31.6 : Gas molecules can physisorb or
chemisorb to a solid surface.

Adsorption, the sticking of a gas molecule to a solid
surface, is always exothermic.

There are two types of adsorption:

Physisorption (physical adsorption) occurs when the
main attractive forces between the adsorbate and the
surface arise from van der Waals interactions.

It is weak: the strength of the interaction is $< 20 \text{ kJ mol}^{-1}$.
and the potential minimum is at
a large distance compared to typical chemical
bonds.

Chemisorption (chemical adsorption) involves
covalent or ionic forces. A bond in the adsorbate
is broken and new chemical bonds are formed
with the solid surface.

This type of interaction is very strong : $250 - 500 \text{ kJ mol}^{-1}$
and the bond is short.

Because chemisorption involves the formation of
chemical bonds to the surface, only a single layer
(or monolayer) of molecules can chemisorb to a surface.

See Fig 31.20

Fig 31.20 shows a very simple viewpoint, where it
is assumed that the surface has only one type of
binding site and that neither the angle at which the
adsorbate approaches the surface nor the orientation
of the adsorbate with respect to the surface matter.

Under these assumptions, the physisorbed state is
plotted relative to the energy of the adsorbate
at infinite separation from the surface.

Direct desorption of the chemisorbed state generates
fragment in the gasphase, of high energy compared
to the adsorbate.

It is possible for the adsorbate to first
physisorb, and then convert to the
chemisorbed state. We can picture
this as a chemical reaction with an
activation energy as shown in Fig 31.20.

$$A(g) + S(s) \underset{k_d}{\overset{k_a}{\rightleftharpoons}} A\text{-}S(s) \qquad K_c = \frac{k_a}{k_d} = \frac{[A\text{-}S]}{[A][S]}$$

Here the rate constants for adsorption and desorption
are independent of the surface coverage
which means we are assuming the adsorbed
molecules do not interact with one another.

Let σ_o = concentration of surface sites (m^{-2} units)
Let θ = fraction of surface sites occupied by adsorbate.

Assume rate of desorption = $v_d = k_d \theta \sigma_o$
rate of adsorption = $v_a = k_a [A] (1-\theta) \sigma_o$

At equilibrium $v_a = v_d \Rightarrow k_d \theta = k_a [A] (1-\theta)$

$$\Rightarrow \frac{1}{\theta} = 1 + \frac{1}{K_c [A]} = 1 + \frac{RT}{K_c P_A} \qquad \text{used } P = cRT \\ \text{ideal gas.}$$
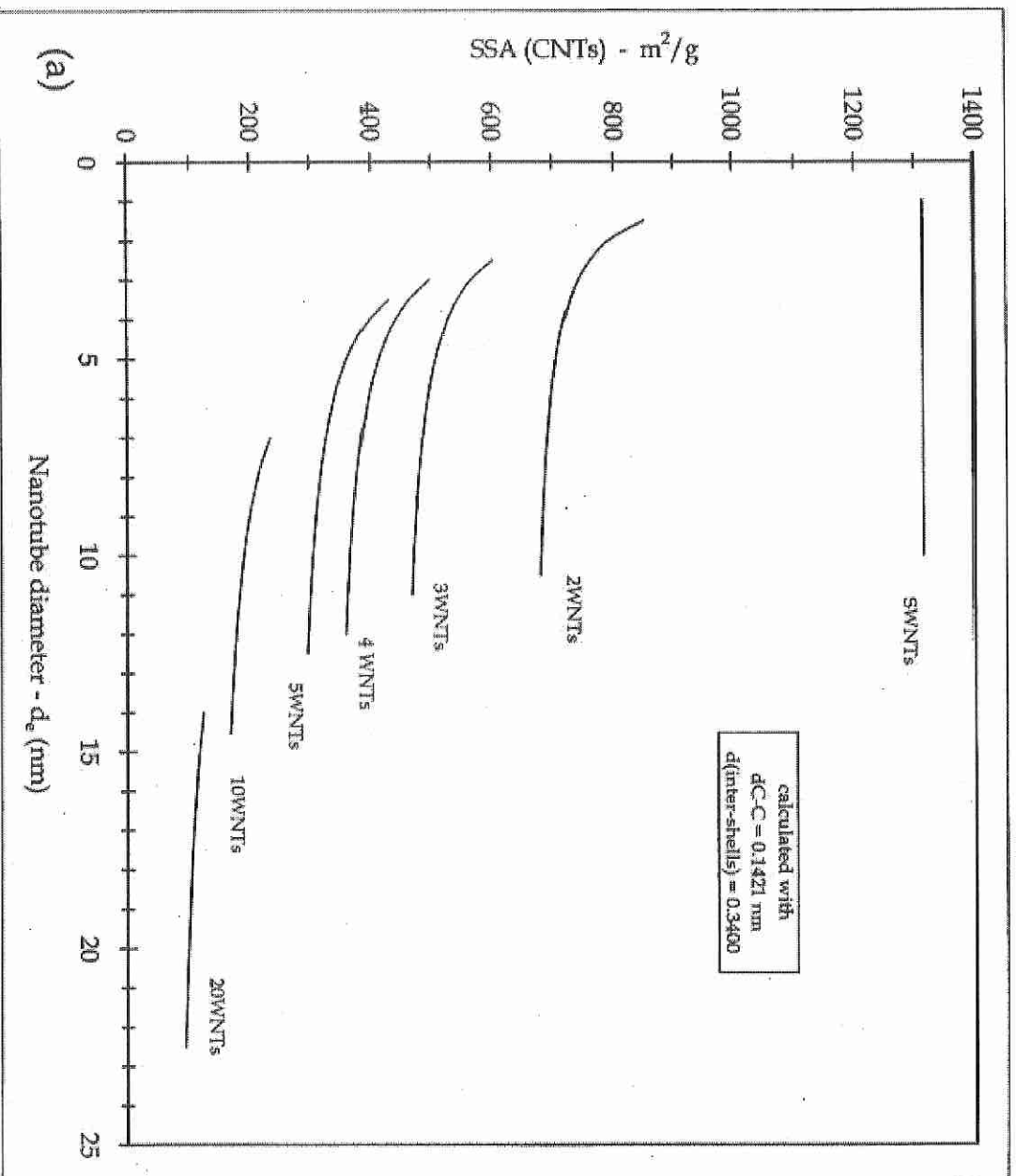
$$\Rightarrow \frac{1}{\theta} = 1 + \frac{1}{b P_A} \qquad , b = K_c / RT$$
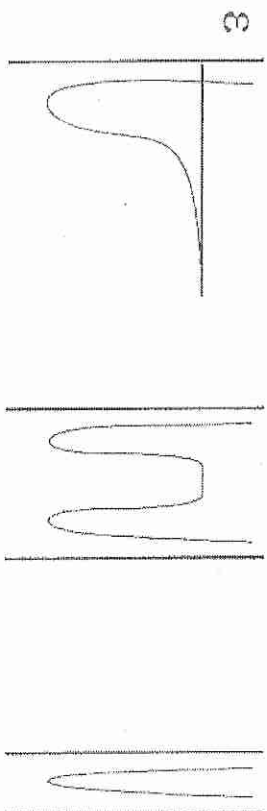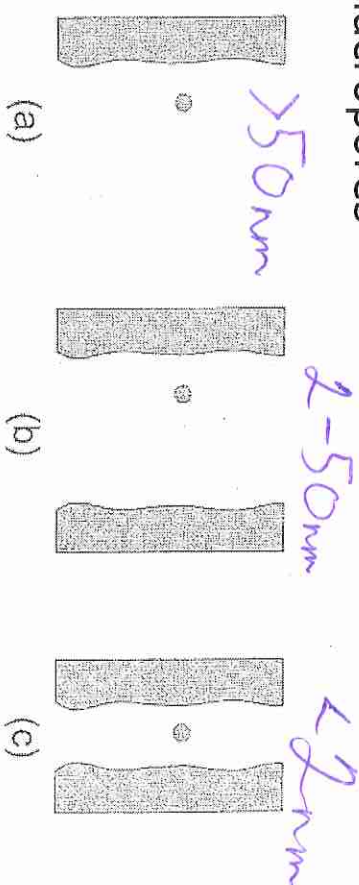
called the Langmuir adsorption isotherm

$\theta \rightarrow 1 \Rightarrow$ monolayer on surface

BET and CNT's

(a) Graph showing SSA (CNTs) - m²/g versus Nanotube diameter - d_e (nm), with curves labeled SWNTs, 2WNTs, 3WNTs, 4WNTs, 5WNTs, 10WNTs, and 20WNTs.

calculated with
dC-C = 0.1421 nm
d(inter-shells) = 0.3400

Peigney et al, CARBON, **39**, 507-514, (2001)

Planar,   mesoporous   microporous
nonporous,
macropores

(a)   (b)   (c)

>50nm   2-50nm   <2nm

ε

Schematic illustration of adsorption potential

BET Assumptions

adsorbate

adsorbent
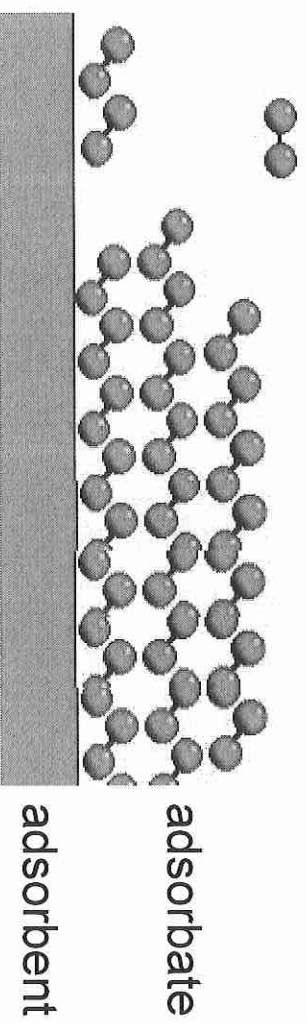
1. Homogeneous surface
2. No lateral interactions between molecules
3. Uppermost layer is in equilibrium with vapor phase
4. First layer: Heat of adsorption;
   Higher layers; Heat of condensation
5. At saturation pressure, the number of layers becomes infinite

molecule dissoci
can be derived fc
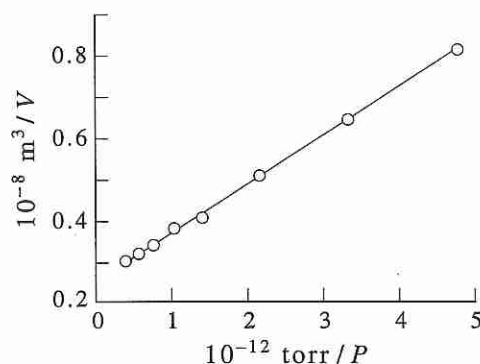
The intercept of the fitted line is 0.252, giving $V_m = 3.96 \times 10^{-8}$ m³. The slope of the fitted line is 1.18×10^{-5} torr·m⁻³, from which we find $b = 2.14 \times 10^{12}$ torr⁻¹.

At 0.00°C and 1.00 atm, 1 mol of gas occupies 2.24×10^{-2} m³. Thus, the number of moles of gas in the volume V_m is

$$\frac{3.96 \times 10^{-8} \text{ m}^3}{2.24 \times 10^{-2} \text{ m}^3 \cdot \text{mol}^{-1}} = 1.77 \times 10^{-6} \text{ mol}$$

which corresponds to

$$(6.022 \times 10^{23} \text{ mol}^{-1})(1.77 \times 10^{-6} \text{ mol}) = 1.06 \times 10^{18} \text{ molecules}$$

Because each molecule occupies a single surface site, there are 1.06×10^{18} sites on the surface. If the mica substrate were a 0.010-m square, the concentration of surface sites would be

$$\sigma_0 = \frac{1.06 \times 10^{18} \text{ molecules}}{(0.010 \text{ m})^2} = 1.06 \times 10^{22} \text{ m}^{-2}$$

Figure 31.22 shows that experimental data for the adsorption of oxygen and carbon monoxide on a silica surface are well described by the Langmuir adsorption isotherm. Example 31–11 derives the adsorption isotherm for the case in which a diatomic
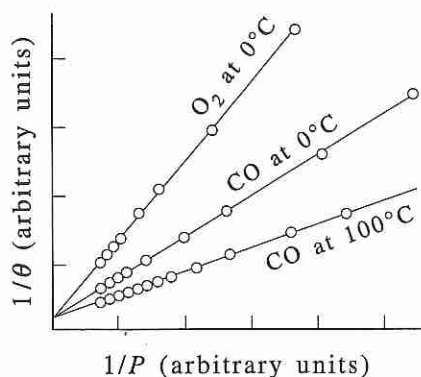
The recipr
an interesting ɟ
curve shown iɪ
be added to thɛ

FIGURE 31.22
A plot of $1/\theta$, the inverse of the fraction of surface sites occupied, as a function of $1/P$ for $O_2(g)$ and CO adsorbed on silica. The data are well described by the Langmuir adsorption isotherm (Equation 31.36). The solid lines are the best fit of the Langmuir adsorption isotherm to the experimental data.

activated chemisorption

Potential energy

C

E_a

P

Precursor state

Distance from surface

$D(A-A)$ gas
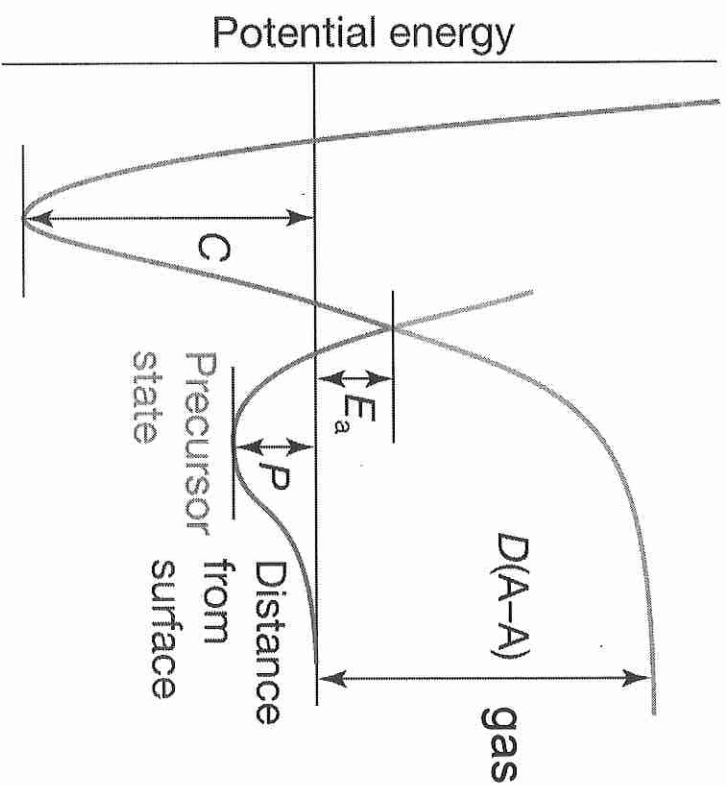
Heterogeneous catalysis

chemisorption   physisorption

Surface area/pore size determination

Modern Methods in Heterogeneous Catalysis Research; 01 Nov 2013; Surface Area and Pore Size Determination; A. Trunschke.

11

$\Gamma = f(p)_T$

The shape of the isotherm of pure fluids depends on

- Interplay between the strength of fluid-wall and fluid-fluid interaction
- Pore space

Classification by the International Union of Pure and Applied Chemistry*
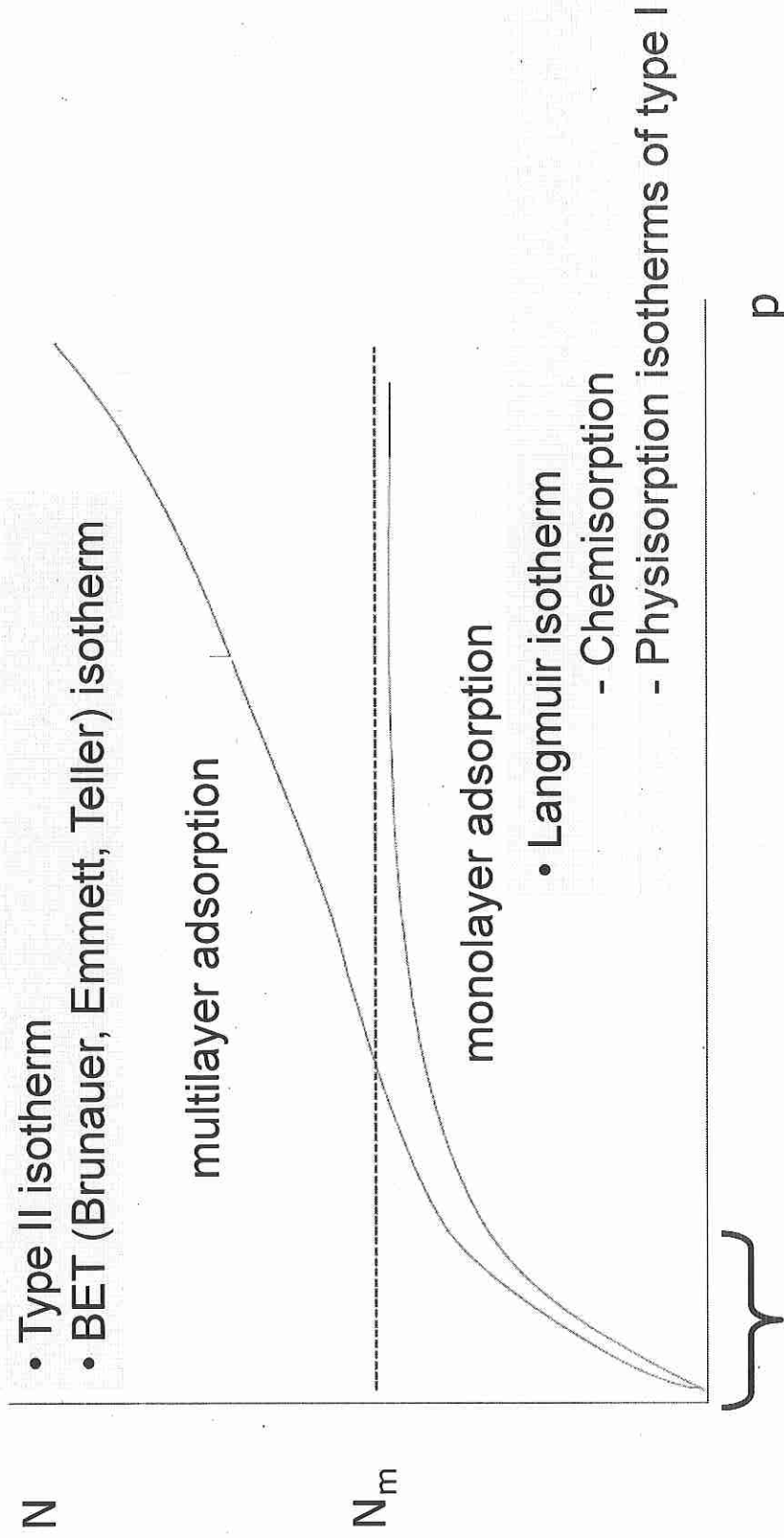
	Width* [nm]
Micropores	< 2
Mesopores	2 ~ 50
Macropores	> 50

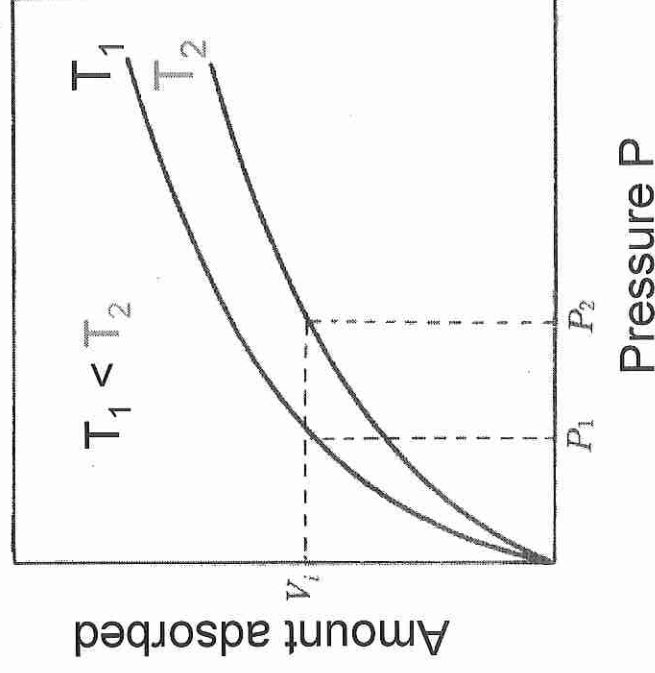- Ultramicropores below 0.7nm
- Supramicropores 0.7~2nm

Width*
- Diameter of a cylindrical pore
- Distance between opposite walls in case of slit pores

* K.S.W. Sing et al., Pure Appl. Chem. 57 (1985) 603.

Other isotherms

- Type II isotherm
- BET (Brunauer, Emmett, Teller) isotherm

multilayer adsorption

N

N_m

monolayer adsorption

- Langmuir isotherm
  - Chemisorption
  - Physisorption isotherms of type I

p

- Freundlich isotherm
  (interaction of adsorbed molecules)
  $$\theta = c_1 p^{1/c_2}$$
- Temkin isotherm
  (adsorption enthalpy is a function of the pressure)
  $$\theta = c_1 ln(c_2 p)$$

$$\Gamma = f(p)_T$$

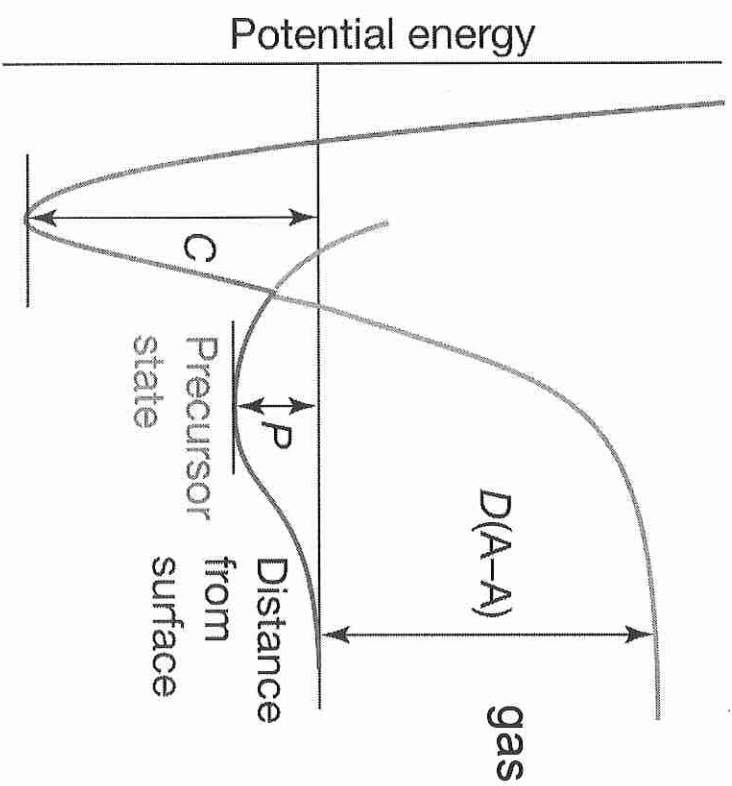Adsorption is favored at lower temperatures

$$\Delta G = \Delta H - T\Delta S$$

Decrease in translation freedom by adsorption: $\Delta S < 0$
Adsorption is a spontaneous process: $\Delta G < 0$

$\rightarrow$

$\Delta H < 0$ Exothermic process

where k_a and k_d are the rate constants for adsorption and desorption, respectively. The fact that k_a and k_d are constants independent of the extent of surface coverage implies that the adsorbed molecules do not interact with one another. Let σ_0 be the concentration of surface sites in units of m^{-2}. If the fraction of surface sites occupied by an adsorbate is θ, then σ, the adsorbate concentration on the surface, is $\theta\sigma_0$, and the concentration of empty surface sites is given by $\sigma_0 - \theta\sigma_0 = (1 - \theta)\sigma_0$. We now assume that the rate of desorption is proportional to the number of occupied surface sites and that the rate of adsorption from the gas phase is proportional to both the number of available (unoccupied) surface sites and the number density of molecules in the gas phase. Mathematically, the rates of desorption and adsorption are given by

$$\text{rate of desorption} = v_d = k_d\theta\sigma_0 \tag{31.33}$$

and

$$\text{rate of absorption} = v_a = k_a(1 - \theta)\sigma_0[A] \tag{31.34}$$

where [A] is the number density or the concentration of A(g). At equilibrium, these rates must be equal, so

$$k_d\theta = k_a(1 - \theta)[A]$$

or

$$\frac{1}{\theta} = 1 + \frac{1}{K_c[A]} \tag{31.35}$$

where $K_c = k_a/k_d$ is the concentration equilibrium constant for Equation 31.32. Generally the pressure of A(g) and not the concentration of A(g) is measured. If the pressure
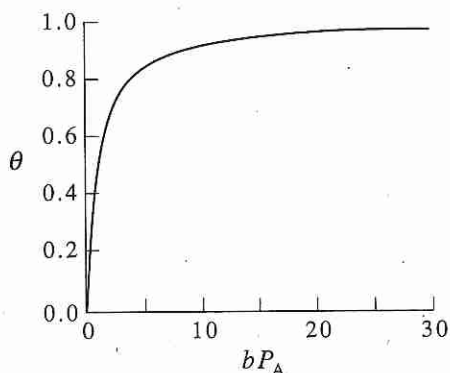

bP_A

FIGURE 31.21
A plot of Equation 31.36, showing that the fraction of the surface covered, θ, is a nonlinear function of the gas pressure.

of A(g) is low e
define $b = K_c/k$

Equation 31.36 i
of θ versus bP_A
monolayer on th
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	Physisorption	Chemisorption
Heat of adsorption	< 50 kJ mol^{-1}	> 500 kJ mol^{-1}
Coverage	Multilayer $\rightarrow$ Measurement of surface area	Monolayer or less, site restriction $\rightarrow$ Titration of active sites
Interaction	No structural changes, reversible	Disruption of chemical bonds may happen
Kinetics	Fast	Activation required
Pores	Pores may be filled $\rightarrow$ Pore volume measurements	-

adsorbate-substrate bond is long compared with the length of the bonds in the bulk solid..

The second type of adsorption is called *chemisorption* (chemical adsorption) and was first proposed by the American chemist Irving Langmuir in 1916. In chemisorption, the adsorbate is bound to the substrate by covalent or ionic forces, much like those that occur between the bonded atoms of a molecule. In chemisorption, a bond of the molecule is broken and new chemical bonds are formed between the molecular fragments and the substrate. Unlike in physisorption, the strength of the substrate-adsorbate bond for a chemisorbed substrate is large; values between 250 and 500 $kJ \cdot mol^{-1}$ are typical. In addition, the length of the substrate-adsorbate bond is shorter for a chemisorbed molecule than for a physisorbed molecule. Because chemisorption involves the formation of chemical bonds to the surface, only a single layer of molecules, or a *monolayer*, can chemisorb to the surface.

Lennard-Jones originally modeled the physisorbed and chemisorbed states in terms of one-dimensional potential-energy curves. Such a model assumes that the substrate has only one type of binding site and that neither the angle at which the adsorbate approaches the substrate nor the orientation of the adsorbate with respect to the substrate is important. If so, the potential energy depends only on z, the distance between the substrate and the adsorbate. Figure 31.20 shows a plot of one-dimensional potential-energy curves for the adsorption of a diatomic molecule, AB, on a surface. We define $V(z) = 0$ to correspond to the infinite separation of the substrate and the diatomic
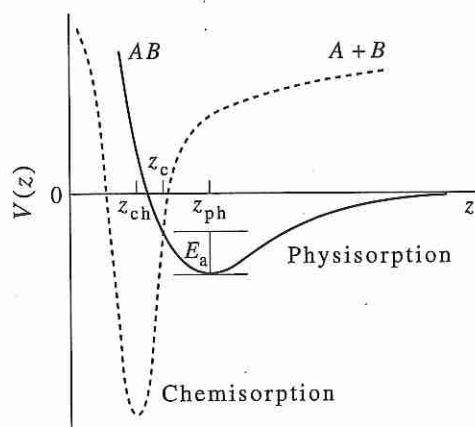

FIGURE 31.20
One-dimensional potential-energy curves for the physisorption of molecule AB (solid line) and the dissociative chemisorption of AB (dashed line). The quantity z is the distance from the surface. In the physisorbed state, the molecule AB is bound to the surface by van der Waals forces. In the chemisorbed state, the AB bond is broken, and the individual atoms are bound covalently to metal atoms on the surface. The points z_{ch} and z_{ph} are the surface-molecule bond lengths for a chemisorbed and physisorbed molecule, respectively. The two potential curves cross at z_c. The activation energy for the conversion from physisorption to chemisorption is measured from the bottom of the physisorbed potential and is E_a.

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physisorbed mol

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crossing is great

31–7. Isother
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A plot of surface
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used to determi
concentration of

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in 1918. Langm
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residence time:

an energy equal to

$E_{ads} = -\Delta H_{ads}$ must be
added to the system to break
the adsorbate-substrate bond.
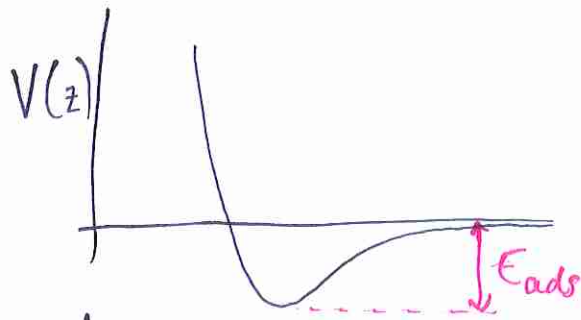
Experimentally we find that k_d obeys Arrhenius-like
behavior.

$$k_d = \tau_o^{-1} e^{-E_{ads}/RT}$$

where $E_{ads} = -\Delta H_{ads}$ and where $\tau_o \approx 10^{-12}$ s

$1/k_d = \tau =$ residence time = lifetime of a molecule on surface.

$$\tau = \tau_o e^{E_{ads}/RT}$$

ex the enthalpy of adsorption of CO on palladium
is -146 kJ/mol. Compute τ at 300 K and 500 K.

$$\tau = (1.0 \times 10^{-12} s) \exp\left(\frac{146 \times 10^3 \text{ J/mol}}{8.314 \text{ JK}^{-1}\text{mol}^{-1} \cdot 300\text{K}} \right)$$

$$= 2.6 \times 10^{13} s$$

At 500 K, $\tau = 1800$ s