Adsorption at Solid-Gas Interfaces

The solid-gas interface

- Adsorption & desorption
- Adsorption – the kinetic view
- Adsorption isotherms
  - Henry’s law model
  - Langmuir model
  - BET model
  - BDDT classification
Figure 13.1 Schematic view of the possible steps involved in a surface chemical reaction between two homonuclear diatomic molecules.

Solid:

Adsorbed gas or vapor:

Molecules incident on a surface

Collision

reflected adsorbed

inelastic elastic precursor state

Molecules gain or lose some energy to the surface

Molecule leaves with all its energy

physisorption

- weak (~10 kcal/mol)
- van der Waals

chemisorption

- strong (~100 kcal/mol)
- chemical bond

reaction desorption
Analogies with coordination chemistry

Less strongly directional
Highly corrugated potential

$\leq 0.3 \text{ eV (30 kJ mol}^{-1}\text{)}, \text{stable only at cryogenic temperatures}$

Weak
Strong

van der Waals attraction
Chemical bond formation

Table 3.1 Comparison between chemisorption and physisorption

<table>
<thead>
<tr>
<th>Chemisorption</th>
<th>Physisorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electron exchange</td>
<td>Polarization</td>
</tr>
<tr>
<td>Chemical bond formation</td>
<td>van der Waals attraction</td>
</tr>
<tr>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>$\geq 1 \text{ eV (100 kJ mol}^{-1}\text{)}$</td>
<td>$\leq 0.3 \text{ eV (30 kJ mol}^{-1}\text{)}, \text{stable only at cryogenic temperatures}$</td>
</tr>
<tr>
<td>Highly corrugated potential</td>
<td>Less strongly directional</td>
</tr>
<tr>
<td>Analogies with coordination chemistry</td>
<td></td>
</tr>
</tbody>
</table>

Any solid is capable of adsorbing a certain amount of gas, the extent of adsorption at equilibrium depending on:

- fractional coverage of adsorbate $\theta$
  
  $\theta = \frac{\# \text{ of surface sites occupied by adsorbate } (N_s)}{\text{total } \# \text{ of substrate adsorption sites } (N)}$

  when $\theta = 1 \Rightarrow \text{monolayer}$

- associative adsorption: molecules adsorbs onto the surface from gas phase without fragmentation
- dissociative adsorption: molecules adsorbs onto the surface from gas phase with fragmentation
Adsorption – The Kinetic View

From the kinetic theory of gases, flux (the rate of molecular impingement) \( I \):

\[
I = \frac{P}{(2\pi mkT)^{1/2}}
\]

<table>
<thead>
<tr>
<th>( P ) (torr)</th>
<th>( I ) (molecules/cm(^2)·s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>760</td>
<td>3 ( \times ) 10(^{23} )</td>
</tr>
<tr>
<td>1</td>
<td>4 ( \times ) 10(^{20} )</td>
</tr>
<tr>
<td>10(^{-3} )</td>
<td>4 ( \times ) 10(^{17} )</td>
</tr>
<tr>
<td>10(^{-6} )</td>
<td>4 ( \times ) 10(^{14} )</td>
</tr>
<tr>
<td>10(^{-9} )</td>
<td>4 ( \times ) 10(^{11} )</td>
</tr>
<tr>
<td>10(^{-12} )</td>
<td>4 ( \times ) 10(^{8} )</td>
</tr>
</tbody>
</table>

In the plot above, there is no barrier to adsorption, indicating that as a molecule approaches the surface, it will reach a position of minimum potential energy & may be trapped in this position.

The probability of escape per unit time is given by absolute reaction rate theory:

\[
v_{des} = v_0 \exp \left( -\frac{\Delta G_{des}^*}{kT} \right)
\]

\( v_{des} \): desorption frequency (s\(^{-1} \))
\( v_0 \): attempt frequency (~ 10\(^{13} \) s\(^{-1} \))

(on the order of atomic vibration frequency of the crystal lattice)

\( \Delta G_{des}^* \): free energy of activation for the escape process
\[
\exp\left[ -\frac{\Delta G_{\text{des}}}{kT} \right] = \left( \frac{f^*}{f} \right) \exp\left[ -\frac{\Delta H_{\text{des}}}{kT} \right] \\
\approx \left( \frac{f^*}{f} \right) \exp\left[ \frac{\Delta E_u}{kT} \right]
\]

\[
\nu_{\text{des}} = \nu_0 \left( \frac{f^*}{f} \right) \exp\left[ -\frac{\Delta H_{\text{des}}}{kT} \right]
\]

“mean stay time for adsorption”
or “mean surface time”

\[
\tau_a = \frac{1}{\nu_{\text{des}}} = \tau_0 \exp\left[ \frac{\Delta H_{\text{des}}}{kT} \right]
\]

\[
\tau_0 = \frac{1}{\nu_0} \left( \frac{f}{f^*} \right)
\]

\(f, f^*\) are molecular partition function of the system in the equilibrium and activated states.

The deeper the potential well (\(\Delta H_{\text{des}}\uparrow\)), the longer the mean stay time. The value of \(\tau_0\) measured experimentally: \(10^{-16} - 10^{-9}\) s, implying \(ff^* \approx 10^{-3} - 10^4\)

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**Table 10.2** Mean Stay Time for Adsorbed Molecules at 300 K for Various Values of the Adsorption Energy, Assuming \(\tau_0 = 10^{-13}\) sec

<table>
<thead>
<tr>
<th>(\Delta H_{\text{des}}) (cal/mol)</th>
<th><strong>Typical Cases</strong></th>
<th>(\tau_a) (sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>Helium</td>
<td>(1.2 \times 10^{-13})</td>
</tr>
<tr>
<td>1.5</td>
<td>H(_2) physisorbed</td>
<td>(1.3 \times 10^{-12})</td>
</tr>
<tr>
<td>3.5-4</td>
<td>Ar, CO, N(_2), CO(_2) (physisorbed)</td>
<td>(1 \times 10^{-10})</td>
</tr>
<tr>
<td>10-15</td>
<td>Weak chemisorption, Organics physisorbed</td>
<td>(3 \times 10^{-6}), to (2 \times 10^{-2})</td>
</tr>
<tr>
<td>20</td>
<td>H(_2) chemisorbed</td>
<td>100</td>
</tr>
<tr>
<td>25</td>
<td>6 \times 10^5 (1 week)</td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>CO chemisorbed on Ni</td>
<td>(4 \times 10^9 (&gt; 100) yr)</td>
</tr>
<tr>
<td>40</td>
<td></td>
<td>(1 \times 10^{17}) (= age of the earth)</td>
</tr>
<tr>
<td>150</td>
<td>O chemisorbed on W</td>
<td>(10^{100}) (= 10(^{1000}) centuries)</td>
</tr>
</tbody>
</table>

\(\tau_a\) is a strong function of both \(\Delta H_{\text{des}}\) and \(T\).
Gas adsorption processes are accompanied by a decrease of entropy & also a decrease of free energy.

\[ \Delta G = \Delta H + \Delta S \]

\[ \Rightarrow \Delta H \text{ always} \]

\[ \therefore T \uparrow, \text{ extent of adsorption} \]

For \( \Delta H_{\text{des}} = 40 \text{ kcal/mol} \) \( (\tau_0 \approx 10^{-13} \text{ s}) \)

At 300 K \( \tau_a \approx 10^{17} \text{ s} \) (age of the earth)

At 600 K \( \tau_a \approx 1 \text{ s} \)

**physisorption**: systems in which the only attractive forces are of van der Waals or dispersion type

\( \Delta H_{\text{des}} \): 100 cal/mol ~ 5000 cal/mol

**chemisorption**: Systems in which hydrogen bonding, covalent chemical bonding or metallic bonding can take place

\( \Delta H_{\text{des}} \): 5 kcal/mol ~ 150 kcal/mol

- ♦ Factors affecting adsorption rate:
  1. 
  2. 
  3. 
  4. 

- ♦ Factors affecting desorption rate:
  1. 
  2. 
  3.
When the system is in adsorptive equilibrium, the net rate of accumulation of gas molecules on the surface = 0.

impingement rate \( I \) = desorption rate \( E \)

In the case of first-order desorption process,

\[
E = \left( \frac{n_a}{\tau_a} \right) \text{ molecules/cm}^2 \cdot \text{s} \quad n_a: \text{surface population of adsorbed molecules per cm}^2
\]

\[
\therefore E = I
\]

\[
\left( \frac{n_a}{\tau_a} \right) = \frac{P}{(2\pi mkT)^{1/2}}
\]

\[
n_a = I\tau_a = \left[ \frac{P}{(2\pi mkT)^{1/2}} \right] \tau_0 \exp\left[ \frac{\Delta H_{\text{des}}}{kT} \right] \quad \star
\]

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**The Henry’s Law Model**

The simplest assumptions:

1. all atoms adsorb independently of one another
   
   \( \Rightarrow \Delta H_{\text{des}}, \tau_a \) are independent of \( n_a \)

2. all positions on the surface are equivalent, independent of where an incoming gas molecule strikes

在這些最簡化的假設情況下，由上式（

\[
n_a = C \left( \frac{P}{T^{1/2}} \right) \exp\left[ \frac{\Delta H_{\text{des}}}{kT} \right]
\]

in which \( C = \frac{\tau_0}{(2\pi mk)^{1/2}} \) constant for any given gas-surface combination
- **Adsorption isotherm**
  Varying $P$ at constant $T$

- **Adsorption isobar**
  Varying $T$ at constant $P$

\[
 n_a = C_2 \left( \frac{1}{T^{1/2}} \right) \exp \left( \frac{\Delta H_{\text{des}}}{kT} \right) \quad \text{ exponential term in } T \text{ dominates}
\]

- **Adsorption isostere**
  Relation between $P$ and $T$ for a constant amount adsorbed

\[
 P = C_3 T^{1/2} \exp \left( -\frac{\Delta H_{\text{des}}}{kT} \right)
\]

\[
 \ln P = -\frac{\Delta H_{\text{des}}}{kT} + C_4 \quad \text{ where the influence of } T^{1/2} \text{ term relative to the exponential term has been neglected}
\]

\[
 \ln P \text{ vs. } \frac{1}{T} \Rightarrow \text{ slope } = -\frac{\Delta H_{\text{des}}}{kT}
\]

**Figure 10.3** Expected equilibrium adsorption behavior in a system following Henry’s law: adsorption isotherms (a), adsorption isobars (b), and adsorption isosteres (c).
“Clausius-Clapeyron equation”

\[
\left( \frac{\partial \ln P}{\partial T} \right)_v = -\frac{\Delta H_{\text{ads}}}{RT^2} \quad (\theta : \text{constant})
\]

integrate \Rightarrow \ln \left( \frac{P_1}{P_2} \right) = \frac{\Delta H_{\text{ads}}}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)

plot \ln \left( \frac{P}{P_0} \right) vs. \frac{1}{T} \quad \text{slope} \propto \Delta H_{\text{ads}}

Do so for several coverage \( \theta \) and we can get \( \Delta H_{\text{ads}}(\theta) \).

---

The Langmuir Model

Assumptions:

1. Surface is
2. Finite # of sites for adsorption
3. No coverage effects – independent adsorption

與 Henry’s law model 最大差別在第(3)點：molecules striking a surface site that is already occupied do not adsorb.

回到 ★ 式：

\( n_u \): surface population of adsorbed molecules per cm\(^2\)

\( n_0 \): # of adsorption sites per cm\(^2\)
solving for $n_a$,

$$n_a + \left( \frac{I \tau_a n_a}{n_o} \right) = I \tau_a$$

$$n_a \left[ 1 + \left( \frac{I \tau_a}{n_o} \right) \right] = I \tau_a$$

$$\left( \frac{n_a}{n_o} \right) \left[ 1 + \left( \frac{I \tau_a}{n_o} \right) \right] = \frac{I \tau_a}{n_o}$$

$$\theta = \left( \frac{n_a}{n_o} \right) = \frac{I \tau_a}{n_o} \left( 1 + \left( \frac{I \tau_a}{n_o} \right) \right)$$

Or, substituting $l = p/(2\pi nkT)^{1/2}$, and defining $\chi = \left( \frac{\tau_a}{n_o} \right) \left( \frac{1}{(2\pi nkT)^{1/2}} \right)$,

one has $\frac{I \tau_a}{n_o} = \chi p$, and thus $\theta = \frac{\chi p}{1 + \chi p}$.

**Figure 10.4** The adsorption isotherm according to the Langmuir model.

Note that at low pressures, where $\chi p << 1$, the equation reduces to the Henry's law relation $\theta = \chi p$, $n_a = n_0 \chi p$.

At high pressures, where $\chi p >> 1$, the equation reduces to $\theta = \frac{\chi p}{\chi^p} = 1$. 
Another consideration of the Langmuir model:

(A) for 1st order Langmuir adsorption

\[ \text{M}(g) + \text{S}_{\text{surface site}} \frac{k_a}{k_d} \text{M} - \text{S} \]  

(Associative adsorption)

rate of adsorption = \( k_a \cdot P(1 - \theta) \)

rate of desorption = \( k_d \cdot \theta \)

at equilibrium:

(B) for 2nd order Langmuir adsorption

\[ \text{M}_{2(g)} + 2 \text{S}_{\text{surface site}} \frac{k_a}{k_d} \text{2(M} - \text{S}) \]  

(Dissociative adsorption)

rate of adsorption = \( k_a \cdot P(1 - \theta)^2 \)

rate of desorption = \( k_d \cdot \theta^2 \)

at equilibrium:
针对1st order Langmuir isotherm 討論：

\[ \theta = \frac{KP}{1 + KP} \]

- \( K \): equilibrium constant, represents the affinity of a particular molecule for a surface

\( K \uparrow \), bond between adsorbate & substrate \( \uparrow \)

limiting conditions:

as \( P \to 0 \), \[ \left( \frac{KP}{1 + KP} \right) \approx 0 \]

when \( KP \ll 1 \), (low \( P \)) \( \theta = KP \)

when \( P \to \infty \), (high \( P \)) \( \theta \approx 1 \)

Summary of the essential features of the Langmuir adsorption isotherm.
決定 total surface area $S_A$ of solid surfaces

$$
\theta = \frac{N_s}{N} = \frac{m}{m_\infty} = \frac{V}{V_\infty} = \frac{KP}{1 + KP}
$$

$m$: mass of gas adsorbed
$m_\infty$: mass of gas adsorbed in a monolayer
$V$: volume of gas adsorbed
$V_\infty$: mass of gas adsorbed in a monolayer

But $N_s$ is usually quite difficult to determine experimentally

故一般使用 $m$ or $V$ (changes after adsorption)

$$
\theta = \frac{m}{m_\infty} \Rightarrow \left( \frac{P}{m} \right) = \frac{1}{m_\infty K} + P\left( \frac{1}{m_\infty} \right)
$$

plot $\left( \frac{P}{m} \right)$ vs. $P$,  
Slope $= 1/m_\infty$
Intercept $= 1/m_\infty K$

或

$$
\theta = \frac{V}{V_\infty} \Rightarrow \left( \frac{P}{V} \right) = \frac{1}{V_\infty K} + P\left( \frac{1}{V_\infty} \right)
$$

plot $\left( \frac{P}{V} \right)$ vs. $P$,  
Slope $= 1/V_\infty$
Intercept $= 1/V_\infty K$
If \( N \) (the total # of sites corresponding to a monolayer) is known & the area of one molecule \( (A_m) \) is known, a priori, the total surface area is:

\[
S_A = N \cdot A_m
\]

\( N \) may be obtained from \( m_\infty \):

\[
\therefore \quad \frac{m_\infty}{\text{M.W.}} = \frac{n_\infty}{N_A} = \frac{N}{N_A} \quad \Rightarrow \quad N = \frac{m_\infty N_A}{\text{M.W.}}.
\]

\( N_A \): Avogadro’s #

\( N \) may also be obtained from \( V_\infty \)

#### Heats of adsorption

\[
A_{(g)} + S_{(surface \, site)} \rightleftharpoons A - S
\]

\( K \): thermodynamic equilibrium constant

\( \Delta G^*_{\text{ad}}, \Delta H^*_{\text{ad}}, \Delta S^*_{\text{ad}} \):
standard Gibbs free energy, enthalpy, and entropy of adsorption
\[
\left[ \frac{\partial}{\partial T} (\log_e K^0) \right]_\theta = \frac{\Delta H_{AD}^0}{RT^2} \quad (1.29)
\]

But rearranging the Langmuir adsorption isotherm
\[
KP = \frac{\theta}{1 - \theta} \quad (1.30)
\]
and taking natural logs of both sides of equation 1.30:
\[
\log_e K + \log_e P = \log_e \left( \frac{\theta}{1 - \theta} \right) \quad (1.31)
\]

Differentiating eqn 1.31 with respect to \( T \) at constant \( \theta \), gives
\[
\left[ \frac{\partial}{\partial T} (\log_e K) \right]_\theta + \left[ \frac{\partial}{\partial T} (\log_e P) \right]_\theta = 0
\]
i.e.
\[
\left[ \frac{\partial}{\partial T} (\log_e K) \right]_\theta = - \left[ \frac{\partial}{\partial T} (\log_e P) \right]_\theta \quad (1.32)
\]
Putting eqn 1.32 in eqn 1.29
\[
\left[ \frac{\partial}{\partial T} (\log_e P) \right]_\theta = - \frac{\Delta H_{AD}^0}{RT^2} \quad (1.33)
\]

Hence, the isosteric (constant coverage) enthalpy of adsorption, \( \Delta H_{AD}^0 \), may be determined from measurements of \( P \) and \( T \) at constant coverage \( \theta \), since integration of eqn 1.33 gives
\[
[\log_e (P_1/P_2)]_\theta = \frac{\Delta H_{AD}^0}{R} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)
\]
and \( P_1, P_2, T_1, \) and \( T_2 \) may be determined from the isotherm obtained at two different temperatures (Fig. 1.3).

Fig. 1.3 Measurement of isosteres.
Note that at all stages, equilibrium between the adsorbed layer and the gas phase must be maintained (\( T_1 > T_2 \)). The dotted line represents the constant value of \( \theta \). The intersection of dotted lines and full lines gives appropriate values of \( T_1, P_1, T_2 \) and \( P_2 \) for use in eqn 1.34.
The BET Model

Assumptions:
(1) Adsorption of the first adsorbate layer is assumed to take place on an array of surface sites of uniform energy.
(2) 2nd layer adsorption can only take place on top of the 1st, 3rd on top of 2nd, 4th on top of 3rd, etc. When \( P = P_0 \) (the saturated vapor pressure of the adsorbate), an infinite # of layers will form.
(3) At equilibrium, the rates of condensation & evaporation are the same for each individual layer.
(4) When the # of adsorbed layers \( \geq 2 \), the equilibrium constants \( K \) are equal and the corresponding values of \( \Delta H_{ad}^* = -\Delta H_{vap}^* \). For the 1st layer, \( \Delta H_{ad}^* \) is as in the Langmuir case.

![Diagram](image.jpg)

**Figure 10.5** The model used for the development of the B.E.T. treatment of adsorption. The surface is broken up, conceptually, into patches covered with 1, 2, 3, \( \ldots \), \( i \) adsorbed layers.

Over a period of time, the fraction of the surface having a given coverage will remain constant. That is, if \( \theta_i \) is that fraction of the surface covered by \( i \) monolayers, at equilibrium, \( d\theta_i/dt = 0 \) for all \( i \), and the total amount of material adsorbed is

\[
    n_a = n_0\theta_1 + 2n_0\theta_2 + 3n_0\theta_3 + \cdots
\]

or

\[
    n_a = n_0\sum_i i\theta_i
\]
Consider the dynamic nature of the adsorptive equilibrium:

\[ \sum \text{(processes increasing } \theta_i \text{)} = \sum \text{(processes decreasing } \theta_i \text{)} \]

\[
\theta_{(i-1)} \text{ 層之吸附 } & \quad \theta_i \text{ 層之吸附 (變 } \theta_{(i+1)} \text{ 層)} \\
\theta_{(i+1)} \text{ 層之脫附 } & \quad \theta_i \text{ 層之脫附 (變 } \theta_{(i-1)} \text{ 層)}
\]

Thus, for \( \theta_0 \):

\[
\left( \frac{n_0}{\tau_{a_1}} \right) \theta_1 = I \theta_0.
\]

For \( \theta_1 \):

\[
I \theta_0 + \left( \frac{n_0}{\tau_{a_2}} \right) \theta_2 = I \theta_1 + \left( \frac{n_0}{\tau_{a_1}} \right) \theta_1.
\]

For \( \theta_2 \):

\[
I \theta_1 + \left( \frac{n_0}{\tau_{a_2}} \right) \theta_3 = I \theta_2 + \left( \frac{n_0}{\tau_{a_1}} \right) \theta_2.
\]

For \( \theta_i \):

\[
I \theta_{(i-1)} + \left( \frac{n_0}{\tau_{a_{(i+1)}}} \right) \theta_{(i+1)} = I \theta_i + \left( \frac{n_0}{\tau_{a_i}} \right) \theta_i.
\]

Subtracting the expression for the change in \( \theta_0 \) from that for the change in \( \theta_1 \), leaves

\[
I \theta_1 = \left( \frac{n_0}{\tau_{a_2}} \right) \theta_2.
\]

By a similar process for the other \( \theta_i \), subtracting the expression for changes in \( \theta_{(i-1)} \) from the expression for changes in \( \theta_i \), leaves a set of simultaneous equations of the form

\[
I \theta_i = \left[ \frac{n_0}{\tau_{a_{(i+1)}}} \right] \theta_{(i+1)}.
\]

When this set of equations is solved, subject to the assumption that \( \tau_{a_2} = \tau_{a_3} = \tau_{a_i} \), one obtains an expression for \( n_a \) of the form

\[
n_a = \frac{k_B n_o x}{(1 + x)(1 - x + k_B x)}, \quad \text{in which} \quad k_B = \frac{\tau_{a_1}}{\tau_{a_2}}, \quad x = \frac{I \tau_{a_2}}{n_o}.
\]
Substituting \( l = \frac{p}{(2\pi nkT)^{1/2}} \) in the expression for \( x \), and making the further substitution that \( \beta = 1/(2\pi nkT)^{1/2} \), one obtains
\[
x = \frac{\beta \tau_{a_2} p}{n_o}.
\]
Note that \( x \) is dimensionless, as \( \beta \tau_{a_2}/n_o \) has units of \((\text{pressure})^{-1}\). It is thus convenient to define another parameter \( q \), having units of pressure, as
\[
q = \frac{n_o}{\beta \tau_{a_2}},
\]
to give
\[
x = \frac{p}{q}
\]

The final expression for adlayer coverage is thus
\[
\theta = \frac{n_a}{n_o} = \left( \frac{k_B p}{q} \right) \left( 1 - \frac{p}{q} \right)^{1 + \frac{k_B p}{q}}.
\]
as \( p \to q \), the denominator in the expression approaches zero. Thus, as \( p \to q \), \( \theta \to \infty \).

It has been customary to associate \( q \) with \( P_0 \) (the saturated vapor pressure) and associate \( \tau_{a_2} \) with \( \Delta H_{\text{vap}} \).

BET equation expressed in linear form:

\[
C = e^{(\Delta H_{\text{des}} - \Delta H_{\text{vap}})/RT} \quad \Delta H_{\text{des}}^o = \text{enthalpy of desorption} = -\Delta H_{\text{ad}}^o
\]

上式亦可以 mass or volume 表示
可求得 both $C$ & $V_\infty$
得知 $V_\infty$ 可得 $N$，即可算 total surface area

**BET isotherms 線性範圍**

$$0.05 < \frac{P}{P_0} < 0.3$$

it underestimates adsorption at low $P$  
it overestimates adsorption at high $P$

**Fig. 1.4** Summary of essential features of the BET isotherm. Note that the existence of a 'knee' at point B is indicative of monolayer completion.
Properties of the BET curves

- The existence of a “knee” corresponds to the completion of the first monolayer.
- When $C > 1$ ($\Delta H_{\text{des}} > \Delta H_{\text{vap}}$), BET describes type II isotherm at low $P$: $(P_0 - P) \sim P_0$, BET reduces to Langmuir as $C \uparrow$, the isotherm resembles more and more the Langmuir adsorption isotherm with the shallow rise at the knee (point B in the previous plot), extending further and further towards $P/P_0 = 1$, relative to the steep rise close to $P/P_0 = 0$.

In the limit as $C \rightarrow \infty$ ($\Delta H_{\text{des}} \gg \Delta H_{\text{vap}}$)

\[
\frac{V}{V_\infty} = \frac{1}{1 - P/P_0}
\]

- When $C < 1$ ($\Delta H_{\text{des}} < \Delta H_{\text{vap}}$), BET describes type III isotherm

BDDT Classification

Different types of isotherms exhibited by real surfaces (types I–V) classified by Brunauer, Denning, Denning and Teller

- **Type I:** resembling “Langmuir” behavior may also correspond to filling of “micropores” with solids [e.g., some activated charcoal, silica gels, zeolites etc.]
- **Type II:** unrestricted monolayer-multilayer adsorption on a heterogeneous substrate may be readily interpreted within a BET isotherm [e.g., N2 adsorption on non-porous or macroporous (pore size > 50 nm) powders (e.g. carbons or oxides) at 77K]
- **Type III:** comparatively rare; adsorbate–adsorbent interactions are weak [e.g., H2O adsorption on graphitized carbons or PE]
• Type IV: the characteristic "hysteresis loop" is indicative of the presence of narrow (2–5 nm) pores that facilitates condensation.

孔隙若大些，則會觀察到 type II 的行為

• Type V: difficult to interpret and occur rarely

• Type VI: each "step" corresponds to the completion of the 1st, 2nd, 3rd ... etc. monolayers [e.g., noble gas adsorption on well-defined uniform solids such as HOPG]


Fig. 1.5 The Brunauer, Denning, Denning, Teller (BDDT) classification of the different types of isotherms exhibited by real surfaces. See text for details.