ACKNOWLEDGEMENT

The author wishes to express his deep appreciation and sincere thanks to Dr. D. Basmadjian, who directed the work, for his encouragement, interest, and many suggestions during the course of this investigation. The financial support from the National Research Council through grant No. A-926 is also gratefully acknowledged.

ABSTRACT

A theoretical study has been made of the adsorption of one component from a gas stream flowing through a large adiabatic fixed bed. Asymptotic solutions were obtained under the assumption that the adsorption occurs in two distinct mass transfer zones moving through the bed, one after the other, as observed by Leavitt (1). Breakthrough concentration and temperature profiles calculated from these solutions are in reasonably good agreement with the experimental results of Leavitt on the adiabatic fixed bed adsorption of CO_2 on molecular sieves. It was also found that the asymptotic solutions to the first mass transfer zone exist for most linear and favorable adsorption isotherms concerned, and that they are always useful in predicting large adiabatic fixed bed performance even when the second mass transfer zone does not attain a constant pattern state.

TABLE OF CONTENTS

LIST OF FIGURES

I INTRODUCTION

An important chemical engineering operation is that in which a certain fluid is passed through a stationary bed for the purpose of removing from it, or adding to it, one or more chemical substances. The purification of gases by passing them through a bed of activated charcoal or molecular sieve adsorbent is an important application of this unit operation (2). In general, it is most economical to conduct this sorption process in semi-continuous arrangement in which the solid phase is present as a fixed bed of granular particles. The fluid phase passes through the interstices of this bed for an extended period of time. A schematic diagram of a typical fixed bed system is shown in Fig. 1. The concentration gradients in the fluid and solid phases display a transient behavior, and their evolution depends upon the pertinent material and energy balances, rates and equilibria. For the design of efficient fixed beds, it is desirable to have a background of theory to predict bed performance from a knowledge of the characteristics and behavior of the individual system variables such as fluid and solid phase diffusivities, adsorption equilibrium data, particle and bed dimensions, etc., all of which affect the overall adsorption. The principal aim in predicting bed performance is to establish the precise time at which the effluent reaches a certain adsorbate concentration level beyond which it is

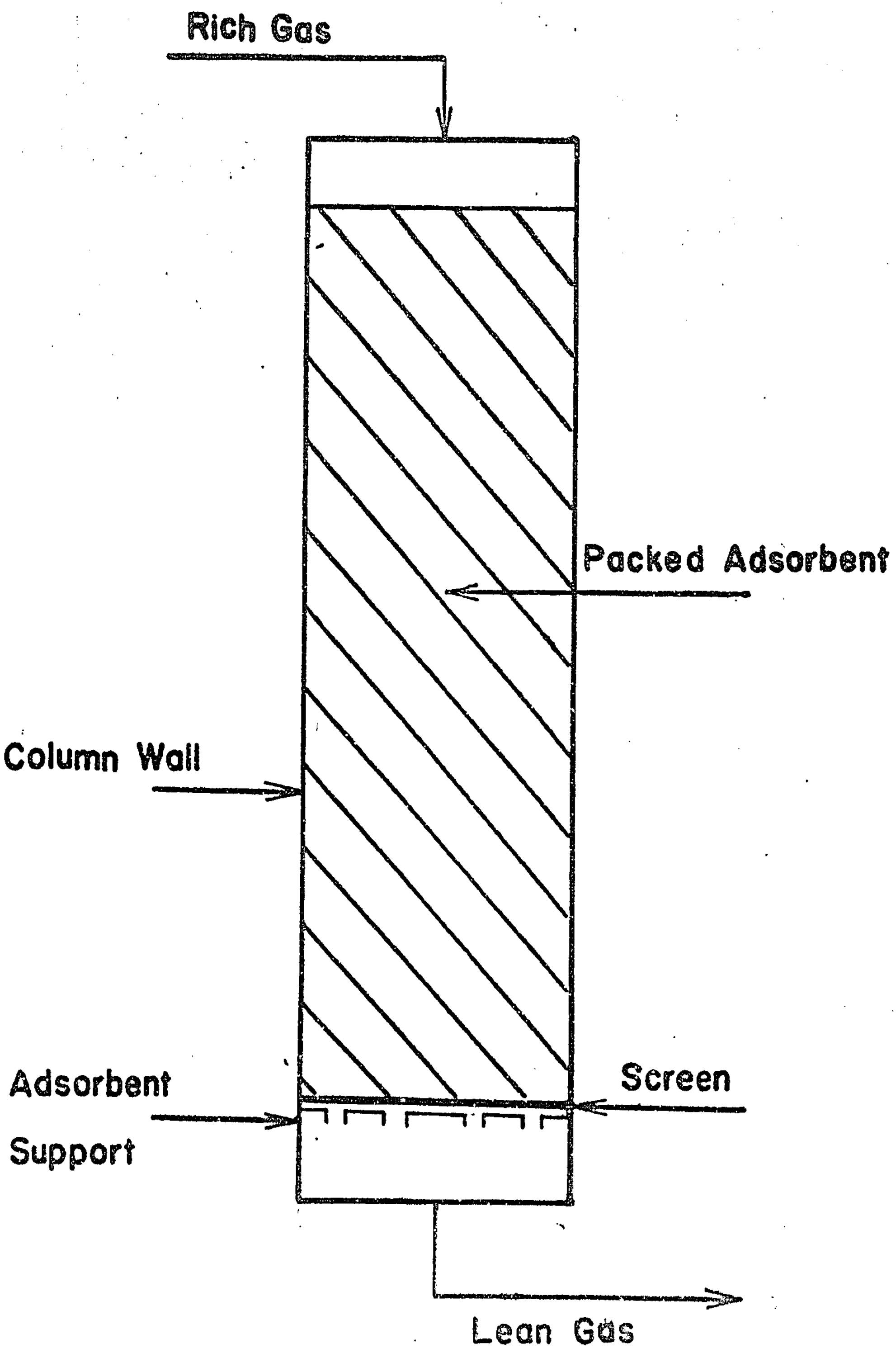

FIG. I. FIXED BED ADSORBER

undesirable to continue operating the bed. At this point the feed stream is diverted to a second bed while the first adsorber is subjected to regeneration by thermal or other means.

This "breakthrough" time of the adsorbate can be calculated for any level, once the concentration profiles are known as a function of time and position. A rigorous treatment of the problem includes a consideration of radial and axial dispersion in the fluid phase as well as taking into account the heat effects associated with the adsorption process (3). The resulting set of partial differential equations describing bed performance is, however, not readily amenable to analytical solution.

In the relatively simple case of isothermal adsorption from a gas feed containing only one adsorbable component, much has been done in the way of predicting bed performance (4). At a high feed concentration, however, the adsorption process is complicated by the non-linear adsorption equilibrium relationship and temperature changes in the bed due to the incomplete removal of the heat of adsorption and the difference between feed and initial bed temperatures. When adsorption occurs in a small-diameter fixed bed, the heat that is generated is readily conducted out through the bed wall; thus the bed may be nearly isothermal. In a large-diameter, industrial-scale bed, however, the heat that is generated in the bed is not easily conducted to the wall ; such conduction may in fact be negligible. As a result, the heat generated in the bed is either carried away by gas flow through the bed or is stored in the bed. The bed temperature may rise significantly, affecting the course of the adsorption step (1). The governing partial differential equations for the adiabatic fixed bed adsorption are, in general, nonlinear, since the rate law for adsorption is usually a non-linear function of concentration and temperature (2). Although no analytical solution to these differential equations has been obtained, it is often useful to derive asymptotic solutions using simplifying assumptions based on experimental observations in long adiabatic fixed bed. These solutions may serve as a good approximation to actual bed performance if the fixed bed is not very short (5). It is the purpose of this study to investigate these asymptotic solutions and their existence.

II LITERATURE SURVEY

A careful study of the literature reveals that very little is known about non-isothermal fixed bed adsorption. This is due to the mathematical complexity of the problem.

Even in the isothermal case, an analytical solution can be obtained only when the adsorption isotherm concerned is either linear or of a Langmuir type non-linear form, and axial dispersion is ignored (6, 7). Since many adsorption isotherms do not conform to either of these cases, researchers in this field have been forced to confine their attention to an even more specialised model or asymptotic case, such as the nondispersive equilibrium model (8) or constant pattern profile case (9).

In isothermal fixed bed adsorption, it has been recognised that axial diffusion and mass transfer resistance have a similar effect on bed performance. They cause a spreading of the adsorbate front as it passes down the fixed bed, that is, both axial diffusion and mass transfer resistance are "dispersive force" (4, 11). On the other hand, in the absence of axial diffusion and mass transfer resistance, it has been shown by De Vault (8) that if the adsorption isotherm concerned is "favorable" (see Fig. 6) - i.e. the second derivative of the solid phase concentration of the adsorbate with respect to the equilibrium fluid phase concentration is always negative, the bed concentration profile will become increasingly sharp and approach a step function as a limit. Whereas this effect is most pronounced in nondispersive equilibrium operations, it also occurs in the presence of dispersive forces. Thus the sharpening effect noted during adsorption of an adsorbate with a "favorable" isotherm opposes the dispersive effect of mass transfer resistance and axial diffusion. In an initially uniformly loaded fixed bed fed at constant rate and composition, these opposing tendencies ultimately come to balance, and the adsorbate front travels down the bed without change in shape (4). This type of behavior is very much easier to treat mathematically since the invariance of the concentration profile allows the elimination of time as an independent variable and results in a considerable simplification of the pertinent differential equations. In fact, when the axial distance is the only independent variable, the mathematical formulation of the problem is reduced to a set of ordinary differential equations. For this reason, the constant pattern assumption is used in most cases of practical importance.

In isothermal fixed bed adsorption of an adsorbate with a favorable isotherm, the existence of the asymptotic solutions, which predict such constant pattern profiles, has been proved mathematically by Lightfoot and Cooney (12). Although the constant pattern is an asymptotic profile which is, strictly speaking, obtained only at distances far removed from the entrance of the bed, it has, nevertheless, been established by Lapidus and Rosen (5) that such a constant pattern is quickly reached inside the bed and may, therefore, be used in design calculation with good accuracy unless the bed is very short. However, if the adsorption isotherm concerned is linear or of the unfavorable type, the constant pattern profile is never reached, since the linear adsorption isotherm has no effect on the shape of the adsorbate profile, and the unfavorable one has the same effect as the mass transfer resistance and axial diffusion (8). In this case, the adsorbate profile will become increasingly diffuse as it travels down the fixed bed. Therefore, in isothermal fixed bed adsorption, the asymptotic profile exists only when the adsorption isotherm concerned is of the favorable type.

For the case of a high feed concentration, Bowen and Donald (13) observed experimentally that the adsorbate concentration profile in a fixed bed is no longer a simple sigmoidal shape as is usually observed in the isothermal case. They detected three different mass transfer zones with the middle one nearly at equilibrium.

This is believed to be caused by the effect of temperature variation on the concentration profile due to the large amounts of heat which can be generated by the process of adsorption when the feed concentration is high.

In a near-adiabatic large fixed bed Leavitt (1) observed that the adsorption occurs in two distinct mass transfer zones that move through the bed, one after the other, with the middle zone at equilibrium. He also proposed a calculation method for the determination of the transfer zone speed and middle zone conditions, but gave no solutions to the concentration and temperature profiles that are useful in calculating the zone length and the breakthrough time when the concentration profiles are not very sharp.

Three non-analytical methods for treating adiabatic fixed bed adsorption may be mentioned: Hougen and Marshall (10) proposed a graphical method of solution for the case of arbitrary adsorption isotherms and negligible axial dispersion. But this is a lengthy trial and error method. A numerical scheme, known as the method of characteristic, was presented by Acrivos (2) for handling the same problem. For the very special case of nondispersive equilibrium operation: negligible axial mass diffusion and heat conduction, and negligible resistances to mass and heat transfer between solid and fluid phases, Lightfoot (4) suggested a simple trial and error numerical method for the determination of the concentration and temperature profiles.

III MATHEMATICAL MODEL OF ADIABATIC FIXED BED ADSORPTION

In order to describe the fixed bed operation quantitatively, we must decided upon a geometrical model to represent the actual system, and then set up differential equations, and initial and boundary conditions based upon this model to provide a mathematical description of the system. It may be easily shown, however, that the detailed behavior of such a system is too complicated to permit quantitative description, and we therefore must set up a simplified model which is simple enough to permit analysis but realistic enough to provide useful results.

1. The Dynamics of Fixed Bed Adsorption

The dynamics of an adsorption process are defined by three transport processes. These are the rates of transfer of momentum, mass and energy. But if we assume plug flow and neglect the effect of pressure drop, there is no need to consider the momentum transfer.

The types of mass transfer present in a fixed bed system are numerous and of varying importance depending on the operating conditions and physical configuration. These include (14, 15):

a) Bulk flow in conjunction with an axial pressure gradient.

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

c) Fluid-phase pore diffusion. Transport inside the pore space of the solid in conjunction with an internal concentration gradient.

d) Adsorption process or phase change. Transport between the fluid phase in close proximity of the solid surface and the solid surface.

e) Solid-phase internal diffusion. Diffusion in a mobile, adsorbed phase covering the pore surface of a porous solid in conjunction with a concentration gradient of the adsorbed solute.

f) Axial and radial transport in the bulk fluid phase as a result of diffusion and turbulence.

All of the transport mechanisms listed above could be significant in the overall model with the possible exception of items (d) and (f), since the rate of surface adsorption is usually very fast compared to the rate of mass transfer (15), and item (f) might be neglected compared to item (a) at high flow rates (3).

The types of energy transport mechanism which might be expected in a fixed bed system are (14):

a) Bulk transport with the flow.

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

c) Convective transport between the fluid and solid phases.

d) Axial and radial conduction and convection in the fluid phase.

e) Axial and radial conduction in the bulk solid phase.

f) Radial conduction within the solid particles.

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

Items (d) and (e) are usually negligible compared to item (d). The rates of items (c) and (f) are fast compared to that of item (b). As a result, the local temperature difference between the fluid and solid phases could be small (16). Further, one might neglect the effect of item (g) in a large-diameter or insulated fixed bed.

In describing the fixed bed adsorption processes, the significant independent variables are:

a) Time

b) Axial 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

The other variables are controllable parameters, such as component identity, feed and initial conditions, and may be used to vary the system.

2. Derivation of Differential Equations

The above list of variables appears to be quite formidable. In this study, a simplified mathematical model with only two independent variables is used - the time and the axial bed position. This model introduces a number of simplifications in that it assumes plug flow through the bed, and neglects the variation of the dependent variables with radial position. Furthermore, the following assumptions are made in the derivation of the equations.

a) The fixed bed is initially uniformly loaded.

b) The feed conditions are constant, and there is only one adsorbable component in the feed.

c) Pressure drop inside the bed is small and the ideal gas law applies to the fluid phase.

d) Mass transfer rate controls the overall adsorption, and the combined resistance to diffusion, consisting of both the external surface film and an intraparticle resistance, is considered together as a diffusional resistance, expressible in the usual manner of the mass transfer "film" theory.

e) Heat transfer rate between the solid and fluid phases is so fast that the local temperatures of the two phases are essentially the same.

f) Heat loss through the bed wall is negligible (adiabatic bed).

g) The carrier gas flow rate and bed porosity are essentially constant throughout the bed.

In order to describe this model system quantitatively, it is necessary to derive partial differential equations relating the composition and temperature in each phase with position in the bed and time; we shall see that these are expressions of conservation of mass and energy. To integrate these differential equations we shall need, in addition to initial and boundary conditions, expressions for the equilibrium distribution of the adsorbate between the solid and gas phases, and for the rate of transfer of the adsorbate between phases.

We may derive these conservation equations by making mass and energy balances over a column segment of length Δz, as shown in Figure 2. The mass balance for the adsorbate is given by

$$\int_{t_1}^{t_2}\left[\left(\frac{G_b y}{1-y} - \rho_g D\,\frac{\partial y}{\partial z}\right)\Bigg|_{z_1} - \left(\frac{G_b y}{1-y} - \rho_g D\,\frac{\partial y}{\partial z}\right)\Bigg|_{z_2}\right] dt$$

$$= \int_{z_1}^{z_2}\left[(\epsilon\rho_g y + \rho_b W)\Big|_{t_2} - (\epsilon\rho_g y + \rho_b W)\Big|_{t_1}\right] dz \qquad (1)$$

Similarly, for the energy balance:

$$\int_{t_1}^{t_2}\left[\left(\frac{G_b H_g}{1-y} - K\,\frac{\partial T}{\partial z}\right)\Bigg|_{z_1} - \left(\frac{G_b H_g}{1-y} - K\,\frac{\partial T}{\partial z}\right)\Bigg|_{z_2}\right] dt$$

$$= \int_{z_1}^{z_2}\left[(\epsilon\rho_g H_g + \rho_b H_s)\Big|_{t_2} - (\epsilon\rho_g H_g + \rho_b H_s)\Big|_{t_1}\right] dz \qquad (2)$$

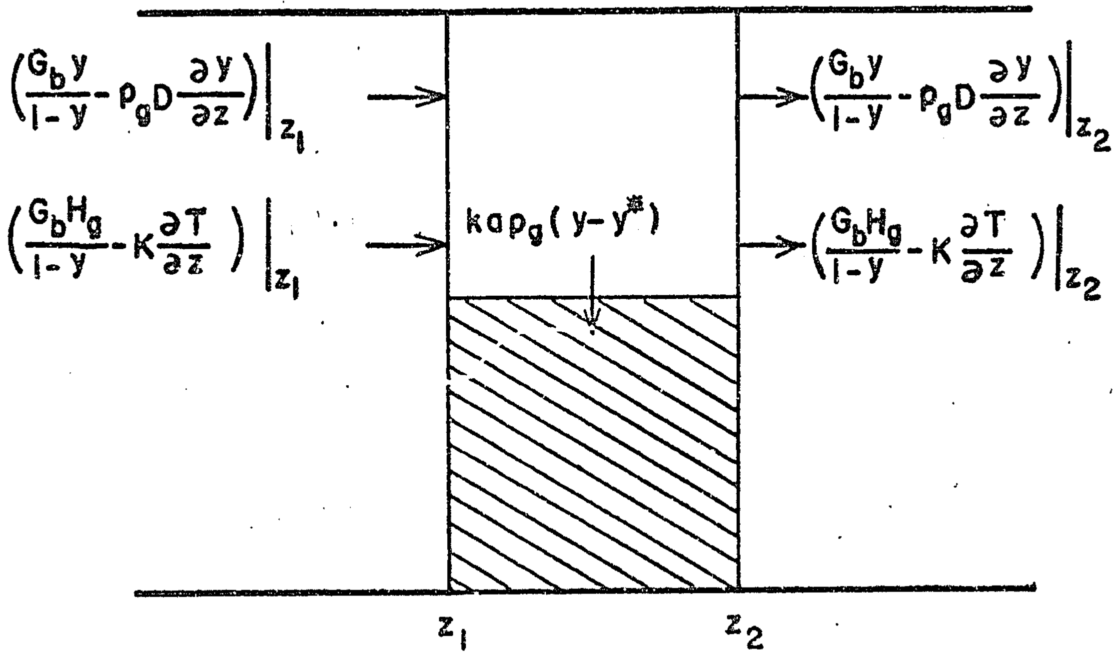

FIG. 2. SEGMENT OF FIXED BED FOR THE FORMULATION OF MASS AND ENERGY BALANCES

Equations (1) and (2) are then transformed, after a twice-repeated application of the mean value theorem, to yield:

$$-\frac{\partial}{\partial s}\left(\frac{G_b y}{1-y} - \rho_g D \frac{\partial y}{\partial s}\right)\Bigg|_{s', t'} \Delta s\, \Delta t = \frac{\partial}{\partial t}\left(\epsilon \rho_g y + \rho_b W\right)\Bigg|_{s'', t''} \Delta s\, \Delta t \tag{3}$$

$$-\frac{\partial}{\partial s}\left(\frac{G_b H_g}{1-y} - K \frac{\partial T}{\partial s}\right)\Bigg|_{s''', t'''} \Delta s\, \Delta t = \frac{\partial}{\partial t}\left(\epsilon \rho_g H_g + \rho_b H_s\right)\Bigg|_{s'''', t''''} \Delta s\, \Delta t \tag{4}$$

where $s_1 < s', s'', s''', s'''' < s_2$

$t_1 < t', t'', t''', t'''' < t_2$

$\Delta s = s_2 - s_1$

$\Delta t = t_2 - t_1$

We now divide by $(\Delta s\, \Delta t)$, let $s_2 \rightarrow s_1$, and $t_2 \rightarrow t_1$. This leads to the following differential equations

$$\frac{\partial}{\partial s}\left(\frac{G_b y}{1-y} - \rho_g D \frac{\partial y}{\partial s}\right) + \frac{\partial}{\partial t}\left(\epsilon \rho_g y + \rho_b W\right) = 0 \tag{5}$$

$$\frac{\partial}{\partial s}\left(\frac{G_b H_g}{1-y} - K \frac{\partial T}{\partial s}\right) + \frac{\partial}{\partial t}\left(\epsilon \rho_g H_g + \rho_b H_s\right) = 0 \tag{6}$$

These two equations are supplemented by the rate equation, which according to assumption (d) can be written as

$$\rho_b \frac{\partial W}{\partial t} = k a \rho_g (y - y^*) \tag{7}$$

In order to reduce the number of dependent variables, reference states for the enthalpies are defined as follows:

a) The adsorbate and carrier gas as gases at 0° F and P.

b) The adsorbent as a solid at 0° F and P.

Therefore, we have

$$H_g = y \int_o^T C'_{pa}\, dT + (1 - y) \int_o^T C'_{pb}\, dT = y\, C_{pa} T + (1 - y)\, C_{pb} T = C_{pg} T \tag{8}$$

$$H_s = \int_o^T C_{ps}\, dT + W \int_o^T C'_{pa}\, dT + \int_o^W \Delta H' dW$$

$$= (C_{ps} + W C_{pa})\, T + W \Delta H \tag{9}$$

It should be noted that $\Delta H'$ and ΔH are functions of both W and T. According to Equations (8) and (9), and the ideal gas law, Equations (5), (6) and (7) may then be written as

$$G_b \frac{\partial}{\partial z} \left(\frac{y}{1 - y}\right) + \rho_b \frac{\partial W}{\partial t} + \frac{\epsilon P}{R} \frac{\partial}{\partial t} \left(\frac{y}{T + 460}\right) - \frac{P}{R} \frac{\partial}{\partial z} \left(\frac{D}{T + 460} \frac{\partial y}{\partial z}\right) = 0 \tag{10}$$

$$G_b \frac{\partial}{\partial z} \left(\frac{C_{pg} T}{1 - y}\right) + \rho_b \frac{\partial (W \Delta H)}{\partial t} + \rho_b C_{ps} \frac{\partial T}{\partial t} + \rho_b \frac{\partial (C_{pa} W T)}{\partial t}$$

$$+ \frac{\epsilon P}{R} \frac{\partial}{\partial t} \left(\frac{C_{pg} T}{T + 460}\right) - \frac{\partial}{\partial z} \left(K \frac{\partial T}{\partial z}\right) = 0 \tag{11}$$

$$\rho_b \frac{\partial W}{\partial t} = \frac{kap}{K} \left(\frac{y - y^*}{T + 460}\right) \tag{12}$$

The boundary and initial conditions for Equations (10), (11) and (12) are

$$W = W_1 \quad T = T_1, \quad y = y_1 = y^*(W_1, T_1) \text{ at } z = 0 \tag{13}$$

$$W = W_3, \; T = T_3, \quad y = y_3 = y^*(W_3, T_3) \text{ at } t = 0 \tag{14}$$

Equations (10), (11) and (12) together with the boundary and initial conditions (13) and (14), and adsorption equilibrium equation $y^* = y^*(W, T)$ describe the dynamic behavior of adiabatic fixed adsorption under assumptions made. The third term in Eq. (10) and the fifth term in Eq. (11) represent the gas phase accumulation of the adsorbate and energy respectively and are usually negligible compared to other terms. The last terms in Equations (10) and (11) represent the axial diffusion and conduction, and are significant only when the bulk flow rate is very low (3). In a small particle bed with low bulk flow rates, y is nearly equal to y^* due to high mass transfer rates or to long residence time (15). Consequently the mass transfer equation (12) drops out in this special case, and the two phases are assumed essentially at equilibrium. This simplification is frequently applied in the mathematical analysis of gas chromatography.

IV ASYMPTOTIC SOLUTIONS TO ADIABATIC FIXED BED ADSORPTION

There seems to be no mathematical method available for solving Equations (10), (11) and (12) analytically, mainly because of the non-linearity of these equations. In this chapter, only some asymptotic solutions will be investigated.

1. Asymptotic Behavior of Adiabatic Fixed Bed Adsorption

Leavitt (1), Bowen and Donald (13) observed three distinct mass transfer zones with the middle one nearly at equilibrium in an adsorber taking a high concentration feed. It is unlikely, therefore, that any theory based on the assumption of a single sigmoidal concentration or temperature profile will be successful in predicting the performance of adsorbers taking a high concentration feed, mainly because the effect of the heat of adsorption cannot be overlooked.

The existence of these zones may be explained as follows: As adsorption proceeds in an adiabatic fixed bed, temperature peaks will develop. After the peak temperature reaches its maximum value, the length of the region which is at this maximum temperature will begin to expand in the direction of flow continuously. Therefore, it is not possible for the entire temperature profile in the bed to reach a constant pattern. Since the temperature and adsorbate concentrations in both phases are not independent of each other, the adsorbate concentration profiles will not reach constant patterns either as far as the *entire* profiles in the bed are concerned. However, when the length of the maximum temperature region is long enough, it is likely that the adsorbate concentrations in both phases will reach an equilibrium condition in that region. With this middle zone at equilibrium, it is possible for the temperature and concentration profiles in the other two zones *before and* after the middle zone to asymptotically approach constant patterns under certain conditions which will be discussed later. The concentration and temperature profiles in each mass transfer zone will then travel along the bed without change in shape. Furthermore, since the temperature and adsorbate concentrations in both phases are dependent of each other, these constant pattern profiles in the same mass transfer zone must travel along the bed at the same speed. Otherwise the constant patterns could not be maintained. However, it is not necessary for the two mass transfer zones to have the same speed.

It seems, therefore, reasonable to postulate asymptotic concentration *and* temperature profiles, as shown in Figure 3, which

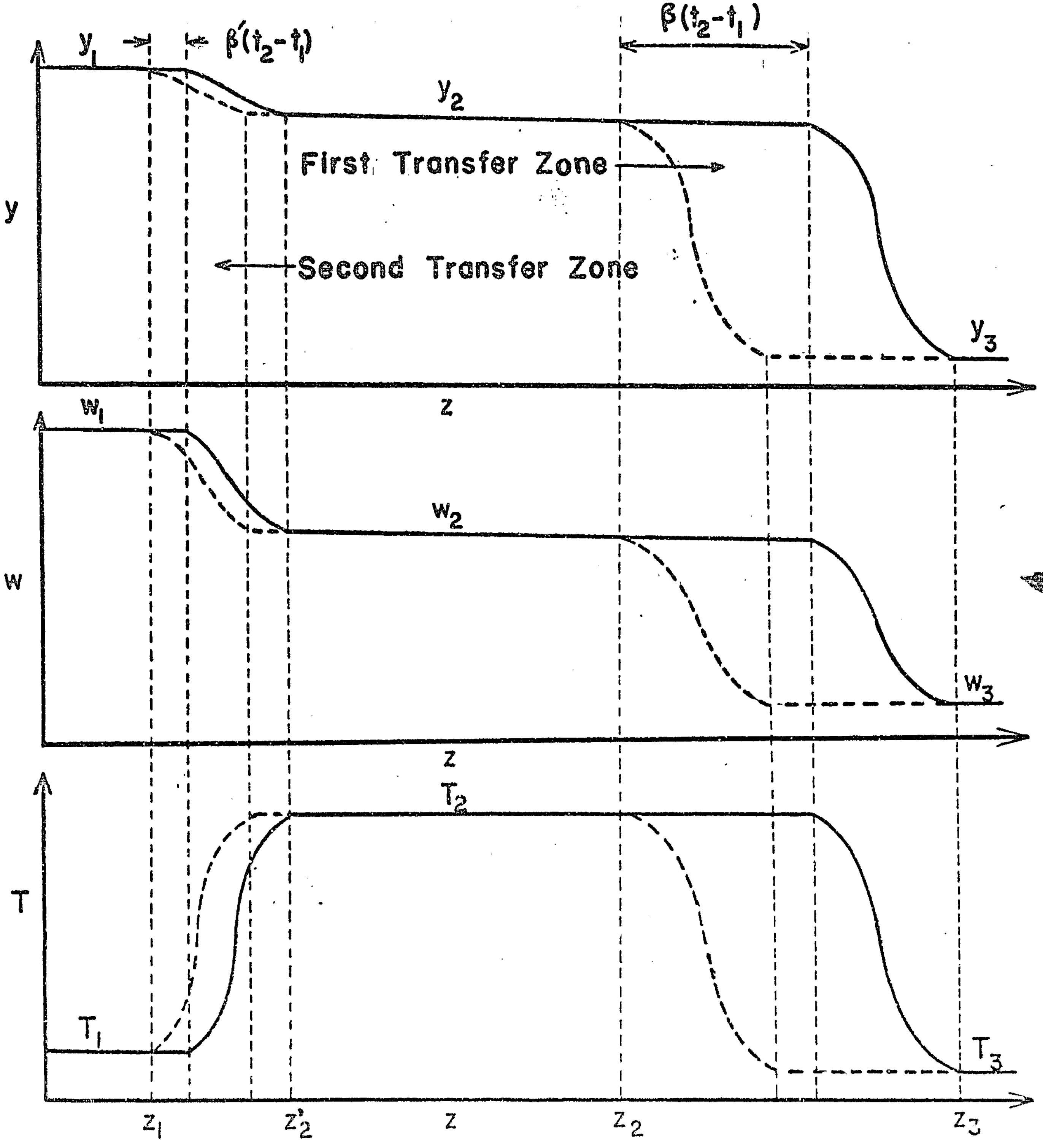

FIG. 3. ASYMPTOTIC CONCENTRATION AND TEMPERATURE PROFILES

---- Profile at time t_1

—— Profile at time t_2

hold provided the fixed bed is long enough. All the shapes of the concentration and temperature profiles in both the first and second mass transfer zones are independent of time. But the distance between these two zones may vary with time, even while the middle zone is essentially at equilibrium.

2. Asymptotic Solutions

(A) Evaluation of the Middle Zone Conditions and Transfer Zone Speeds

Each mass transfer zone speed and middle zone conditions can be easily determined through use of mass and energy balances between z_2 and z_3 for the first transfer zone and between z_1 and z_2' for the second transfer zone as shown in Fig. 3. Accumulation of the adsorbate in both phases per unit time per unit cross-sectional area across the first transfer zone is given by:

$$G_b\left(\frac{y_2}{1-y_2}-\frac{y_3}{1-y_3}\right)=\beta\left[\epsilon(\rho_{g2}y_2-\rho_{g3}y_3)+\rho_b(W_2-W_3)\right] \qquad (15)$$

where β is the first transfer zone speed. Accumulation of energy in both phases per unit time per unit cross-sectional area across the first transfer zone is given by:

$$G_b\left(\frac{H_{g2}}{1-y_2}-\frac{H_{g3}}{1-y_3}\right)=\beta\left[\epsilon(\rho_{g2}H_{g2}-\rho_{g3}H_{g3})+\rho_b(H_{s2}-H_{s3})\right] \qquad (16)$$

From these two relations and Equations (8) and (9), it follows that

$$\beta = G_b \left(\frac{y_2}{1-y_2} - \frac{y_3}{1-y_3}\right)\left[\rho_b (W_2 - W_3) + \frac{\epsilon P}{R}\left(\frac{y_2}{T_2 + 460} - \frac{y_3}{T_3 + 460}\right)\right]^{-1}$$

$$= G_b \left(\frac{C_{pg2} T_2}{1-y_2} - \frac{C_{pg3} T_3}{1-y_3}\right)\left\{\rho_b \left[(W_2 \Delta H_2 - W_3 \Delta H_3) + C_{ps} (T_2 - T_3) + (C_{pa2} W_2 T_2 - C_{pa3} W_3 T_3)\right] + \frac{\epsilon P}{R}\left(\frac{C_{pg2} T_2}{T_2 + 460} - \frac{C_{pg3} T_3}{T_3 + 460}\right)\right\}^{-1} \quad (17)$$

Similarly for the second transfer zone, we have

$$\beta' = G_b \left(\frac{y_1}{1-y_1} - \frac{y_2}{1-y_2}\right)\left[\rho_b (W_1 - W_2) + \frac{\epsilon P}{R}\left(\frac{y_1}{T_1 + 460} - \frac{y_2}{T_2 + 460}\right)\right]^{-1}$$

$$= G_b \left(\frac{C_{pg1} T_1}{1-y_1} - \frac{C_{pg2} T_2}{1-y_2}\right)\left\{\rho_b \left[(W_1 \Delta H_1 - W_2 \Delta H_2) + C_{ps} (T_1 - T_2) + (C_{pa1} W_1 T_1 - C_{pa2} W_2 T_2)\right] + \frac{\epsilon P}{R}\left(\frac{C_{pg1} T_1}{T_1 + 460} - \frac{C_{pg2} T_2}{T_2 + 460}\right)\right\}^{-1} \quad (18)$$

where β' is the second transfer zone speed. Values of y_2, W_2, T_2, β and β' can be determined from Equations (17) and (18), and adsorption equilibrium equation $y_2 = y^*(W_2, T_2)$ if feed and initial conditions are known.

(B) Concentration and Temperature Gradients

Once the middle zone conditions and zone speed are known, we may proceed to calculate the concentration and temperature profiles of each transfer zone separately. The following derivations are only for the first transfer zone. Since the procedure is entirely the same for the second transfer zone, it will not be repeated here.

Under our constant pattern profile assumption the following relations must be true

$$\left(\frac{\partial z}{\partial t}\right)_y = \left(\frac{\partial z}{\partial t}\right)_W = \left(\frac{\partial z}{\partial t}\right)_T = \beta \tag{19}$$

Integrating the above equations, yields

$$f_1(y) = z - \beta t \tag{19a}$$

$$f_2(W) = z - \beta t \tag{19b}$$

$$f_3(T) = z - \beta t \tag{19c}$$

It follows that y, W and T are functions of $(z - \beta t)$ only. Let

$$x = z - \beta t \tag{20}$$

Then

$$\left(\frac{\partial y}{\partial z}\right)_t = \frac{dy}{dx}\left(\frac{\partial x}{\partial z}\right)_t = \frac{dy}{dx}$$

$$\left(\frac{\partial y}{\partial t}\right)_z = \frac{dy}{dx}\left(\frac{\partial x}{\partial t}\right)_z = -\beta\,\frac{dy}{dx}$$

Similarly, for the functions W and T we have

$$\left(\frac{\partial W}{\partial z}\right)_t = \frac{dW}{dx}, \quad \left(\frac{\partial W}{\partial t}\right)_z = -\beta \frac{dW}{dx}$$

$$\left(\frac{\partial T}{\partial z}\right)_t = \frac{dT}{dx}, \quad \left(\frac{\partial T}{\partial t}\right)_z = -\beta \frac{dT}{dx}$$

By these transformations, Equations (10), (11) and (12) can be reduced to the following ordinary differential equations:

$$G_b \frac{d}{dx}\left(\frac{y}{1-y}\right) - \beta\left[\rho_b \frac{dW}{dx} + \frac{\epsilon P}{R}\frac{d}{dx}\left(\frac{y}{T+460}\right)\right] - \frac{P}{R}\frac{d}{dx}\left(\frac{D}{T+460}\frac{dy}{dx}\right) = 0 \tag{21}$$

$$G_b \frac{d}{dx}\left(\frac{C_{pg}T}{1-y}\right) - \beta\left[\rho_b \frac{d(W\Delta H)}{dx} + \rho_b C_{ps}\frac{dT}{dx} + \rho_b \frac{d(C_{pa}WT)}{dx} + \frac{\epsilon P}{R}\frac{d}{dx}\left(\frac{C_{pg}T}{T+460}\right)\right] - \frac{d}{dx}\left(K\frac{dT}{dx}\right) = 0 \tag{22}$$

$$\frac{dW}{dx} = \frac{k\,a\,p}{\beta\,\rho_b\,R} \cdot \frac{y^* - y}{T+460} \tag{23}$$

Since the constant pattern profiles can only be approached for large distances (as $z \to \infty$) or for large times (as $t \to \infty$), the boundary and initial conditions (13) and (14) reduce to the following conditions:

$$y = y_3,\ W = W_3,\ T = T_3,\ \text{as } x = (z-\beta t)\Big|_{\substack{t\,=\,0 \\ z \to +\infty}} \longrightarrow +\infty \tag{24}$$

$$y = y_2,\ W = W_2,\ T = T_2,\ \text{as } x = (z-\beta t)\Big|_{\substack{t \to \infty \\ z \text{ in middle zone}}} \longrightarrow -\infty \tag{25}$$

Equations (21), (22) and (23), together with boundary conditions (24) and (25), and pertinent adsorption equilibrium equation describe the asymptotic behavior of adiabatic fixed bed adsorption under assumptions made.

Equations (21) and (22) can be easily integrated once. The second integration is usually more difficult and will be discussed in greater detail in the subsequent section. Integrating Equations (21) and (22) once with the aid of boundary condition (24), we obtain

$$\frac{PD}{R(T+460)}\frac{dy}{dx} = G_b\left(\frac{y}{1-y} - \frac{y_3}{1-y_3}\right) - \beta\left[\rho_b(W - W_3) + \frac{\epsilon P}{R}\left(\frac{y}{T+460} - \frac{y_3}{T_3+460}\right)\right] \tag{26}$$

$$K\frac{dT}{dx} = G_b\left(\frac{C_{pg}T}{1-y} - \frac{C_{pg3}T_3}{1-y_3}\right) - \beta\left[\rho_b(W\Delta H - W_3\Delta H_3) + \rho_b C_{ps}(T_2 - T_3) + \rho_b(C_{pa}WT - C_{pa3}W_3T_3) + \frac{\epsilon P}{R}\left(\frac{C_{pg}T}{T+460} - \frac{C_{pg3}T_3}{T_3+460}\right)\right] \tag{27}$$

Equation (23) may also be formally integrated, yielding

$$x = \frac{\beta\rho_b R}{pa}\int_{\overline{W}}^{W} \frac{T+460}{k(y^* - y)}\,dW = \emptyset(W) - \emptyset(\overline{W}) \tag{28}$$

where $\overline{W}$ is defined such that $W = \overline{W}$ as $x = 0$. Asymptotic concentrations and temperature profiles can be obtained from Equations (26) (27) and (28) and the adsorption equilibrium equation. Various special solutions will be discussed in section (C).

The evaluation of $\overline{W}$ in Eq. (28) requires some discussion: Its value can in principle be determined through use of a material balance for the adsorbate over the entire fixed bed (17). Assuming that the constant pattern profiles begin to develop at the start of the operation, we have the following conservation equation for the adsorbate:

$$G_b \left(\frac{y_2}{1-y_2} - \frac{y_3}{1-y_3}\right) t = \rho_b \int_0^\infty (W - W_3)\, dz + \int_0^\infty \epsilon(\rho_g y - \rho_{g3} y_3)\, dz \qquad (29)$$

where $W = W_2$ at $z = 0$.

Since the gas phase accumulation is usually small, we may neglect the last term of Eq. (29). Further, it follows from Equation (28) that W is a function of $\left[x + \phi(\overline{W})\right]$ or $\left[z - \beta t + \phi(\overline{W})\right]$ only. Equation (29) may therefore be written in the following form:

$$G_b \left(\frac{y_2}{1-y_2} - \frac{y_3}{1-y_3}\right) t = \rho_b \int_{-\beta t + \phi(\overline{W})}^{\infty} (W - W_3)\, d\left[x + \phi(\overline{W})\right] \qquad (30)$$

Referring to Fig. 4a, we see that

$$\int_{-\beta t + \phi(\overline{W})}^{\infty} (W - W_3)\, d\left[x + \phi(\overline{W})\right] = -(W' - W_3)\left[-\beta t + \phi(\overline{W})\right] + \int_{W_3}^{W} \phi(W)\, dW \qquad (31)$$

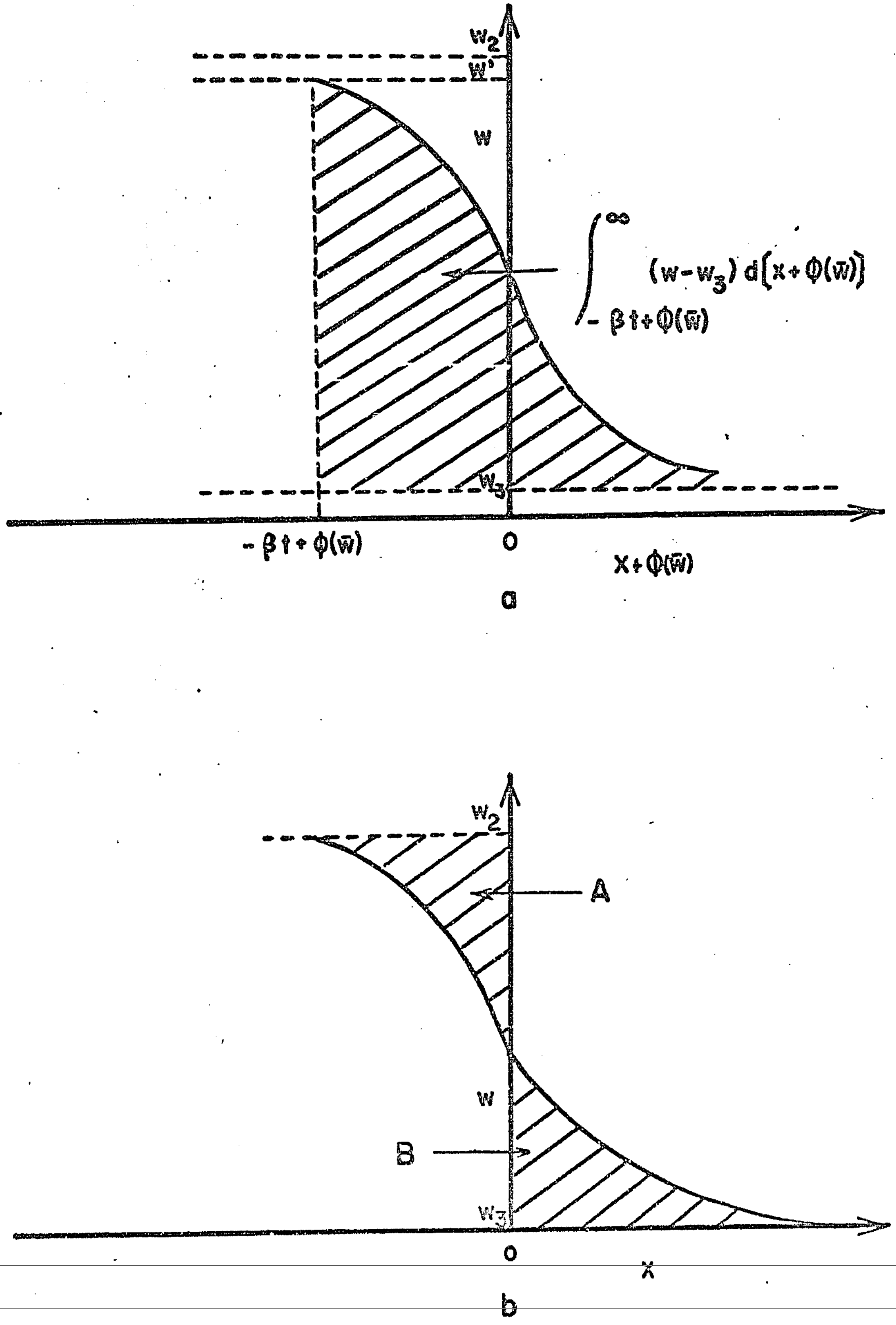

FIG. 4. CONCENTRATION PROFILE IN THE FIRST TRANSFER ZONE

Substituting this relation into Equation (30), yields

$$G_b \left(\frac{y_2}{1-y_2} - \frac{y_3}{1-y_3}\right) t = \rho_b \left\{ (W' - W_3) \left[\beta t - \phi(\overline{W})\right] + \int_{W_3}^{W'} \phi(W)\, dW \right\} \qquad (32)$$

Since t is large, W' approaches W_2 and Eq. (32) becomes

$$\int_{W_3}^{W_2} \phi(W)\, dW - (W_2 - W_3)\, \phi(\overline{W}) = \left[\frac{G_b}{\rho_b} \left(\frac{y_2}{1-y_2} - \frac{y_3}{1-y_3}\right) - \beta (W_2 - W_3)\right] t \qquad (33)$$

From Eq. (17), we see that the right hand side of Eq. (33) is equal to zero, if we neglect the gas phase accumulation term. It follows then, that

$$\phi(\overline{W}) = \frac{1}{W_2 - W_3} \int_{W_3}^{W_2} \phi(W)\, dW \qquad (34)$$

This is the equation used for evaluating $\phi(\overline{W})$ provided Eq. (28) can be integrated analytically. Since $x = \phi(W) - \phi(\overline{W})$, Eq. (34) may also be put into the following form:

$$\int_{W_3}^{W_2} x\, dW = 0 \qquad (35)$$

If Equation (28) cannot be integrated analytically we may use Eq. (35) to estimate the value of $\overline{W}$. Referring to Fig. 4b Eq. (35) means that the area A should be equal to the area B. In the special case where the curve W vs. x is symmetric with respect to the point $W = (W_2 + W_3)/2$, we have $\overline{W} = (W_2 + W_3)/2$. Although the curve W vs. x is not necessarily symmetric with respect to that point, some authors (4, 11) have adopted this simplification in their treatment of the isothermal case.

(C) Special Solutions

We now carry out the second integration of Equations (26) and (27) by introducing additional simplifying assumptions.

Case (a). Negligible Axial Mass Diffusion and Heat Conduction

$(D = 0,\ K = 0,\ k = \text{finite})$

From Equations (26) and (27), we have

$$G_b \left(\frac{y}{1-y} - \frac{y_3}{1-y_3}\right) - \beta \left[\rho_b (W - W_3) + \frac{\epsilon P}{R} \left(\frac{y}{T+460} - \frac{y_3}{T_3 + 460}\right)\right] = 0 \qquad (36)$$

$$\begin{aligned} G_b \left(\frac{C_{pg} T}{1-y} - \frac{C_{pg3} T_3}{1-y_3}\right) - \beta \Big[& \rho_b (W\Delta H - W_3 \Delta H_3) + \rho_b C_{ps} (T - T_3) \\ & + \rho_b (C_{pa} W T - C_{pa3} W_3 T_3) + \frac{\epsilon P}{R} \left(\frac{C_{pg} T}{T+460} - \frac{C_{pg3} T_3}{T_3 + 460}\right)\Big] = 0 \qquad (37) \end{aligned}$$

If we neglect the terms of gas phase accumulation of the adsorbate and energy in Equations (36) and (37) then these equations can be simplified to the following forms:

$$\frac{y}{1 - y} = c W + d \tag{38}$$

$$T = \left\{ \beta \rho_b (1 - y_3)(W \Delta H - W_3 \Delta H_3) + T_3 \left[G_b C_{pg3} - \beta \rho_b (1 - y_3)(C_{ps} + C_{pa3} W_3) \right] \right\} x$$

$$\left\{ G_b C_{pg} - \beta \rho_b (1 - y_3) \left[C_{ps} + C_{pg} W_3 + (C_{pa} - C_{pg}) W \right] \right\}^{-1} \tag{39}$$

where

$$c = \frac{\beta \rho_b}{G_b} \tag{40}$$

$$d = \frac{y_3}{1 - y_3} - \frac{\beta \rho_b}{G_b} W_3 \tag{41}$$

Further, if $C_{pa} = C_{pg}$ = constant, or $(C_{pa} - C_{pg}) W \ll C_{ps}$ then Equation (39) can be reduced to a linear form between T and W:

$$T = e W + f \tag{42}$$

where

$$e = \frac{\beta \rho_b (1 - y_3) \Delta H}{G_b C_{pg} - \beta \rho_b (1 - y_3)(C_{ps} + C_{pg} W_3)} \tag{43}$$

$$f = T_3 - \frac{\beta \rho_b (1 - y_3)\, W_3 \Delta H_3}{G_b C_{pg} + \beta \rho_b (1 - y_3)(C_{ps} + C_{pg} W_3)} \qquad (44)$$

It is seen then that the relations among $y/(1 - y)$, W, and T are all linear provided ΔH is constant.

The concentration profile W as a function of x can be calculated from Equations (28), (36) and (37), and the pertinent adsorption equilibrium equation. In general Equation (28) has to be integrated graphically or numerically, mainly because of the exponential temperature dependence of the equilibrium as shown, for example, by Langmuir's adsorption isotherm (18).

$$y = \frac{k_o}{Pe_o} \left[\frac{2\pi m_a R(T + 460)}{N}\right]^{\frac{1}{2}} \left[\exp \frac{\Delta H'}{R(T + 460)}\right] \frac{W}{W_m - W} \qquad (45)$$

Analytical integration of Equation (28) has so far been found possible only for the following special case:

$$y^* = \frac{(T + 460)\, W}{a' - b W} \qquad \text{Volmer's isotherm} \qquad (46)$$

$y \ll 1$

ΔH = constant

$C_{pa} = C_{pg}$ = constant or $(C_{pa} - C_{pg})\, W \ll C_{pa}$

k = constant

Negligible gas phase accumulation of the adsorbate and energy

The procedure for this case is as follows. Substituting Equations (38), (42) and (46) into Equation (28) and carrying out the integration we obtain for this special case

$$x = \phi(W) - \phi(\overline{W}) = \frac{\beta \rho_b R}{k a P} \left[\frac{Q}{2A} \ln (A W^2 - B W - C) + \left(\frac{E}{\sqrt{q}} - \frac{B Q}{2A \sqrt{q}} \right) \ln \left(\frac{2AW - B - \sqrt{q}}{2AW - B + \sqrt{q}} \right) - F W \right] - \phi(\overline{W}) \tag{47}$$

where

$$A = bc + e \tag{47a}$$

$$B = a'c - bd - f - 460 \tag{47b}$$

$$C = a'd \tag{47c}$$

$$q = B^2 + 4AC \tag{47d}$$

$$Q = a'e - a(f + 460) - \frac{(a'c - bd - f - 460)\, be}{bc + e} \tag{47e}$$

$$E = a'(f + 460) - \frac{a'bde}{bc + e} \tag{47f}$$

$$F = \frac{be}{bc + e} \tag{47g}$$

The integration constant $\phi(\overline{W})$ can be calculated from Equations (34) and (47). The result is

$$\phi(W) = \frac{\beta \rho_b R}{2AkaP(W_2 - W_3)} \left\{ \left(\frac{Q}{2A} + \frac{E}{\sqrt{q}} + \frac{BQ}{2A\sqrt{q}}\right) \left[(2AW - B - \sqrt{q}) \ln (2AW - B - \sqrt{q}\right.\right.$$

$$\left. - (2AW - B - \sqrt{q}) \right] + \left(\frac{Q}{2A} - \frac{E}{\sqrt{q}} - \frac{BQ}{2A}\right) \left[(2AW - B + \sqrt{q}) \ln (2AW - B + \sqrt{q}) \right.$$

$$\left.\left. - (2AW - B + \sqrt{q}) \right] - (Q \ln 4A)\, W - A F W^2 \right\} \Bigg|_{W_3}^{W_2} \qquad (48)$$

Case (b). Negligible Mass Transfer Resistance and Axial Heat

Conduction ($y = y^*$, $K = 0$, $D > 0$)

The mass transfer equation (28) drops out, and we are left with Equations (26) and (37), and the relation $y = y^*$. Formally integrating Equation (26), yields

$$x = \frac{P}{R} \int_{\bar{y}}^{y} D \left\{ (T + 460) \left[G_b \left(\frac{y}{1 - y} - \frac{y_3}{1 - y_3}\right) - \beta \rho_b (W - W_3) \right.\right.$$

$$\left.\left. - \frac{B \epsilon P}{R} \left(\frac{y}{T + 460} - \frac{y_3}{T_3 + 460}\right) \right] \right\}^{-1} dy \qquad (49)$$

where

$$\bar{y} = y^*(\overline{W}, \overline{T}) \doteq y^* \left(\frac{W_2 + W_3}{2}, \frac{T_2 + T_3}{2}\right) \qquad (50)$$

The last relation holds since for $x = 0$, $W = \overline{W} = \frac{W_2 + W_3}{2}$ and consequently from Equation (42) $\overline{T} = \frac{T_2 + T_3}{2}$. The integration of Eq. (49) may be carried out graphically or numerically with the aid of Eq. (37) and adsorption equilibrium data.

Case (c). Negligible Mass Transfer Resistance and Axial Mass Diffusion ($y = y^*$, $D = 0$, $K > 0$)

The mass transfer equation (28) drops out again, and we are left with Equations (27) and (36), and the relation $y = y^*$. Integrating Equation (27), yields

$$x = \int_{\overline{T}}^{T} K \left\{ G_b \left(\frac{C_{ps} T}{1 - y} - \frac{C_{ps3} T_3}{1 - y_3} \right) - \beta \left[\rho_b (W \Delta H - W_3 \Delta H_3) + \rho_b C_{ps} (T - T_3) \right. \right.$$

$$\left. \left. + \rho_b (C_{pa} W T - C_{pa3} W_3 T_3) + \frac{\epsilon P}{R} \left(\frac{C_{ps} T}{T + 460} - \frac{C_{ps3} T_3}{T_3 + 460} \right) \right] \right\}^{-1} dT \quad (51)$$

where $\overline{T}$ can be obtained from the following relation

$$\overline{y} = \left(\frac{y_2}{1 - y_2} + \frac{y_3}{1 - y_3} \right) / \left(\frac{1}{1 - y_2} + \frac{1}{1 - y_3} \right) = y^* (\overline{W}, \overline{T}) = y^* \left(\frac{W_2 + W_3}{2}, \overline{T} \right) \quad (52)$$

Again, this relation holds since for $x = 0$, $W = \overline{W} \doteq \frac{W_2 + W_3}{2}$ and from Equation (38), $\overline{y} \doteq \left(\frac{y_2}{1 - y_2} + \frac{y_3}{1 - y_3} \right) / \left(\frac{1}{1 - y_2} + \frac{1}{1 - y_3} \right)$. The integration of Equation (51) may be carried out graphically or numerically with the aid of Equation (36) and adsorption equilibrium data. Substituting the results together with the relation $y = y^* (W, T)$ into Eq. (36) gives the concentration profile y as a function of x.

Case (d). Negligible Mass Transfer Resistance
$(y = y^*, \ D > 0, \ K > 0)$ Applicable to Beds of Small
Particles With Low Gas Flow Rates

The governing equations for this case are Equations (26) and (27) and $y = y^* (W \ T)$. Dividing Equation (27) by (26), yields

$$\frac{dT}{dy} = \left(\frac{PD}{R(T+460)K}\right) \left\{ G_b \left(\frac{C_{pg} T}{1-y} - \frac{C_{pg3} T_3}{1-y_3}\right) - \beta \left[\rho_b (W\Delta H - W_3 \Delta H_3) + \rho_b C_{ps} (T_2 - T_3) \right.\right.$$

$$\left.\left. + \rho_b (C_{pa} WT - C_{pa3} W_3 T_3) + \frac{\epsilon P}{R} \left(\frac{C_{pg} T}{T+460} - \frac{C_{pg3} T_3}{T_3 + 460}\right) \right] \right\} \times$$

$$\left\{ G_b \left(\frac{y}{1-y} - \frac{y_3}{1-y_3}\right) - \beta \left[\rho_b (W - W_3) + \frac{\epsilon P}{R} \left(\frac{y}{T+460} - \frac{y_3}{T_3+460}\right) \right] \right\}^{-1} \tag{53}$$

It should be noted that Equation (53) is indeterminate at $y = y_2$ and y_3, since both dy/dx and dT/dx in Equations (26) and (27) vanish at these points. Hence there is difficulty in starting the integration from the point y_2 or y_3. A simplified method for resolving this situation is to use the following approximate relation:

$$W = \frac{W_2 + W_3}{2}, \quad T = \frac{T_2 + T_3}{2} \text{ as } y = \left(\frac{y_2}{1 - y_2} + \frac{y_3}{1 - y_3}\right) \Big/ \left(\frac{1}{1 - y_2} + \frac{1}{1 - y_3}\right) \tag{54}$$

This relation is estimated from Equations (26) and (27) and by neglecting the axial diffusion and conduction, and the gas phase accumulation of the adsorbate and energy. Integrating Eq. (53) numerically with the aid of adsorption equilibrium data and the boundary condition (54), and then substituting the results together with the relation $y = y^* (W, T)$ into Equation (49), we can calculate the concentration profile y as a function of x for this case.

Case (e). Finite Mass Transfer Resistance and Non-zero Axial Mass Diffusion and Heat Conduction (k = finite, $D > 0$, $K > 0$)

This is the most general case under the assumptions made and the governing equations are Equations (23), (26) and (27). From these equations we have

$$\frac{dy}{dW} = \frac{\beta \rho_b}{D k a (y^* - y)} \left[\frac{R(T + 460)}{P}\right]^2 \left[G_b \left(\frac{y}{1 - y} - \frac{y_3}{1 - y_3}\right) - \beta \rho_b (W - W_3) - \frac{\beta \epsilon P}{R} \left(\frac{y}{T + 460} - \frac{y_3}{T_3 + 460}\right)\right] \tag{55}$$

$$\frac{dT}{dW} = \frac{\beta \rho_b R (T + 460)}{P K k a (y^* - y)} \left\{ G_b \left(\frac{C_{pg} T}{1 - y} - \frac{C_{pg3} T_3}{1 - y_3}\right) - \beta \left[\rho_b (W \Delta H - W_3 \Delta H_3) + \rho_b C_{ps} (T - T_3) + \rho_b (C_{pa} W T - C_{pa3} W_3 T_3) + \frac{\epsilon P}{R} \left(\frac{C_{pg} T}{T + 460} - \frac{C_{pg3} T_3}{T_3 + 460}\right)\right]\right\} \tag{56}$$

Both Equations (55) and (56) are indeterminate at $W = W_2$ and W_3. The approximate boundary condition (54) used in case (d) can be applied here. Numerical integration, such as the method of Runge-Kutta one-third rule for a system (see Appendix), is needed for solving Equations (55) and (56) to obtain

$$y = f_4(W) \tag{57}$$

$$T = f_5(W) \tag{58}$$

The concentration profile W as a function of x can then be calculated from Equations (28), (57) and (58) and the pertinent adsorption equilibrium equation.

3. Existence of Asymptotic Solutions

There are some limits to the conditions under which the asymptotic solutions exist and these will now be discussed in some detail.

The conditions for the existence of the first constant pattern transfer zone may be found by examining under what conditions solutions of Equations (23), (26) and (27) can satisfy the boundary conditions (24) and (25). The same argument applies to the second constant pattern transfer zone. It should be noted that although Equations (23), (26) and (27) already satisfy the following relations

$$y = y_3, \quad W = W_3, \quad T = T_3, \quad \frac{dy}{dx} = \frac{dW}{dx} = \frac{dT}{dx} = 0 \tag{59}$$

$$y = y_2, \quad W = W_2, \quad T = T_2, \quad \frac{dy}{dx} = \frac{dW}{dx} = \frac{dT}{dx} = 0 \, , \tag{60}$$

this does not mean that solutions of Equations (23), (26) and (27) will satisfy boundary conditions (24) and (25), since it still remains to be proved that $y = y_3$ as $x \rightarrow +\infty$, and $y = y_2$ as $x \rightarrow -\infty$.

In order for the solutions of Eqs. (23), (26) and (27) to satisfy boundary conditions (24) and (25), Equations (23), (26) and (27) must satisfy the following conditions, in addition to conditions (59) and (60).

$$\frac{dy}{dx} < 0, \quad \frac{dW}{dx} < 0, \quad \frac{dT}{dx} < 0, \quad \text{for } y_3 < y < y_2 \tag{61}$$

If $dy/dx = f(y, W, T) < 0$ for $y_3 < y < y_2$, then $1/f(y, W, T)$ is always negative for $y_3 < y < y_2$, and becomes negative infinite as $y \rightarrow y_{3+}$ and $y \rightarrow y_{2-}$, since according to conditions (59) and (60), $dy/dx = 0$ at $y = y_2$, y_3. Now since

$$x = \int_{\bar{y}}^{y} \frac{dy}{f(y, W, T)} \tag{62}$$

it follows that

$$x \rightarrow +\infty, \quad \text{as} \quad y \rightarrow y_3$$

$$x \rightarrow -\infty, \quad \text{as} \quad y \rightarrow y_2$$

Hence, the solution of $dy/dx = f(y, W, T)$, or equivalently of Equation (26), satisfy conditions (24) and (25). The same reasoning applies to Equations (23) and (27).

In fact, the condition (61) can be derived as follows: the condition $dW/dx < 0$, or equivalently $y - y^* > 0$ according to Equation (23), means that there exists a mass transfer driving force for the adsorption process to proceed. This is a necessary condition. Further, since the relations among W, $y/(1 - y)$ and T are usually almost linear as shown by Equations (26) and (27) and case (a), it follows from the condition $\frac{dW}{dx} < 0$ for $y_3 < y < y_2$, that $\frac{dy}{dx} < 0$ and $\frac{dT}{dx} < 0$ in the same interval $y_3 < y < y_2$, must also be necessary conditions.

In the isothermal adsorption case, it has been recognized that the constant pattern concentration profile exists only when the adsorption isotherm concerned is of the favorable type (12). This is because solutions of Equations (23) and (26) can satisfy condition (61) only when the adsorption isotherm concerned is favorable. However, in the adiabatic case, this is not necessarily so, since the temperature variation may have a considerable effect on the concentration profiles. There are some limits to the conditions under which two separate constant pattern transfer zones will arise during adiabatic fixed bed adsorption. As mentioned before, the relations among $y/(1 - y)$, W and T are usually almost linear. It can be easily shown that the adiabatic operating line W vs. y is always somewhat concave upward, but the shape and position of the adiabatic equilibrium curve, W vs. y^* are, in general, strongly dependent on the effects of temperature changes upon the adsorption isotherm, the magnitude of the heat of adsorption, and the operating conditions. Figures 5 and 6 show the various adiabatic operating lines and equilibrium curves obtained by assuming linear relations among $y/(1 - y)$, W and T. For $\bar{W} = (W_2 + W_3)/2$ we have

$$\bar{T} = (T_2 + T_3)/2 \quad \text{and} \quad \bar{y} = \left(\frac{y_2}{1 - y_2} + \frac{y_3}{1 - y_3}\right) / \left(\frac{1}{1 - y_2} + \frac{1}{1 - y_3}\right).$$

It is seen that the effect of temperature changes upon the adsorption isotherm has a considerable effect on the magnitude of the mass transfer driving force $(y - y^*)$. If the adiabatic equilibrium curve always lies to the left of the adiabatic operating line, as shown in Figures 5 and 6, then $(y - y^*)$ is always non-negative over the range concerned, and condition (61) will be satisfied. Consequently the constant pattern transfer zone exists.

A sufficient condition for $(y - y^*) > 0$ in the first transfer zone can be derived as follows. Since we have

$$(y - y^*) = 0, \quad \text{at } T = T_2, T_3 \tag{63}$$

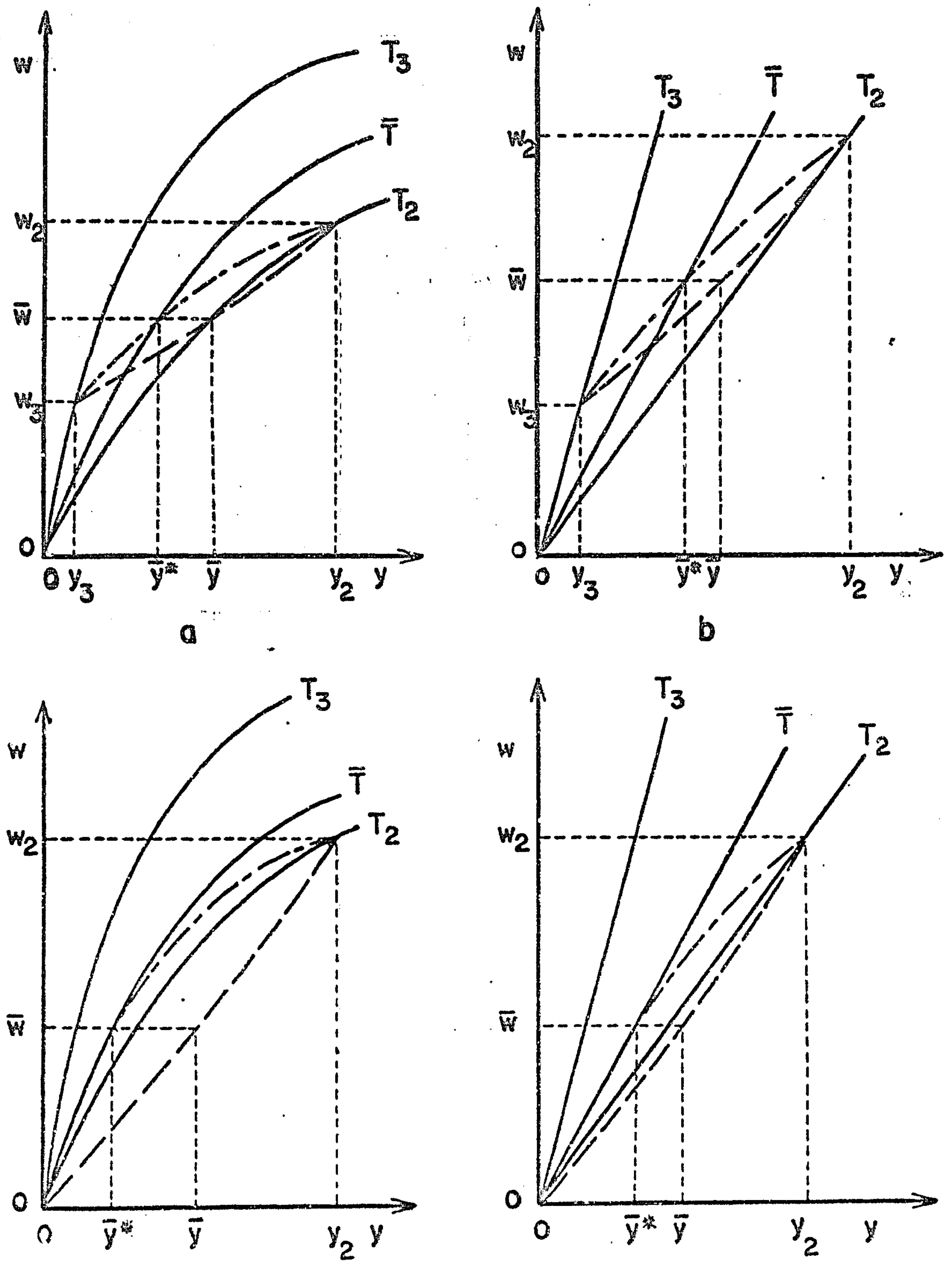

FIG. 5. ADIABATIC OPERATING LINES AND EQUILIBRIUM CURVES IN THE FIRST TRANSFER ZONE

— — — Adiabatic operating line : Eq.(38)

— - — - Adiabatic equilibrium curve

——— Adsorption isotherm

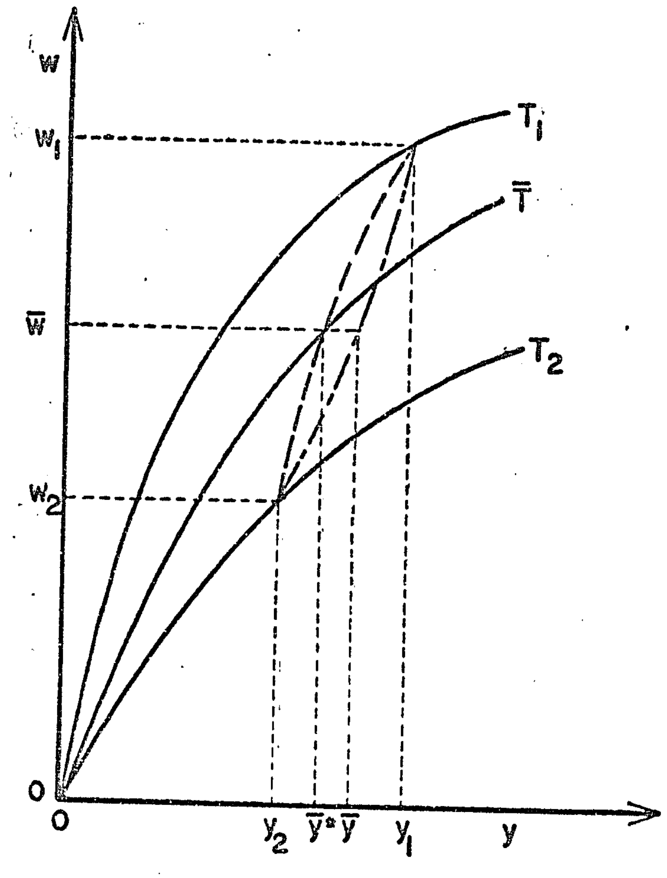

FIG. 6. ADIABATIC OPERATING LINES AND EQUILIBRIUM CURVES IN THE SECOND TRANSFER ZONE

–·–·–·– Adiabatic operating line

— — — Adiabatic equilibrium curve

——— Adsorption isotherm

then if

$$\frac{d^2(y - y^*)}{dT^2} < 0, \quad \text{in } T_3 < T < T_2 \tag{64}$$

$(y - y^*)$ will be always greater than zero in the first transfer zone $(T_3 < T < T_2)$. Now we have

$$\frac{d\left[y - y^*(W, T)\right]}{dT} = \frac{dy}{dT} - \left(\frac{\partial y^*}{\partial T}\right)_W - \frac{dW}{dT}\left(\frac{\partial y^*}{\partial W}\right)_T \tag{65}$$

$$\frac{d^2\left[y - y^*(W, T)\right]}{dT^2} = \frac{d^2y}{dT^2} - \frac{d^2W}{dT^2}\left(\frac{\partial y^*}{\partial T}\right)_W - \left(\frac{\partial^2 y^*}{\partial T^2}\right)_W$$

$$- 2\frac{dW}{dT}\left[\frac{\partial}{\partial T}\left(\frac{\partial y^*}{\partial W}\right)_T\right]_W - \left(\frac{dW}{dT}\right)^2\left(\frac{\partial^2 y^*}{\partial W^2}\right)_T \tag{66}$$

and assuming Equations (38) and (42) hold, and ΔH is a constant, we have

$$\frac{d^2y}{dT^2} = -\frac{2e}{c}\left[T - f + \frac{e}{c}(1 + d)\right]^{-3} \tag{67a}$$

$$\frac{dW}{dT} = \frac{1}{e} > 0 \tag{67b}$$

$$\frac{d^2W}{dT^2} = 0 \tag{67c}$$

It follows then from condition (64) and Equations (66) to (67c) that a sufficient condition for the first constant pattern transfer zone to exist is:

$$\frac{2e}{c}\left[T - f + \frac{e}{c}(1 + d)\right]^{-3} + \left(\frac{\partial^2 y^*}{\partial T^2}\right)_W + \frac{2}{e}\left[\frac{\partial}{\partial T}\left(\frac{\partial y^*}{\partial W}\right)_T\right]_W + \frac{1}{e^2}\left(\frac{\partial^2 y^*}{\partial W^2}\right)_T > 0$$

$$\text{in } T_3 < T < T_2 \qquad (68)$$

The first term in the inequality (68) is positive, the third term is positive for most adsorption isotherms, and the last term is positive and zero for favorable and linear adsorption isotherms respectively. It is clear then that condition (68) can be satisfied by favorable and linear adsorption isotherms if the derivative $\left(\frac{\partial y^*}{\partial T}\right)_W$ increases or decreases slightly with increasing T for the same W. Figures 5a and 5b show that $(y - y^*) > 0$ in the interval $y_3 < y < y_2$ when $\left(\frac{\partial y^*}{\partial T}\right)_W$ decreases slightly with increasing T for the same W. Volmer's isotherm (Eq. (46)) and Langmuir isotherm (Eq. (45)), for example, can be shown to fulfil condition (68). It should be pointed out, however, that condition (68) is not a necessary one in some cases. In the most common case of no initial bed loading ($W_3 = 0$), for example the value of $(y - y^*)$ is <u>always</u> positive in $y_3 = 0 < y < y_2$ for favorable and linear adsorption isotherms that may not even satisfy condition (68). Figures 5c and 5d show that, in this instance, the adiabatic equilibrium curve is by necessity to the left of the adiabatic operating line, since all the pertinent isotherm points through which the adiabatic equilibrium curve passes lie to the left of the adiabatic operating line.

Since the gas phase adsorbate concentration drop over the second transfer zone is usually small, it is better to derive a sufficient condition for the second constant pattern transfer zone to exist in the following form

$$\frac{d^2\left[W^*(y, T) - W\right]}{dT^2} = \left(\frac{\partial^2 W^*}{\partial T^2}\right)_y + \frac{2e'}{c'}\left[T - f' + \frac{e'}{c'}(1 + d')\right]^{-2}\left[\frac{\partial}{\partial T}\left(\frac{\partial W^*}{\partial y}\right)_T\right]_y$$

$$+ \left(\frac{e'}{c'}\right)^2\left[T - f' + \frac{e'}{c'}(1 + d')\right]^{-4}\left(\frac{\partial^2 W^*}{\partial y^2}\right)_T$$

$$- \frac{2e'}{c'}\left[T - f' + \frac{e'}{c'}(1 + d')\right]^{-3}\left(\frac{\partial W^*}{\partial y}\right)_T < 0 \qquad (69)$$

where c', d', e' and f' according to Equations (38) and (42) are

$$c' = \frac{\beta' \rho_b}{G_b} \qquad (70)$$

$$d' = \frac{y_2}{1 - y_2} - \frac{\beta' \rho_b}{G_b} W_2 \qquad (71)$$

$$e' = \frac{\beta' \rho_b (1 - y_2)\, \Delta H}{G_b C_{pg} - \beta' \rho_b (1 - y_2)(C_{ps} + C_{pg} W_2)} \qquad (72)$$

$$f' = T_2 - \frac{\beta' \rho_b (1 - y_2) W_2 \Delta H_2}{G_b C_{pg} - \beta' \rho_b (1 - y_2)(C_{ps} + C_{pg} W_2)} \qquad (73)$$

It should be noted that the term $\left(\frac{\partial W^*}{\partial y}\right)_T$ is always positive, the term

$\left(\frac{\partial^2 W^*}{\partial y^2}\right)_T$ is always negative for favorable adsorption isotherms.

and the term $\left[\frac{\partial}{\partial T}\left(\frac{\partial W^*}{\partial y}\right)_T\right]_y$ is negative for most adsorption isotherms. Since in most cases, $\frac{e'}{c'} < -10^3$, $T - f' < 0$, and $0 < d' < 1$, it is likely that condition (69) will be satisfied by favorable adsorption isotherms if $\left(\frac{\partial^2 W^*}{\partial T^2}\right)_y$ is negative, or equivalently $-\left(\frac{\partial W^*}{\partial T}\right)_y$ increases with increasing T for the same y, as shown in Figure 6. Again it should be emphasized that condition (69) is just a sufficient condition for the second constant pattern transfer zone to exist.

Even if the second constant pattern transfer zone does not exist, i.e., the concentration and temperature profiles in this zone become increasingly diffuse, it is still possible for the profiles in the first transfer zone to reach the asymptotic state provided the bed is long enough for the equilibrium middle zone to form. The asymptotic solutions for the first transfer zone in this case remain unchanged, since Equation (17) and the right hand side relation of Equation (18) are always true as long as an equilibrium middle zone exists behind the first transfer zone. This can be proved by making mass and energy balances between feed inlet and the middle zone as follows:

$$G_b \left(\frac{y_1}{1-y_1} - \frac{y_2}{1-y_2}\right)(t) = \int_0^{z_2} \left[\rho_b (W - W_2) + \frac{\in P}{R}\left(\frac{y}{T+460} - \frac{y_2}{T_2+460}\right)\right] dz$$

$$= z \left[\rho_b (W - W_2) + \frac{\in P}{R}\left(\frac{y}{T+460} - \frac{y_2}{T_2+460}\right)\right] \Bigg|_0^{z_2}$$

$$- \int_{W_1, y_1, T_1}^{W_2, y_2, T_2} z\, d\left[\rho_b (W - W_2) + \frac{\in P}{R}\left(\frac{y}{T+460} - \frac{y_2}{T_2+460}\right)\right]$$

$$= \int_{W_2, y_2, T_2}^{W_1, y_1, T_1} z\, d\left[\rho_b (W - W_2) + \frac{\in P}{R}\left(\frac{y}{T+460} - \frac{y_2}{T_2+460}\right)\right] \qquad (74)$$

where z_2 is in the equilibrium middle zone. Applying the mean value theorem to Equation (74) we obtain

$$\frac{\bar{z}}{t} = G_b \left(\frac{y_1}{1-y_1} - \frac{y_2}{1-y_2}\right)\left[\rho_b (W_1 - W_2) + \frac{\in P}{R}\left(\frac{y_1}{T_1+460} - \frac{y_2}{T_2+460}\right)\right]^{-1} \qquad (75)$$

where $0 < \bar{z} < z_2$. Similarly, for the energy balance, we have

$$\frac{\bar{z}'}{t} = G_b \left(\frac{C_{pg1} T_1}{1-y_1} - \frac{C_{pg2} T_2}{1-y_2}\right)\Bigg\{\rho_b \Big[(W_1 \Delta H_1 - W_2 \Delta H_2) + C_{ps}(T_1 - T_2) + (C_{pa1} W_1 T_1 - C_{pa2} W_2 T_2)\Big] \frac{\in P}{R}\left(\frac{C_{pg1} T_1}{T_1+460} - \frac{C_{pg2} T_2}{T_2+460}\right)\Bigg\}^{-1} \qquad (76)$$

where $0 < \bar{z}' < z_2$. It is seen that both $\bar{z}$ and $\bar{z}'$ are proportional to time. Since the concentration and temperature profiles are always associated together and both $\bar{z}$ and $\bar{z}'$ must be within these profiles no matter how large t, it follows that $\bar{z}$ must be equal to $\bar{z}'$. From Equations (75) and (76) we may obtain the same relation as that on the right hand side of Eq. (18). This proves that the middle zone conditions are not altered, and that consequently the first zone temperature and concentration profiles remain unchanged.

4. Comparison of Theory With Experimental Results

The only available experimental results on near-adiabatic fixed bed adsorption are those obtained by Leavitt (1). The bed in which the adsorption step was carried out was composed of activated Linde Molecular Sieve Type 5 A in the form of pellets 1/8 inch in diameter and about 0.21 inch in average length. The bed length was 5.05 ft. The wall of the adsorbent vessel was kept near 96°F by passing water at 96°F into the water jacket surrounding the vessel. Strictly speaking, the bed was not in an adiabatic condition, but since the bed was large, the heat loss might be negligible for short operating times. The operating conditions given by Leavitt (1) are:

D_b = 0.66 ft.

P = 20.6 psia

ρ_b = 47 lbs./ft.^{3}

G_b = 3.18 lb. mole/hr. ft.^{2}

T_1 = 96° F

T_3 = 91° F

y_1 = 0.132

y_3 = 0

W_1 = 0.00338 lb. mole/lb.

The additional data needed in calculating the concentration and temperature profiles are as follows.

C_{ps} = 0.25 B.t.u./lb. °F (19)

ρ_p = 76.7 lb./ft.^{3}, ϵ_i = 0.374 (Determined by Fuels Division, Department of Mines and Technical Surveys, Ottawa)

a = 308 ft.^{2}/ft.^{3}

ϵ = 0.332

C_{pa} = 8.60 + 0.00245 T (20)

C_{pb} = 6.96 B.t.u./lb. mole °F (21)

$C_{pg} = y\,C_{pa} + (1 - y)\,C_{pb} = 6.96 + 1.64\,y + 0.00245\,y\,T$

$D = 0.457 \left(\frac{T + 460}{537}\right)^{1.82}$ at P = 20.6 psia

$\overline{G}$ = 3.42 lb. mole/(ft.^{2}) (hr.)

ρ_g = 0.00315 lb. mole/ft.^{3}, at 150° F and 20.6 psia

μ = 0.0472 lb./ft. hr. at 150° F for y = 0.066

There is some uncertainty regarding the values of ΔH and D_s. ΔH is obtained from a plot of Clausius-Clapeyron equation:

$$\left[\frac{\partial \ln (Py)}{\partial (\frac{1}{T+460})}\right]_W = \frac{\Delta H'}{R} \tag{77}$$

between 122° F and 212° F (see Figures 7 and 8). We may reasonably assume that we are in the bulk diffusion region (24), and therefore

$$D_s = \epsilon_i^2 D = 0.0639 \left(\frac{T+460}{537}\right)^{1.82} \tag{22}$$

k_f and k_s may be calculated from the following equations(4).

$$\left(\frac{k_f}{\epsilon v}\right) \left(\frac{\mu}{\rho_g D}\right)_f^{\frac{2}{3}} = (0.91)^2 \left(\frac{G}{0.91\ a\ \mu_f}\right)^{-0.51} \tag{78}$$

$$k_s = \frac{5}{3} \left(\frac{a\ D_s}{1-\epsilon}\right) \tag{79}$$

Therefore

$$k_f = 113 \left(\frac{T+460}{537}\right)^{1.21} \tag{80}$$

$$k_s = 53.1 \left(\frac{T+460}{537}\right)^{1.82} \tag{81}$$

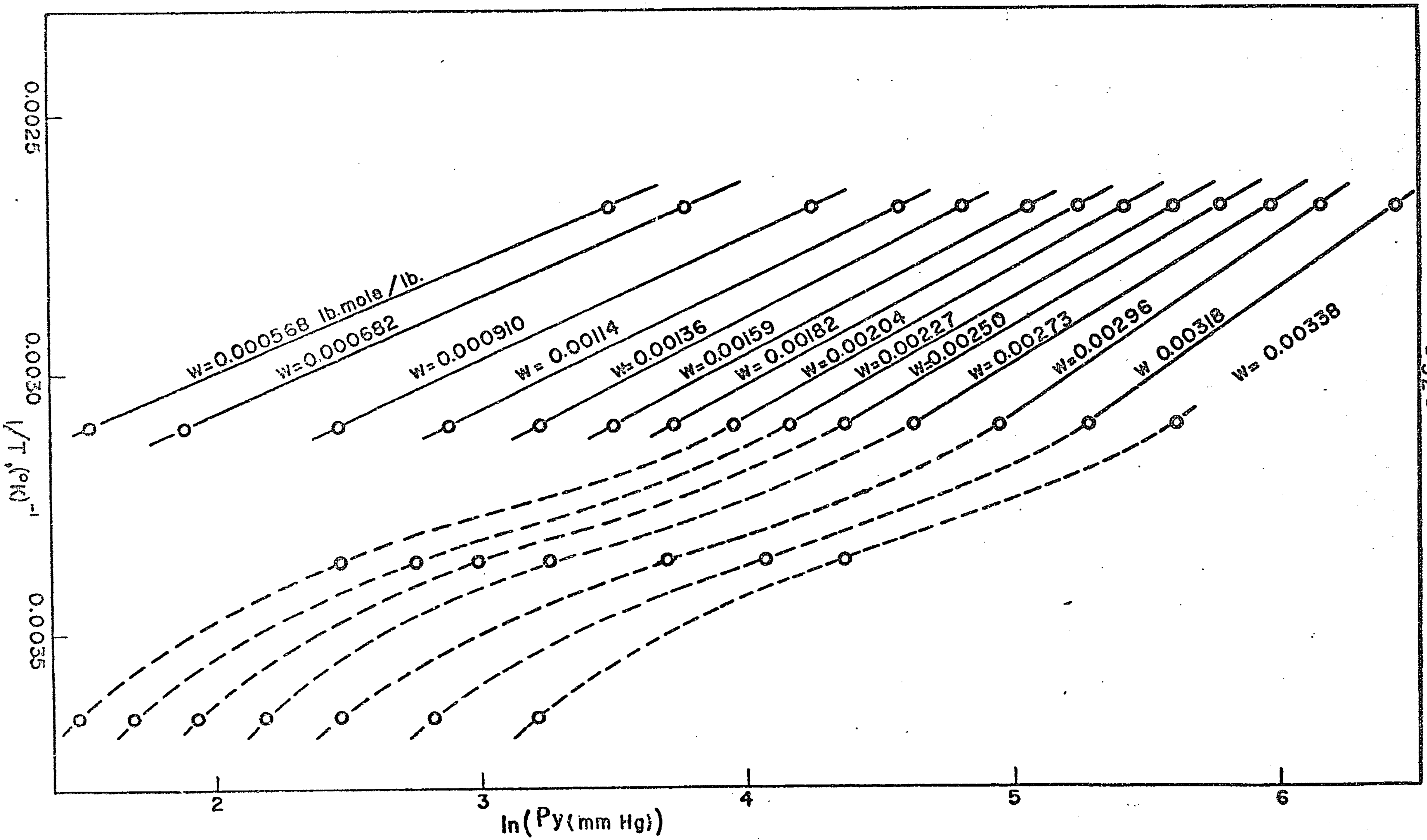

FIG. 7. ADSORPTION ISOSTERES. CO_2 ADSORBED ON MOLECULAR SIEVE TYPE 5A (23)

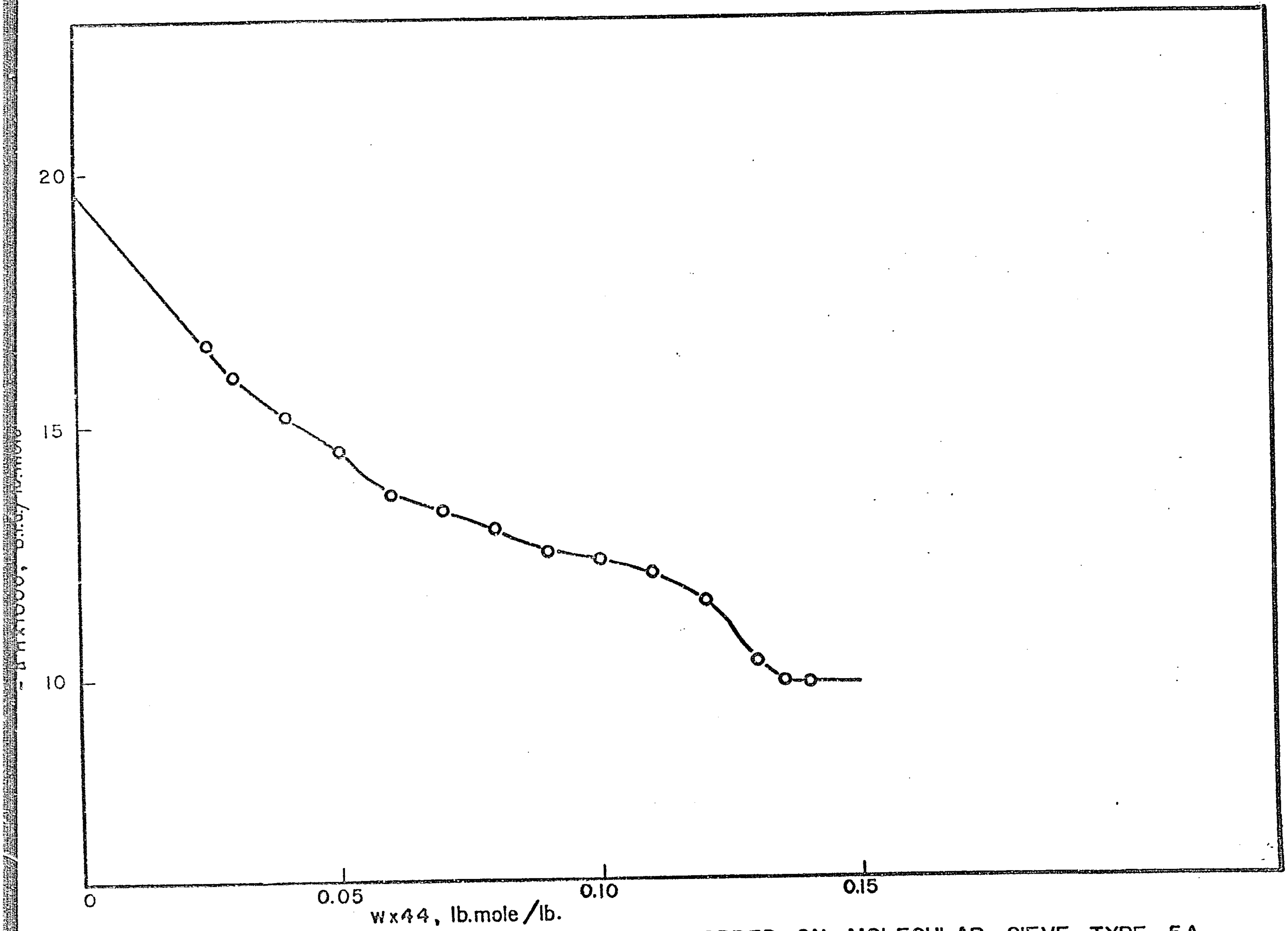

FIG. 8. DIFFERENTIAL HEAT OF ADSORPTION. CO_2 ADSORBED ON MOLECULAR SIEVE TYPE 5A

Since

$$k = \left(\frac{1}{k_f} + \frac{1}{k_s}\right)^{-1} \tag{82}$$

it follows that

$$k = \left[0.00885\left(\frac{537}{T + 460}\right)^{1.21} + 0.0188\left(\frac{537}{T + 460}\right)^{1.82}\right]^{-1} \tag{83}$$

(A) Determination of the Middle Zone Conditions and Transfer Zone Speeds

From Equations (17) and (18) we have

$$\frac{\dfrac{y_2}{1 - y_2}}{W_2} = \frac{\dfrac{C_{pg2}T_2}{1 - y_2} - 633}{W_2 \Delta H_2 + 0.25\,(T_2 - 91) + C_{pa2} W_2 T_2} \tag{84}$$

$$\frac{0.152 - \dfrac{y_2}{1 - y_2}}{0.00338 - W_2} = \frac{798 - \dfrac{C_{pg2}T_2}{1 - y_2}}{0.25(96 - T_2) - (\Delta H_2 + C_{pa2}T_2)\,W_2 - 41.9} \tag{85}$$

Solving Equations (84) and (85) with the aid of Figures 7 and 8 for y_2, T_2 and W_2, we obtain the middle zone conditions as follows

$y_2 = 0.104$

$W_2 = 0.00127$ lb. mole/lb.

$T_2 = 210°F$

Again from Equations (17) and (18), we have

$\beta = 6.20$ ft./hr.

$\beta' = 1.15$ ft./hr.

If the concentration profiles are very sharp, then the breakthrough time of the adsorbate can be simply obtained as follows

$$t_b = \frac{z}{\beta} = \frac{5.05}{6.20} = 0.815 \text{ hr.}$$

$$t_b' = \frac{z}{\beta'} = \frac{5.05}{1.15} = 4.40 \text{ hr.}$$

(B) Determination of the Concentration and Temperature Profiles in the First Transfer Zone

For this system we may reasonably assume zero axial mass diffusion and heat conduction (Case (a)). From Equations (38), (39) and (28), we obtain

$$y = \frac{91.6\ W}{1 + 91.6\ W} \tag{86}$$

$$T = \frac{4610 - 292\ W\Delta H}{72.8 - 3.18\ C_{pg} + 292\ W\ (C_{pa} - C_{pg})} \tag{87}$$

$$x = 0.492 \int_{\frac{0.00127}{2}}^{W} \frac{T + 460}{k\ (y^* - y)}\ dW \tag{88}$$

Values of y, T and W at any x can be calculated from Equations (83), (86), (87) and (88) with the aid of Figures 7 and 8. Figures 9 and 10 show the calculated temperature and concentration profiles in the first transfer zone as functions of x.

(C) Determination of the Concentration and Temperature Profiles in the Second Transfer Zone

Following the same procedure and similar equations as in the previous section, we obtain

$$y = \frac{17\,W + 0.0945}{17\,W + 1.0945} \tag{89}$$

$$T = \frac{3130 + 48.4\,W\Delta H}{3.12\,C_{pg} - 48.4\,(C_{pa} - C_{pg})\,W - 12.1} \tag{90}$$

$$x = 0.0912 \int_{\frac{(0.00338 + 0.00127)}{2}}^{W} \frac{T + 460}{k\,(y^{*} - y)}\,dW \tag{91}$$

Figures 9 and 10 show the calculated temperature and concentration profiles in the second transfer zone as functions of x'.

(D) Comparison of Calculated Results With Experimental Results

The experimental results obtained by Leavitt are shown in Figures 11 and 12. The middle zone conditions are: $T_2 = 200°F$,

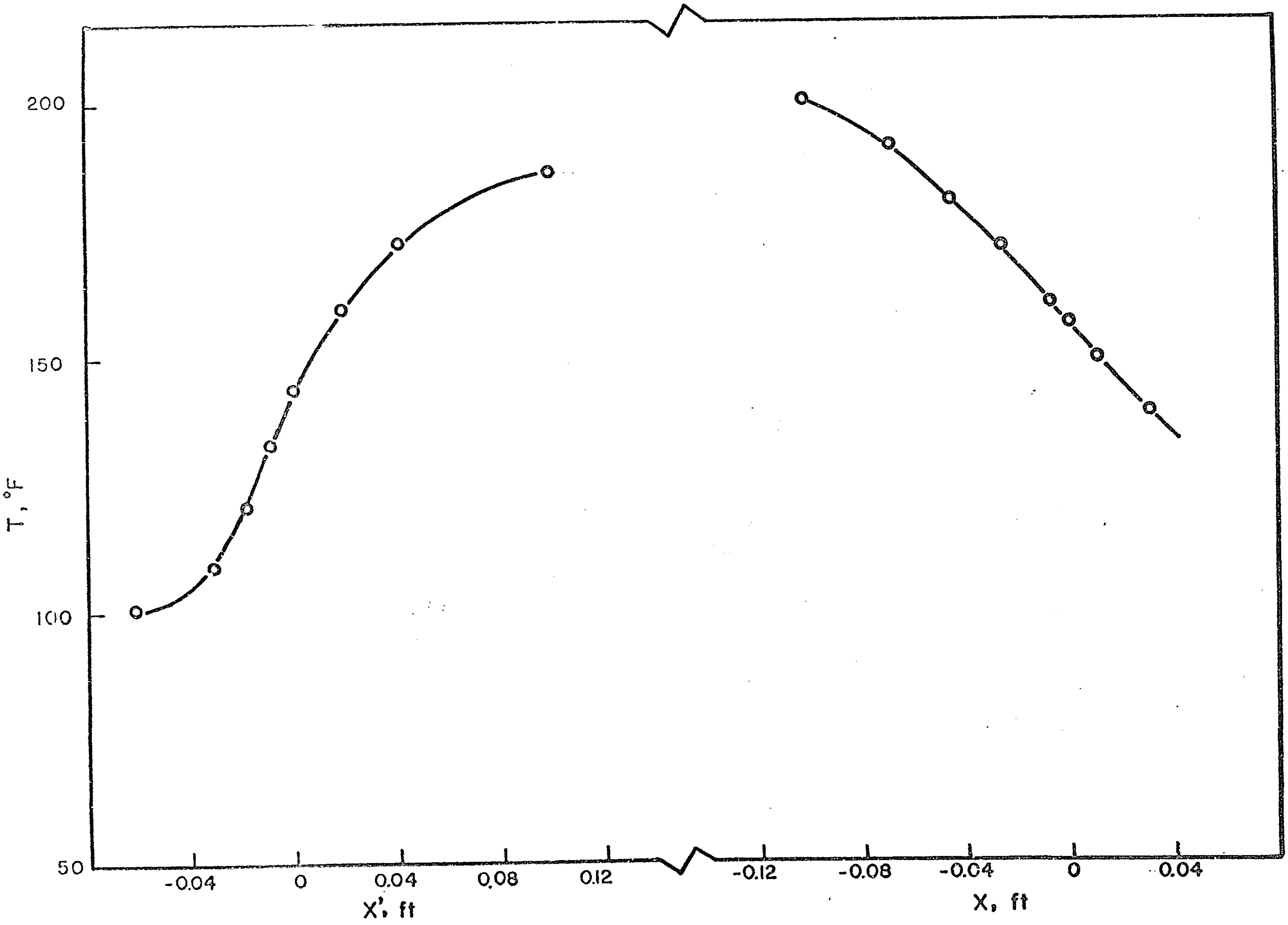

FIG. 9 CALCULATED TEMPERATURE PROFILE

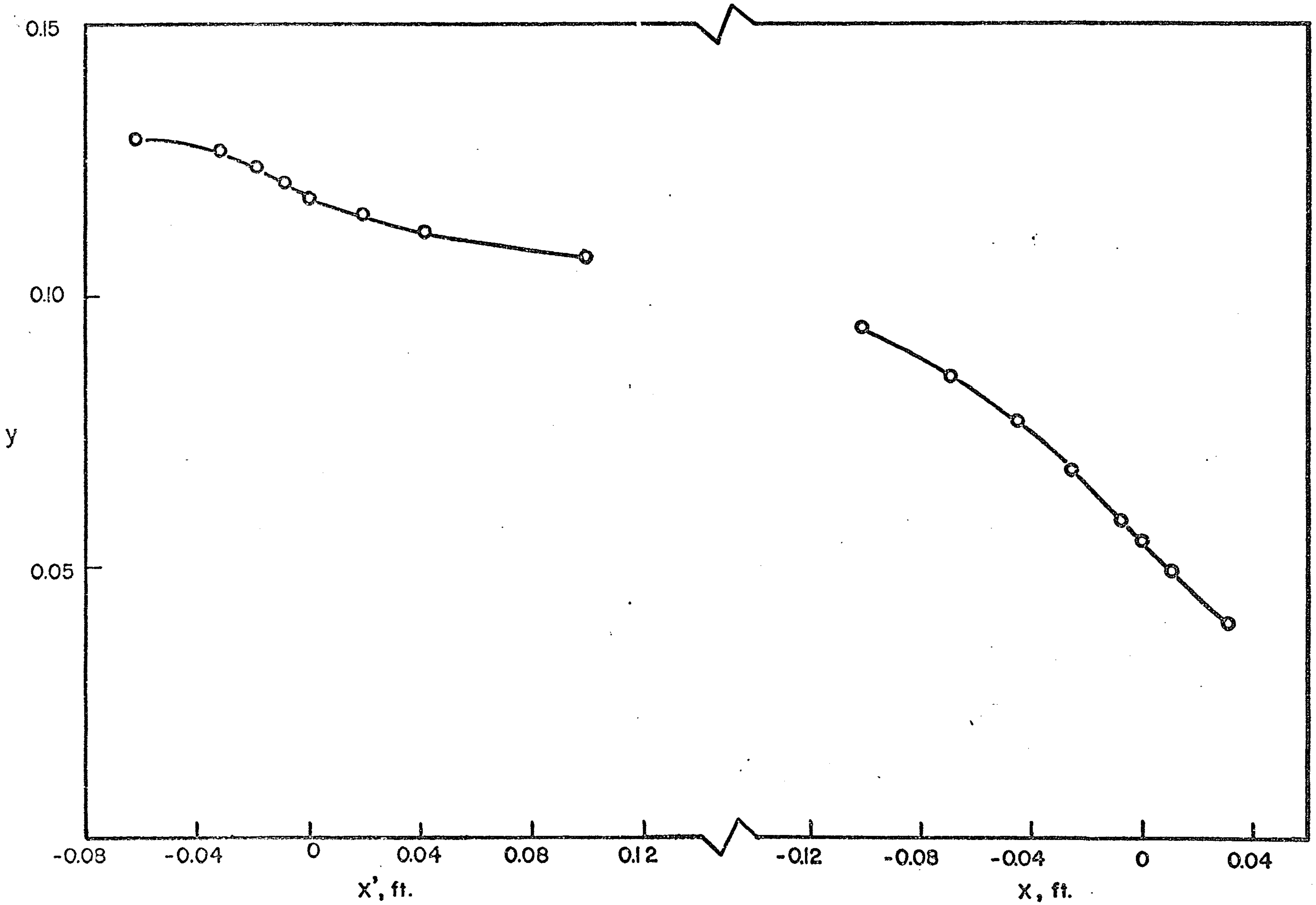

FIG. 10. CALCULATED GAS PHASE CONCENTRATION PROFILE

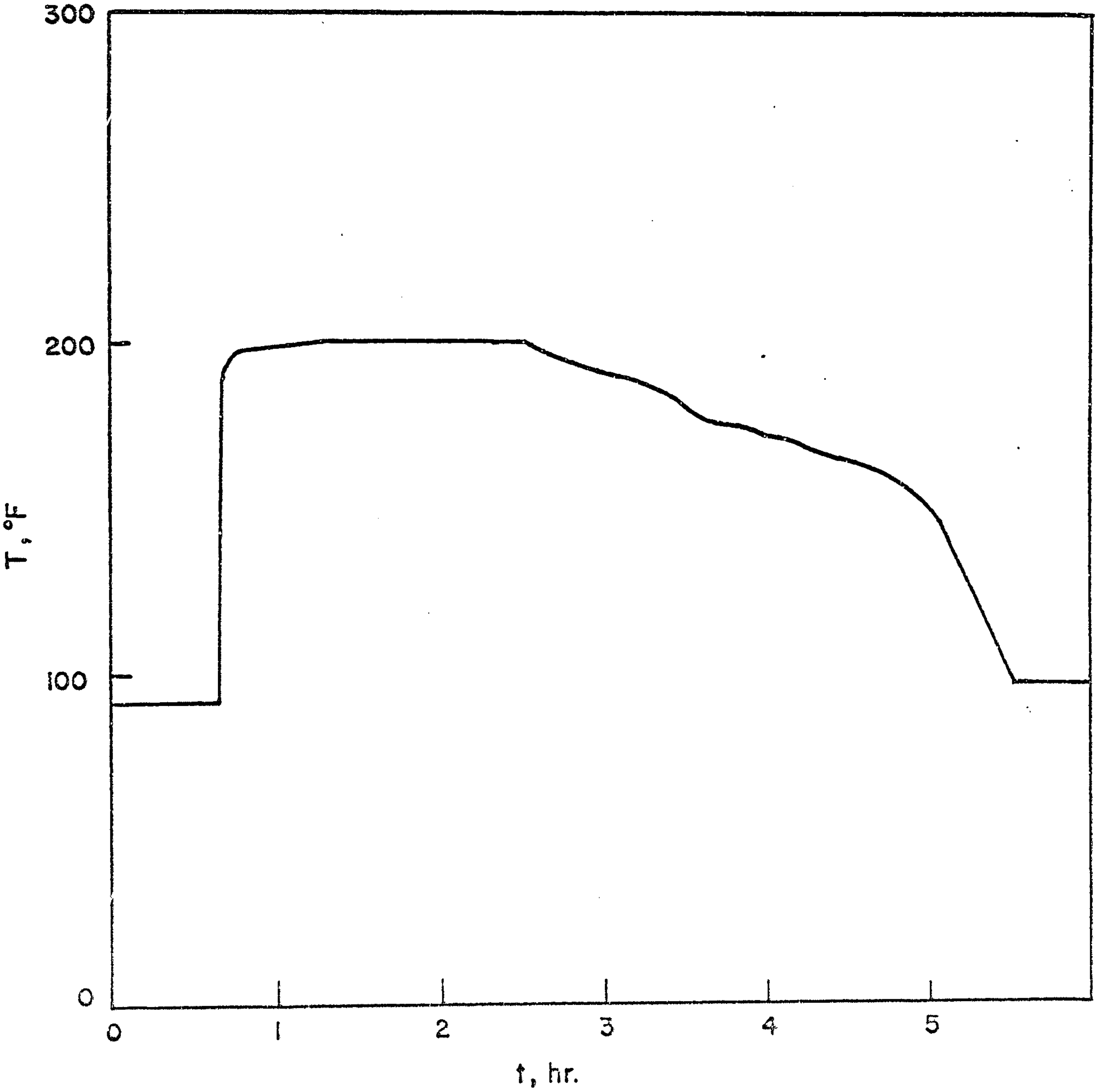

FIG. 11. MEASURED TEMPERATURE IN ADSORBENT BED, 2 IN. FROM EXIT END (1)

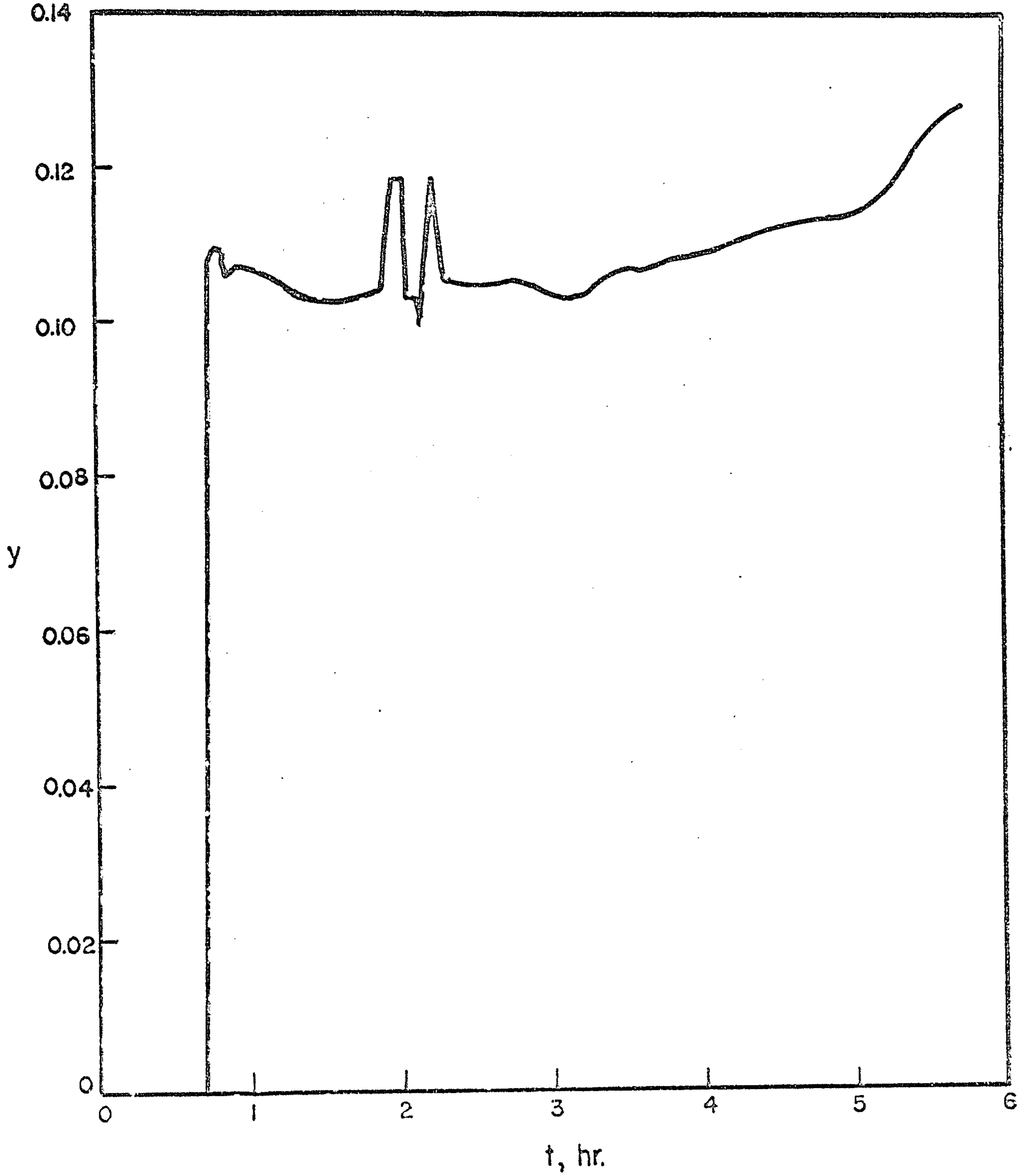

FIG. 12. MEASURED COMPOSITION OF EFFLUENT GAS FROM ADSORBENT BED (I)

$y_2 = 0.105$. The breakthrough time of the first transfer zone is about 0.7 hr.*, and the concentration and temperature profiles in this zone are extremely sharp. Unfortunately Leavitt does not report his profiles with sufficient accuracy to permit a comparison with the calculated profiles shown in Figures 9 and 10.

It should be pointed out that the comparison of calculated results with experimental results can only be rough, since there is some uncertainty regarding the values of ΔH and D_s. The calculated middle zone conditions are: $T_2 = 210°F$, $y_2 = 0.104$. The calculated concentration and temperature profiles in both transfer zones are very sharp, and the breakthrough times are 0.815 hr. for the first zone, and 4.40 hr. for the second zone. All the calculated results are in reasonably good agreement with Leavitt's measured values. It should be noted that the decreasing temperature after 2.5 hr. shown in Figure 11 is due to heat loss to the bed wall as pointed out by Leavitt (1).

---

* In Leavitt's original paper presented at an A. I. Ch. E. meeting, the breakthrough time of the first transfer zone is 0.8 hr.

V DISCUSSION OF RESULTS

1. Strictly speaking, constant pattern profiles are only approached asymptotically in very long fixed beds, but in practice, they may be considered as approximate solutions to actual adiabatic adsorbers.

2. The breakthrough time for any adsorbate concentration level can be calculated from the asymptotic solution and the height of the fixed bed. Since it takes time for the two constant pattern transfer zones to form and separate from each other, the breakthrough time can only be approximately predicted by the asymptotic solutions based on the assumption that the two constant pattern transfer zones begin to develop at the start of the bed operation (this assumption is needed in calculating $\overline{W}$, see Equation (29)), or equivalently the ratio of the bed length passed by the first transfer zone to that passed by the second transfer zone is always equal to the speed ratio β/β'. However, since the speed of the second transfer zone is usually much slower than that of the first transfer zone (1), the error associated with the first zone breakthrough time predicted by the asymptotic solution would be small, provided the fixed bed is not very short.

3. It should be noted that the breakthrough time can be simply obtained by dividing the height of the fixed bed with the first transfer zone speed if the adsorbate concentration profile in that zone is very sharp, or if the breakthrough concentration is defined as

$$y = \left(\frac{y_2}{1 - y_2} + \frac{y_3}{1 - y_3}\right) / \left(\frac{1}{1 - y_2} + \frac{1}{1 - y_3}\right)$$

Since at $x = 0$, or $t = \frac{z}{\beta}$, y is approximately equal to the above value for most cases.

4. If the feed conditions happen to be the same as that of the middle zone, then there is only one constant pattern transfer zone in the bed, namely the first transfer zone. The asymptotic solutions, in this case, exist for most linear and favorable adsorption isotherms, and give very accurate breakthrough times if the fixed bed is long enough to reach its asymptotic state.

VI CONCLUSIONS

1. A mathematical model was developed for the adiabatic operation of a fixed-bed adsorber, and asymptotic solutions to the governing partial differential equations were investigated under the assumption of two constant pattern transfer zones as the ultimate dynamic behavior of the adiabatic fixed bed adsorption.

2. There are some limitations to the existence of two constant pattern transfer zones. It was found that the first constant pattern transfer zone exists for most ~~linear~~ and favorable adsorption isotherms. The second constant pattern transfer zone exists, in most cases, when the absolute value of the derivative, $(\partial W^*/\partial T)_y$ of the adsorption isotherm increases with increasing T for the same y. Nevertheless, even if the second constant pattern transfer zone does not exist, the solutions for the first constant pattern transfer zone are still useful in fixed bed design work provided the bed is long enough for the equilibrium middle zone to form behind the first transfer zone.

NOMENCLATURE

A = defined by Eq. (47a)

a = mass transfer area per unit volume of adsorbent bed, sq. ft./cu. ft.

a' = constant in Volmer's isotherm, Eq. (46)

B = defined by Eq. (47b)

b = constant in Volmer's isotherm, Eq. (46)

C = defined by Eq. (47c)

C_{pa} = mean heat capacity of the adsorbate as a gas between 0°F and T, B.t.u./(lb. mole) (°F)

C'_{pa} = heat capacity of the adsorbate as a gas at temperature T, B.t.u./(lb. mole) (°F)

C_{pb} = mean heat capacity of the carrier gas between 0°F and T B.t.u./(lb. mole) (°F)

C'_{pb} = heat capacity of the carrier gas at temperature T B.t.u./(lb. mole) (°F)

C_{pg} = mean heat capacity of the gas mixture of composition y between 0°F and T, B.t.u./(lb. mole) (°F)

C_{ps} = heat capacity of the adsorbent, B.t.u./(lb.) (°F)

c = defined by Eq. (49)

c' = defined by Eq. (70)

D = effective axial diffusivity sq. ft./hr.

D_s = effective diffusivity through the stationary phase, sq. ft./hr.

D_b = fixed bed diameter, ft.

d = defined by Eq. (41)

d' = defined by Eq. (71)

E = defined by Eq. (47f)

e = defined by Eq. (43)

e' = defined by Eq. (72)

F = defined by Eq. (47g)

f = defined by Eq. (44)

f' = defined by Eq. (73)

$\overline{G}$ = average superficial flow rate of the gas mixture lb. mole/(hr.) (sq. ft.)

G_b = superficial flow rate of the carrier gas lb. mole/(hr.) (sq. ft.)

H_g = enthalpy of the gas mixture, defined by Eq. (8) B.t.u./lb. mole

H_s = enthalpy of the adsorbent plus the adsorbate adsorbed, defined by Eq. (9), B.t.u./lb. adsorbent

K = effective axial thermal conductivity B.t.u./(ft.) (hr.) (°F)

k = overall mass transfer coefficient ft./hr.

k_f = gas phase mass transfer coefficient ft./hr.

k_o = desorption rate constant

k_s = stationary phase mass transfer coefficient ft./hr.

m_a = mass of adsorbate molecule

N = Avogadro's number, molecule/lb. mole

P = operating pressure of the fixed bed, psia

q = defined by Eq. (47d)

Q = defined by Eq. (47e)

R = gas constant (psia) (cu. ft.)/(lb. mole) (°F)

T = temperature, °F

$\overline{T}$ = value of T at $x = 0$, °F

t = time, hr.

t_b = breakthrough time of the first transfer zone, hr.

t'_b = breakthrough time of the second transfer zone, hr.

t_o = time required for the equilibrium middle zone to form, hr.

v = superficial linear velocity of the gas mixture, ft./hr.

W = loading of the adsorbate on the adsorbent lb. mole/ lb. adsorbent

W^* = loading of the adsorbate on the adsorbent in equilibrium with y at temperature T, lb. mole/lb. adsorbent

$\overline{W}$ = value of W at $x = 0$, lb. mole/lb. adsorbent

W_m = loading of the adsorbate on the adsorbent when the adsorbent surface is covered with a complete unimolecular layer, lb. mole/lb. adsorbent

x = distance coordinate, defined by Eq. (20), ft.

x' = $z - \beta' t$, ft.

y = mole fraction of the adsorbate in the gas phase

$\bar{y}$ = value of y at $x = 0$

y^* = mole fraction of the adsorbate in the gas phase in equilibrium with the solid phase concentration W at temperature T

z = axial distances from column inlet in direction of flow, ft.

$\bar{z}$ = defined by Eq. (75)

$\bar{z}'$ = defined by Eq. (76)

$\Delta H'$ = differential heat of adsorption, B.t.u./lb. mole

$(W\Delta H)$ = integral heat of adsorption when the loading of the adsorbate on the adsorbent is W at temperature T, B.t.u./lb. adsorbent

α_o = condensation coefficient on the bare adsorbent surface

β = speed of the first constant pattern mass transfer zone, ft./hr.

β' = speed of the second constant pattern mass transfer zone, ft./hr.

ϵ = fixed bed porosity, cu. ft./cu. ft.

ϵ_i = macropore volume of the adsorbent, cu. ft./cu. ft.

ρ_b = bulk density of the adsorbent, lb./cu. ft.

ρ_g = gas phase density, lb. mole/cu. ft.

ρ_p = adsorbent particle density, lb./cu. ft.

μ = gas phase viscosity, lb./(ft.) (hr.)

ϕ = function defined by Eq. (28)

Subscripts

1 = refers to the feed conditions

2 = refers to the equilibrium middle zone conditions

3 = refers to the initial bed conditions

REFERENCES

1. Leavitt, F.W., Chem. Eng. Progr. 58, 54 (1962)
2. Acrivos, A., Ind. Eng. Chem. 48, 703 (1956)
3. Basmadjian, D., Can. J. Chem. Eng. 41, 269 (1963)
4. Lightfoot, E.N., Sanchez-Palma, R.J., and Edwards, D.O., "Chromatography and Allied Fixed Bed Separations Processes", New Chemical Engineering Separation Techniques, Schoen, H.M., ed., Interscience Publishers, New York, 1962
5. Lapidus, L., and Rosen, J.B., Ion Exchange, Chem. Eng. Progr. Symposium Series 50, No. 14, 97 (1954)
6. Rosen, J.B., J. Chem. Phys. 20, 387 (1952)
7. Thomas, H.C., J. Am. Chem. Soc., 66, 1664 (1944)
8. De Vault, D., J. Am. Chem. Soc. 65, 532 (1943)
9. Michaels, A.S., Ind. Eng. Chem. 44, 1922 (1952)
10. Hougen, O.A., and Marshall, W.R., Chem. Progr. 43, 197 (1947)
11. Acrivos, A., Chem. Eng. Sci. 13, 1 (1960)
12. Cooney, D.O., and Lightfoot, E.N., Ind. Eng. Chem. Fundamentals 4, 233 (1965)
13. Bowen, J.H., and Donald, M.B., Chem. Eng. Sci. 18, 599 (1963)
14. Loschelt, C.P., Ph.D. thesis, Louisiana State University, 1964
15. Vermeulen, T., "Separation by Adsorption Methods", Advances in Chemical Engineering, Vol. II, Drew, T.B., and Hoopers, J.W., Jr., eds., Academic Press, New York, 1958
16. Gonzales, L.O., and Spencer, E.H., Chem. Eng. Sci. 18, 753 (1963)

17. Tychonov, A. N., and Samarski, A. A., Partial Differential Equations of Mathematical Physics; Tr. by Redding, S., pp 140 - 149, Holden-Day, San Francisco, 1964

18. Brunauer, S., The Adsorption of Gases and Vapors, p. 64, Princeton University Press, Princeton, N. J., 1945

19. Hersh, C. K., Molecular Sieves, p. 55, Reinhold Publishing Corporation, New York, 1961

20. Din, F., Thermodynamic Functions of Gases, Vol. 1, p. 125, Butterworths, London, 1956

21. Ibid., Vol. 3, p. 151 (1961)

22. Wakao, N., and Smith, J. M., Chem. Eng. Sci. 17, 828 (1962)

23. Linde Molecular Sieves Isotherm Data Sheet No. SD 22 and 23, Tonawanda Development Laboratory, Linde Company

24. Chu, K. P., M. Sc. thesis, University of Ottawa, 1963

APPENDIX

Runge-Kutta One Third Rule for a System:

For the following system

$$\frac{dy}{dW} = f_4 \ (y, T, W)$$

$$\frac{dT}{dW} = f_5 \ (y, T, W)$$

we have

$$\Delta y = \frac{1}{6} \ (\Delta' y + 2\,\Delta'' y + 2\,\Delta''' y + \Delta'''' y)$$

$$\Delta T = \frac{1}{6} \ (\Delta' y + 2\,\Delta'' T + 2\,\Delta''' T + \Delta'''' T)$$

where

$$\Delta y = y\,(W + h) - y\,(W)$$

$$\Delta T = T\,(W + h) - T\,(W)$$

$$\Delta' y = h f_4 \,(y, T, W)$$

$$\Delta' T = h f_5 \,(y, T, W)$$

$$\Delta'' y = h f_4 \,(W + \frac{h}{2}, \ y + \frac{\Delta' y}{2}, \ T + \frac{\Delta' T}{2})$$

$$\Delta'' T = h f_5 \,(W + \frac{h}{2}, \ y + \frac{\Delta' y}{2}, \ T + \frac{\Delta' T}{2})$$

$$\Delta''' y = h f_4 \,(W + \frac{h}{2}, \ y + \frac{\Delta'' y}{2}, \ T + \frac{\Delta'' T}{2})$$

$$\Delta''' T = h f_5 \,(W + \frac{h}{2}, \ y + \frac{\Delta'' y}{2}, \ T + \frac{\Delta'' T}{2})$$

$$\Delta''''y = hf_4 (W + h, y + \Delta'''y, T + \Delta'''T)$$

$$\Delta''''T = hf_5 (W + h, y + \Delta'''y, T + \Delta'''T)$$