers were punched and verified on IBM, 80-column, cards by the personnel of the Louisiana State University Computer Research Center. A Fortran-IV computer program, Appendix C, was written and "de-bugged" to process these cards. The IBM 7040 system at the Computer Research Center was used to first calculate the values of concentration for print-out by the IBM 1401 system. The values of $Y_{00}$ and $Y_{0E}$ as interpreted from this print-out were used to recalculate the concentrations as mass ratio according to the
transformation of Chapter II. The output from this pass was punched on cards.

The experimental temperature data is presented in units of degrees Fahrenheit and plotted exactly as was the experimental concentrations. The experimental data was processed by the same technique used for the experimental concentration data. The computer program for the calculation is exhibited in Appendix B and the output from the program was on cards.

The experimental data was plotted by a Cal-Comp Plotter controlled by an IBM 1620 computer which is another digital computer system available at the Computer Research Center. Two Fortran II programs were written to plot the experimental temperature (Appendix D) and concentration (Appendix E) data. The programs required several subprograms (PLOT, AXIS, DRAW) which are contained in a deck of plotting subprograms devised by Proctor and Gamble. The deck is a standard library subprogram available at the Computer Research Center at Louisiana State University. The experimental data is presented in the form of these plots in Figures 4 through 27.

The experimental data may be analyzed first by a qualitative approach. The dynamic effects of the inlet concentration may be predicted qualitatively on the basis of a material balance and the capacity of the adsorbent for the adsorbate. Approximate calculations, using these two principles, indicate that increasing the adsorbate concentration, at the same carrier flow, results in a decrease in the time required for the adsorption wave to reach a specific point in the bed. This is easily verified, for the experimental study, by observation of
any two runs with the same carrier gas flow rate and initial bed conditions; for example, runs 2-1 and 2-4.

Similar qualitative arguments may be used to predict the effects of initial conditions and flow rate. Increasing the initial bed concentration causes a decrease in the time required for the wave to reach a point, all other conditions being constant; i.e., runs 2-1 and 2-5. Increasing the carrier flow has a similar effect as may be observed from runs 2-6 and 3-2.

Figures 16 through 27 demonstrate another wave phenomena which may be observed for fixed bed adsorption systems operating under non-isothermal conditions. The second wave phenomenon is the temperature wave which moves through the bed in conjunction with the concentration wave. The temperature wave occurs as a result of the energy release from the phase change of the adsorbate and therefore is dynamically dependent upon the rate of movement of the concentration wave. The maximum temperature is also dependent on the velocity of the concentration wave as may be seen by comparing runs 2-5 and 3-1.

The dynamic dependence of the temperature wave on the concentration wave is an implicit relation in that the concentration wave is also dynamically dependent upon the temperature. This reciprocal dependence cannot be expressed by any simple quantitative relationship. For this reason, the quantitative discussion is presented in section three of this chapter.

The preceding discussion indicates the qualitative effects of the inlet feed rate and composition and the initial adsorbent composition. The effects of the other controllable parameters mentioned in
Chapter I are also of interest. The additional parameters are the physical properties of the components of the system, inlet feed temperature and initial solid temperature, system pressure and the temperature of the surroundings. However, a detailed experimental study of all of the additional variables would be extremely time consuming and of little use unless some sort of generalized relations might be developed to represent the dynamic behavior of the system. This requires, initially, a transformation of the independent variables into a form which could be used to represent a particular system of components by one relation.

The transformations of Chapter II were selected because they did not require any additional assumptions which might cause a discrepancy between the theoretical results and the experimental results. These transformations may be evaluated in terms of the correlation of runs at various values of flow rate and various initial and inlet concentrations by comparing the experimental data in the transformed coordinate system.

Figures 28 and 29 are presented in order to evaluate the effectiveness of the time transformation of Chapter II in yielding a generalized solution. Figures 28 and 29 are plots of the transformed gas phase concentration, $R$, versus the transformed time, $\theta$, at a particular point in the bed.

The effect of varying the initial bed composition in the transformed coordinate system can be seen by observing that the concentration wave reaches position five (5) in run 2-5 prior to the time that it reaches the same position in run 2-1. This effect is typical of all runs for which only the initial bed composition varies. Increasing the inlet feed concentration demonstrates the same effect as
Figure 28. The effect of initial and inlet concentration on the concentration wave at a point.

- ○ $0.138 \ 0.0058$ (Run 2-1)
- △ $0.144 \ 0.0220$ (Run 2-5)
- □ $0.280 \ 0.0056$ (Run 2-4)

**Axes:**
- X-axis: Transformed time ($\phi$)
- Y-axis: Adsorbate concentration in gas ($R$)
FIGURE 29. THE EFFECT OF CARRIER GAS FLOW RATE ON THE EXPERIMENTAL CONCENTRATION WAVE AT A POINT

○ Gs=11.33 (Run 2-6)
△ Gs=7.73 (Run 3-2)
an increase in initial adsorbent concentration as can be seen by comparing runs 2-4 and 2-1 at the same position.

Figure 29 demonstrates that the effect of a change in carrier flow rate is not compensated for by the transformation of time proposed in Chapter II. All conditions except the carrier gas flow rate are approximately the same in runs 2-6 and 3-2 but still a difference in the dynamics exists in the transformed system. This failure of the time transformation to generalize the solution does not preclude its use, however, in the theoretical solution of the mathematical model. The dimensionless parameters obtained from the transformation might prove effective in correlations of the experimental data, if desired.

The transformations of the dependent variables appear sufficient to accomplish the objective of the transformations. The objective in transforming these variables is to reduce the variable to a form such that the initial and inlet conditions are incorporated in the transformed variable and such that the range of the transformed variables is the same. This can be easily accomplished for the gas phase concentration \( Y \) and the solid concentration \( w \). The temperature transformations were not as easily defined in that a maximum temperature would have to be known for each run to permit the range to be the same for all values of initial and inlet conditions. Thus the choice of the transformation of the temperatures was rather arbitrary. However, the concentration transformations were very effective in permitting the comparison of various runs as can be seen from figures 28 and 29.

3. Results of Theoretical Calculations

The primary purpose of this study is to develop a method of
calculating the dynamic behavior of fixed bed adsorption systems. A
model of the system was presented in Chapter II, represented by a set of
mathematical equations, and a solution technique which had been found
sufficient for simple adsorption cases was explained. This solution
technique was programmed in Fortran IV for use with an IBM 7040 Digital
Computer System. The results obtained were compared with experimental
results to evaluate the overall solution technique. This section will
describe the procedure used to obtain the final form of the solution
technique.

The initial computer program was written to perform the calcula-
tions as described in Chapter II. Values of \( N_1 \) and \( N_2 \) were estimated
for run 2-1 using the correlations obtained by Gamson, Thodos and
Hougen(14) and by Wilke and Hougen.(14) The particle diameter was
estimated to be 0.0109 ft. as determined from pressure drop studies
and the assumption of a surface to unit volume ratio midway between
that of a cube and a tetrahedron. The specific surface was determined
as 685 ft.\(^2\)/ft.\(^3\). The modified Reynolds number for this run was calcu-
lated to be 3.18 which is below the range of experimental data of Wilke
and Hougen. Values of the mass transfer parameter \( N_1 \) and heat trans-
fer parameter \( N_2 \) were calculated, using the above data, to be 270
and 5000 respectively. The values calculated for \( H_{DG} \) and \( H_{HG} \) as .00143
and .001065 feet respectively.

The value calculated for \( H_{DG} \) (as defined by Wilke and Hougen)
was 0.00143 feet. However, the height of a mass transfer unit in this
study is defined in terms of mole fraction concentrations where that
of Wilke and Hougen is in terms of partial pressures. It can be shown
that the height of the mass transfer unit as defined herein is equal to the total pressure \( P_{AVG} = 14.8 \text{ PSIA} \) times the calculated value above; or, 0.0212 feet. The height of the heat transfer unit herein is consistent with that of Wilke and Hougen and was found to be 0.001065 feet.

The solution technique was programmed in Fortran IV for the 7040 digital computer. The date of the initial compilation (6/1/64) was used to identify the program. This method of identification was used throughout the theoretical study for revised forms of the solution technique. The calculated results of the initial solution technique were found to oscillate in the region of the adsorption wave where the concentrations were near the inlet. These oscillations were observed to dissipate for low values of the mass transfer parameter \( N_L < 100 \) and to lead to an unstable solution for higher values \( N_L > 400 \). Reduction of the increment sizes used did not eliminate the oscillations even though the answers from successive calculations with decreasing increment sizes showed no significant change.

The initial theoretical results led to several changes in the mathematical model. The first change provided a method of specifying the dynamic behavior of the inlet gas concentration by a function other than just a step function. This function was defined as follows:

\[
R_0 = 1 - \exp \left(-\frac{t}{b}\right),
\]

where

- \( R_0 \) - transformed gas phase concentration at the bed inlet.
- \( t \) - time (min)
- \( b \) - time constant (positive only).

It can be seen that the function fits the desired limits:
\[
\begin{align*}
t = 0 & \text{ implies } R_0 = 0 \ ; \text{ hence: } Y_0 = Y_{0E} \\
\lim_{t \to \infty} (R_0) & = 1 \ ; \ R_0 = 1 \text{ implies } Y_0 = Y_{00}
\end{align*}
\]

This additional factor did not remove the previous oscillations for values of the time constant which resulted in theoretical values of \( R_0 \) which were similar to experimental values. However, the function defined above could be used to simulate the experimental values of \( R_0 \) better than did the step function. Since the function above adds an additional degree of freedom to the theory, it was utilized in subsequent studies. The value of the time constant used was 0.667.

The study of the effect of the mass transfer parameter indicated another deviation between experimental and theoretical results. The experimental temperatures were observed to increase to a maximum as the adsorption wave passed a particular point and to decrease steadily at a significant rate following the passage of the wave. In contradiction the calculated temperatures were observed to approach a maximum as the wave passed a particular position and then to decrease at an almost imperceptible rate following several oscillations. This discrepancy was interpreted as being a possible discrepancy in the theoretical model which should be given some consideration.

Three possible explanations were postulated which might account for the discrepancy noted. The obvious explanation is that the assumption of adiabatic conditions is not correct. The other possibilities are that a significant longitudinal heat flux may exist in the solid or that the experimental temperatures may be in error at the sample point as a result of heat conduction through the sample port. The last
explanation would require a revision in the experimental apparatus or technique and is noted here for future experiments.

Theoretical models may be postulated to describe the other two possibilities. Both may be described mathematically and included in the mathematical model. However, it was reasoned that a rigorous derivation was not justified at this time, in that the primary assumptions regarding the use of overall transfer coefficients had not yet been justified. In order to provide some method of correcting this discrepancy, if further studies verified its existence, a radial heat loss term was included in the mathematical model.

This heat flux was assumed to be a linear function of the gas temperature and the initial solid temperature. The heat source was assumed to be the solid since the heat capacity of the gas phase is small compared to the heat capacity of the solid. The revision to the mathematical model which results from this assumed heat flux is an additional term in the solid heat balance. The revised form of equation (II-68) is:

\[ D_4 = \frac{\partial T_s}{\partial \theta} = -\frac{D_1 \lambda}{C_s} (1+Y) \frac{C_p G}{C_s} D_3 - N_4 \left( T_G - T_{S0} \right) \]  

(IV-2)

where \( N_4 \) is a number to be determined by comparison with experimental data. The radial heat loss term (in units consistent with the energy balance of Chapter II) may be written as:

\[ q_R = U_{AR} \left( T_G - T_{S0} \right) = \frac{4U}{D} \left( T_G - T_{S0} \right) \]

from which it can be shown that:

\[ N_4 = \frac{4L}{D C_s} U \]  

(IV-3)
where:  
D - the column diameter,
L - the length of packed bed,
C_s - the specific heat of the solid phase,
U - Overall heat transfer coefficient for a steady state heat flux.

The theoretical answers available at this point also indicated that the solution technique would not be sufficient to calculate answers comparable with the experimental data. It was decided to improve the solution technique by using a technique similar to that of Gonzalez and Spencer.(3) This technique is developed from a powers series for the dependent variable, M, in the following paragraphs,

Let M(X) be an element of the range of a function of X and t at a particular value of t. Assume that this function can be defined by a polynomial in X as follows:

\[ M(X) = A_0 + A_1X + A_2X^2 + A_3X^3 + \ldots + A_nX^n. \]  \hspace{1cm} (IV-4)

The derivative of M(X) is:

\[ D(X) = \frac{\partial}{\partial X} [M(X)] = A_1 + 2A_2X + 3A_3X^2 + \ldots + nA_nX^{n-1}, \]  \hspace{1cm} (IV-5)

where \( X_1 = 0 \) implies:

\[ A_1 = D(X_1) \]
\[ A_2 = \frac{1}{2} \frac{\partial}{\partial X} [D(X_1)] \]
and \[ A_n = \left( \frac{1}{n!} \right) \frac{\partial^{n+1}}{\partial X^{n-1}} [D(X_1)] \]

It can also be seen that:

\[ M(X_1) = M(X_1 - \Delta X) + \int_{X_1 - \Delta X}^{X_1} D(X) \, dX. \]  \hspace{1cm} (IV-6)
The integration in (IV-6) may be performed by truncating fourth order and greater terms of equation (IV-4) and substituting for $D(X)$ from the resulting form of (IV-5):

$$D(X) = A_1 + 2A_2X + 3A_3X^2$$  \hspace{1cm} (IV-7)

The coefficients ($A_2$ and $A_3$) may be determined by substitutions obtained from subtracting and adding the forward and backward Taylor series expansions of $D(X_1)$. The expressions obtained for $A_2$ and $A_3$ are presented after truncation of third order and higher terms as:

$$A_2 = \frac{D(X_1 + \Delta X) - D(X_1 - \Delta X)}{4\Delta X}$$  \hspace{1cm} (IV-8)

$$A_3 = \frac{D(X_1 + \Delta X) - 2D(X_1) + D(X_1 - \Delta X)}{6(\Delta X)^2}$$  \hspace{1cm} (IV-9)

The results of the integration after substitution are:

$$\int_{X_1-\Delta X}^{X_1} D(X) dX = \int_{-\Delta X}^{0} D(X) dX$$

$$= \left[ \frac{5}{12} D(X_1-\Delta X) + \frac{2}{3} D(X_1) - \frac{1}{12} D(X_1-\Delta X) \right] (\Delta X)$$  \hspace{1cm} (IV-10)

and

$$M(X_1) = M(X_1-\Delta X) + \left[ \frac{5}{12} D(X_1 - \Delta X) + \frac{2}{3} D(X_1) - \frac{1}{12} D(X_1 - \Delta X) \right] (\Delta X).$$  \hspace{1cm} (IV-11)

The desired form of (IV-11) is obtained by performing a translation of the $X$ axis defined by:

$$X = \xi - \xi_0$$  \hspace{1cm} (IV-12)

and

$$M(X) = M(\xi).$$  \hspace{1cm} (IV-13)

Equation (IV-11) may be written in terms of $\xi$ at $X_1 = 0$ or by
equation (IV-12) at $\xi = 0$ as:

$$M(\xi_0) = M(\xi_0 - \Delta \xi) + \left[ \frac{5}{12} D(\xi_0 - \Delta \xi) + \frac{2}{3} D(\xi_0) - \frac{1}{12} D(\xi_0 + \Delta \xi) \right] (\Delta \xi).$$

(IV-14).

Equation (IV-14) may be written using subscript notation, by defining

$$I = \frac{\xi_0}{\Delta \xi},$$

as follows:

$$M_I = M_{I-1} + \left[ \frac{5}{12} D_{I-1} + \frac{2}{3} D_{I} - \frac{1}{12} D_{I+1} \right] (\Delta \xi) \quad (IV-15)$$

A first order correct expression may be developed by a similar derivation for the last bed position, $N_M$, in terms of the next to last position, $N$, by also truncating the third order term of equation (IV-4). This yields the following expression:

$$M_{NM} = M_N + \left[ D_N + D_{NM} \right] \frac{(\Delta \xi)}{2}. \quad (IV-16)$$

Equations (II-65 and II-67) are used to obtain $NM$ expressions for $Y$ and $T_G$. The first $N$ equations for the two variables are as follows:

$$A_{1I} Y_{I-1} + B_{1I} Y_I + C_{1I} Y_{I+1} = D_{1I} \quad (IV-17)$$

and

$$A_{2I} T_{G_{I-1}} + B_{2I} T_{G_I} + C_{2I} T_{G_{I+1}} = D_{2I} \quad (IV-18)$$

where

$$A_{1I} = \frac{1}{(N_1)(\Delta \xi)} - \frac{5}{12} \left( 1 - y_{E_{I-1}} \right)$$

$$B_{1I} = - \frac{1}{(N_1)(\Delta \xi)} - \frac{2}{3} \left( 1 - y_{E_I} \right)$$

$$C_{1I} = \frac{1}{12} \left( 1 - y_{E_{I+1}} \right)$$

$$D_{1I} = - \frac{5}{12} y_{E_{I+1}} - \frac{2}{3} y_{E_I} + \frac{1}{12} y_{E_{I+1}}$$

$$A_{2I} = \frac{1}{(N_2)(\Delta \xi)} - \frac{5}{12}$$
\[ B_{2I} = -\frac{1}{(N_2)(\Delta \xi)} - \frac{2}{3} \]

\[ C_{2I} = \frac{1}{12} \]

\[ D_{2I} = \frac{5}{12} T_{s_{I-1}} - \frac{2}{3} T_{s_I} + \frac{1}{12} T_{s_{I+1}} \]

and
\[ y_{E_K} = \frac{y_{E_N}}{1 + y_{E_N}} \]

The last equations may be expressed by specifying the coefficients of equations \( \text{(IV-17)} \) and \( \text{(IV-18)} \) for \( I = NM; \)

\[ A_{1NM} = \frac{2}{(N_1)(\Delta \xi)} - (1 - y_{E_N}) \]

\[ B_{1NM} = -\frac{2}{(N_1)(\Delta \xi)} - (1 - y_{E_{NM}}) \]

\[ C_{1NM} = 0 \]

\[ D_{1NM} = -y_{E_N} - y_{E_{NM}} \]

\[ A_{2NM} = \frac{2}{(N_2)(\Delta \xi)} - 1 \]

\[ B_{2NM} = -\frac{2}{(N_2)(\Delta \xi)} - 1 \]

\[ C_{2NM} = 0 \]

\[ D_{2NM} = -T_{S_N} - T_{S_{NM}} \]

The changes were incorporated in two steps. The first step consisted of the incorporation of the heat loss term. Several calculations were made with this program \((6/23/64)\) in order to compare the two solution techniques. The revision in the method of calculating the
spatial derivatives was added to the program (6/26/64) and several runs were made for comparison. Figure 30 graphically displays the difference in the two solution techniques for adiabatic conditions. The data input for both runs was the same. The actual values used for \( N_1 \) and \( N_2 \) respectively were 200 and 600. Values are presented at position 4 only for this comparison.

The obvious improvement in the solution obtained from the revised solution technique certainly justifies the revision. The approximate computer time requirements increased from 0.05 to 0.067 minutes of 7040 time per minute of real time which is not prohibitive. These arguments were considered sufficient to justify using the revised solution technique for the remainder of the theoretical study.

The next phase of the theoretical study was to determine the effect of the various parameters on the system and to attempt to determine the values for which the theoretical solution approximated the experimental data. The order in which the parameters was tested was:

(a) \( N_4 \) - the heat loss parameter
(b) \( N_1 \) - the mass transfer parameter
(c) Equilibrium data.

The heat transfer parameter was not studied individually since the effect had already been determined to be insignificant compared to the mass transfer parameter. For the remainder of the runs the heat transfer parameter was arbitrarily set equal to the mass transfer parameter except for the heat transfer studies where it was arbitrarily set at three times the mass transfer parameter. Proof of this assumption will be presented after the solution technique is verified,
FIGURE 30. COMPARISON OF THE RESULTS OF THE SECOND AND THE THIRD ORDER CORRECT SOLUTION TECHNIQUES

- Second Order
- Third Order

Adsorbate Concentration in Gas (Y)

Position

Time (MIN)
Five runs were made with $N_4$ as a variable for boundary conditions approximately the same as those determined from experimental run 2-1. The equilibrium parameters used were those tabulated in Table I. The remainder of the input data is listed below:

$$Y_0 = 0.1380$$

$$T_{G_0} = 77^\circ F$$

$$Y_{O_E} = 0.0053$$

$$T_{S_0} = 77^\circ F$$

$$N_1 = 200$$

$$N_2 = 600$$

$$N_3 = 1000 \text{ MIN}$$

$$\Delta \xi = 0.015625$$

$$\Delta \theta = 0.0005$$

The values of $N_4$ used were 0.0, 2.0, 4.0, 6.0 and 8.0. The effects of this parameter on the gas phase concentration profile are presented by Figure 31 and on the gas phase temperature by Figure 32.

The effect of the rate of heat transferred through the column wall may be summarized as follows:

a) The slope of the temperature wave prior to reaching the maximum temperature, decreases with an increase in the rate of heat transfer.

b) The maximum temperature decreases with an increase in the rate of heat transfer.

c) The slope of the temperature wave beyond the maximum temperature decreases with an increase in the rate of heat transfer.
FIGURE 31. THE EFFECT OF THE HEAT LOSS PARAMETER (N₄) ON THE THEORETICAL GAS PHASE CONCENTRATION WAVE AT A POINT

○ N₄ = 0.0
△ N₄ = 4.0
□ N₄ = 8.0

POSITION 4

TIME (MIN)
FIGURE 32. THE EFFECT OF THE HEAT LOSS PARAMETER ($N_4$) ON THE THEORETICAL GAS PHASE TEMPERATURE WAVE AT A POINT

- $N_4 = 0.0$
- $N_4 = 4.0$
- $N_4 = 8.0$

Position 4
The effect of the rate of heat transfer on the slope of the concentration wave may be summarized by noting that the slope prior to the inflection point decreases as the rate of heat transfer increases and that the maximum concentration is approached at a slower rate beyond that point. It may also be noticed that the time required for the concentration wave to reach a particular position in the bed increases with an increase in the rate of heat transfer. This may be explained by noting that the capacity of the adsorbent increases with decreasing temperature. This increase in adsorbent capacity qualitatively explains the lag in the concentration wave.

The effect of the mass transfer parameter, \( N_1 \), was studied next. The values of \( N_1 \) used were for a range of 175 to 25 in order to magnify the effect for graphical presentation. The series of runs were made at adiabatic conditions and for the same boundary conditions as the previous series of runs. The concentration results obtained at position five for three of the runs are displayed in Figure 33.

This initial study was followed by a comparison of experimental and theoretical data in order to determine how well the revised mathematical model could simulate the experimental results. The experimental run which was used in this study was Run 2-5. It was chosen on the basis of its apparent consistency and because the initial bed concentrations and temperatures were fairly constant. The present solution technique assumes that the initial values are constant.

Several runs were made using the equilibrium data presented in Chapter II and program 6/26/64. The values of the boundary conditions and other data for this series of runs are listed below.
FIGURE 33. THE EFFECT OF THE MASS TRANSFER PARAMETER ($N_1$) ON THE THEORETICAL GAS PHASE CONCENTRATION WAVES AT A POINT.

- $N_1 = 150$
- $N_1 = 100$
- $N_1 = 50$
The runs were made primarily to determine the values of the mass transfer parameter and the heat loss parameter which best simulated the experimental results. Figures 34 and 35 are the results of this series of runs which seemed to compare the best of those studied. The values obtained for the mass transfer parameter ($N_1$) and heat loss parameter ($N_4$) were 250 and 6.0 respectively.

The deviation between the two sets of data (experimental and theoretical) presents a subject for considerable discussion. The deviation that is most noticeable is the difference in the time for the wave to pass the two points plotted. The only deviation in the initial conditions of any significance between the experimental run and theoretical calculation is in the initial bed temperature.

The experimental initial temperature of the bed at position 4 was 1°F greater than the average used for the theoretical calculation while at position 6, they were equal. This temperature difference would predict that the solid concentration (at position 4) would be lower at initial equilibrium conditions for the experimental run than for the theoretical run. This lower concentration initially would yield a higher capacity, other conditions being constant, which would result in the experimental wave passing after the theoretical wave. This minor difference in initial temperatures does not explain the

\[
\begin{align*}
Y_0 & = 0.1440 \\
T_{G0} & = 80.0°F \\
Y_{OE} & = 0.0220 \\
T_{SO} & = 79.0°F \\
N_3 & = 1058 \text{ min} \\
\Delta \xi & = 0.015625 \\
\Delta \theta & = 0.0005
\end{align*}
\]
FIGURE 34. COMPARISON OF EXPERIMENTAL AND THEORETICAL GAS PHASE CONCENTRATIONS

- Adsorbate Concentration in Gas (Y)
- Time (MIN)

○ Experimental (Run 2-5)
△ Theoretical

Positions:
- Position 4
- Position 6
FIGURE 35. COMPARISON OF EXPERIMENTAL AND THEORETICAL GAS TEMPERATURES

○ Experimental (Run 2-5)
△ Theoretical
difference in the time of the wave front passage as displayed in Figures 34 and 35.

Another explanation might be based on the temperature deviation displayed in Figure 35. This can be proven to be incorrect. The higher theoretical temperatures decrease the capacity of the adsorbent which causes the fronts to pass a specific point earlier than for lower temperatures. For this reason it can be seen that an increase in the rate of heat loss from the system would magnify the observed difference in the wave velocities.

An increase in the rate of heat loss will also cause another deviation to occur and a further increase in the magnitude of two deviations that may be seen in the solution displayed. The additional deviation that would occur would be a decrease in the maximum temperatures calculated. Increasing the heat loss term to a value sufficient to approximate the temperature observed experimentally after the maximum temperature occurs would result in the maximum temperature for the theoretical case being lower than the experimental maximum.

The deviations that would be increased in magnitude are those which can be seen by comparing the experimental and theoretical concentration curves. It can be seen that the slope of the predicted concentration curves is less than that of the experimental curves and that the theoretical curves approach a lower maximum at a slower rate than the experimental curves. An increase in the heat loss term would magnify these deviations as determined by the study of the heat loss parameter (see Figure 30).

All of the deviations observed might be explained by an error
in the equilibrium data. Figures 31 and 33 indicate that an increase in the mass transfer parameter or a decrease in the heat loss parameter both result in an increase in the slope of the concentration wave but do not change the maximum concentration obtained or the capacity of the adsorbent. A change in the equilibrium data can be shown to produce a change in the adsorbent capacity and additional case studies were used to demonstrate the desired increase in maximum gas phase concentration obtained. The first change can be seen by observing the effect of a change in the term $d$ of the expression:

$$f_0 = cw^d.$$  

The results are presented in Table V, for the following specified data.

<table>
<thead>
<tr>
<th>$T_s$</th>
<th>79°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>$Y_0$</td>
<td>0.144</td>
</tr>
<tr>
<td>$Y_{OE}$</td>
<td>0.022</td>
</tr>
</tbody>
</table>

It can be seen that decreasing the exponent ($d$) results in two changes both of which are apparently desirable. The term, $w_{OE} - w_0$, can be used to indicate the adsorbent capacity even though it is calculated for an isothermal condition. The decrease in capacity which results from a decrease in the exponent ($d$) will accelerate the concentration wave velocity. The corresponding increase in $m$ will increase the heat of adsorption and permit an increase in the heat loss term while still maintaining the same maximum temperatures.

One final deviation was considered significant enough to merit discussion. The deviation may be discerned by close examination of time derivative of the temperature in the region past the maximum
<table>
<thead>
<tr>
<th>$d$</th>
<th>$w_0$</th>
<th>$w_{OE}$</th>
<th>$w_{OE} - w_0$</th>
<th>$\bar{m}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-.54</td>
<td>.0108</td>
<td>.0397</td>
<td>.0289</td>
<td>2.48</td>
</tr>
<tr>
<td>-.52</td>
<td>.0093</td>
<td>.0348</td>
<td>.0255</td>
<td>2.52</td>
</tr>
<tr>
<td>-.50</td>
<td>.0078</td>
<td>.0302</td>
<td>.0224</td>
<td>2.56</td>
</tr>
<tr>
<td>-.48</td>
<td>.0065</td>
<td>.0258</td>
<td>.0193</td>
<td>2.62</td>
</tr>
<tr>
<td>-.45</td>
<td>.0049</td>
<td>.0199</td>
<td>.0150</td>
<td>2.70</td>
</tr>
</tbody>
</table>

d - Exponent of $f_0 = cw^d$ (See Chapter II).

$w_0$ - Initial solid concentration.

$w_{OE}$ - Solid concentration in equilibrium with $Y_0$ at $T_{s0}$.

$\bar{m}$ - Arithmetic mean of $m$ and $m_f$.

$m$ - $m$ evaluated at $w_0$ and $T_{s0}$.

$m_f$ - $m$ evaluated at $w_{OE}$ and $T_{s0}$. 
temperature. It can be seen that the experimental temperature in this region displays some second order dependence while the theoretical temperature is almost exactly linear. A revision in the heat loss term which might yield this behavior would be the use of the square of the temperature difference in the heat loss expression. This revision was incorporated in program 6/29/64 for evaluation.

A series of additional theoretical calculations demonstrated that all of the desired effects postulated in the discussion of the previous series of runs were obtained with the exception of one. The effect of the change in the heat loss expression was not as significant as was desired to eliminate the deviation in the functional form of the experimental temperature curve.

During this series of runs, however, an additional property of the solution technique was determined. Attempts to use larger values of the mass transfer parameter \(N_1 = 300\) with the same increment sizes yielded unstable solutions. This led to an investigation of the effect of increment size. Previous investigations showed that decreasing the dimensionless time increment \(\Delta \theta\) by a factor of 5 (from 0.0005 to 0.0001) resulted in insignificant changes in the theoretical answers.

It was noted that the first signs of an unstable solution occurred immediately following the calculation of the first negative values of \(A_l\) as defined in equation (IV-17). The use of smaller spatial increment \(\Delta \xi = 0.0078125\) was attempted but the resulting answers duplicated those of the previous calculations. Previous studies also indicated that the ratio of increment sizes \(\Delta \theta/\Delta \xi\) was also a criterion for stability. An additional decrease in the dimensionless time
increment ($\Delta \theta = .00025$) resulted in eliminating the instability. The criteria for stability postulated above were tested at $N_1 = 600$ with the first indication of instability occurring exactly as predicted. These criteria for stability may be summarized by two inequalities which are sufficient for a stable solution.

$$\frac{1}{(N_1)(\Delta \xi)} > \frac{5}{12} (1-y_E) \quad \text{for all } \xi, \theta$$

and

$$\frac{\Delta \theta}{\Delta \xi} \leq 0.033.$$

The final form of the solution technique was obtained by the incorporation of numerical integration techniques to determine material and energy balances for the calculated results. For the purpose of these calculations, variations in the gas phase accumulation terms were assumed negligible. Two percentages were defined to specify the balances.

$$PC_{MB} = \frac{O_{MB} + A_{SMB}}{I_{MB}} \times 100 \quad (IV-19)$$

$$PC_{HB} = \frac{O_{HB} + A_{SHB}}{I_{HB}} \times 100 \quad (IV-20)$$

where

- $O$ - output from the column ($0 \leq \theta \leq \theta_o$)
- $I$ - input to the column ($0 \leq \theta \leq \theta_o$)
- $A_s$ - accumulation in the solid phase ($0 \leq \xi \leq 1$.)

The values of the terms listed above were obtained by integration using the numerical technique referred to as the "trapezoidal rule."

The results of the various revisions are displayed in Figures
36 and 37. The values used for this series of runs were the same as for the previous series with the exception of those listed below:

\[
N_1 = 300 \\
N_4 = 0.8
\]

The effects postulated by the change in equilibrium data may be checked by comparison of the results shown in Figures 36 and 37 for \( d = -0.52 \) and \(-0.50\). It can be seen that the wave velocity has been increased until the predicted wave passes position 6 prior to the time of the experimental passage. The differences between the experimental and theoretical concentration values in the higher concentration region still exists.

The final study was made to check the effect of lower rates of heat loss. The value \((d = -0.52)\) was chosen for these calculations since a decrease in the rate of heat loss will decrease the wave velocity and therefore yield answers that most closely approximate the experimental results. The remaining variables were specified to be the same as for the previous run. Figures 38 and 39 display the results at position 5 for various values of the rate of heat loss \((N_4 = 0.4, 0.2, 0.05)\).

The results of these calculations indicate a distinct discrepancy between experimental and theoretical values. Figure 38 indicates that, at some value of \(N_4\) between 0.2 and 0.05, the theoretical solution should very closely approximate the experimental concentration values. However, in this range a large discrepancy is noted in the theoretical and experimental temperature values. Increasing the rate of heat transfer through the boundaries causes large deviations.
FIGURE 36. COMPARISON OF EXPERIMENTAL AND THEORETICAL GAS PHASE CONCENTRATIONS AFTER SMALL EQUILIBRIUM VARIATIONS

- Adsorbate concentration in gas (Y)

- Time (min)

- Experimental (Run 2-5)

- Theoretical
  - \( d = -0.52 \)
  - \( d = -0.50 \)
FIGURE 37. COMPARISON OF EXPERIMENTAL AND THEORETICAL GAS TEMPERATURES AFTER SMALL EQUILIBRIUM VARIATIONS

- Experimental (Run 2-5)
- Theoretical
  - △ d = -0.52
  - □ d = -0.50

Gas Temperature (°F)

Time (MIN)
FIGURE 38. COMPARISON OF EXPERIMENTAL AND THEORETICAL GAS PHASE CONCENTRATIONS FOR VARYING RATES OF HEAT LOSS (REVISED)

- **Experimental (Run 2-5)**
- **Theoretical**
  - $N_4 = 0.4$
  - $N_4 = 0.2$
  - $N_4 = 0.05$

Axes:
- **Y-axis**: Adsorbate concentration in gas (Y)
- **X-axis**: Time (MIN)
FIGURE 39. COMPARISON OF EXPERIMENTAL AND THEORETICAL GAS TEMPERATURES FOR VARYING RATES OF HEAT LOSS (REVISED)

Legend:
- ○ Experimental (Run 2-5)
- △ Theoretical
  - $N_q = 0.4$
  - $N_q = 0.2$
  - $N_q = 0.05$

Note:
- Position 4
- Position 6
in the concentration values and does not correct the temperature plots. This can be proved by observing that the theoretical temperatures do not agree with either the maximum experimental temperature or with the temperatures following the maximum temperature for all values of the parameter $N^*$. 

A localized area of high heat transfer in the vicinity of the sample port is the obvious explanation for the discrepancies noted. The three brass sample ports at each sampling level present a heat transfer path from the bed, through the insulation to the surroundings. This could cause the observed temperatures to be lower in the vicinity of the sampling position than in the positions between.

An additional source of temperature differences may be a result of inconsistent equilibrium data. The heat of adsorption is calculated directly from information taken from an isotere plot without experimental verification. In addition, the extrapolation of enthalpy and fugacity data beyond the pure component critical point is also subject to question.

Additional explanations possible for the experimental and theoretical temperature difference are experimental heat losses which might result from conduction of heat from the thermocouple bead through the lead wires and longitudinal heat transfer by conduction through the adsorbent. Errors resulting from the first possibility might be eliminated by improving the thermocouples probes. The latter possibility might explain the initial $0.4 - 0.6^\circ F$ temperature rise prior to the passage of the main adsorption wave. This may be observed in Figure 39 at position 6 during the time interval from 36 to 47 minutes.
If one assumes that the experimental temperatures are in error, then Figure 38 indicates that the solution technique simulates the experimental concentration profiles very well for a particular set of parameter values. The theoretical solutions presented show the effect of the rate of radial heat loss on the system. It can be seen that at low values of this parameter ($N_4$), the maximum concentrations obtained agree very well with the experimental data. The slope of the wave appears to be too steep at these low values but this could be corrected by decreasing the mass transfer parameter ($N_1$) as demonstrated in Figure 33.

Earlier evidence indicated that the heat transfer parameter ($N_2$) had little effect on the actual dynamics of the system under consideration. This may be attributed to the low heat capacity of the gas as compared to that of the solid. Theoretical justification of this fact is presented in Table VI for three values of $N_2$. The actual difference between the gas phase concentrations at the same time for the three values was a maximum of 0.0007. The equilibrium solid concentration is presented to show the combined effect on solid temperature and solid concentration.

The material balances obtained for the final series of runs may be used to judge the accuracy of the solution technique. The initial material balances may be expected to be considerably in error due to the inaccuracy of the integration method for very few increments. However, after the initial period the results were very good. A typical material balance after 10 minutes of simulated time was 100.251%, which decreased steadily to 100.00013% after 60 minutes and to 99.99989%
TABLE VI

THE EFFECT OF VARIOUS VALUES OF THE HEAT TRANSFER PARAMETER (\(N_2\)) ON GAS PHASE CONCENTRATION AND EQUILIBRIUM SOLID CONCENTRATION

<table>
<thead>
<tr>
<th>Time</th>
<th>(N_2 = 300)</th>
<th>(N_2 = 600)</th>
<th>(N_2 = 1200)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(Y)</td>
<td>(Y_E)</td>
<td>(Y)</td>
</tr>
<tr>
<td>10</td>
<td>.0222</td>
<td>.0222</td>
<td>.0222</td>
</tr>
<tr>
<td>11</td>
<td>.0223</td>
<td>.0222</td>
<td>.0223</td>
</tr>
<tr>
<td>12</td>
<td>.0225</td>
<td>.0223</td>
<td>.0223</td>
</tr>
<tr>
<td>13</td>
<td>.0230</td>
<td>.0226</td>
<td>.0230</td>
</tr>
<tr>
<td>14</td>
<td>.0244</td>
<td>.0235</td>
<td>.0243</td>
</tr>
<tr>
<td>15</td>
<td>.0277</td>
<td>.0254</td>
<td>.0275</td>
</tr>
<tr>
<td>16</td>
<td>.0344</td>
<td>.0299</td>
<td>.0343</td>
</tr>
<tr>
<td>17</td>
<td>.0465</td>
<td>.0389</td>
<td>.0465</td>
</tr>
<tr>
<td>18</td>
<td>.0642</td>
<td>.0540</td>
<td>.0644</td>
</tr>
<tr>
<td>19</td>
<td>.0845</td>
<td>.0740</td>
<td>.0849</td>
</tr>
<tr>
<td>20</td>
<td>.1026</td>
<td>.0942</td>
<td>.1031</td>
</tr>
<tr>
<td>21</td>
<td>.1156</td>
<td>.1100</td>
<td>.1160</td>
</tr>
<tr>
<td>22</td>
<td>.1233</td>
<td>.1200</td>
<td>.1235</td>
</tr>
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<td>23</td>
<td>.1274</td>
<td>.1256</td>
<td>.1274</td>
</tr>
<tr>
<td>24</td>
<td>.1293</td>
<td>.1283</td>
<td>.1292</td>
</tr>
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<td>25</td>
<td>.1303</td>
<td>.1297</td>
<td>.1301</td>
</tr>
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<td>26</td>
<td>.1307</td>
<td>.1303</td>
<td>.1305</td>
</tr>
<tr>
<td>27</td>
<td>.1310</td>
<td>.1307</td>
<td>.1308</td>
</tr>
<tr>
<td>28</td>
<td>.1312</td>
<td>.1309</td>
<td>.1310</td>
</tr>
<tr>
<td>29</td>
<td>.1314</td>
<td>.1311</td>
<td>.1312</td>
</tr>
<tr>
<td>30</td>
<td>.1316</td>
<td>.1313</td>
<td>.1313</td>
</tr>
</tbody>
</table>

\(N_1 = 300\)
\(N_3 = 1058\)
\(N_4 = 0.2\)
Position 4
after 100 minutes. The results of the energy balance were not as good as those above. The assumption of a negligible accumulation of enthalpy in the gas phase is probably the source of the deviation from 100% for the adiabatic case.

Estimates of the heat loss as a percent of the total entering enthalpy may be made using the actual values of the heat balance computed. The heat loss term was not included in the energy balance for this purpose. Approximate values of the percentage heat loss may be obtained by subtracting the calculated heat balance from 100%. Figure 40 displays the calculated heat balance for several rates of heat loss. It appears that a heat loss of 10% after 80 minutes might best simulate the experimental conditions.

An additional subject for discussion may be discerned by noting the effect of a small change in the heat loss parameter \( N_4 \). The resulting 2-3°F temperature difference between theoretical calculations has a significant effect on the adsorption wave downstream from the point of the temperature difference. This can be seen by noting the difference between the calculated temperatures (Figure 39) at position 4 for \( N_4 \) equal to 0.4 and to 0.2. A significant difference may be observed in the calculated concentrations (Figure 38) at position 6 as a result of this difference. On the basis of these unverified theoretical temperature results one might conclude that the dynamic behavior, of systems of this type, is very sensitive to small temperature variations.

It may be recalled that a large portion of this discussion was concerned with differences between experimental and calculated
FIGURE 40. ENERGY BALANCES FOR SEVERAL VALUES OF THE HEAT LOSS PARAMETER (REVISED)
temperatures. It may also be recalled that the differences were of an order of magnitude of 4-6°F and in several cases even less. However, these relatively small temperature differences were shown to make a significant effect on the shape of the adsorption wave. It may be also noted that for the cases studied the time for the concentration wave to reach a particular point did not vary greatly as a result of the temperature differences.

In conclusion, one might observe that the values of the mass transfer parameter used for the theoretical calculations are of the same order of magnitude as determined from the data of Wilke and Hougen. Sufficient information concerning the effects of the various parameters has been presented to permit further improvements in the theoretical simulation of the experimental system if desired.
CHAPTER V

CONCLUSIONS AND RECOMMENDATIONS

The following conclusions and recommendations are offered based on the experimental and theoretical results presented in the previous chapter.

(a) One of the purposes of the experimental investigation has been accomplished. A fixed bed adsorption system has been fabricated which enabled a study of adsorption as a method of separating gases under non-isothermal conditions. The effects of the flow rate and the initial and inlet concentrations on the dynamic behavior of the system were found to be the same (qualitatively) as one would predict for an isothermal system.

(b) A mathematical model of considerable rigor was developed for adiabatic operation. An iterative solution technique (patterned after the more recent techniques of Gonzales and Spencer) is presented and is shown to solve the mathematical model very precisely. The material balance values of 100% and the essentially constant heat balance value of 99% justify this conclusion.

(c) Deviations between the experimental system and the mathematical model preclude making any conclusions as to the accuracy of the solution technique. These deviations are listed below.

(1) The estimated average rate of heat loss through the walls is 10-20% of the total entering enthalpy after 80 minutes of operation.
(2) An estimated rate of heat loss in the vicinity of the sample ports appears to be two to three times the rate above.

An attempt to correct for the first deviation was incorporated by the assumption of a non-rigorous rate equation. No attempt to correct for the second deviation was made, but on the basis of the concentration data presented, it appears that the correction for the first deviation is sufficient to simulate the experimental concentration values obtained. Considerable deviations between experimental and calculated temperatures were observed for all rates of heat loss attempted which may be attributed to (2) above.

(d) Two criteria for a stable solution were postulated and checked. They may be expressed as two inequalities and are presented below.

\[ \frac{1}{(N_1)(\Delta S)} > \frac{5}{12} (1 - y_E) \]

(2) \[ \frac{\Delta \theta}{\Delta S} \leq 0.033 \]

(e) The calculated results obtained from the solution technique for the mathematical model presented certainly justify further studies in this area. The evidence presented herein indicates that further studies with improved experimental apparatus might prove the applicability of this model in simulating non-isothermal fixed bed adsorption systems for a wide range of concentrations and forms of equilibrium relations.

(f) The following recommendations are offered to extend this study.

(1) Improvements on the experimental apparatus to eliminate the heat loss in the vicinity of the sample ports.
(2) Improvements on the experimental apparatus or in the form of the heat loss function to lend more rigor in this area.

(3) A study of the thermodynamic equilibrium theory as applied to gas-solid systems to develop and justify satisfactory forms for the relations involved and to test for consistency of the results predicted.
SELECTED BIBLIOGRAPHY


APPENDIX A

NOMENCLATURE AND SYMBOLS

a - specific surface of the solid, ft$^2$ of transfer area per ft$^3$ of bed volume.

$a_m$ - a constant in the correlation of experimental data for the slope of the equilibrium isotherms, $m = a_m y + b$.

B - a constant in the expression for determining the latent heat of vaporization as a function of temperature, $\lambda_s = A + BT$.

C - heat capacity of the adsorbent, BTU/(lb)(°F).

$C_A$ - heat capacity of the adsorbed adsorbate, BTU/(lb)(°F).

$C_{PA}$ - heat capacity at constant pressure of the adsorbate in the gas phase, BTU/(lb)(°F).

$C_{PB}$ - heat capacity at constant pressure of the carrier gas in the gas phase, BTU/(lb)(°F).

$C_{PG}$ - heat capacity at constant pressure of the gas phase mixture, BTU/(lb)(°F).

$C_s$ - corrected heat capacity of the solid phase mixture, BTU/(lb)(°F).

D - inside diameter of the column, ft.

$D_1$, $D_2$, $D_3$, $D_4$ - partial derivatives as defined by equations (II-65, 66, 67, 68).

exp(b) - functional notation for $e^b$.

f - fugacity, PSIA.

$f_o$ - intercept of the equilibrium isotherms as defined by equation (II-37).

$f_s$ - fugacity of the pure component, saturated liquid, PSIA.

$F_e$ - fractional void space of the bed excluding the internal voids of the solid.

G - mass velocity of the gas mixture through the bed per unit of empty, column, cross-sectional area, lbs/(hr)(ft$^2$).
\( \bar{G} \) - geometric mean of the initial mass velocity \((Y = Y_0)\) and the mass velocity of \(Y\) a maximum, lbs/(hr)(ft\(^2\)).

\( \bar{C}_s \) - mass velocity of the pure component carrier gas, lbs/(hr)(ft\(^2\)).

\( h \) - gas phase heat transfer coefficient, BTU/(Hr)(ft\(^2\))(\(\circ\)F).

\( H \) - enthalpy above specified reference conditions, BTU/lb.

\( H_A \) - enthalpy of the pure component adsorbate, BTU/lb adsorbate.

\( H_G \) - enthalpy of the gas mixture, BTU/lb gas.

\( H_s \) - enthalpy of the solid phase, BTU/lb adsorbent.

\( H_{AD} \) - heat of adsorption or the enthalpy difference associated with the phase change of the adsorbate for the particular values of \(T_s\) and \(w\) and \(T_C = T_s\), BTU/lb adsorbate.

\( H_{AD}^0 \) - heat of adsorption at the reference conditions specified.

\( H_{HG}, H_{DG} \) - height of a gas phase heat and mass transfer unit, respectively, as defined by equations (II-19) and (II-24), ft.

\( K_y \) - overall gas mass-transfer coefficient for equimolal counter diffusion using mole fraction concentration units, lb-moles/(hr)(ft\(^2\)).

\( K'y \) - overall gas mass-transfer coefficient for unicomponent diffusion using mole fraction concentration units, lb moles/(hr)(ft\(^2\)).

\( K'_Y \) - overall gas mass-transfer coefficient for unicomponent diffusion using mole ratio concentration units, lb moles/(hr)(ft\(^2\)).

\( L \) - length of packed bed, ft.

\( \ln \) - natural logarithm

\( m \) - slope of the equilibrium isoteres.

\( M_A, M_B, M_G \) - molecular weight of the adsorbate, carrier-gas and the gas mixture.

\( N \) - mass flux of the adsorbate from the gas phase to the adsorbent, lbs/(hr)(ft\(^2\)).

\( N_1 \) - number of gas phase mass transfer units in the system as defined by equation (II-63).

\( N_2 \) - number of gas phase heat transfer units in the system as defined by equation (II-64).
- conversion factor to obtain time (t) from the dimensionless time (θ) as defined by equation (II-47), min.

- radial heat transfer parameter.

- total pressure, PSIA.

- vapor pressure, PSIA.

- heat flux from the solid phase to the gas phase, BTU/(hr)(ft²).

- transformed gas phase concentration, \((Y - Y_{OE})/(Y_{00} - Y_{OE})\).

- transformed gas phase concentration at the bed inlet.

- transformed solid phase concentration, \((w - w_0)/(w_{OE} - w_0)\).

- elapsed time, min.

- temperature, °F.

- gas phase temperature, °F.

- gas phase temperature at \(t = 0\) for \(0 < z \leq L\), °F.

- gas phase temperature at \(z = 0\) for \(t > 0\), °F.

- reference temperature, °F.

- solid phase temperature, °F.

- solid phase temperature at \(t = 0\) for \(0 \leq z \leq L\), °F.

- transformed gas phase temperature, \((T_G - T_0)/(T_0 - T_R)\).

- transformed solid phase temperature, \((T_S - T_{SO})/(T_{SO} - T_R)\).

- solid phase concentration, mass ratio.

- solid phase concentration at \(t = 0\) for \(0 \leq z \leq L\), mass ratio.

- solid phase concentration that would be in equilibrium with the inlet gas phase concentration \((Y_{OE})\) at \(T_0\), mass ratio.

- liquid phase concentration for vapor-liquid equilibrium, mole fraction.

- solid phase concentration for gas-solid equilibrium, mole fraction.

- gas phase concentration for vapor-liquid and gas-solid equilibrium respectively, mole fraction.
\( y \) - gas phase concentration, mass fraction.

\( y_{BM} \) - log mean of the carrier gas concentrations on each side of the gas "film," mole fraction.

\( y_E \) - gas phase concentration in equilibrium with solid phase concentration \( w \) at \( T_s \), mole fraction.

\( Y \) - gas phase concentration, mass ratio.

\( Y_E \) - gas phase concentration in equilibrium with solid phase concentration \( w \) at \( T_s \), mass ratio.

\( Y_0 \) - gas phase concentration at the bed inlet, mass ratio.

\( Y_{OE} \) - gas phase concentration in equilibrium with the solid phase concentration \( w_0 \) at \( T_{SO} \), mass ratio.

\( Y_{00} \) - steady state gas phase concentration at the bed inlet, mass ratio.

\( z \) - length of packed bed measured from the inlet end, ft.

\( \gamma \) - activity coefficient.

\( \theta \) - transformed time, \( \theta = (G_s/\rho_p L)t \), dimensionless.

\( \lambda_s \) - modified latent heat of vaporization (enthalpy of the liquid relative to the ideal gas), BTU/lb.

\( \mu_l \) - micro-liter.

\( \nu \) - fugacity coefficient.

\( \xi \) - transformed length, \( \xi = z/L \), dimensionless.

\( \rho_B \) - bulk density of the adsorbent, lbs adsorbent/ft\(^3\) of column volume.

\( \rho_G \) - gas phase density, lbs gas/ft\(^3\) gas.
A FORTRAN IV PROGRAM FOR CONCENTRATION DATA PROCESSING

1. LIST OF PROGRAM STATEMENTS

   DIMENSION HEAD1 (12)
9   PAUSE
   READ 100, HEAD1
   PUNCH 101, HEAD1
   PUNCH 105
1   READ 102, YO, YOS, V, A, B, C, D
2   READ 103, TIME, IPOS, XNP, XEP, KAN, KAE
   IF (IPOS) 10, 10, 7
7   IF (KAN) 2, 3, 4
4   AN = KAN
3   IF (KAE) 2, 5, 6
6   AE = KAE
5   XEPC = XEP * AE
   XNPC = XNP * AN
   Y = XEPC / (XEPC + XNPC)
   Y = A + Y * (B + Y * (C + Y * D))
   Y = Y / (1. - Y)
   A1 = (Y - YOS) / (YO - YOS)
   IZ = IPOS - 3
   IF (IZ) 15, 16, 16
15  IZ = 0
16  Z = IZ
   XI (I) = Z * 8. / 64.
   TH = V * TIME
   PUNCH 104, TIME, IPOS, Y, TH, XI, A1
   GOTO 2
10   PUNCH 106
   GOTO 9
100  FORMAT (12A6)
101  FORMAT (12A6), //
102  FORMAT (7F10.6)
103  FORMAT (F10.1, I5, 2F10.1, 215)
104  FORMAT (F10.1, I6, 4F9.4)
105  FORMAT (6X, 4HTIME, 3X, 3HP0S, 6X, 1HY, 16X, 5HTHETA, 6X, 2HXI, 7X, 1HR)
106  FORMAT (10X, 10HEND OF RUN, /1H1)
END
2. DEFINITION OF INPUT AND OUTPUT VARIABLES USED IN PROGRAM STATEMENTS

HEAD1 - Alphameric problem identification data card.
YO - Yool.
YOS - Yoe1.
V - ratio of \( \Theta/t^1 \).
A, B, C, D - constants in the equation for expressing the gas phase concentration (weight %) as a function of the ethane peak height (expressed as a per-cent of the sum of the peak heights corrected to an attenuation of one).
TIME - t^1.
IPOS - position in the bed where the sample was obtained. The position in inches may be obtained by multiplying the difference of IPOS and 3 by a factor 8.
XNP - observed nitrogen peak height as a per cent of total scale read from the chromatograph chart paper.
XEP - observed ethane peak height as above.
KAN - attenuation used for the nitrogen peak.
KAE - attenuation used for the ethane peak.
Y - Y1.
TH - \( \Theta^1 \).
XI - \( \xi^1 \).
A1 - \( R^1 \).

3. SAMPLE INPUT DATA

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4. ANSWERS FOR SAMPLE INPUT DATA

RUN NO 2-5

\(^1\)As defined in Appendix A.
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APPENDIX C

A FORTRAN IV PROGRAM FOR TEMPERATURE DATA PROCESSING

1. LIST OF PROGRAM STATEMENTS

DIMENSION T(12), TO(12), TW(12), U(12), XI(12), 
HEAD1(12)

1 DO10 I=3,11
J=I-3
10 XI(I)=Z*8./64.
READ101, HEAD1
PUNCH 109, HEAD1
PUNCH 104,
PUNCH 110, HEAD1
PUNCH 106, (XI(I), I=3,11)
PUNCH 105
READ108, TR, V

2 K=1
READ100, TIME, (T(I), I=1,12)
IF(ABS(TIME)-.01)8,8,9
9 IF (TIME) 1, 1, 21
8 K=2
20 IF(T(12)-.01)20,20,3
20 T(12)=TS
3 DO4 I=3,11
IF(T(I)-.01)6,6,5
5 TW(I)=T(I)-T(12)+TR
GOTO(11,12), K
12 TO(I)=TW(I)
11 U(I)=(TW(I)-TO(I))/(TO(I)-TR)
GOTO4
6 TW(I)=0.
U(I)=0.
4 CONTINUE
PUNCH 102, TIME, (TW(I), I=3,11)
TH=V*TIME
PUNCH 103, TIME, TH, (U(I), I=3,11)
TS=T(12)
GOTO2

100 FORMAT (13F5.1)
101 FORMAT (12A6)
102 FORMAT (1X,F5.1, 9F6.1,19X,1H1)
103 FORMAT (1X,F5.1,F6.4,9F6.3,13X,1H2)
104 FORMAT (5H TIME,4X,1H3,5X,1H4,5X,1H5,5X,1H6,5X,1H7, 
15X,1H8,5X,1H9,4X,2H10,4X,2H11,21X,1H1)
105 FORMAT (11H TIME THETA,4X,1H3,5X,1H4,5X,1H5,5X,1H6,5X,1H7, 
11H7,5X,1H8,5X,1H9,4X,2H10,4X,2H11,15X1H2)
106 FORMAT (6H XI = ,9F6.3,19X,1H2)
108 FORMAT (2F10,4)
109 FORMAT (12A6,7X,1H1)
110 FORMAT (12A6,7X,1H2)
END
2. DEFINITIONS OF INPUT AND OUTPUT VARIABLES USED IN PROGRAM STATEMENTS

HEAD1 - alphanumeric problem identification data card
TR - $T_R^1$.
V - ratio of $\Theta$/t$^1$.
TIME - t$^1$
T(I) - observed gas phase temperature at position I,°F.
I Position
1,2 positions monitored prior to the bed inlet.
3-11 positions in the bed as previously defined.
12 position in an ice bath used to correct for recorder drift.
TW(I) - observed gas phase temperature at position I corrected for recorder drift,°F.
TH - $\Theta^1$.
U - u$^1$.

3. SAMPLE INPUT DATA
HEAD1 - Run No 2-5
TR - 32.0
V - 0.000946

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4. ANSWERS FOR SAMPLE INPUT DATA

RUN NO 2-5

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1As defined in Appendix A.
APPENDIX D

A FORTRAN II PROGRAM FOR PLOTTING PROCESSED CONCENTRATION DATA

1. LIST OF PROGRAM STATEMENTS

1 READ101, C1, C2, C3, SI3
   CALL PLOT(0., 0., 3)
   PAUSE
   IF (SENSE SWITCH1) 5, 6

5 READ 104, X1, Y1, NC1, SI1, AN1, ZM1, DZ1
   READ 104, X2, Y2, NC2, SI2, AN2, ZM2, DZ2
   CALL AXIS (X1, Y1, NC1, SI1, AN1, ZM1, DZ1)
   CALL AXIS (X2, Y2, NC2, SI2, AN2, ZM2, DZ2)

6 READ 102, TIME, IPOS, Y, TH, XI, R
   IF (TIME+.01) 8, 8, 30

30 IF (SENSE SWITCH 2) 20, 23

23 Y = (Y - ZM2) * C2

3 X = TIME * C1

24 CALL PLOT(X, Y, 3)
   IF (SENSE SWITCH4) 10, 9

9 PUNCH TAPE 4

4 FORMAT (18H110555592207777933)

12 P = X + .03
   Q = Y - .04
   VAR = IPOS
   CALL DRAW(2, P, Q, SI3, 0., VAR, -1)
   GO TO 6

8 PRINT103
   PAUSE
   GO TO 1

20 Y = (R - ZM2) * C3
   IF (SENSE SWITCH 3) 22, 3

22 X = TH * C1
   GO TO 24

10 PUNCH TAPE11

11 FORMAT (20H22066669333308888944)
   GOTO12

101 FORMAT (4F10.6)

102 FORMAT (F10.1, I6, 4F9.4)

103 FORMAT (13HTIME NEGATIVE)

104 FORMAT (2F5.2, I5, 4F10.2)

END
2. DEFINITION OF INPUT VARIABLES USED IN PROGRAM STATEMENTS

C1, C2, C3 - Scaling factors for plotting data
S13 - height of characters for subroutine DRAW.
X1, Y1 - starting coordinates for axis 1
NC1 - number of characters in the label for axis 1
S11 - length of the axis, in.
AN1 - angle of the axis, degrees.
ZM1 - value of the variable at the starting coordinates.
DZ1 - variable increment per inch.
TIME, IPOS, Y, TH, XI, R - as defined in Appendix B.

3. SAMPLE INPUT DATA

<p>| | |</p>
<table>
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The remainder of the input is the output from the concentration data processing program (Appendix B) after removal of the identifier cards.

4. Figure 7 displays the output from this program using all of the data of experimental run 2-5.
A FORTRAN II PROGRAM FOR PLOTTING PROCESSED TEMPERATURE DATA

1. LIST OF PROGRAM STATEMENTS

```fortran
DIMENSION T(I1)
1 READ101,C1,C2,S13,J,K,L
   CALL PLOT(0.,0.,3)
   PAUSE
   IF(SENSE SWITCH1)5,30
5 READ 104, X1,Y1,NC1,S11,AN1,ZM1,DZ1
   READ 104, X2,Y2,NC2,S12,AN2,ZM2,DZ2
   CALL AXIS(X1,Y1,NC1,S11,AN1,ZM1,DZ1)
   CALL AXIS(X2,Y2,NC2,S12,AN2,ZM2,DZ2)
30 IF (SENSE SWITCH 2) 20,6
6 READ102,TIME,(T(I),I=3,11)
   IF(TIME+.01)8,8,3
   X=TIME*C1
21 DO 7 I=J,K,L
   IF(ABS(T(I))-.001)7,7,23
23 Y=(T(I)-ZM2)*C2
24 CALL PLOT(X,Y,3)
   IF(SENSE SWITCH4)10,9
9 PUNCH TAPE 4
4 FORMAT (18H110555592207777933)
12 P=X+.03
   Q=Y-.04
   VAR=I
   CALL DRAW(2,P,Q,S13,0.,VAR,-1)
7 CONTINUE
GO TO30
8 PRINT103
   PAUSE
   GO TO 1
20 READ 102, TIME, THETA,(T(I),I=3,11)
   IF (SENSE SWITCH 3) 22,3
22 X = THETA*C1
   GO TO 21
10 PUNCH TAPE11
11 FORMAT (20H22066669333308888944)
GOTO12
101 FORMAT(3F10.6,3T5)
102 FORMAT(12F6.2)
103 FORMAT(13HTIME NEGATIVE)
104 FORMAT(2F5.2,T5,4F10.2)
END
```

APPENDIX E
2. DEFINITION OF INPUT VARIABLES USED IN PROGRAM STATEMENTS

C1, C2 - scaling factors for plotting data
SI3 - height of characters for subroutine DRAW.
J, K, L - integers to determine which bed positions are to be plotted.
X1, Y1, NC1, SI1, AN1, ZM1, DZ1 - as defined in Appendix D.
TIME, T(I) - as defined in Appendix C.

3. SAMPLE INPUT DATA

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</tr>
<tr>
<td>AN1</td>
<td>0</td>
</tr>
<tr>
<td>ZM1</td>
<td>0</td>
</tr>
<tr>
<td>DZ1</td>
<td>20</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Variable</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>X2</td>
<td>0.</td>
</tr>
<tr>
<td>Y2</td>
<td>0.</td>
</tr>
<tr>
<td>NC2</td>
<td>40</td>
</tr>
<tr>
<td>SI2</td>
<td>5</td>
</tr>
<tr>
<td>AN2</td>
<td>90</td>
</tr>
<tr>
<td>ZM2</td>
<td>60</td>
</tr>
<tr>
<td>DZ2</td>
<td>10</td>
</tr>
</tbody>
</table>

The remainder of the input is the output from the temperature data processing program (Appendix C) after removal of the identifier cards.

4. Figure 19 displays the output from the program using all of the data of experimental run 2-5.
APPENDIX F

A FORTRAN IV PROGRAM FOR PREDICTING THEORETICAL RESULTS

1. LIST OF PROGRAM STATEMENTS

1. LIST OF PROGRAM STATEMENTS

    DIMENSION W(129,4), TS(129,4), XM(129), YE(129),
    CA(129), CD(129), FF(129), GG(129), Y(129), TG(129),
    D1(129), D2(129,4), D3(129), D4(129,4),
    CB(129), CC(129), YYE(129)

    PAUSE

    READ900, AM, BM, CFO, DFO
    READ900, AFS, BFS, CFS, ALM, BLM, CLM
    READ900, CPA, CPB, C, WMA, WMB

    900 FORMAT(7F10.0)

    READ901, ICM1, ICM2, IPM

    901 FORMAT(5I5)

    READ902, NM, DLTH, PAV

    902 FORMAT(15, 3F15.0)

    READ900, YOO, TGO, YOE, WO, TSO, TR, WOE

    4 READ 900, XN1, XN2, XN3, XN4, BTC

    I=6400/NM

    INC=800/I

    AI=I

    DLXI=AI/6400.

    DLTH=DLTH*1000./XN3

    N=NM

    NM=NM+1

    NMA=NM-2

    PRINT 910, ICM1, ICM2, IPM

    PRINT 907, DLXI, DLTH

    PRINT 908, YOO, TGO, YOE, WO, TSO, TR, WOE

    PRINT 909, XN1, XN2, XN3, XN4, BTC

    DO20 I=1, NM

    W(I,1)=WO

    20 TS(I,1)=TSO

    TH=0.

    PCMB=100.

    PCHB=100.

    DLTH2=DLTH/2.

    IP=0

    JP=2

    J=1

    LOJ=1

    39 IC2=0

    40 IC2=IC2+1

    41 DO42K=1, NM
XM(K) = AM*W(K,J)**BM
FC = CFO*W(K,J)**DFO
FS = 10.*(AFS+BFS/(CFS+TS(K,J)))
YE(K) = (FS/FO)**XM(K)/PAV
YE(K) = YE(K)/(1.-YE(K))
YE(K) = YE(K)*WMA/WMB

42 YYE(K) = YE(K)/(1.+YE(K))
TIME = TH*XN3
RO = 1.-EXP(BTC*TIME)
YO = RO*(YOO-YOE)+YOE

50 Q1 = 1./(XN1*DLXI)
DO 51 K = 2,N
CA(K) = Q1-5.*(1.-YYE(K-1))/12.
CB(K) = -Q1-2.*(1.-YYE(K))/3.
CC(K) = (1.-YYE(K+1))/12.
CD(K) = -5.*YYE(K-1)/12.-2.*YYE(K)/3.+YYE(K+1)/12.
CD(2) = CD(2) - CA(2)*YO
CA(2) = 0.
DO 52 K = 2,N
FF(K) = CB(K) - CA(K)*CC(K-1)/FF(K-1)
GG(K) = (CD(K) - CA(K)*GG(K-1))/FF(K)
CA(NM) = 1.-YYE(N)-2.*Q1
CB(NM) = 2.*Q1+1.-YYE(NM)
FF(NM) = CB(NM) - CA(NM)*CC(N)/FF(N)
Y(NM) = (YYE(NM)+YYE(N)-CA(NM)*GG(N))/FF(NM)
DO 53 I = 1,NMA
K = NM-I

53 Y(K) = GG(K) - CC(K)*Y(K+1)/FF(K)
Y(1) = YO

55 Q2 = 1./XN2*DLXI
DO 56 K = 2,N
CA(K) = Q2-5./12.
CB(K) = -Q2-2./3.
CC(K) = 1./12.
CD(K) = -5.*TS(K-1,J)/12.-2.*TS(K,J)/3.+TS(K+1,J)/12.
CD(2) = CD(2) - CA(2)*TG0
CA(2) = 0.
DO 57 K = 2,N
FF(K) = CB(K) - CA(K)*CC(K-1)/FF(K-1)
GG(K) = (CD(K) - CA(K)*GG(K-1))/FF(K)
CA(NM) = 2.*Q2-1.
CB(NM) = -2.*Q2-1.
FF(NM) = CB(NM) - CA(NM)*CC(N)/FF(N)
TG(NM) = (-TS(N,J)-TS(NM,J)-CA(NM)*GG(N))/FF(NM)
DO 58 I = 1,NMA
K = NM-I

58 TG(K) = GG(K) - CC(K)*TG(K+1)/FF(K)
TG(1) = TG0

60 D1(K) = -XN1*(Y(K)-YE(K))/(1.+YE(K))

64 GO TO (98,70,70,70),J
SB1 = Y(1) * DLTH2
SB2 = Y(NM) * DLTH2
STBl = SB1 * CA(1)
STB2 = SB2 * (CA(NM) + CB(NM) * (TG(NM) - TG(1)))
SB40 = (W(1,J) + W(NM,J)) / 2.
DO 200 K = 2, N
SB40 = SB40 + W(K,J)
SB40 = SB40 * DLXI
STB40 = (CC(1) * (TS(1,J) - TG(1)) + CC(NM) * (TS(NM,J) - TG(1))) / 2.
DO 203 K = 2, N
STB40 = STB40 + CC(K) * (TS(K,J) - TG(1))
STB40 = STB40 * DLXI
GO TO 71
70 DO 75 K = 1, NM
XLMDA = ALM + BLM * TS(K,J) + CLM * TS(K,J)**2
CA(K) = XLMDA + XM(K)
XLMDA = XM(K) * XLMDA + (1. + BM) - CPA * (TS(K,J) - TG(K))
CS = C + W(K,J) * (CPA - XM(K) * BLM)
CC(K) = CS
CPG = CPB + Y(K) * CPA
CB(K) = CPG
D2(K,J) = -D1(K)
75 D4(K,J) = -(XLMDA * D1(K) + (1. + Y(K)) * CPA * D3(K) + XN4 * (TG(K) - TSO) / CS
IF (J-1) .GE. 65, 72
71 DO 76 K = 1, NM
W(K,J+1) = W(K,J) + DLTH * D2(K,J)
76 TS(K,J+1) = TS(K,J) + DLTH * D4(K,J)
J = 2
TH = TH + DLTH
GO TO 41
72 COTO (73, 81, 85), LOJ
73 IF (IC2 - ICM1) .LE. 74, 74, 90
74 DO 77 K = 1, NM
W(K,J) = W(K,J-1) + DLTH * (D2(K,J-1) + D2(K,J-1)) / 2.
77 TS(K,J) = TS(K,J-1) + DLTH * (D4(K,J) + D4(K,J-1)) / 2.
GO TO 40
79 LOJ = 2
DO 80 K = 1, NM
W(K,J+1) = W(K,J-1) + 2.* DLTH * D2(K,J)
80 TS(K,J+1) = TS(K,J-1) + 2.* DLTH * D4(K,J)
TH = TH + DLTH
J = 3
GOTO 39
81 IF (IC2 - ICM2) .LE. 78, 78, 90
78 DO 82 K = 1, NM
W(K,J) = W(K,J-1) + DLTH * (D2(K,J) + D2(K,J-1)) / 2.
82 TS(K,J) = TS(K,J-1) + DLTH * (D4(K,J) + D4(K,J-1)) / 2.
GOTO 40
83 LOJ = 3
88 DO 84 K = 1, NM
W(K,J+1) = W(K,J-1) + 2.* DLTH * D2(K,J)
84 \( TS(K,J+1) = TS(K,J-1) + 2 \cdot DLTH \cdot D4(K,J) \)
\( TH = TH + DLTH \)
\( J = 4 \)
GOTO39
85 IF (IC2 - ICY2) 62, 62, 90
62 DO86K = 1, NM
\( W(K,J) = W(K,J-1) + DLTH \cdot (D2(K,J) + D2(K,J-1))/2. \)
86 \( TS(K,J) = TS(K,J-1) + DLTH \cdot (D4(K,J) + D4(K,J-1))/2 \).
GO TO 40
89 DO87K = 2, 3
DO87K = 1, NM
\( D2(K,L) = D2(K,L+1) \)
\( D4(K,L) = D4(K,L+1) \)
\( W(K,L) = W(K,L+1) \)
87 \( TS(K,L) = TS(K,L+1) \)
\( J = 3 \)
GOTO88
90 \( SB1 = SB1 + Y(1) \cdot DLTH2 \)
\( SB2 = SB2 + Y(NM) \cdot DLTH2 \)
\( Q = (W(1,J) + W(NM,J))/2. \)
DO 201 K = 2, N
201 \( Q = Q + W(K,J) \)
\( SB4 = Q \cdot DLXI - SB40 \)
\( PCMB = (SB2 + SB4) \cdot 100. / SB1 \)
\( SB1 = SB1 + Y(1) \cdot DLTH2 \)
\( SB2 = SB2 + Y(NM) \cdot DLTH2 \)
\( Q1 = CA(1) \cdot Y(1) \cdot DLTH2 \)
\( Q2 = (CA(NM) + CB(NM) \cdot (TG(NM) - TG(1)) \cdot Y(NM) \cdot DLTH2 \)
\( STB1 = STB1 + Q1 \)
\( STB2 = STB2 + Q2 \)
\( Q = (CC(1) \cdot (TS(1,J) - TG(1)) + CC(NM) \cdot (TS(NM,J) - TG(1)))/2. \)
DO 202 K = 2, N
202 \( Q = Q + CC(K) \cdot (TS(K,J) - TG(1)) \)
\( STB4 = Q \cdot DLXI - STB40 \)
\( PCMB = STB2 + STB4) \cdot 100. / STB1 \)
\( STB1 = STB1 + Q1 \)
\( STB2 = STB2 + Q2 \)
98 CALL SSWITCH (1, LL)
GO TO (106, 92), LL
106 IP = -1
GO TO 91
92 IF (IP) 99, 93, 99
93 IP = IP - IPM
IPOS = 2
DO 95 I = 1, NM, INC
IPOS = IPOS + 1
IF (IPOS - JP) 97, 96, 97
97 IF (ABS (TS(I,J-1) / TS(I,J) - 1) - 0.001) 95, 96, 96
96 CALL SSWITCH (2, LL)
GOTO (110, 111), LL
110 PUNCH903, IPOS, TH, Y(I), YE(I), TG(I), W(I,J), TS(I,J)
GOTO95
111 R = (Y(I) - YOE) / (YAO - YOE)
\[ RE = \frac{(Y(I) - YOE)}{(YO - YOE)} \]
\[ S = \frac{(W(I,J) - WO)}{(WO - WO)} \]
\[ U = \frac{(TG(I) - TGO)}{(TGO - TR)} \]
\[ V = \frac{(TS(I,J) - TSO)}{(TSO - TR)} \]

PUNCH904, IPOS, TH, R, RE, U, S, V

95 CONTINUE

101 IF(JP-11)101,102,102

102 JP=JP+1

GOTO91

91 TIME=XN3*TH

PRINT905, TH, TIME, YO

IPOS=2

DO 94 I=1, NM, INC

IPOS=IPOS+1

PRINT906, IPOS, Y(I), YE(I), TG(I), W(I,J), TS(I,J), XM(I)

PRINT 907, PCMB, PCHB

CALL SSWTCH (4, LL)

GO TO (107, 99), LL

107 PAUSE4

CALL SSWTCH (3, LL)

GO TO (1, 141), LL

141 IF(Y(NM)/YO-.9)99,99,103

99 IP=IP+1

GOTO (70, 79, 83, 89), J

100 PAUSE1

GOTO1

103 PAUSE2

READ901,LLL

GOTO (1, 2, 3, 4, 5), LLL

903 FORMAT(20X, I3, F11.6, 2F9.4, F9.1, F9.4, F9.1)

904 FORMAT(20X, I3, F11.6, 5F9.5)

905 FORMAT(20X, 9HTHETA = F9.6, 8HTIME = F11.2, F10.4, //, 20X,

15HPOSIT, 7X, 1HY, 8X, 2HYE, 9X, 2HTG, 8X, 1HW, 9X, 2HTS, 23X, 1HM)

906 FORMAT(20X, I3, F12.4, F10.4, F10.1, F10.5, F10.1, 15X, F10.2)

907 FORMAT(20X, 3F15.8)

908 FORMAT(20X, F10.4, F10.2, 2F10.4, 2F10.2, F10.4)

909 FORMAT(20X, 4F10.1, F10.3)

910 FORMAT(20X, 515)

END
2. DEFINITION OF INPUT AND OUTPUT VARIABLES USED IN PROGRAM STATEMENTS

\( AM, BM \) - constants in the equation for \( m^1 \) as a function of \( \omega^1 \).

\( CF0, DF0 \) - constants in the equation for \( f_0^1 \) as a function of \( \omega^1 \).

\( AFS, BFS, CFS \) - constants in the equation for \( f_s^1 \) as a function of \( T_s^1 \).

\( ALM, BLM, CLM \) - constants in the equation for \( \lambda_s^1 \) as a function of \( T_s^1 \).

\( CPA \) - \( C_{PA}^1 \).

\( CPB \) - \( C_{PB}^1 \).

\( C \) - \( C^1 \).

\( WMA \) - \( M_A^1 \).

\( WMB \) - \( N_B^1 \).

\( ICM1 \) - number of Euler improvement cycles for the initial time increment.

\( ICM2 \) - as above for all other time increments.

\( IPM \) - number of time increments between print-outs.

\( NM \) - number of spatial increments.

\( DLTH \) - transformed time increment.

\( PAV \) - average pressure in the bed.

\( Y00 \) - \( Y_{00}^1 \).

\( TGO \) - \( T_{Go}^1 \).

\( YOE \) - \( Y_{OE}^1 \).

\( W0 \) - \( W_0^1 \).

\( TSO \) - \( T_{So}^1 \).

\( TR \) - \( T_R^1 \).

\( WOE \) - \( W_{OE}^1 \).

\( XN1 \) - \( N^1_1 \).

\( XN2 \) - \( N^1_2 \).

\( XN3 \) - \( N^1_3 \).

\( XN4 \) - \( N^1_4 \).

\( BTC \) - negative reciprocal of the time constant for the variation of the inlet gas phase concentration.

\(^1\text{As defined in Appendix A.}\)
3. **SAMPLE INPUT DATA**

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>AM</td>
<td>1,5753</td>
</tr>
<tr>
<td>BM</td>
<td>0.11647</td>
</tr>
<tr>
<td>CFO</td>
<td>59.141</td>
</tr>
<tr>
<td>DFO</td>
<td>-0.52</td>
</tr>
<tr>
<td>AFS</td>
<td>4.1037</td>
</tr>
<tr>
<td>BFS</td>
<td>-600.8</td>
</tr>
<tr>
<td>CFS</td>
<td>330.2</td>
</tr>
<tr>
<td>ALM</td>
<td>175.0</td>
</tr>
<tr>
<td>BLM</td>
<td>-0.53</td>
</tr>
<tr>
<td>CLM</td>
<td>0.0</td>
</tr>
<tr>
<td>CPA</td>
<td>0.42</td>
</tr>
<tr>
<td>CPB</td>
<td>0.25</td>
</tr>
<tr>
<td>C</td>
<td>0.25</td>
</tr>
<tr>
<td>WMA</td>
<td>30.07</td>
</tr>
<tr>
<td>WMB</td>
<td>28.016</td>
</tr>
<tr>
<td>ICM1</td>
<td>15</td>
</tr>
<tr>
<td>ICM2</td>
<td>1</td>
</tr>
<tr>
<td>IPM</td>
<td>4</td>
</tr>
<tr>
<td>NM</td>
<td>128</td>
</tr>
<tr>
<td>DLTH</td>
<td>0.00025</td>
</tr>
<tr>
<td>PAV</td>
<td>14.8</td>
</tr>
<tr>
<td>Y00</td>
<td>0.144</td>
</tr>
<tr>
<td>TGO</td>
<td>80.0</td>
</tr>
<tr>
<td>YOE</td>
<td>0.022</td>
</tr>
<tr>
<td>WO</td>
<td>0.009256</td>
</tr>
<tr>
<td>TSO</td>
<td>79.0</td>
</tr>
<tr>
<td>TR</td>
<td>32.0</td>
</tr>
<tr>
<td>WOE</td>
<td>0.034789</td>
</tr>
<tr>
<td>XN1</td>
<td>300.0</td>
</tr>
<tr>
<td>XN2</td>
<td>300.0</td>
</tr>
<tr>
<td>XN3</td>
<td>1058.0</td>
</tr>
<tr>
<td>XN4</td>
<td>0.4</td>
</tr>
<tr>
<td>BTC</td>
<td>-1.5</td>
</tr>
</tbody>
</table>

4. Figure 38 displays a partial plot of the answers obtained from the input data above.
EVALUATION OF EQUILIBRIUM CONSTANTS

1. BASIC ISOTHERM DATA

The isotherm data was obtained from Pittsburgh Chemical Company. The data is taken from a report on an experimental study of the adsorption isotherms of normal paraffin hydrocarbons on Pittsburgh Activated Carbon (Type BPL). The isotherm data for ethane at three temperatures is listed below. This data was plotted on log-log graph paper to facilitate the plotting of isotherms.

<table>
<thead>
<tr>
<th>EQUILIBRIUM PRESSURE (PSIA)</th>
<th>AMOUNT ADSORBED (G/100G CARBON)</th>
<th>-9°F</th>
<th>77°F</th>
<th>170°F</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>2.25</td>
<td>0.66</td>
<td>0.195</td>
<td></td>
</tr>
<tr>
<td>0.3</td>
<td>3.65</td>
<td>1.24</td>
<td>0.390</td>
<td></td>
</tr>
<tr>
<td>0.5</td>
<td>4.7</td>
<td>1.62</td>
<td>0.540</td>
<td></td>
</tr>
<tr>
<td>1.0</td>
<td>6.4</td>
<td>2.35</td>
<td>0.85</td>
<td></td>
</tr>
<tr>
<td>2.0</td>
<td>8.5</td>
<td>3.41</td>
<td>1.32</td>
<td></td>
</tr>
<tr>
<td>4.0</td>
<td>10.9</td>
<td>4.8</td>
<td>2.00</td>
<td></td>
</tr>
<tr>
<td>7.0</td>
<td>13.2</td>
<td>6.4</td>
<td>2.8</td>
<td></td>
</tr>
</tbody>
</table>

2. SATURATION FUGACITY DATA

The saturation fugacity data was obtained by use of a fugacity coefficient and vapor pressure data (extrapolated beyond the critical point where necessary). The data used for this study is listed below. This data is also to be used in the isotherm plot.
ETHANE SATURATION FUGACITY DATA

<table>
<thead>
<tr>
<th>T(°F)</th>
<th>P_S(ATM)</th>
<th>T_R</th>
<th>P_R</th>
<th>\nu_{T,P_S}</th>
<th>f_s^*(ATM)</th>
<th>f_s^*(PSIA)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-50</td>
<td>6.30</td>
<td>0.74</td>
<td>0.130</td>
<td>0.89</td>
<td>5.60</td>
<td>82.4</td>
</tr>
<tr>
<td>0</td>
<td>14.9</td>
<td>0.83</td>
<td>0.32</td>
<td>0.80</td>
<td>11.9</td>
<td>175.</td>
</tr>
<tr>
<td>50</td>
<td>30.0</td>
<td>0.93</td>
<td>0.62</td>
<td>0.72</td>
<td>21.6</td>
<td>318.</td>
</tr>
<tr>
<td>100</td>
<td>52.0</td>
<td>1.01</td>
<td>1.08</td>
<td>0.64</td>
<td>33.2</td>
<td>489.</td>
</tr>
<tr>
<td>150</td>
<td>82.5</td>
<td>1.11</td>
<td>1.71</td>
<td>0.60</td>
<td>49.4</td>
<td>726.</td>
</tr>
<tr>
<td>200</td>
<td>121.</td>
<td>1.20</td>
<td>2.52</td>
<td>0.59</td>
<td>71.4</td>
<td>1050.</td>
</tr>
<tr>
<td>250</td>
<td>170.</td>
<td>1.30</td>
<td>3.54</td>
<td>0.65</td>
<td>110.5</td>
<td>1630.</td>
</tr>
</tbody>
</table>

The following expression was determined for expressing the data above:

\[ \log f_s^* = 4.1037 - \frac{600.8}{T + 330.25} \]

where:

- \( f_s^* \) - saturation fugacity, PSIA,
- \( T \) - temperature, °F.

3. ISOTERE DATA

The isotherm plot in conjunction with the fugacity data above was used to plot the adsorption equilibrium fugacity versus the pure component saturation fugacity for a particular solid concentration. This plot was used to obtain the intercept and slope of the isoterres as defined in Chapter II. The data used for obtaining the constants of Chapter II is presented below.
4. ENTHALPY DATA

The difference of the enthalpy of the adsorbate as an ideal gas and adsorbed on the solid was determined from the relations of Chapter II. The relation requires the slope of the isotheres (m) and corrected latent heat of vaporization as defined in Appendix A. The heat of vaporization and the corrected heat of vaporization for ethane are presented below:

<table>
<thead>
<tr>
<th>$T_{(OF)}$</th>
<th>$T_R$</th>
<th>$P_R$</th>
<th>$H_v^k$</th>
<th>$H_v - H_L^k$</th>
<th>$H_v - H_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>.83</td>
<td>.32</td>
<td>-537</td>
<td>4590</td>
<td>5127</td>
</tr>
<tr>
<td>50</td>
<td>.93</td>
<td>.62</td>
<td>-1100</td>
<td>3420</td>
<td>4520</td>
</tr>
<tr>
<td>100</td>
<td>1.01</td>
<td>1.08</td>
<td>-3670</td>
<td>0</td>
<td>3670</td>
</tr>
<tr>
<td>200</td>
<td>1.11</td>
<td>1.71</td>
<td>-2870</td>
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AUTOBIOGRAPHY

The author was born November 4, 1935 in Elfers, Florida. He received his elementary and secondary education in the public school systems of Florida and Wisconsin. In 1956, he received the degree of B.E. in Chemical Engineering from Vanderbilt University. He was designated a Naval Aviator in 1957 and spent the following two and one-half years as a pilot and as an Officer of the Operations and Supply Departments of Patrol Squadron Five (VP-5), U.S. Navy. In September, 1960, following his release from active duty, he entered the Graduate School of Louisiana State University where he received the degree of M.S. in Chemical Engineering in January, 1962. At present he is a candidate for the degree of Doctor of Philosophy in Chemical Engineering at that same institution and is employed as a Process Design Engineer at Ethyl Corporation in Baton Rouge, Louisiana.
Candidate: Cecil Paul Loechelt

Major Field: Chemical Engineering

Title of Thesis: The Dynamic Behavior of Non-Isothermal, Fixed Bed Adsorption Systems

Approved:

Frank E. Proctor, Jr.
Major Professor and Chairman

Max Goodrich
Dean of the Graduate School

EXAMINING COMMITTEE:

Date of Examination:

July 29, 1964