CHAPTER 2

CONCEPTS OF ADSORPTION

In any heterogeneous system consisting of atoms, molecules, or ions, the interactions between the phases begin with chemical or physical interactions at the phase interface. This surface interaction phenomenon can be observed at interfaces between gas and solid, gas and liquid, liquid and solid, between two liquids, and even between two solid phases. The types of interactions between the phases of an heterogeneous system depends on the properties and composition of all the components of the system. On the stand point of the distribution of the substances to be sorbed, two types of sorption can occur : adsorption and absorption. Adsorption takes place when the molecules or atoms sorbed are concentrated on the surfaces only, absorption takes place when the molecules or atoms are distributed in the bulk of the interacting phases. As a rule, adsorption takes place when one of the phases consists of a solid. The fluid phase is called the adsorbate while the solid phase is called the adsorbent.

2.1 Adsorbents

Adsorbents are porous solids which may be

manufactured from materials such as bone or coal chars , calcined clays , iron oxide , calcined bauxite , etc. The important physical characteristics of adsorbents include pore volume , pore size distribution , and surface area. Also of practical importance are bulk density , crush strength , and erosion resistance. Surface area of adsorbents can be determined by a method called the BET method. In characterizing the pore volume , both total pore volume and its distribution over the pore diameter are important. Pore size distributions are measured by mercury porosimetry for pores larger than 100 - 150 $^{\circ}$A and by N_2 desorption for pores in the range 10 - 250 $^{\circ}$A.

2.1.1 Activated carbon

Activated carbon adsorbents are made from materials such as wood , peat , coals , petroleum coke , bones , coconut shells , and fruit nuts. Starting with the initial pores present in the raw material , more pores , with desired size distributions , are created by activation. The unique surface property of activated carbon , in contrast to the other major adsorbents , is that it has a nonpolar surface. This unique property gives activated carbon the following advantages : it does not require stringent moisture removal before use ; because of large internal surfaces it adsorbs more non-polar and weakly polar organic molecules to a larger extent than other adsorbents (methane adsorption in

activated carbon is twice that in molecular sieve -5A) ; and with a lower bond strength stripping of adsorbed molecules is easier.
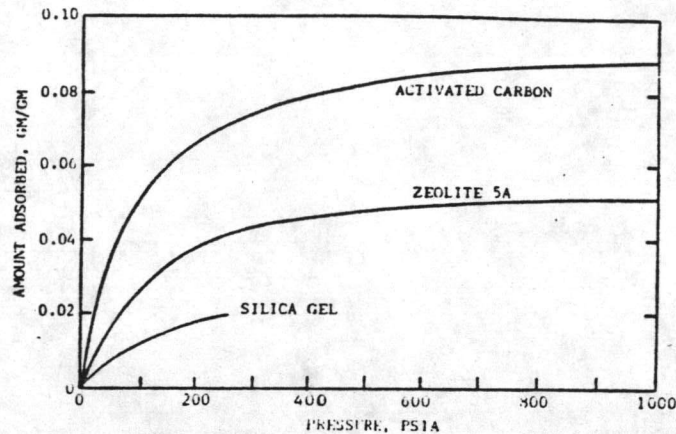

Figure 2.1 Equilibrium sorption of methane at 25 °C on silica gel , zeolite 5A , and activated carbon.[1]

Activated carbons have large surface areas (between 300 and 2,500 m^2/g). They have pore diameters equal to or greater than 30 °A for liquid - phase carbons , whereas the pore diameters of gas - phase carbons are mostly in the range of 10 °A to 25 °A. But a polymodal pore - size distribution is generally found in activated carbons. The pore structure may be pictured as having large pores called feeder pores or transport pores with many small pores branching out called adsorption pores. According to the International Union of Pure and Applied Chemistry (IUPAC) classification [1] , the pores are subdivided into macropores (d > 500 °A) , mesopores (20 °A < d < 500 °A) , and micropores (d < 20 °A). The cumulative pore - volume distribution of the fine pores for a typical gas - phase activated carbons is

shown , along with four other adsorbents , in Figure 2.2.

2.1.2 Molecular - Sieve Carbons

Since they are less hydrophilic than zeolites , molecular - sieve carbons (MSC) can be used more efficiently in separation processes involving wet - gas streams and have received a great deal of interest lately. One major application has been the production of nitrogen from air.

2.1.3 Activated aluminas

Activated alumina is a material which has high surface areas and great affinity for water and is used for drying gases and dewatering liquids. A partial list of industrial gases that can be dried by activated alumina includes : Ar , He , H_2 , low alkanes (mainly C_1 - C_3) and hydrocarbons , Cl_2 , HCl , SO_2 , NH_3 , and Freon fluorochloralkanes. However it loses adsorption capacity with time due to coking and contamination.

2.1.4 Silica gels

Silica gels are a continuous networks of spherical particles of colloidal silicas. There are a number of preparation methods for silica gel , which result in different pore structures.
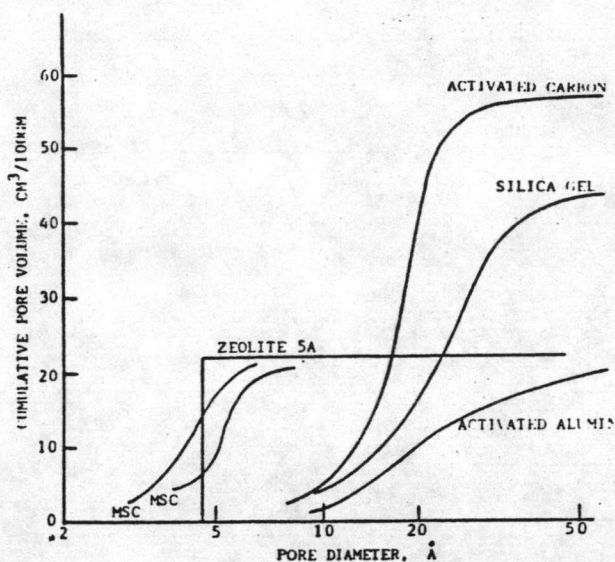
Figure 2.2 Pore - size distribution for activated carbon , silica gel , activated alumina , molecular sieve carbon.[1]

Commercially , silica gel is prepared by mixing a sodium silicate solution with an acid. The reaction produces a concentrated dispersion of finely divided particles of hydrated SiO_2 , known as silica hydrosol or silicic acid as follows

$$Na_2SiO_3 + 2HCl + nH_2O \longrightarrow 2NaCl + SiO_2 \cdot nH_2O + H_2O$$
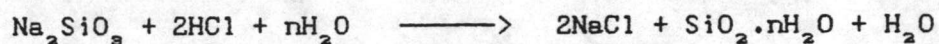
The hydrosol polymerizes slowly into a white jellylike precipitate which is then washed , dried , and activated to produce silica gel. Various silica gels with a wide range of properties such as surface area , pore volume and strength

are made by varying silica concentration , temperature , pH and activation temperature. Two typical types of silica gels are regular - density and low - density silica gels (although both have the same densities). Regular - density gel however has a surface area of 750 - 850 m^2/g and an average pore diameter of 22 - 26 $^{\circ}$ A , whereas for low - density gel the equivalent values are 300 - 350 m^2/g and 100 - 150 $^{\circ}$ A.

Silica gel , along with activated alumina , is a desirable adsorbent for drying because of its high surface area and unique surface properties.

The heat of adsorption of water vapor on silica gel is as low as for activated alumina (approximately 11 kcal/mole). Regeneration of silica gel is achieved by heating to only about 150 $^{\circ}$ C (as compared to 350 $^{\circ}$ C for zeolites)

2.1.5 Zeolites

Zeolites are crystalline aluminosilicates of alkali or alkali earth elements such as sodium , and calcium , and are represented by the formula

$$M_{x/n}[(AlO_2)_x(SiO_2)_y]zH_2O$$
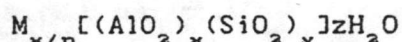
The zeolite skeleton has a regular structure of cages , which are usually interconnected by six windows in each cage of sizes averaging 3 $^{\circ}$ A to 10 $^{\circ}$ A. And sorption may occur with

great   selectivity because of size of the window aperture —
hence the name **molecular sieve.**

At least forty species of naturally occuring zeolites
have been found and more than 150 types of zeolites have
been synthesized ; they are designated by a letter or group
of letters — Type A , Type X , Type Y , Type ZSM , and so on.

2.2 Adsorption forces

The basic forces causing adsorption can be divided
into   two   groups : intermolecular or Van der   Waals , and
chemical. Thus , if in the process of   adsorption , the
individuality of the adsorbed molecules and of the adsorbent
surface   are preserved , we have physical adsorption.   If ,
between the adsorbate and adsorbent , any electron   transfer
or   sharing   occurs , or if the adsorbate breaks   up   into
atoms   or   radicals   bound separately , then   we   have
chemisorption.

The following parameters can be used to evaluate   an
adsorbate — adsorbent   system to establish   the   type   of
adsorption:

1. Heat of physical adsorption is of the same   order
of magnitude as the heat of liquefaction , while heat   of
chemisorption is of the same order of magnitude as   heats
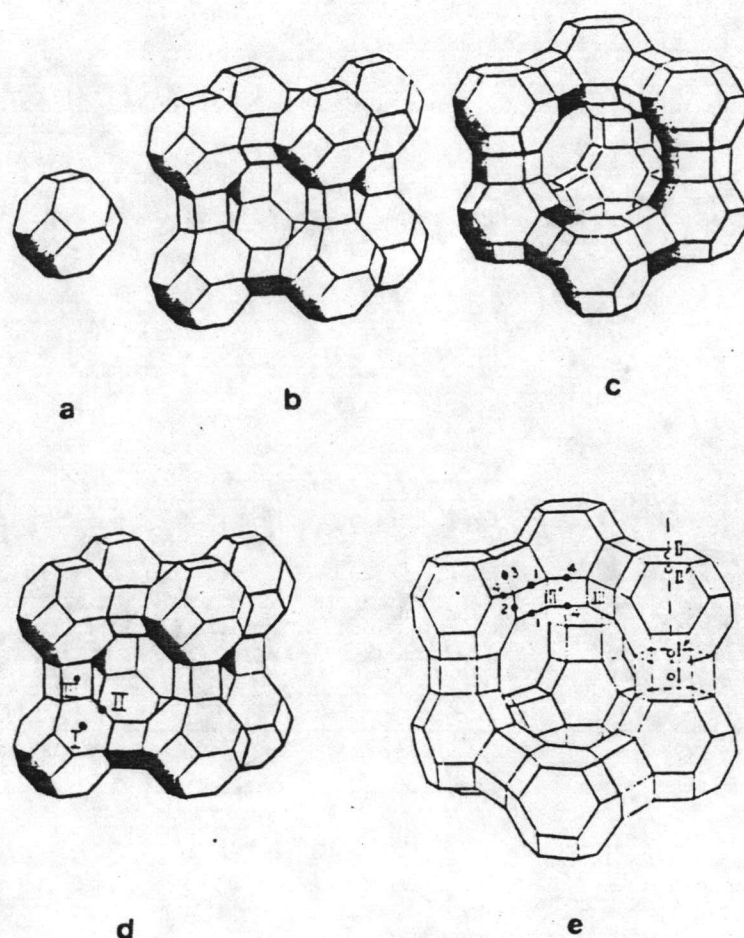of chemical reactions.

Figure 2.3 Line representation of the zeolite structure : (a) sodalite cage ; (b) type A zeolite " unit cell " ; (c) " unit cell " for type X and Y ; (d) cation sites for type A ; (e) cation sites for type X and Y.

2. Physical adsorption occurs under suitable temperatures and pressures in any gas - solid system , while chemisorption takes place only if the gas is capable of forming a chemical bond with the surface.

3. A physical adsorbed molecule can be removed

unchanged at a reduced pressure at the same temperature where the adsorption took place. The removal of the chemisorbed layer is more difficult.

4. Physical adsorption can involve the formation of multimolecular layers, while chemisorption is always at the monolayer level.

5. Physical adsorption is instantaneous (it is the diffusion into porous adsorbents which is time - consuming), while chemisorption may be instantaneous , but generally requires an activation energy threshhold.

2.3 Gas - Phase Adsorption

The number of gas molecules present at the surface of an adsorbent depends on the number that diffuse through the pores to reach the active surface and the time they spend on the surface. According to de Boer [6] , if n molecules strike a unit area of a surface per unit time , and remain there for an average time , t , then σ is the number of molecules present per unit area of surface:

$$\sigma = nt \qquad (2.1)$$

n is for example the number striking 1 cm^2 of adsorbent surface per second and is a function of velocity of the molecules within the system. The relationship used to calculate n is given as [6]

$$n = 3.52 * 10^{22} * \frac{P}{MT} \qquad (2.2)$$

where   P = pressure in Hg , mm

          M = molecular weight

          T = absolute temp , K

From this equation at 20 °C and 750 mm Hg pressure , the following values can be obtained:

for H_2 : n = 11.0 * 10^{23} molecules/cm^2/sec

for N_2 : n = 2.94 * 10^{23} "

for O_2 : n = 2.75 * 10^{23} molecules/cm^2/sec

The molecule residence time , t , on the surface is more difficult to determine. Clausing [6] used a method involving the estimation of the velocity with which molecules of a gas pass through narrow capillaries at low pressures to measure t. Experimenting with argon in glass capillaries , Clausing obtained the following results:

at 90 K   :   t = 3.1 * 10^{-5} sec

at 78 K   :   t = 75 * 10^{-5} sec

Same orders of magnitude were obtained also for nitrogen on glass , but for neon the following value was obtained:

$$t = 2 * 10^{-7} \text{ sec} \quad \text{at } 90 \text{ K}$$

Frenkel [6] treated t as function of temperature and presented the following equation

$$t = t_o e^{Q/RT} \tag{2.3}$$

where t_o is the time of oscillation of the molecule in the adsorbed state , and Q is the heat of adsorption.

2.4 Adsorption equilibrium

Adsorption equilibrium is reached when the number of molecules arriving on the surface is equal to the number of molecules leaving the surface. The adsorbed molecules exchange energy with the structural atoms of the surface and , provided that the time of adsorption is long enough , they will be in thermal equilibrium with the surface atoms.

2.4.1 Adsorption isotherms

Isotherms can yield qualitative information about the adsorption process and also indicate the fraction of surface coverage.

The five basic types of adsorption isotherms are presented in figure 2.4 [1]. Type I isotherms represent systems in which adsorption does not proceed beyond the formation

of a monomolecular layer. Type II isotherms indicate an indefinite multilayer formation after the completion of the monolayer. Type III isotherms are obtained when the amount of adsorbed gas increases without limit as its relative saturation approaches unity. Type IV isotherms are variations of type II , but with a finite multilayer formation corresponding to complete filling of the capillaries. Type V isotherms are similar variations of type III.
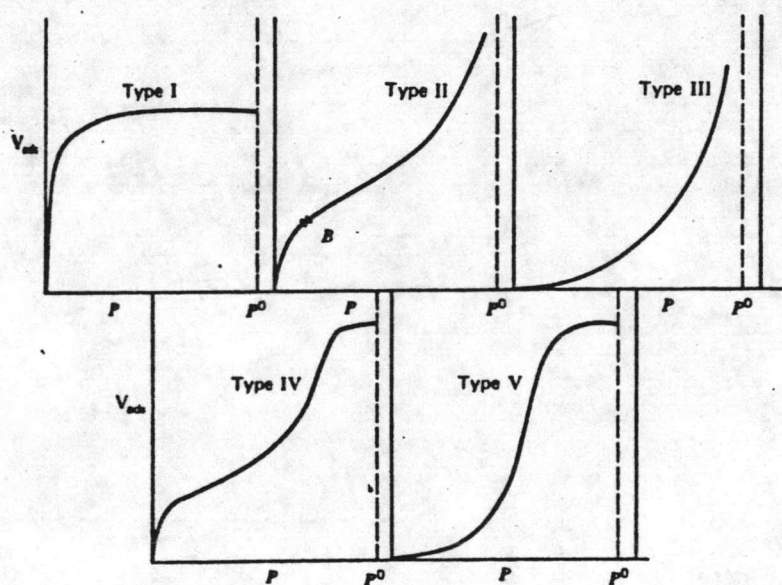

Figure 2.4 The five types of adsorption isotherms (according to the BET classification).

2.4.1.1 The Langmuir adsorption isotherm.

The simplest and still the most useful isotherm , for both physical and chemical adsorption , is the Langmuir

isotherm. The Langmuir isotherm in its usual form is based on the following assumptions[1]:

1. The adsorbed molecule or atom is held at definite , localized sites.

2. Each site can accommodate one and only one molecule or atom.

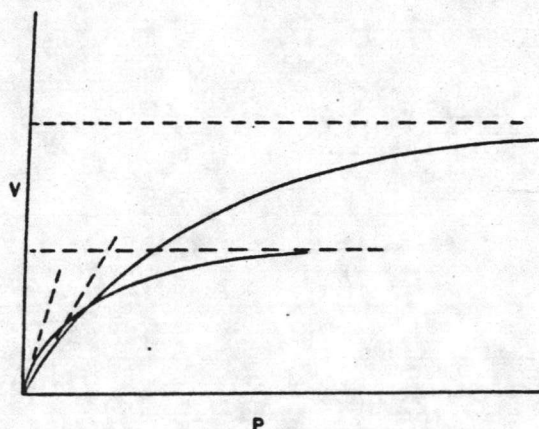3. The energy of adsorption is a constant over all sites , and there is no interaction between adsorbates.

Figure 2.5 Langmuir isotherms [1]

2.4.1.2 BET adsorption isotherms.

Adsorption isotherms do not resemble to Langmuir isotherms. Brunauer , Emmett , and Teller (BET)[1] considered that there are five principal forms , as illustrated in figure 2.4. Type I is the Langmuir type , type II corresponds to a multilayer formation. Type III is relatively rare — a recent example is that of the adsorption of nitrogen on ice. Type IV and V are considered to reflect a capillary

condensation phenomena in that they level off before the saturation pressure is reached and may show hysteresis effects.
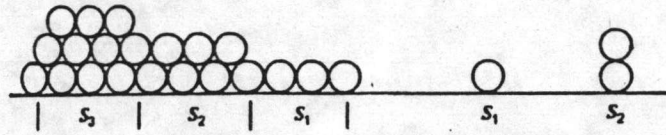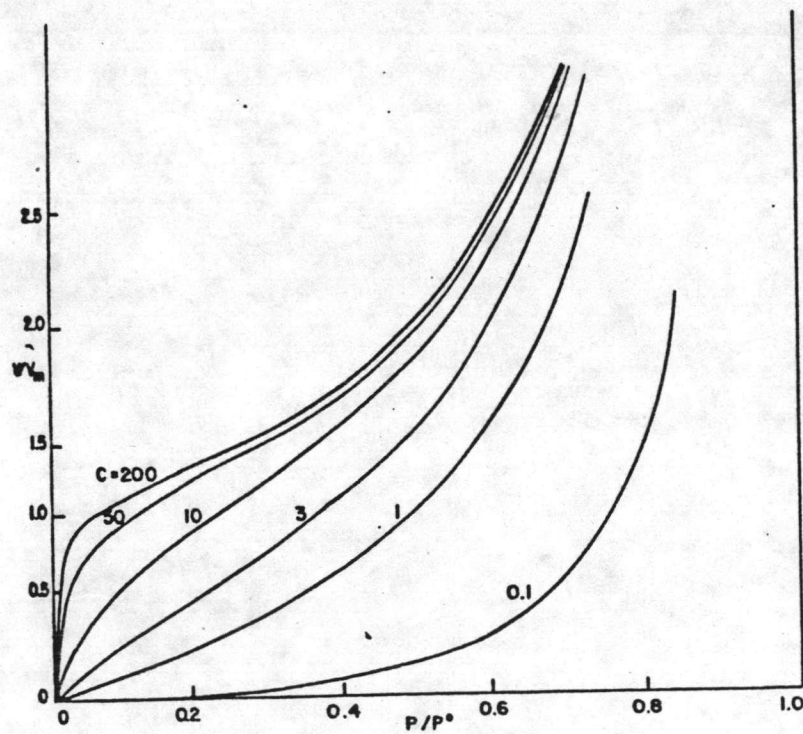

Figure 2.6 The BET model.[1]
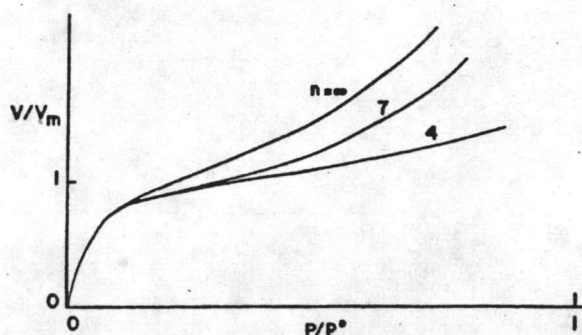

Figure 2.7 BET isotherms.[7]

Figure 2.8 BET isotherms with adsorption limited to n layers.[7]

The basic assumption of the BET model is that the Langmuir equation applies to each layer, but that for the first layer the heat of adsorption may have some special value. A further assumption is that evaporation and condensation can occur only from or on exposed surfaces. As illustrated in figure 2.6, the picture is one of portions of uncovered surface S_o, of surface covered by a single layer S_1, by a double layer S_2, and so on. The condition for equilibrium is taken to be such that the amount of each type of surface reaches a steady state value with respect to the next deeper.

2.4.1.3 The Potential theory

A still different approach to multilayer adsorption is one which considers that there is a potential field at the surface of a solid into which adsorbate molecules " fall

". The adsorbed layer thus resembles the atmosphere of a planet - it is most compressed at the surface of the solid and decreases in density outward. The general idea is quite old and was first formalized by Polanyi in about 1914. And the details of this model was described in a previous reference [6].

2.4.1.4 The polarization model

De Boer and Zwikker [7] suggested that the adsorption of nonpolar molecules could be explained by assuming that the polar adsorbent surface induces dipoles in the first adsorbed layer and that these in turn induce dipoles in the next layer , and so on.

2.4.1.5 Capillary condensation

Below the critical temperature of the adsorbate , adsorption is generally multilayer in type , and the presence of pores may have the effect not only of limiting the possible number of layers of adsorbate but also of introducing capillary condensation phenomena. The most general characteristic of such adsorption systems is that of hysteresis ; as illustrated in figure 2.9.
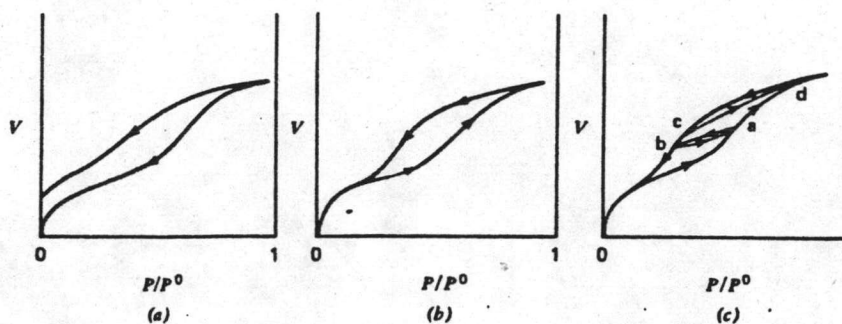
Figure 2.9 Hysteresis loops in adsorption [7]

2.4.2 Adsorption isobars

If we keep the pressure constant we will get a
direct correlation between the number of molecules adsorbed
and the temperature which is the adsorption isobars:

TABLE I

Adsorption isobars [1]

Nitrogen at 133 millibars		n - Pentane at 1.33 millibars	
Temperature ($^\circ$C)	amount adsorbed (g/g)	($^\circ$C)	(g/g)
-79	0.0200	-63.7	0.36
0	0.0030	-15.2	0.24
30	0.0016	0	0.20
80	0.0008	20.5	0.15
151.5	0.0002		

2.4.3 Adsorption isosteres

The adsorption isostere is a relationship between pressure and temperature according to the same degree of surface coverage. In the other hand adsorption isostere is a relationship that show the amount of fluid in adsorbed phase at any temperature and pressure. The adsorption isosteres are shown in table II

TABLE II

Ammonia pressure over charcoal and over water [1]

temperature($^\circ$C)	P(millibars)	P_w(millibars)
0	39	39
30	141	192
80	747	1411

2.4.4 The ideal solution theory.

The ideal solution theory is a method of prediction of adsorption equilibrium of gases mixture from the single component adsorption isotherms. The ideal solution theory method may be summarized as follows[8]

$$y_1 = \frac{\text{length of line DE}}{\text{length of line FE}}$$

$$x_1 = \frac{\text{length of line DC}}{\text{length of line BC}}$$

where

y_1 = mole fraction in gas phase

x_1 = mole fraction in adsorbed phase

The line DE , FE , DC , and BC shown in figure 2.10. The spreading pressure may be determined as follows

$$\pi A \, / \, RT = K_1 P_1 = n_1 = n_2 = \text{amount adsorbed}$$

where

π = spreading pressure

A = specific area of adsorbent

R = gas constant

T = absolute temperature

K = Henry's law constant

P_1 = equilibrium pressure for pure component

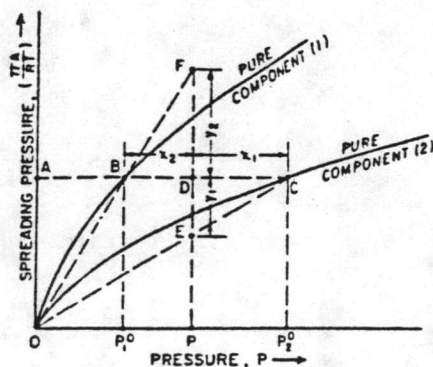and at constant T and π , we have

$$K_1 P_1 = K_2 P_2$$

Figure 2.10 Calculation of mixture adsorption equilibria from pure component spreading pressures.