# Chapter 3

Physical Adsorption at the Fluid-Solid Interface

3.1 Introduction

Two types of adsorption may occur at the gas-solid interface:

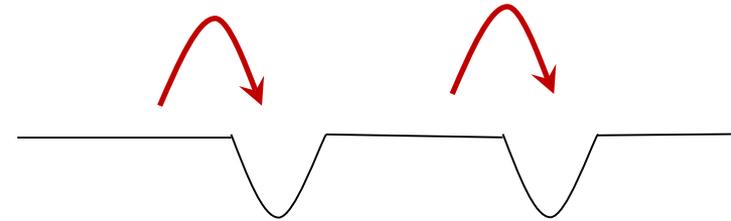**(1) Physical adsorption (physisorption) :**

1. Nonspecific and similar to condensation
2. No structure change on surface
3. No activation energy required
   (energy comparable to liquefaction)
4. More than one layer of adsorption could occur
5. Reversible process (adsorption ⟷ desorption)
6. Adsorbates are free to move on the surface
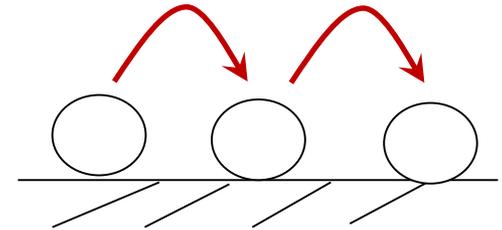
(2) Chemical adsorption (chemisorption) :

1. Site-specific
2. Chemical bonds are formed
3. Associated with activation energy
4. Only single layer formed
5. Usually irreversible

$$(e.g.\ C_{(S)} + O_2 \xrightarrow{\text{Chemisorption}} C(O) \xrightarrow{\text{adsorption}} CO\ or\ CO_2\ )$$

6. Adsorbates are localized at certain points

This course discusses physical adsorption only.
We will start from adsorption on nonporous solids.
Porous materials will be discussed later.

3.2 Experimental and Theoretical Adsorption Isotherms: An Overview

(1) Adsorption isotherm:
   Representation of the amount adsorbed as a function of equilibrium gas pressure at a fixed temperature.

(2) Adsorption studies are conducted in a vacuum system.
   (all gases have to be removed prior to the addition of the adsorbate)

   ➔ **Heating and pumping are required (surface cleaning)**

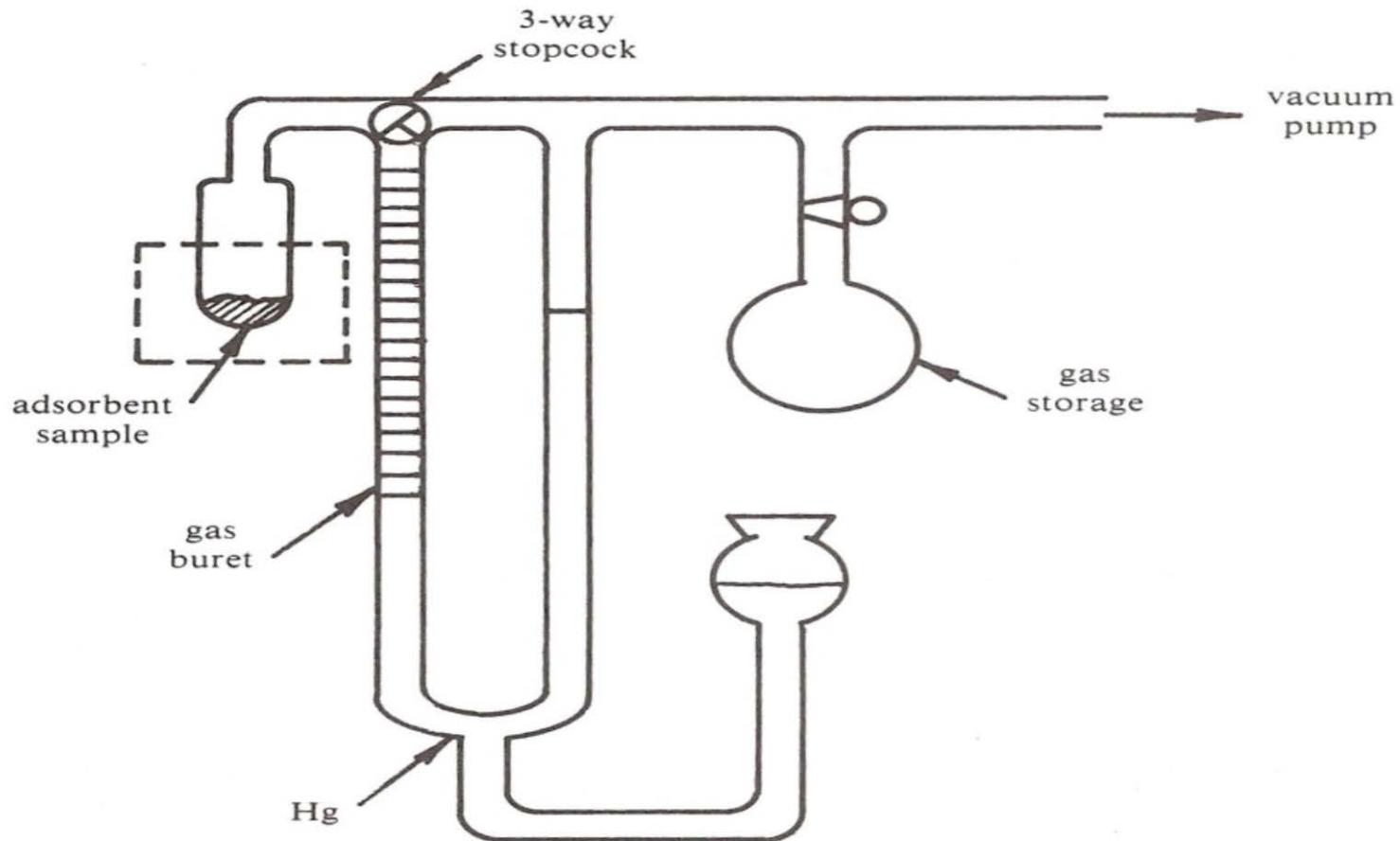**(3) The range of the adsorption pressure is usually between zero and P_o (saturation pressure of the adsorbate).**

Figure 9.1   Schematic illustration of a gas adsorption apparatus.

Experimental Steps:

1. **Sample tube and gas buret are evacuated, and then a non-adsorbing gas (helium usually, smaller molecular size) is introduced into the gas buret. The volume (V_1) and pressure (P_1) of gas in the buret can be obtained.**

2. The 3-way stopcock is opened to connect buret with sample tube. The new pressure (P_2) and volume (V_2) in the buret can be read.
   ➔ The dead space (= sample tube volume – sample volume can be determined. *different samples, different dead space***

3. Pump out helium, the buret then filled with adsorbate. Record the volume (V_3), pressure (P_3) and temperature (T).
   ➔ The initial number of adsorbate molecules can be determined.

4. 3-way stopcock is opened to connect buret and sample tube. Measure the volume (V_4) and pressure (P_4), then the final number of molecular can be calculated (because the dead space is known).

Initial – final = number of molecules adsorbed

5. Repeat steps 3 and 4 by adjusting Hg level, then:

不同壓力下的吸附量

P_4

Amount adsorbed

An isotherm
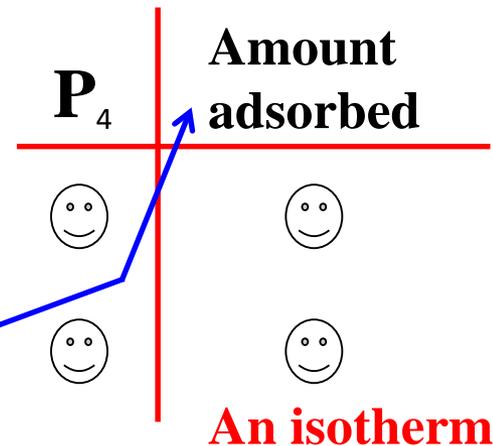
Example 3.1:

The following pressure –volume (P-V) data were collected at a temperature of 22°C. The V's are volumes in the gas buret and the numerical subscripts refer to the steps itemized above. With helium, $P_1 = 21.71$ torr, $V_1 = 12.90$ cm^3 ; $P_2 = 16.50$ torr, $V_2 = 10.90$ cm^3. With adsorbate, $P_3 = 12.85$ torr, $V_3 = 13.70$ cm^3, $P_4 = 3.24$ torr, $V_4 = 5.00$ cm^3.
What is the volume of the dead space?
How many moles are adsorbed at the final equilibrium pressure, 3.24 torr?

Solution:

Use idea gas law, i.e.

where R = gas constant 【≡】 $\dfrac{cm^3\ torr}{K\ mol}$

$$P_1V_1 = P_2(V_2 + V_d)$$
$$(21.71)(12.90) = (16.5)(10.90 + V_d)$$
$$V_d = 6.07 cm^3$$

∴ **amount adsorbed at 3.24 torr**
$$= n_i - n_f$$
$$= 7.26 \times 10^{-6}\ mol$$

In step 3 $\quad n_i = \dfrac{P_3V_3}{RT} = \dfrac{(12.85)(13.70)}{(62360)(295K)} = 9.57 \times 10^{-6}\ mol$

In step 4 $\quad n_f = \dfrac{P_4(V_4 + V_d)}{RT} = \dfrac{(3.24)(5.00+6.07)}{(62360)(295K)} = 1.95 \times 10^{-6}\ mol$

The Langmuir Equation – Theory

We will discuss this equation using a solution system.

$\begin{cases} \text{Solvent : component 1} \\ \text{Solute : component 2} \end{cases}$

Assumption:

They occupy the same area when they are adsorbed on a surface.

Process:

Adsorbed solvent + solute in solution

➔ Adsorbed solute + solvent in solution

➔ $K' = \dfrac{a_2^{s} \, a_1^{b}}{a_1^{s} \, a_2^{b}}$

where a = activity, s = surface of solid, b = bulk soltion

Assume:

Two-dimensional surface solution is ideal, and surface is completely covered by solvent and solute molecules.

$a^s \propto x^s$ (mole fraction)

K: Langmuir constant

➤ $K' = \dfrac{x_2^s a_1^b}{x_1^s a_2^b}$ $\quad x_1^s + x_2^s = 1$

Let $X_i^s = \theta_i$ (surface coverage)
 = fraction of surface
 occupied by component i

➤ $K' = \dfrac{x_2^s a_1^b}{(1 - x_2^s) a_2^b}$

$\theta_1 + \theta_2 = 1$
(surface completely occupied)

➤ $X_2^s = \dfrac{K' \dfrac{a_2^b}{a_1^b}}{(K' \dfrac{a_2^b}{a_1^b}) + 1}$

$\theta_2 = \dfrac{Ka_2^b}{Ka_2^b + 1} = \dfrac{Ka}{Ka + 1}$

(drop b and 2 for simplicity)

∵ **dilute solution**

∴ $\dfrac{K'}{a_1^b} = \text{constant} = K$ $\quad X_2^s = \dfrac{Ka_2^b}{Ka_2^b + 1}$

Two limiting cases:

1. a $\longrightarrow$ 0, $\theta_2 = K\,a$

2. K a >> 1, $\theta_2 = 1$ (saturation of surface, i.e , a is large)

Slope= K= Langmuir constant

Adsorption capacity:

(people usually not measuring the fraction of coverage)

$\dfrac{n_2^s}{W}$ = number of moles of solute adsorbed per unit weight of adsorbent

$\dfrac{n_2^s}{A}$ = number of moles of solute adsorbed per unit area of adsorbent

$$\frac{n_2^s}{A} = \frac{n_2^s}{A_{sp} W}$$

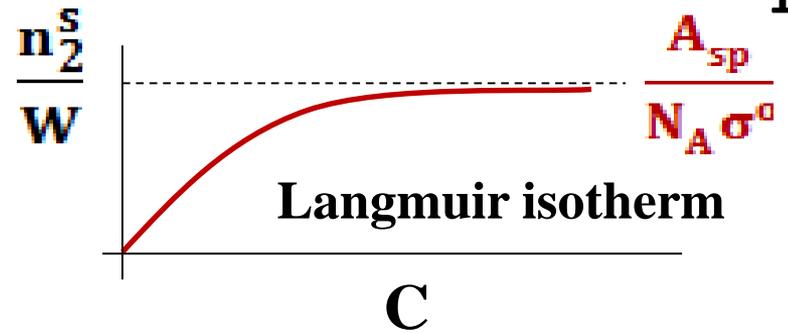$$\theta = \frac{n_2^s N_A \sigma^0}{A} = \frac{n_2^s N_A \sigma^0}{A_{sp} W}$$

A_{sp} = specific surface area

σ^0: molecular area ; A: Avogadro's number
A_{sp}: specific surface area

Saturation adsorption: $\theta = 1$

$$\left(\frac{n_2^s}{W}\right)_{sat} = \frac{A_{sp}}{N_A \sigma^0} \quad \text{or} \quad \left(\frac{n_2^s}{A}\right)_{sat} = \frac{1}{N_A \sigma^0}$$

$$\frac{n_2^s}{W} \qquad \frac{A_{sp}}{N_A \sigma^0}$$

Langmuir isotherm

C

The Langmuir equation: application to results

$$\theta = \frac{N_A \sigma^0}{A_{sp}} \left(\frac{n_2^s}{W}\right) = \frac{KC}{KC+1}$$

By plotting y vs. x:
  slope = m ; intercept = b

$$\text{Let } m = \frac{N_A \sigma^0}{A_{sp}}$$

$$\frac{m}{b} = K$$

$$m\left(\frac{n_2^s}{W}\right) = \frac{(m/b)C}{(m/b)C+1}$$

Then you can get Langmuir constant from m/b = K

$$\frac{C}{n_2^s/W} = mC+b$$

$$\frac{c}{n_2^s/W}$$

Slope=m

b

C

(applied to y = mx + b)

Example 3-2

11
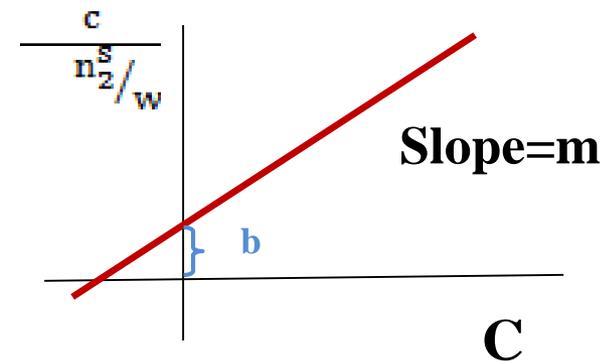
The moles of solute B adsorbed per gram of solid C were determined by measuring concentration changes in the solution. The accompanying results report the adsorption versus the concentration of the equilibrium solution:

C(mole B liter^{-1})	0.75	1.40	2.25	3.00	3.35	4.25
n/w × 10^4 (mol B (gC)$^{-1}$)	6.00	8.00	9.57	10.0	10.4	10.8

Plot these data in the form suggested by $\dfrac{C}{n_2^s/W} = mc + b$ and evaluate the slope and intercept.

If A_{sp} for solid C is known by independent study to be 325 m^{2}g^{-1}, what is σ^0 for the adsorbate? Alternatively, suppose σ^0 for the adsorbate is known to be 0.25 nm^2 on this surface.
What value of A_{sp} is consistent with the adsorption data?

Solution

The ratio c/(n/w) is evaluated as required to test Eq.

$C(n/w)^{-1} \times 10^{-3}(gC\ liter^{-1})$ 1.25 1.75 2.35 3.00 3.35 3.95

A plot of these values against the equilibrium concentration is shown in Figure. The slope and intercept of the line drawn are 769 g C (mole B)$^{-1}$ and 0.0700 g C liter^{-1}, respectively.

$$\sigma^0 = \frac{mA_{sp}}{N_A} = \frac{(769)(325)(10^9)^2}{6.02*10^{23}} = 0.42\ nm^2$$

And if σ^0 is known,

$$A_{sp} = \frac{N_A \sigma^0}{m} = \frac{(6.02 \times 10^{23})(0.25)(10^{-18})}{769} = 196\ m^2g^{-1}$$

The value of K is given by the ratio m/b according to $K = \dfrac{m}{b}$.

For this (hypothetical) system, K=(769)/(0.0700)=1.10×10^4 liter(mole B)$^{-1}$, these reciprocal concentration units are appropriate for K, since the activity of the bulk solvent has been absorbed into definition of K.

$$K = \frac{K'}{a_1^b} = \frac{a_2^s}{a_1^s a_2^b}$$

Solution

$$\frac{c}{n_2^s\,w} \times 10^{-3}$$

$(g\ C\ l^{-1})$

4.0

3.0

2.0

1.0

1   2   3   4   5

$C(mole\ Bl^{-1})$
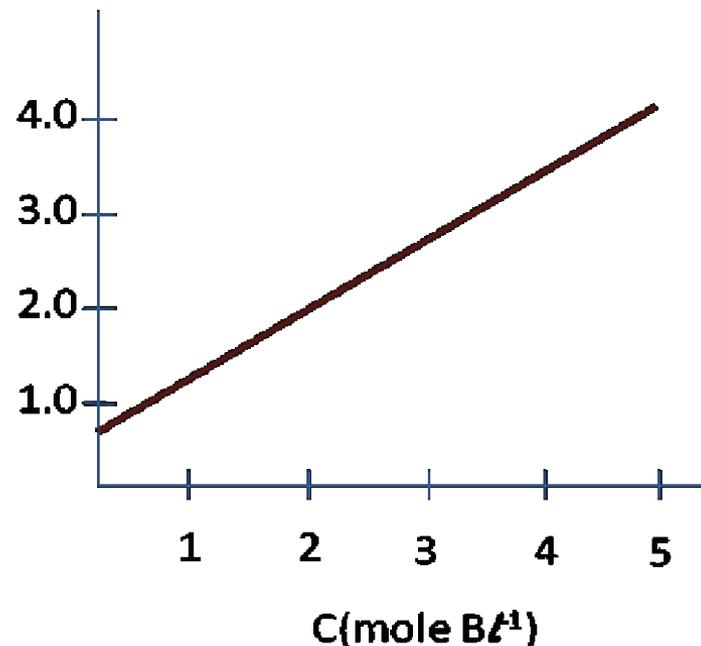
The method of example applied,
to the adsorption of benzene,
naphthalene and anthracene on
 carbon black from heptane solutions
gives values of 0.42, 0.67, and 0.83 nm²,
respectively, for σ^0.
The progression of sizes indicates that the molecular lie flat on the
surface of the carbon.
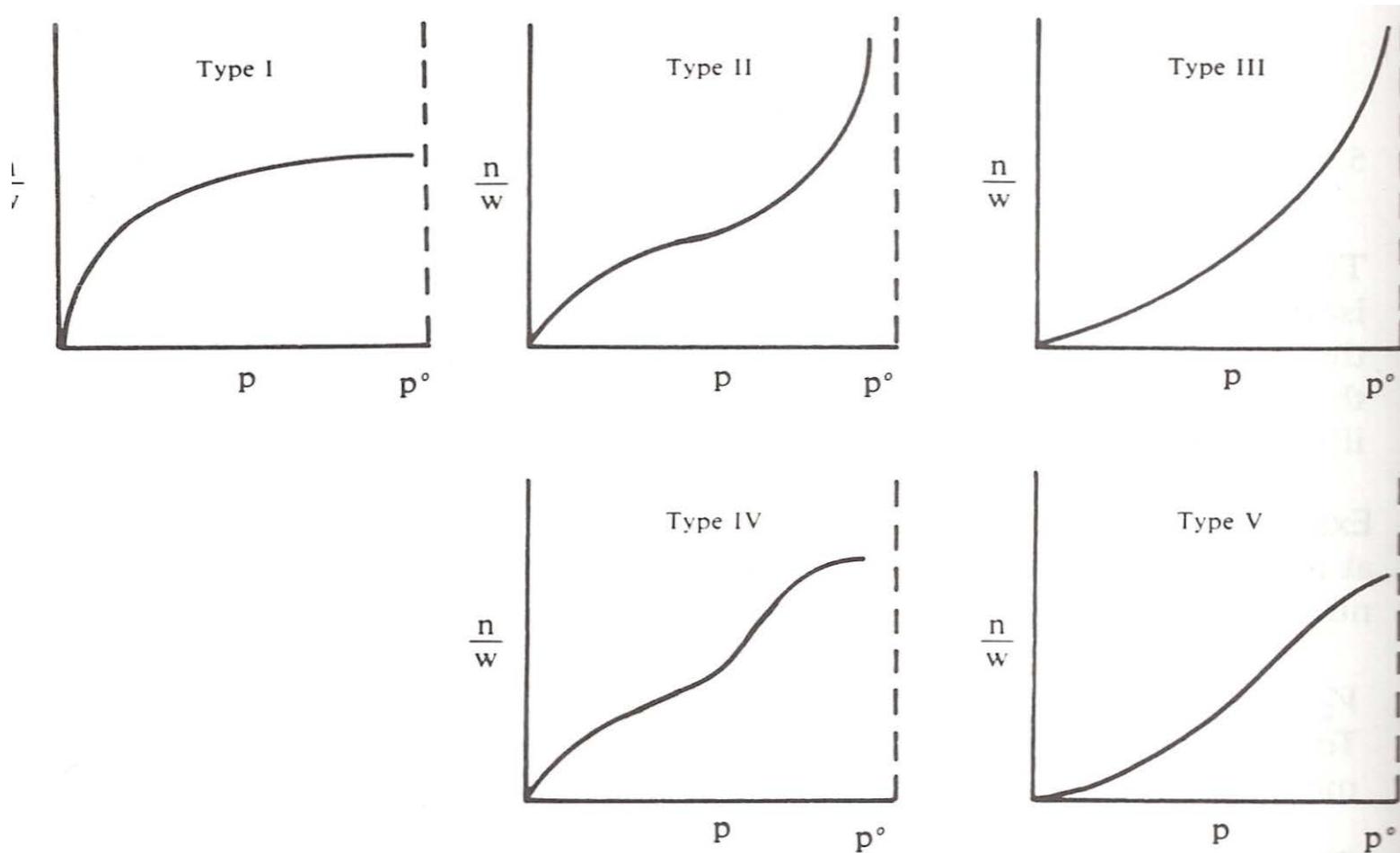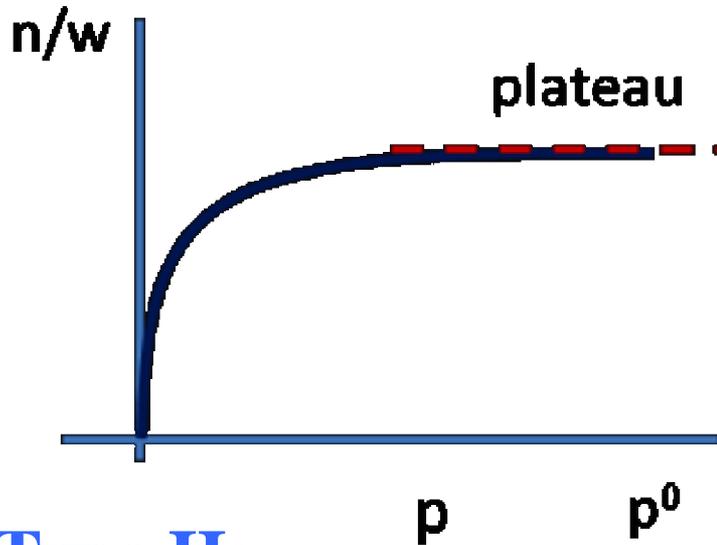
Gas adsorption

Gas adsorption isotherm can be classified into five types:

Figure 9.2 Qualitative shapes of the five general types of gas adsorption isotherms (see text for a discussion of their physical significance).
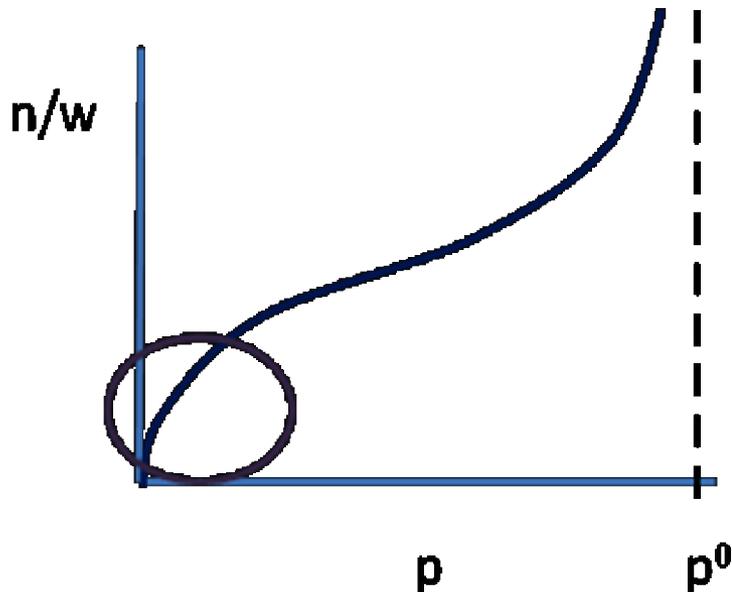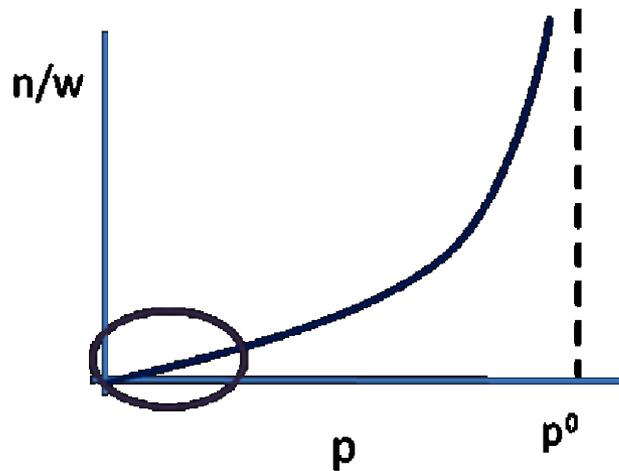
Type I:

Langmuir isotherm:

the plateau indicating monolayer coverage for nonporous adsorbents. This implies a specific interaction between adsorbate and adsorbent (more typical of chemisorption).

Type II:

Multilayer adsorption
(single layer → multilayer →condensation)

Type III:

n/w

p   p⁰
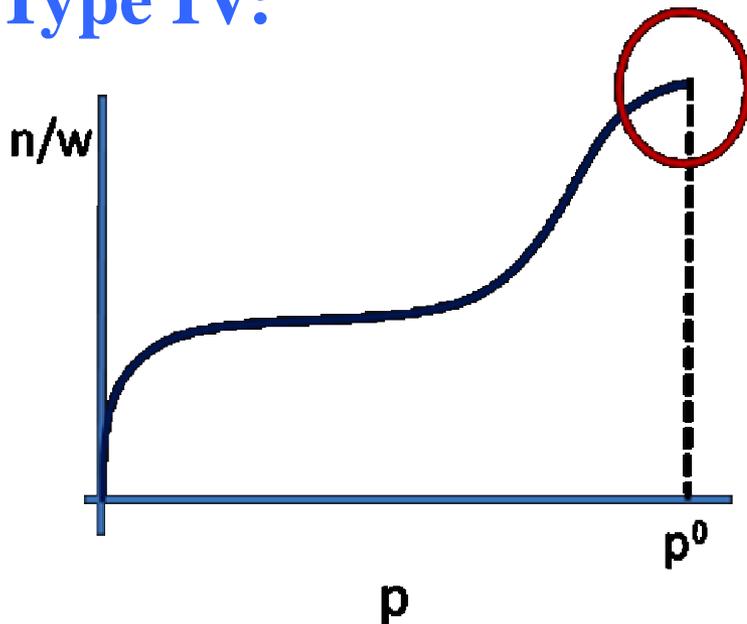
在low pressure時的n/w
較type2小

開始時,氣體通過表面的吸附差

Heat of liquefaction > heat of adsorption

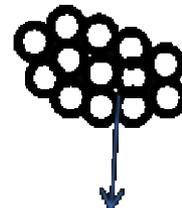**(adsorbate-adsorbed layer interaction**
> adsorbate-adsorbent interaction)

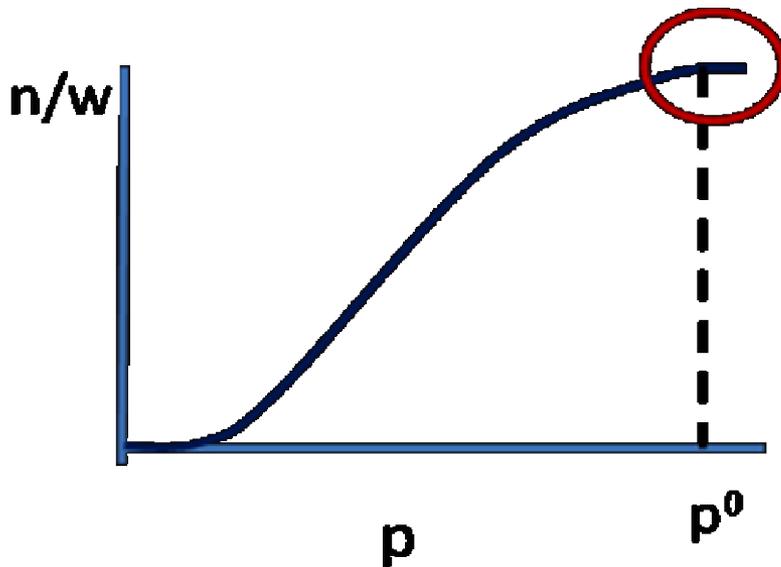# Type IV:

n/w

p   p⁰

Mesopore are filled up

2-100nm
mesopores

Type V:

Types IV and V:

Analogs of types II and III, except for the leveling off occurs at $P < P_0$.

There should be mesopores contained (these materials are not microporous).

If the specific area is the information required, the amount of adsorption at monolayer coverage must be measured. **Monolayer coverage is impossible for physisorption.**

This requires theoretical isotherms.

◆ However, it turns out that a set of experiment data can often be fitted by more than one theoretical isotherm.

◆ **From a practical point of view:**

Any theory that correctly predicts the adsorption results may be regarded as a success.

From a theoretical point of view:
You have to describe adsorption in terms of molecular properties and an equation of state.

E.g. the BET equation:
criticized by theoreticians;
but at the same time, a standard equation for A_{sp}.

To present an accurate picture
→ present both of these viewpoints.