Lecture 13
Surface Dynamics

Irving Langmuir 1881–1957
Concepts of adsorption, desorption, various kinds of adsorption, energetics of adsorption, adsorption isotherms

\[ A + S = AS \quad \Delta_{ads} H < 0 \]

Adsorption isotherms

Langmuir adsorption isotherm

Assumptions
1. Adsorption does not occur beyond monolayer
2. Sites are equivalent and surface is uniform
3. Adsorption at one site is independent of occupancy at another site
Adsorption,

\[ \frac{d\Theta}{dt} = k_a PN(1 - \Theta) \]

Desorption,

\[ -\frac{d\Theta}{dt} = k_d N \Theta \]

\[ K = \frac{k_a}{k_d} \]

\[ P = \Theta \frac{K}{K(1 - \Theta)} \quad or \quad \Theta = \frac{KP}{1 + KP} \]

It is possible to deduce this equation from first principles.
Surface area measurements
Measurements use often pressure of the gas.
Example of CO adsorption on charcoal.

Methods to measure adsorption
Flash desorption
Gravimetry – quartz crystal microbalance
**Dissociative Adsorption**

\[ kd\Theta^2 = ka(1 - \Theta)^2 P \]

\[ \frac{\Theta}{1 - \Theta} = \frac{ka^{1/2} P^{1/2}}{kd^{1/2}} \]

\[ \Theta = \frac{KP^{1/2}}{1 + KP^{1/2}} \]

\[ K = (k_a/k_d)^{1/2} \]
Adsorption and reaction

Adsorbed state