Adsorption of gases on solids

(focus on physisorption)
Adsorption

- Solid surfaces show strong affinity towards gas molecules that it comes in contact with and some amount of them are trapped on the surface.
- The process of trapping or binding of molecules to the surface is called adsorption.
- Desorption is removal of these gas molecules from the surface.
Adsorption

• Two types of adsorption
  – Physical adsorption:
    generally a molecule is physisorbed if the bond energy is less than 10 kcal/mole
  – Chemical adsorption:
    chemisorbed if bond energy is more than 10 kcal/mole

• In chemisorption there is a direct chemical bond involved while Vanderwaals forces are responsible for physical bonding
## Adsorption and Reaction at Surfaces

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**Weak, Long Range Bonding**

- Van der Waals interactions (e.g. London dispersion, dipole-dipole)

**Chemisorption**

- Strong, short-range bonds
- Bonds are formed between the adsorbate and the surface

**Physisorption**

- Weak, long-range bonding
- Bonds are formed through dispersion forces

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**Surface Specific**

- Chemisorption of hydrogen takes place on transition metals but not on gold or mercury.

**Not Surface Specific**

- Physisorption takes place between all molecules on any surface providing the temperature is low enough.

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**Adsorption and Reaction at Surfaces**

- **Adsorption**
  - Langmuir Isotherm used to model adsorption equilibrium.
  - Surface reactions may take place: dissociation, reconstruction, catalysis.
  - Can be activated, in which case equilibrium can be slow and increasing temperature can favour adsorption.
  - Non-activated with equilibrium achieved relatively quickly. Increasing temperature always reduces surface coverage.

- **DH_{ads}**
  - 50 … 500 kJ mol⁻¹

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**Diagram**

- [Diagram of Adsorption and Reaction at Surfaces]
### Adsorption and Reaction at Surfaces

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**Adsorption**

- Langmuir Isotherm used to model adsorption equilibrium.
- BET Isotherm used to model adsorption equilibrium.
- Surface reactions may take place: Dissociation, reconstruction, catalysis.
- No surface reactions.
- Can be activated, in which case equilibrium can be slow and increasing temperature can favour adsorption.
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**DH\textsubscript{ads}**

\[
DH\textsubscript{ads} = 50 \ldots 500 \text{ kJ mol}^{-1}
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**Surface Specific**

- E.g. Chemisorption of hydrogen takes place on transition metals but not on gold or mercury.

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**STRONG, SHORT RANGE BONDING**

- Chemical bonding involving orbital overlap and charge transfer.

**Chemisorption**

**Physisorption**
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![Diagram showing physisorption and chemisorption](image-url)
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Adsorption and Reaction at Surfaces

\[ \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \]
Lennard-Jones Potential

Lennard-Jones Potential

physisorption

\[ \Delta H_{\text{ads}} < 50 \text{ kJmol}^{-1} \]

- attractive van der Waals interactions
- repulsive Coulombic interactions
- Pauli repulsion

\[ \Delta H_{\text{ads}} \]

\[ Z \text{ physisorbed} \]

\[ Z \text{ physisorbed} \]
Lennard-Jones Potential
chemisorption

activated chemisorption

un-activated chemisorption
Lennard-Jones Potential
un-activated chemisorption

\[ \Delta H_{\text{ads}} > 50 \text{ kJmol}^{-1} \]
Lennard-Jones Potential
activated chemisorption

\[ \Delta E_{\text{ads}} \]

\[ \Delta H_{\text{ads}} \]

\[ \Delta E_{\text{diss}} \]

Chemisorption 2

\[ N_2 \]

\[ Z \]

\[ 2N \]

\[ N_2^{\text{physisorbed}} \]

\[ Z_{\text{chemisorbed}} \]

\[ 2N_{\text{chemisorbed}} \]
Isotherm

- Isotherm is an equation which relates the amount of substance attached to the surface to its concentration in the gas phase at a fixed temperature.
- Langmuir: for monolayer adsorption
- BET: for multilayer
This simplest physically plausible isotherm is based on three assumptions:

1. Adsorption cannot proceed beyond monolayer coverage.
2. All surface sites are equivalent and can accommodate, at most, one adsorbed atom.
3. The ability of a molecule to adsorb at a given site is independent of the occupation of neighboring sites.

The dynamic equilibrium is

\[ A(g) + M(\text{surface}) \leftrightarrow AM(\text{surface}) \]
Langmuir adsorption

Rate of adsorption = collision rate \{ \frac{P}{(2\pi mkT)^{0.5}} \} \times \text{probability of finding a suitable site } f(\Theta) \times \text{prob of being in correct orientation } \kappa \times \text{probability of overcoming the adsorption barrier } \exp\left(-\frac{E_a}{RT}\right) \text{ (this may be 1 if there is no barrier, e.g. physisorption)}

f(\Theta) \text{ is dependant on the type of adsorption:}

(1 - \Theta) \text{ if the adsorbate requires a vacant site}

(1 - \Theta)^2 \text{ if the adsorbate requires two vacant sites (e.g. dissociative adsorption).}
Langmuir adsorption

Rate of desorption = rate constant \( k = A \exp(-\frac{Ed}{RT}) \times \text{coverage term} \ g(\theta) \)

\( g(\theta) \) tells us the kinetic order of desorption:

- \( = 1 \) zero order - constant coverage, e.g. a solid or multilayer film,
- \( = \theta \) first order - adsorbate remains intact,
- \( = \theta^2 \) second order - adsorbate recombines during desorption.
Hence if $r_a = r_d$ at eqm,

$$P = (2pmkT)^{0.5} (A/k) \{g(\theta)/f(\theta)\} \exp(E_a - E_d)/RT$$

$E_a - E_d$ is just the heat of adsorption, $q$

For non-dissociative (Langmuir) adsorption with no multilayer formation $g(\theta) = \theta$ and $f(\theta) = (1 - \theta)$,

giving $P = \theta / b (1 - \theta)$

where $1/b = (2pmkT)^{0.5} (A/k) \exp(-q)/RT$