CHAPTER 3

DETERMINATION OF ADSORPTION RATE CONSTANTS OF METHANE , PROPANE ,

AND CARBONDIOXIDE ON MOLECULAR SIEVE CARBON -5A

3.1 The determination of adsorption rate constants

The design of fixed-bed adsorbers for fluid-solid systems must use the concentration-time , or breakthrough curve , of the effluent stream. The mechanisms of gas adsorption in fixed beds are as follows[9].

a) Diffusion of the component from the main body of the gas phase to the external surface of the adsorbent particle (external diffusion).

b) Diffusion through the porous network of the particle (internal diffusion).

c) The adsorption process itself.

The purpose of this study is to find the values of the diffusion coefficients and adsorption rate constants that describe the three steps using chromatographic measurements. The overall validity of the methods can be ascertained by comparing breakthrough curves measured experimentally with those predicted using the rate constants.

3.1.1 The initial equations and assumptions.

The assumptions used in this study are as follows

1.   Adsorption   is   proportional to   the   gas   —
phase concentration and independent of the fraction of the
surface   covered   with   adsorbate.   Thus   the   equilibrium
relationship between adsorbed molecules and those in the gas
phase is linear. This is a reasonable assumption for small
concentrations.

2. Axial diffusion in the bed is negligible.

3. Concentrations do not vary in the radial direction.

With   these   restrictions the concentration C(Z,t)   is
determined as follows (derivations of the following equations
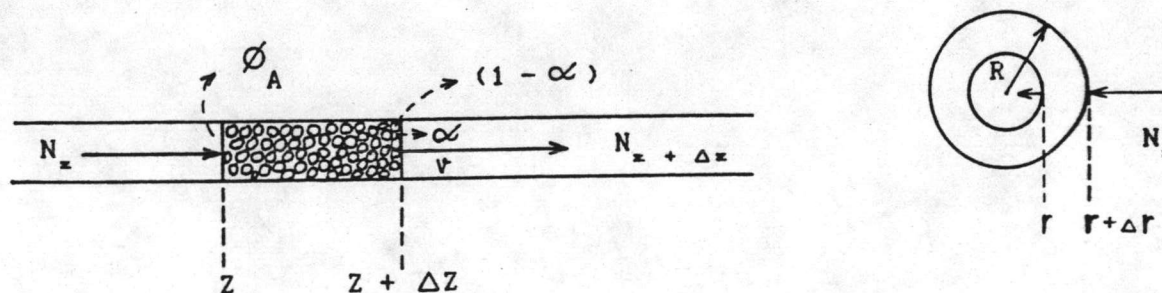are   shown   in appendix c)

Figure 3.1 Component balance in gas phase and in
particles.

the component balance in the gas phase may be written as

$$\frac{1}{\alpha} E_A \frac{\partial^2 C}{\partial Z^2} - \frac{v}{\alpha} \frac{\partial C}{\partial Z} - \frac{\partial C}{\partial t} - \frac{3D_c}{\alpha} \frac{(1-\alpha)}{\alpha} \left(\frac{\partial C_1}{\partial r}\right)_{r=R} = 0 \qquad (3.1)$$

the component balance in the particles may be written as

$$\frac{D_c}{\beta} \frac{2}{R} \frac{\partial C_1}{\partial r} + \frac{\partial^2 C_1}{\partial r^2} - \frac{\partial C_1}{\partial t} - \frac{\rho_p}{\beta} \frac{\partial C_{ads}}{\partial t} = 0 \qquad (3.2)$$

and the rate of adsorption (assumed to be linear) is given as

$$\frac{\partial C_{ads}}{\partial t} = k_{ads} (C_1 - C_{ads}/K_A) \qquad (3.3)$$

the external diffusion boundary condition is given as

$$D_c \left(\frac{\partial C_1}{\partial r}\right)_{r=R} = k_f (C - C_1) \qquad (3.4)$$

and the internal diffusion boundary condition is given as

$$\frac{\partial C_1}{\partial r} = 0 \quad at \quad r = 0 \quad for \quad t > 0 \qquad (3.5)$$

and the initial conditions are

$$C = 0 \quad at \quad Z > 0 \quad for \quad t = 0 \qquad (3.6)$$

$$C_1 = 0 \quad at \quad r >= 0 \quad for \quad t = 0 \qquad (3.7)$$

Conditions (3.6) and (3.7) state that the adsorbent does not contain any adsorbed species as the start of the run. Then condition (3.8) specifies that at the bed inlet the

concentration of the adsorbable species is maintained constant , thus

$$C = C_o \quad \text{at} \quad Z = 0 \quad \text{for} \quad t > 0 \qquad (3.8)$$

For the case where only intraparticle diffusion is significant and neglecting axial dispersion ($E_A = 0$) we have

$$v\frac{\partial C}{\partial Z} + \alpha \frac{\partial C}{\partial t} + \frac{3D_e}{R}\frac{\rho_B}{\rho_p}\left(\frac{\partial C_1}{\partial r}\right)_{r = R} = 0 \qquad (3.9)$$

Now application of the Laplace transform reduces the problem to the solution of the following expression[21]

$$\frac{C(Z,t)}{C_o} = \frac{1}{2} + \frac{2}{\pi}\int_o^\infty \frac{1}{y}\exp[A_1(y)]\sin[A_2(y)]\,dy \qquad (3.10)$$

with

$$A_1(y) = -3D[w_1 + E(w_1 + w_2)]/[(1 + Ew_1)^2 + (Ew_2)^2] \qquad (3.11)$$

$$A_2(y) = D\{A\mathcal{T}y^2 - [3w_2/[(1 + Ew_1)^2 + (Ew_2)^2]]\} \qquad (3.12)$$

$$w_1 = [\emptyset_1\sin(2\emptyset_1) + \emptyset_2\sinh(2\emptyset_2)]/[\cosh(2\emptyset_2) - \cos(2\emptyset_1)] - 1 \qquad (3.13)$$

$$w_2 = [\emptyset_2\sin(2\emptyset_1) + \emptyset_1\sinh(2\emptyset_2)]/[\cosh(2\emptyset_2) - \cos(2\emptyset_1)] \qquad (3.14)$$

$$\emptyset_1 = -\sqrt{Ay^2/[2(y^4 + 1)(\sqrt{y^4 + 1} + y^2)]} \qquad (3.15)$$

$$\phi_2 = \sqrt{Ay^2 / [2(y^4 + 1)(\sqrt{y^4 + 1} - y^2)]} \qquad (3.16)$$

In these equations $\mathcal{T}$ is a normalized time

$$\mathcal{T} = t/t_o \qquad (3.17)$$

where t_o is the time necessary for saturation of the adsorbent under conditions where there is no resistance at all. It is given by

$$t_o = \frac{1 - \alpha}{\alpha} \rho_p K_A \frac{Z}{v} \qquad (3.18)$$

The dimensionless parameters D,E, and A are defined as follows :

$$D = \frac{D_c}{R^2} \left(\frac{1 - \alpha}{\alpha} \right) \frac{Z}{v} \qquad (3.19)$$

$$E = \frac{D_c}{k_f R} \qquad (3.20)$$

$$A = \frac{R^2 k_{ads} \rho_p}{D_c} \qquad (3.21)$$

They contain the rate constants which describe external diffusion , internal diffusion , and adsorption rate , and are therefore characteristic of these processes.

When the constants D_c , k_f and k_{ads} are known , it is possible to calculate by means of equations (3.10) to (3.21)

the $\quad C = C(t, Z = $ const.) curve , point by point. However , the values of the constants are rarely known.

Kubin and Kucera [3] describe the movement of an adsorbable substance in a chromatographic column which may be described by the same differential equations as that of the adsorber. The only difference between the two cases is the bed inlet condition. Instead of equation (3.8) , the pulse unit can be described by the square function [19]

$$C = C_o \quad \text{at} \quad Z = 0 \quad \text{for} \quad 0 <= t <= t_{oA}$$
$$C = 0 \quad \text{at} \quad Z = 0 \quad \text{for} \quad t > t_{oA} \quad\quad\quad (3.22)$$

where t_{oA} is the injection time of adsorbable gas of concentration C_o. The solution of $C(Z,t)$ in the Laplace domain is as follows

$$s(Z,p) = C_o [1 - \exp(-pt_{oA})]\exp(- \gamma Z) \quad\quad\quad (3.23)$$

where

$$\gamma = - \frac{v\alpha}{2E_A} + \sqrt{\left(\frac{v\alpha}{2E_A}\right)^2 + \frac{p\alpha}{E_A}[1 + h(p)]} \quad\quad\quad (3.24)$$

and

$$h(p) = \frac{3k_f}{R} \frac{1-\alpha}{\alpha}\left[1 - \frac{\sinh(R\sqrt{\lambda})}{p \quad (pD_e/k_f)\sqrt{\lambda}\cosh(R\sqrt{\lambda}) + p[1 - (D_e/Rk_f)]\sinh(R\sqrt{\lambda})}\right]$$

$$(3.25)$$

$$\lambda = \frac{p\beta}{D_c}\left[1 + \frac{(\rho_p/\beta)K_A k_{ads}}{K_A p + k_{ads}}\right]$$ (3.26)

Though it does not appear feasible to invert the transform analytically , it is possible to obtain directly from $s(Z,p)$ explicit expressions for the moment of the chromatographic curve $C(Z,t)$.

3.1.3 The moments method

The nth absolute moment , μ_n' , of the function , $C(Z,t)$, is defined as

$$\mu_n' = m_n / m_o$$ (3.27)

where

$$m_n = \int_0^\infty t^n C(Z,t)dt \qquad (n = 0,1,2,3,\ldots\ldots)$$ (3.28)

The nth central moment μ_n is defined as

$$\mu_n = (1/m_o)\int_0^\infty (1 - \mu_1')^n C(Z,t)dt$$ (3.29)

The first absolute moment characterizes the position of the center of gravity of the chromatographic curve , whereas the second central moment characterizes the width of the curve. The evaluation of the moments [5] from a knowledge of $s(Z,p)$ is based on the following position

$$m_n = (-1)^n \lim_{p \to 0} \frac{d^n}{dp^n} [s(Z,p)/p] \tag{3.30}$$

By using equations (3.27) to (3.30) together with equations (3.23) to (3.26) the first absolute, and second and third central moments can be expressed as follows:

$$\mu_1' = (Z/v)(1 + b_o) + (t_o A/2) \tag{3.31}$$

$$\mu_2 = (2Z/v)[b_1 + (E_A/\alpha)(1 + b_o)^2(1/v^2)] + (t_o A/12) \tag{3.32}$$

$$\mu_3 = (3Z/v)[b_2 + 4(E_A/\alpha)b_1(1 + b_o)(1/v^2)$$

$$+ 4(E_A/\alpha)^2(1 + b_o)^3(1/v^4) \tag{3.33}$$

$$b_o = [(1 - \alpha)\beta/\alpha][1 + (\rho_a/\beta)K_A] \tag{3.34}$$

$$b_1 = [(1 - \alpha)\beta/\alpha]\left[\frac{\rho_p}{\beta} \frac{K_A}{k_{ads}} \right.$$

$$\left. + \frac{R^2\beta}{15}\left(1 + \frac{\rho_p K_A}{\beta}\right)^2\left(\frac{1}{D_c} + \frac{5}{k_f R}\right) \right] \tag{3.35}$$

$$b_2 = \lim_{p \to 0} \frac{d^2}{dp^2}[h(p)] \tag{3.36}$$

Experimental chromatographic curves of the effluent from the bed can be used in equations (3.27) to (3.29) to evaluate moments μ_1' and μ_2. Datas at different velocities

and particle radii R , will give the moments as a function of these two variables. Then equations (3.31),(3.32),(3.33), and (3.34) can be used to evaluate the axial dispersion coefficient E_A , the intraparticle diffusion coefficient D_e , adsorption rate constant k_{ads} , the mass transfer coefficient k_f , as well as the adsorption equilibrium K_A . Then all the constants necessary for the prediction of the breakthrough curve by means of equations (3.10) to (3.21) are available.

3.1.4 Determination of adsorption isotherms.

3.1.4.1 The adsorption isotherms of single components.

From experimental breakthrough curves which have a shape as shown in figure 3.2 , we can find the amount of gas adsorbed on molecular sieve carbon-5A by area integration.

The amount of gases adsorbed on molecular sieve carbon-5A at any concentration be obtained and the plot of the amount of gases adsorbed on molecular sieve carbon-5A vs the concentration (partial pressure) give the adsorption isotherms as shown in figure 5.1.

The equilibrium constants can be obtained from these adsorption isotherms by the following relation

$$K = C_{adsorbed}/C_o$$

where

$C_{adsorbed}$ = the amount of gas adsorbed on

MSC-5A.

C_o = the concentration of gas input.
The results were shown in table.IV.
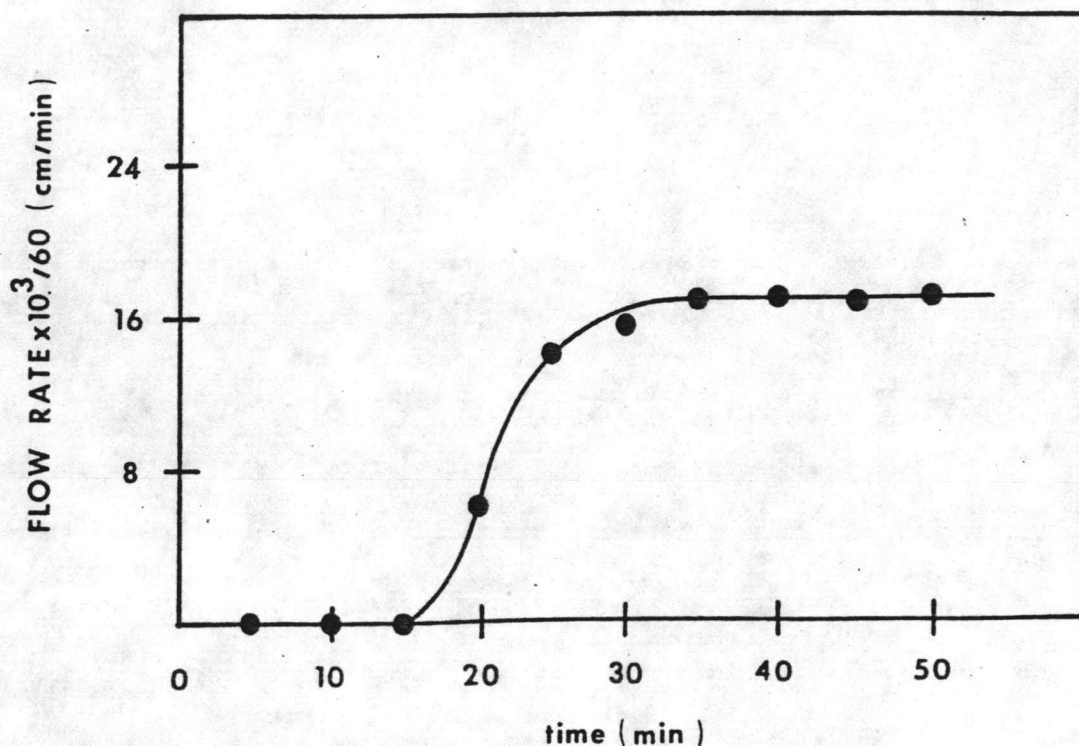

Figure 3.2 Breakthrough curve of carbondioxide at a partial pressure of 0.0685 and at 45 °C.

3.1.4.2 The adsorption isotherms of mixture.

Similarly as for single component adsorption isotherms we can find the amount of gas adsorbed from the chromatographic curves which have a shape as shown in figure 3.3. The experimental data obtained are in the range of low concentrations of hydrocarbon as shown in figure 3.4 and 3.5.
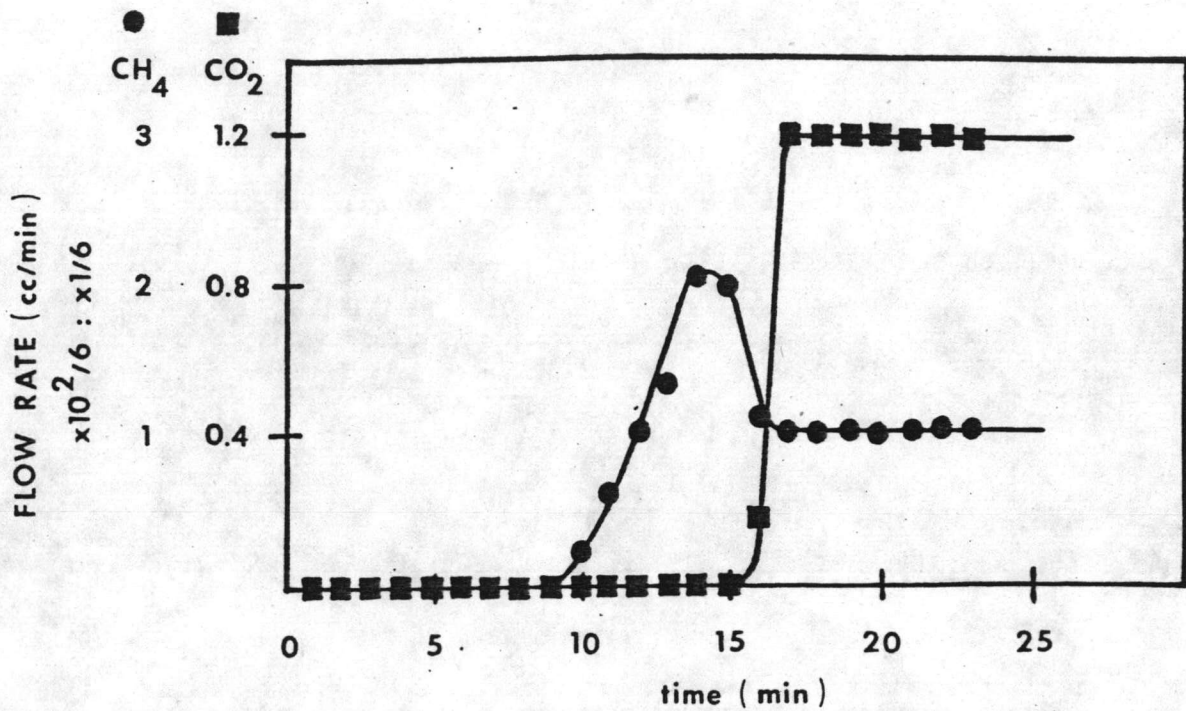
Figure 3.3   The breakthrough curve of mixture of carbondioxide and methane at 0.5 bar and 45 ° C.

The results of adsorption isotherms of mixture presented in figure 5.2 and 5.3 are predicted from single component adsorption isotherms using the ideal solution theory of Myers and Prausnitz [8] as shown in chapter 2.
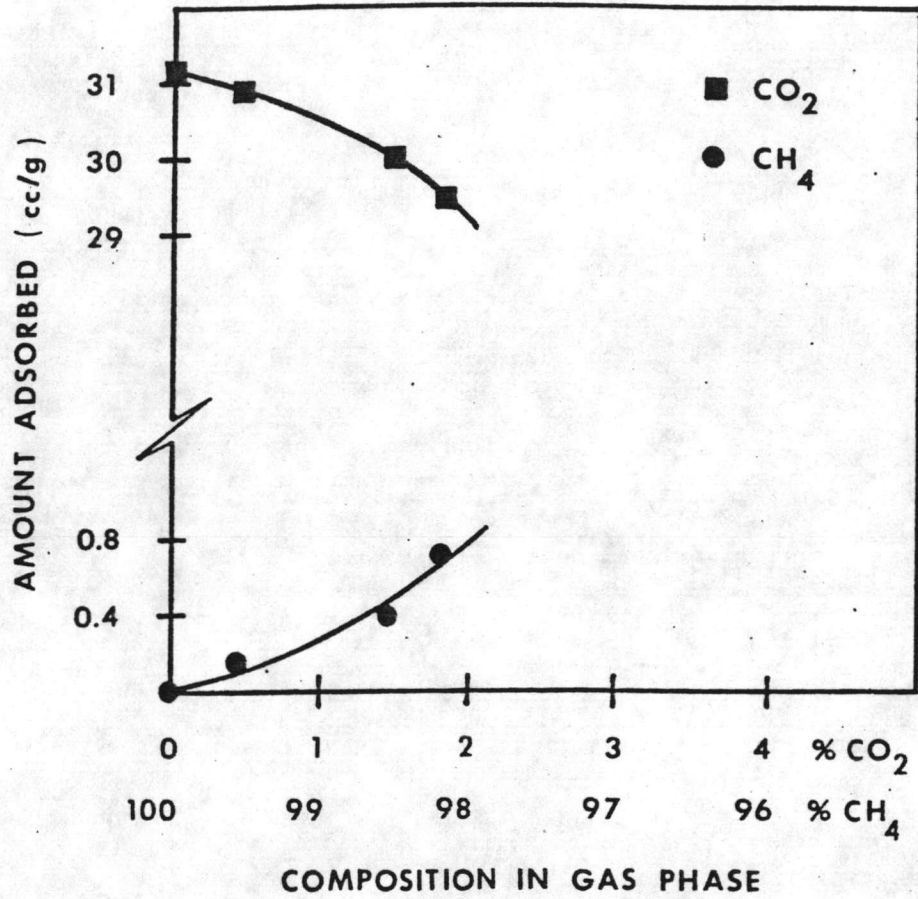
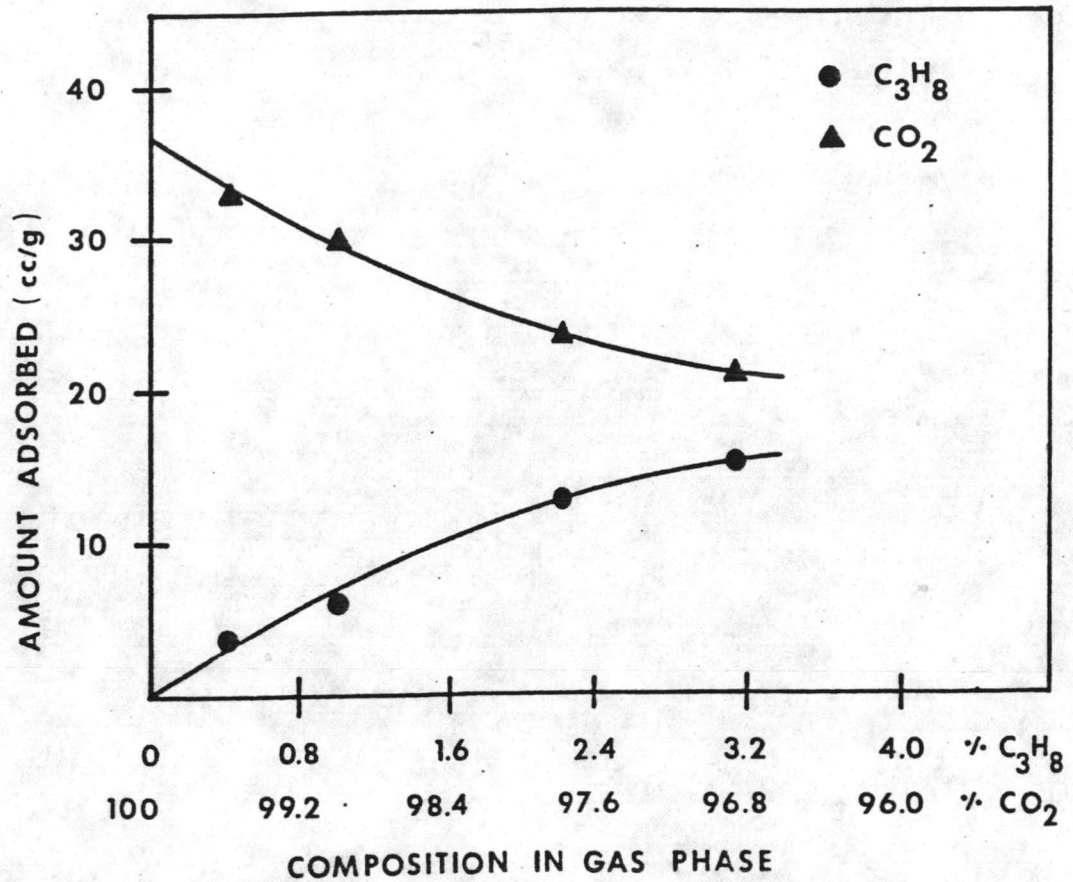Figure 3.4   The equilibrium curve of a mixture of methane and carbondioxide at 45 ° C and 0.5 bar.

Figure 3.5   The   equilibrium   curve   of a   mixture   of carbondioxide   and   propane   at   45 ° C   and   0.5   bar.

3.1.5 Determination   of   the   constants   parameters.

3.1.4.1 First   absolute   moments (equilibrium   constants)

From   equations (3.31) and (3.34) it   follows   that

$$\frac{\Delta \mu_1' - t_{oA}/2}{\frac{1 - \alpha}{\alpha} \beta} = \frac{\rho_p K_A}{\beta} \left(\frac{Z}{v} \right) \qquad (3.37)$$

where

$$\Delta \mu_1' = \mu_1' - (\mu_1')_{inert} \qquad (3.38)$$

The first absolute moment for a nonadsorbable substance is given by equation (3.31) with $K_A = 0$ and $t_{oA} = 0$. Hence

$$(\mu_1')_{inert} = 1 + \left(\frac{1 - \alpha}{\alpha} \beta\right) \frac{Z}{v} \qquad (3.39)$$

The plot of the reduced moment vs Z/v for equation (3.37) should be a straight line passing through the origin. Furthermore , data for different sizes of MSC-5A particles should fall on the same line. The values of K_A are determined from the slopes of the lines using equation (3.37).

3.1.4.2 Second central moments.

Equations (3.32),(3.34), and (3.35) relate the second central moments of the chromatographic peak at the column outlet to the width of the injected pulse (t_{oA}) , the parameters which characterize the column and the adsorbent (Z ,β,α,ρ_p,R) , the constants which describe the adsorption (K_A , k_{ads}) , and the diffusional transport coefficients (D_c, k_f). Furthermore the second central moment depends on the velocity of the carrier gas. In order to analyze the experimental data , equation (3.32) was transformed into the following form

$$\frac{\mu_2 - t_{oA}^2/12}{2(Z/v)} = b_a + b_1 + b_e + \frac{E_A}{\alpha} (1 + b_o)^2 \frac{1}{v^2} \qquad (3.40)$$

where

$$\mho_{\bullet} = \left(\frac{1-\alpha}{\alpha}\beta\right)\left(\frac{\rho_p}{\beta}\right)\frac{K_A^2}{k_{ads}} \tag{3.41}$$

$$\mho_1 = \mho_0 \frac{R^2}{15} \left[1 + \rho_p K_A\right] \frac{1}{D_c} \tag{3.42}$$

$$\mho_{\bullet} = \mho_0 \frac{R^2}{15} \left[1 + \rho_p K_A\right] \frac{5}{k_f R} \tag{3.43}$$

$$\mho_{\bullet} + \mho_1 + \mho_{\bullet} = \mho_1 \tag{3.44}$$

The mass transfer coefficient k_f , in equation (3.43) depends on the velocity and the diameter of the particles. In analogy to the correlation of the heat transfer coefficient for forced convection around a sphere , the following correlation for mass transport has been proposed:[5]

$$N_{Nu} = 2.0 + 0.60(N_{Re})^{1/2}(N_{Sc})^{1/3} \tag{3.45}$$

The Nusselt number (N_{Nu}) for mass transfer is defined as

$$N_{Nu} = \frac{2Rk_f}{D_{AB}}$$

and the Reynolds and Schmidt numbers have their usual meanings. At very low values of Reynolds number , $N_{Nu} = 2.0$ according to equation (3.45) and the mass transfer coefficient is given by

$$k_f R = D_{AB} \qquad\qquad (3.46)$$

The calculation of the binary molecular diffusivity D_{AB} is shown in appendix G. Thus we can find the external mass transfer coefficient using equation (3.46). Accordingly, the mass transfer coefficient at low Reynolds numbers does not depend on velocity and is inversely proportional particle size. Therefore experimental data plotted as the left side of equation (3.40) vs $1/v^2$ should be a straight line with a slope equal to $E_A (1 + b_o)^2 / \alpha$ and an intercept equal to $(b_a + b_1 + b_a)$.

3.1.4.3 Axial dispersion coefficients.

As K_A (and hence , b_o) is known from the analysis of the first absolute moment , the axial dispersion coefficients , E_A , can be obtained from the slopes of the straight line as before.

3.1.4.4 Adsorption rate constants.

Since k_f is given by equation (3.46) it is possible to determine the adsorption rate constant k_{ads} , and the effective internal diffusion coefficient D_c. With reference to equation (3.44) the plot of b_1 vs R^2 should be a straight line with an intercept equal to b_a . k_{ads} can then be calculated from equation (3.41).

3.1.4.5 Intraparticle diffusivity.

The slope of the straight line between b_1 and R^2 is equal to $(b_1 + b_-)/R^2$. Since k_f and K_A are known, b_- can be determined and used with these slopes to establish values of b_1. Then D_c is obtained from equation (3.42).