In modern surface science, important technological processes often involve the adsorption of molecules in gaseous form onto a surface. We can treat this adsorption problem by using thermodynamics or kinetics. The nature of the adsorption process depends on gas-surface interactions.

- Thermodynamics approach

**Gibbs model:** Assume that the concentrations of the two bulk phases are uniform up to a mathematical “dividing surface” of zero thickness appropriately chosen to stimulate the real system.

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**Figure 5.1** Composition variation across an interface in a two-component system. (a) The real system. (b) According to the Gibbs model.
**Langmuir isotherm**: Assume the ideal lattice gas model. I.e. $N$ particles are assumed to bound to $M$ adsorption sites (with $N < M$) with an identical energy. We can show the adlayer coverage $\theta$ is:

$$\theta = \frac{\chi P}{1 + \chi P}$$

where the “mole fraction” is

$$\chi = q \exp(-\mu^0/kT)$$

and $q$ is the partition function and $\mu^0$ is the standard chemical potential.

From these simple models, we can evaluate all the standard thermodynamic variables corresponding to a multi-component system.
• Kinetics approach

Figure 5.6  The Langmuir adsorption isotherm.

Figure 9.3  One-dimensional potential energy diagram for an atom approaching a solid surface along a path perpendicular to the surface.
To do this, we need to know the change in the potential energy of the system as the molecule approaches the surface, i.e. gas-surface interactions. Depending upon the strength of these interactions, we may loosely classify the adsorption as either physisorption (< 5 kcal/mol) or chemisorption (> 5 kcal/mol).

One common technique to probe the gas-surface interactions is by atom scattering. We can consider this classically or quantum mechanically. A generic potential energy curve of this kind of gas-surface interaction resembles that of the formation of the hydrogen molecule.
Figure 9.11  Potential energy (solid curve) and kinetic energy (dotted curve) for an atom approaching a solid surface.

Figure 9.14  Scattering of atoms from a rough surface corrugation. Scattering occurs at the local specular angle, giving rise to "rainbow scattering."

Figure 9.15  Scattering trajectory plots for the impingement of a gas atom on surfaces of differing corrugation amplitude. The maximum deviation from specular scattering is associated with the inflection point of the corrugation.
We can derive the so-called fundamental kinetic equation for adsorption equilibrium by assuming...
essential first order kinetics for the desorption. [See hand-written note.]

<table>
<thead>
<tr>
<th>$\Delta H_{\text{des}}$</th>
<th>Typical Cases</th>
<th>$\tau_0$ (sec)</th>
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<tbody>
<tr>
<td>100 cal/mol</td>
<td>Helium</td>
<td>$1.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>1.5 kcal/mol</td>
<td>$H_2$ physisorbed</td>
<td>$1.3 \times 10^{-12}$</td>
</tr>
<tr>
<td>3.5-4 kcal/mol</td>
<td>Ar, CO, N$_2$, CO$_2$ (physisorbed)</td>
<td>$1 \times 10^{-10}$</td>
</tr>
<tr>
<td>10-15 kcal/mol</td>
<td>Weak chemisorption, Organics physisorbed</td>
<td>$3 \times 10^{-6}$, to $2 \times 10^{-2}$</td>
</tr>
<tr>
<td>20 kcal/mol</td>
<td>$H_2$ chemisorbed</td>
<td>100</td>
</tr>
<tr>
<td>25 kcal/mol</td>
<td>CO chemisorbed on Ni</td>
<td>$6 \times 10^5$ (1 week)</td>
</tr>
<tr>
<td>30 kcal/mol</td>
<td>CO chemisorbed on Ni</td>
<td>$4 \times 10^9$ (&gt; 100 yr)</td>
</tr>
<tr>
<td>40 kcal/mol</td>
<td>CO chemisorbed on Ni</td>
<td>$1 \times 10^{17}$ (= age of the earth)</td>
</tr>
<tr>
<td>150 kcal/mol</td>
<td>O chemisorbed on W</td>
<td>$10^{100}$ (= $10^{1000}$ centuries)</td>
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**Figure 10.3** Expected equilibrium adsorption behavior in a system following Henry's law: adsorption isotherms (a), adsorption isobars (b), and adsorption isosteres (c).
From this and the basic assumptions used in the Langmuir model, we obtain the same equation for the adsorption isotherm as that derived using statistical thermodynamics (see above). Note that the Langmuir model works best for strong adsorption systems (i.e. with large $\Delta H_{\text{des}}$) or chemisorption and not so good for physisorption.

A model that explicitly relaxes one of the restriction of the Langmuir model so that adlayers can have a value $\theta > 1$ was formulated by *Braunauer, Emmett and Teller* (1938). This so-called B.E.T. model works best for physisorption where multilayer adsorption is common. In this model, we assume that adsorption equilibrium has been obtained. We break down the surface into *patches*, each with a different number of monolayers covered.
- **Experimental Techniques**

A common technique to examine adsorption behaviour is Thermal Desorption Spectrometry (or Temperature-Programmed Desorption Mass Spectrometry), i.e. TDS or TPD. [See hand-written note here.]

See note on Quantitative analysis of P-T curves.
Fig. 5.1. Comparison of (a) thermal desorption and (b) flash desorption curves showing the $\alpha$, $\beta_1$, and $\beta_2$ states of CO on W (Goymour & King, 1973; Ehrlich, 1961b).
Fig. 5.2. Evolution curves for first and second order desorption with the same activation energy, and identical heating curves (Ehrlich, 1961c).

Fig. 5.4. An arbitrary desorption peak with full width at half maximum \( \omega \), and low and high temperature half-widths \( \tau \) and \( \delta \).
Fig. 5.5. Activation energy of desorption $E_d$ as a function of $T_0$ for a first order reaction and a linear temperature sweep, assuming $v = 10^{15} \text{s}^{-1}$ (Redhead, 1962).

Fig. 5.6. The theoretical shapes of first and second order desorption peaks (Redhead, 1962).
Fig. 5.12. Desorption traces for $\text{H}_2$ absorbed on W[100] at $\sim 100$ K with co-adsorbed CO showing binding state shift. CO exposure (a) 0, (b) $3.5 \times 10^{-2}$ torr s, (c) $69 \times 10^{-2}$ torr s, (d) $56 \times 10^{-7}$ torr s, (e) $66 \times 10^{-6}$ torr s (Yates & Madey, 1971).
The other commonly used techniques are Electron Stimulated Desorption (ESD) and Photon Stimulated Desorption (PSD). For ESD, an electron beam is used to excite an adsorbate to an repulsive excited electronic state, which causes the adsorbate to undergo dissociative desorption from the surface. In the case of PSD, a photon (or UV light or laser) is used for the electronic excitation.
Fig. 5.14. Schematic potential curves for interaction between a surface M and an atom A, and between M and the ion A⁺. A possible electronic transition resulting in ESD at A⁺ is indicated by the shaded region.

Fig. 5.15. Additional schematic potential curves for interaction between a surface M and an adsorbed atom A. Possible excited states including an ionic state (M + A⁺ + e⁻), a metastable atomic state (M + A⁺) and an antibonding state (M + A⁺) are shown. The shaded zones show possible electronic transitions from the ground state to the various excited states.
Fig. 5.17. PSD yield curve of O$^+$ emission from O adsorbed on W[100] compared with the energy derivative ESD from the same surface and with the optical absorption spectrum of a W foil. All curves are normalised to constant incident photon or electron flux, while the ESD is offset in energy by 5 eV as an approximate work function correction to give the same excitation energy relative to the Fermi level (after Woodruff et al., 1981).