Lecture 5

Selected aspects of thermodynamics for adsorption, diffusion and desorption

Physisorption
Chemisorption
Surface Bonding
Mechanisms of adsorption/diffusion/desorption

References:
1) Zangwill, Chapter 8, 9, 14
2) Attard and Barnes, p.1-17, 27-34, 71-75
3) Woodruff & Delchar, Chapter 5, p.356
4) Kolasinski, Chapter 3 and 4
5) Somorjai, Chapter 3.8, 4, 5

Force and Energy Diagram

\[ F_{\text{net}} = F_{\text{attractive}} + F_{\text{repulsive}} \]
\[ F_{\text{ATTR}} = \frac{(Z_1 e)(Z_2 e)}{4\pi\varepsilon_0 a^2} \]
\[ F_{\text{REP}} = -\frac{nb}{a^n} \]

\( n \) and \( b \) are constants; \( n = 7 - 9 \)

\[ F_{\text{NET}} = 0 = -\frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 a^2} = \frac{bn}{a^{n+1}} \]

\[ n = 9; \quad \frac{Z_1 Z_2 e^2}{4\pi\varepsilon_0 a^2} = \frac{9b}{a^8} \]

\[ b = \frac{Z_1 Z_2 e^2 a^8}{4\pi\varepsilon_0 \times 9} = \frac{1}{36} \frac{Z_1 Z_2 e^2 a^8}{\pi\varepsilon_0} \]
5.1 Basics of Collision Process

(a) Elastic Scattering
(b) Inelastic Scattering

Adsorb
(c) Chemisorption
(d) Physisorption
Surface diffusion
Surface reaction
Desorption

Figure 3.14 A one-dimensional representation of nonactivated adsorption: (a) elastic scattering trajectory; (b) direct inelastic scattering trajectory; (c) sticking event (chemisorption); (d) sticking event (physisorption).

Cf. Kolasinski

Physisorption vs Chemisorption

<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 attractions</td>
</tr>
<tr>
<td>Strong</td>
<td>Weak</td>
</tr>
<tr>
<td>&gt; 1 eV (100 kJ mol(^{-1}))</td>
<td>&lt; 0.3 eV (30 kJ mol(^{-1}))</td>
</tr>
<tr>
<td>Highly corrugated potential</td>
<td>Stable only at cryogenic temperatures (N(_2) 77K, He 4K)</td>
</tr>
<tr>
<td>Analogies with coordination chemistry</td>
<td>Less strongly directional</td>
</tr>
<tr>
<td>Second phase can form for suitable T and P</td>
<td>Multilayers can form</td>
</tr>
<tr>
<td>O/Fe, Al, Si</td>
<td>H(_2)/ Fe, Au</td>
</tr>
<tr>
<td>H/Pd</td>
<td>H(_2)O/Au</td>
</tr>
<tr>
<td>NH(_3)/Cu</td>
<td>NH(_2)/Cu</td>
</tr>
</tbody>
</table>
5.2 Binding Sites and Diffusion

The binding energy of an adsorbate depends on its position on the surface, or on the **binding site**

![Images of different binding sites](image)

**Effects of T on diffusion:**
Diffusion rate in a system will increase with temperature:

\[
D = D_0 \times e^{\frac{E_A}{RT}}
\]

- \(D\) – diffusivity, m\(^2\)/s
- \(D_0\) – proportionality constant, m\(^2\)/s, independent of T
- \(E_A\) – activation energy for diffusing species, J/mol
- \(R\) – molar gas constant; \(R = 8.314\) J mol\(^{-1}\) K\(^{-1}\)
Fick’s first law of diffusion

\[ J = -D \frac{dC}{dx} \]

For steady-state diffusion condition (no change in the system with time), the net flow of atoms is equal to the diffusivity \( D \) times the diffusion gradient \( \frac{dC}{dx} \).

\[ f \left( \frac{\text{atoms}}{m^2 \text{s}} \right) = -D \left( \frac{m^3}{s} \right) \frac{dC}{dx} \left( \frac{\text{atoms}}{m^3} \times \frac{1}{m} \right) \]

'-' sign: flux direction is from the higher to the lower concentration; i.e., it is the opposite to the concentration gradient.

Diffusivity \( D \) depends on:
1. Diffusion mechanism
2. Temperature of diffusion
3. Type of crystal structure (bcc > fcc)
4. Crystal imperfections
5. Concentration of diffusing species

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Diffusivity (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solvent (host structure)</td>
<td>500°C (932°F)</td>
</tr>
<tr>
<td>1. Carbon</td>
<td>FCC iron</td>
</tr>
<tr>
<td>2. Carbon</td>
<td>BCC iron</td>
</tr>
<tr>
<td>3. Iron</td>
<td>FCC iron</td>
</tr>
<tr>
<td>4. Iron</td>
<td>BCC iron</td>
</tr>
<tr>
<td>5. Nickel</td>
<td>FCC iron</td>
</tr>
<tr>
<td>6. Manganese</td>
<td>FCC iron</td>
</tr>
<tr>
<td>7. Zinc</td>
<td>Copper</td>
</tr>
<tr>
<td>8. Copper</td>
<td>Aluminum</td>
</tr>
<tr>
<td>9. Copper</td>
<td>Copper</td>
</tr>
<tr>
<td>10. Silver</td>
<td>Silver (crystal)</td>
</tr>
<tr>
<td>11. Silver</td>
<td>Silver (grain boundary)</td>
</tr>
<tr>
<td>12. Carbon</td>
<td>HCP titanium</td>
</tr>
</tbody>
</table>

Non-Steady-State Diffusion

In practice the concentration of solute atoms at any point in the material changes with time – non-steady-state diffusion.

For non-steady-state condition, diffusion coefficient, \( D \) - NOT dependent on time:

Second Fick’s law of diffusion:

\[ \frac{dC_s}{dt} = \frac{d}{dx} \left( D \frac{dC_s}{dx} \right) \]

If \( D \neq D(x) \), in 1D case:

\[ \frac{dC_s}{dt} = D \frac{\partial^2 C}{\partial x^2} \]

The rate of compositional change is equal to the diffusivity times the rate of the change of the concentration gradient.

In 3D case:

\[ \frac{dC_s}{dt} = D \left( \frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \]
Non-Steady-State Diffusion (continued)

With specific initial or boundary conditions this partial differential equations can be solved to give the concentration as function of spatial position and time 

\[ c(x, y, z, t) \]

Let us consider two rods with different concentrations \( c_1 \) and \( c_2 \) which are joined at \( x=0 \) and both are so long that mathematically they can be considered as infinitely long. The concentration profile at \( t = 0 \) is discontinuous at \( x = 0 \):

\[ x < 0, \quad c = c_1; \quad x < 0, \quad c = c_2 \]

We can obtain solution of:

\[ \frac{dC}{dt} = D \frac{\partial^2 C}{\partial x^2} \]

\[ c(x, t) - c_1 = \frac{c_2 - c_1}{\sqrt{\pi}} \int_{-\infty}^{x} e^{-z^2} d\xi = \frac{c_2 - c_1}{2} \left( 1 + \text{erf}\left( \frac{x}{2\sqrt{Dt}} \right) \right) \]

where \( \text{erf} (z) = \frac{2}{\sqrt{\pi}} \int_{0}^{z} e^{-\xi^2} d\xi \), is known as the error function \( \frac{x}{2\sqrt{Dt}} \)

Gas diffusion into a solid

Let us consider the case of a gas \( A \) diffusing into a solid \( B \)

\[ \frac{C_s - C}{C_s - C_0} = \text{erf}\left( \frac{x}{2\sqrt{Dt}} \right) \]

\( C_0 \) – surf. C of element in gas diffusing into the surface
\( C_0 \) – initial uniform concentration of element in solid
\( x \) – distance from surface
\( D \) – diffusivity of diffusing solute element
\( t \) – time
\( \text{erf} \) – mathematical function called **error function**
Error function

Curve of the error function $\text{erf}(z)$ for

$$z = \frac{x}{2\sqrt{Dt}}$$

<table>
<thead>
<tr>
<th>$z$</th>
<th>$\text{erf} , z$</th>
<th>$z$</th>
<th>$\text{erf} , z$</th>
<th>$z$</th>
<th>$\text{erf} , z$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0</td>
<td>0.4</td>
<td>0.4284</td>
<td>0.85</td>
<td>0.7707</td>
</tr>
<tr>
<td>0.025</td>
<td>0.0282</td>
<td>0.45</td>
<td>0.4755</td>
<td>0.90</td>
<td>0.7970</td>
</tr>
<tr>
<td>0.05</td>
<td>0.0564</td>
<td>0.50</td>
<td>0.5205</td>
<td>0.95</td>
<td>0.8209</td>
</tr>
<tr>
<td>0.10</td>
<td>0.1125</td>
<td>0.55</td>
<td>0.5633</td>
<td>1.0</td>
<td>0.8427</td>
</tr>
<tr>
<td>0.15</td>
<td>0.1680</td>
<td>0.60</td>
<td>0.6039</td>
<td>1.1</td>
<td>0.8802</td>
</tr>
<tr>
<td>0.20</td>
<td>0.2227</td>
<td>0.65</td>
<td>0.6420</td>
<td>1.2</td>
<td>0.9103</td>
</tr>
<tr>
<td>0.25</td>
<td>0.2763</td>
<td>0.70</td>
<td>0.6778</td>
<td>1.3</td>
<td>0.9340</td>
</tr>
<tr>
<td>0.30</td>
<td>0.3286</td>
<td>0.75</td>
<td>0.7112</td>
<td>1.4</td>
<td>0.9523</td>
</tr>
<tr>
<td>0.35</td>
<td>0.3794</td>
<td>0.80</td>
<td>0.7421</td>
<td>1.5</td>
<td>0.9661</td>
</tr>
</tbody>
</table>

Example...

If boron is diffused into a thick slice of Si with no previous B in it at $T=1100^\circ$C for 5 h, what is the depth below the surface at which the concentration is $10^{17}$ atoms/cm$^3$ if the surface concentration is $10^{18}$ atoms/cm$^3$? $D = 4 \times 10^{-13}$ cm$^2$/s for B diffusing in Si at $1100^\circ$C.
Atomistics of Solid State Diffusion

• Diffusion mechanisms:

1. **Vacancy** (substitutional) diffusion – migration of atom in a lattice assisted by the presence of vacancies
   
   Ex.: self diffusion of Cu atoms in Cu crystal

2. **Interstitial** diffusion – movement of atoms from one interstitial site to another neighboring interstitial site without permanent displacement any of the atoms in the matrix crystal lattice

   Ex.: C diffusion in BCC iron

Vacancy (Substitutional) Diffusion Mechanism

Substitutional (in homogeneous system - self-diffusion, in heterogeneous system – solid state solutions)

• Vacancies are always present at any T
• As T increases ⇒ # of vacancies increases ⇒ diffusion rate increases
• Move atom A (from (1) to (2)) = move vacancy from (2) to (1).?

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting point (°C)</th>
<th>Crystal structure</th>
<th>Temperature range studied (°C)</th>
<th>Activation energy</th>
<th>Activation energy</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zinc</td>
<td>419</td>
<td>HCP</td>
<td>240–418</td>
<td>91.6</td>
<td>21.9</td>
</tr>
<tr>
<td>Aluminum</td>
<td>660</td>
<td>FCC</td>
<td>400–610</td>
<td>165</td>
<td>39.5</td>
</tr>
<tr>
<td>Copper</td>
<td>1083</td>
<td>FCC</td>
<td>700–990</td>
<td>196</td>
<td>46.9</td>
</tr>
<tr>
<td>Nickel</td>
<td>1452</td>
<td>FCC</td>
<td>900–1200</td>
<td>293</td>
<td>70.1</td>
</tr>
<tr>
<td>α iron</td>
<td>1530</td>
<td>BCC</td>
<td>808–884</td>
<td>240</td>
<td>57.5</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2600</td>
<td>BCC</td>
<td>2155–2540</td>
<td>460</td>
<td>110</td>
</tr>
</tbody>
</table>

higher $T_{melt}$ ⇒ stronger bonding between atoms ⇒ high activation energy to move V
Ehrlich-Schwoebel Barrier, $E_S$

Exchange mechanism of diffusion
(important for metal-on-metal growth)

STM image of chromium decorated steps of Cu(111)

Possible mechanisms of self-diffusion and their activation energy

1. Neighboring atoms exchange sites
2. Ring mechanism
3. Vacancy mechanism
4. Direct interstitial mechanism
5. Indirect interstitial mechanism

<table>
<thead>
<tr>
<th>Migration</th>
<th>Formation</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>8 eV</td>
<td>8 eV</td>
</tr>
<tr>
<td>3</td>
<td>1 eV</td>
<td>2 eV</td>
</tr>
<tr>
<td>4</td>
<td>0.6 eV</td>
<td>4 eV</td>
</tr>
<tr>
<td>6</td>
<td>0.2 eV</td>
<td>3.6 eV</td>
</tr>
</tbody>
</table>
5.3 Physisorption

Physisorption arises from dispersion forces. Instantaneous fluctuations in charge distribution interact with instantaneous dipole moments in neighboring species

\[ E_{\text{attr}} = -\frac{C}{r^6}; \quad \text{where} \quad C = f(a_i, \mu_i) \]

The 6-12 Lennard-Jones potential is commonly used to describe both Van der Waals and steeply rising repulsive interaction potential

\[ E \equiv 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] + \frac{C}{r^6} \]

Physisorption energy of Xe on a metal surface

Factors affecting binding energy
- Roughness
- Local adsorbate density
- Proximity of substrate
- Bulk vaporization energy
- Geometry in binding sites
- Adsorbate-adsorbate interactions
- Order/disorder phenomena, phase transitions
- Distinction between adsorbate and substrate

1 eV/atom (molecule) = 23.05 kcal/mol = 96.47 kJ/mol.

Figure 6.29. Heat of xenon adsorption on the stepped palladium (100) \times (110) surface as a function of coverage [45].
5.4 Nondissociative Chemisorption

- Sequential filling of binding sites
- Binding energies depend on crystal face
- Steps, defects affect adsorption energies
- 2D alloyed layers, compound layers can exist when no such bulk phase is known
- Adsorption chemistry is analogous to cluster inorganic chemistry

The Blyholder Model of CO Chemisorption

CO has longed served as a model adsorbate

- MO of gas-phase CO
- The wavefunction changes sign in going from the region shown by different color

Isolated CO:

- 6π
- 2π
- 5π
- 1π
- 4σ
- 3σ

A

B
Molecular Oxygen Chemisorption

- Three distinct vibrational frequencies \( \Rightarrow \) three molecular species
- Decreasing frequency \( \Rightarrow \) increasing M-O_2 bonding

adapted from Surf. Sci. 334, 19

5.5 Reactive (Dissociative) Chemisorption

Chemisorption associated with molecular decomposition

Other Reactive Processes:
- Catalysis (\( A_2 + B_2(\text{ads}) \rightarrow 2AB \))
- Substrate reaction (Oxidation, etc)
- Desorption (+"Chemistry with a sledge hammer"!)
Dissociate Adsorption Examples

$\text{O}_2$ on Al(111)
- At 80K pairs for oxygen adatoms with interatomic distances 1-3 Al spacing

$\text{Cl}_2$ on Si(111)
- At 80K pairs for oxygen adatoms with interatomic distances 1-3 Al spacing

Prediction from Heat of Adsorption

Given dissociative adsorption: is molecular or atomic desorption preferred?

$$|\Delta H_{\text{ads}}| < E_A \quad \text{or} \quad |\Delta H_{\text{ads}}| > E_A$$

Ni-H$_2$
- $M + 2A_{(g)}$

W-O$_2$
- $M + A_{(g)} + A_{(g)}$

Molecular desorption

Atomic desorption