

Lecture 13

Surface Dynamics



Irving Langmuir 1881–1957

Nobel Prize in Chemistry 1932 "for his discoveries and investigations in surface chemistry".

Concepts of adsorption, desorption, various kinds of adsorption, energetics of adsorption, adsorption isotherms



Adsorption isotherms

Concept of theta, Θ
surface coverage

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,

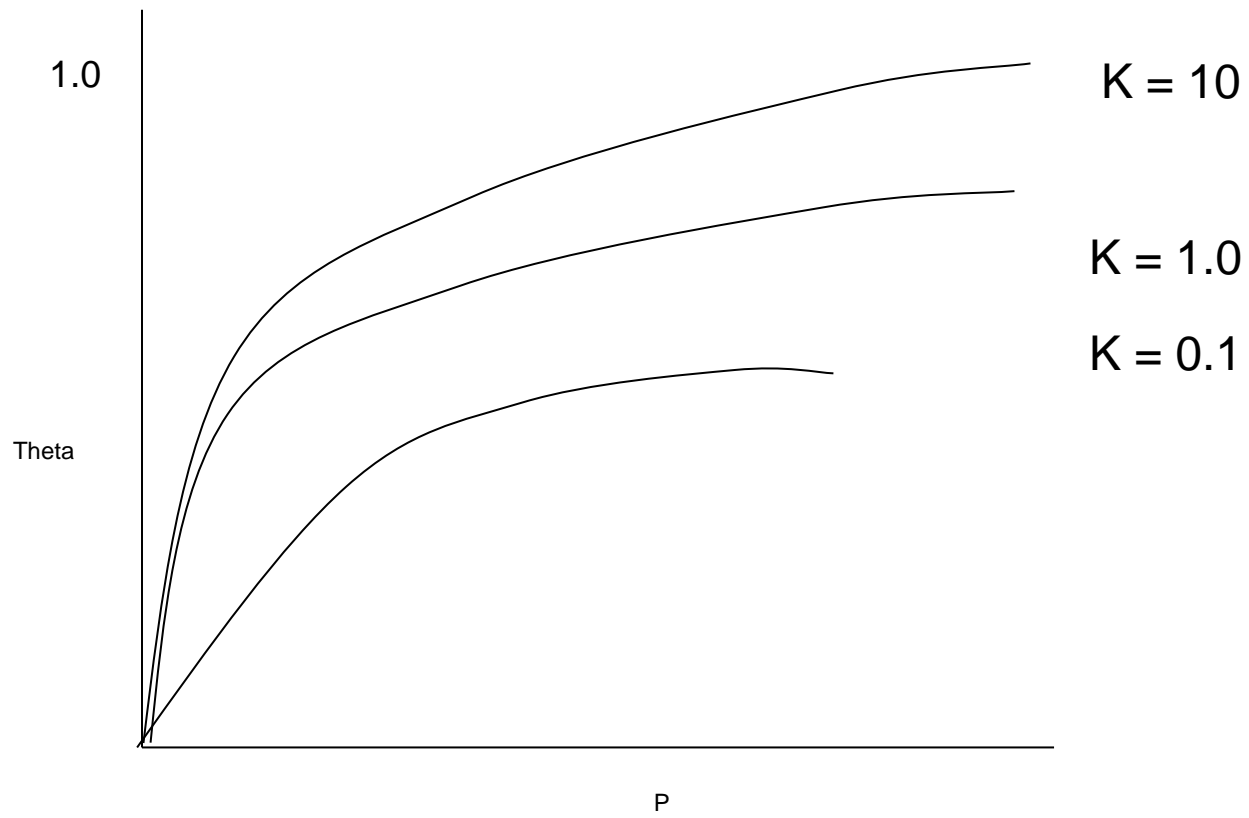
$$d\Theta/dt = k_a PN(1 - \Theta)$$

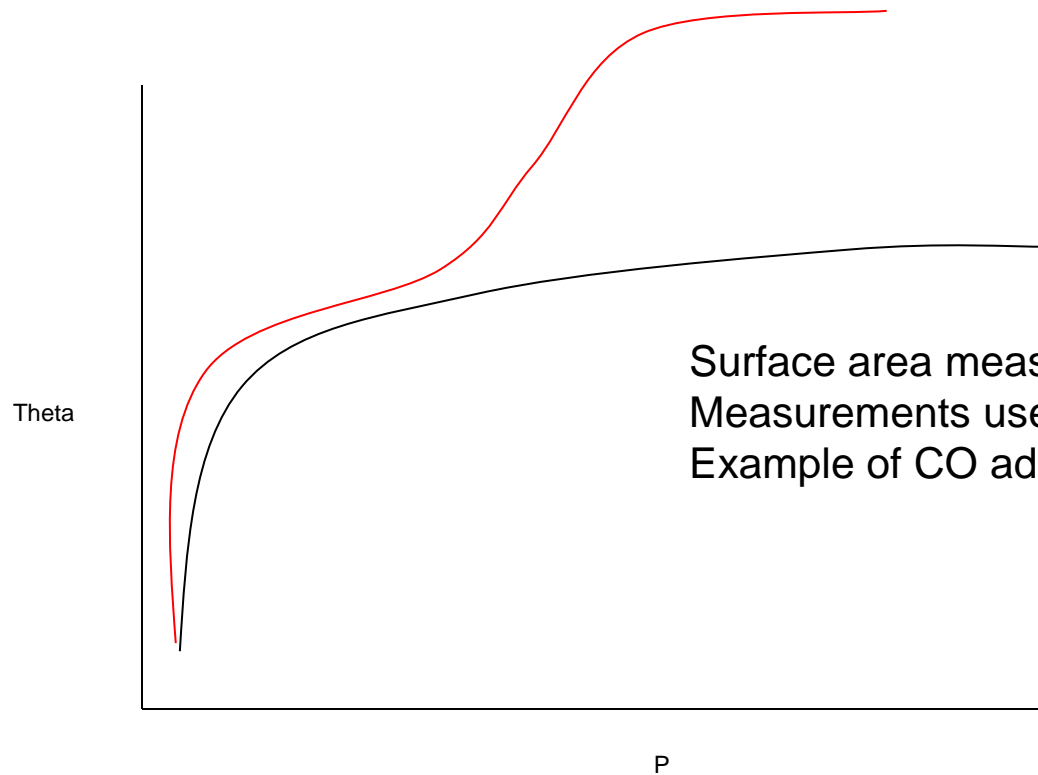
Desorption,

$$d\Theta/dt = -k_d N\Theta$$

$$K = k_a/k_d \quad P = \frac{\Theta}{K(1 - \Theta)} \quad \text{or} \quad \Theta = \frac{KP}{1 + KP}$$

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

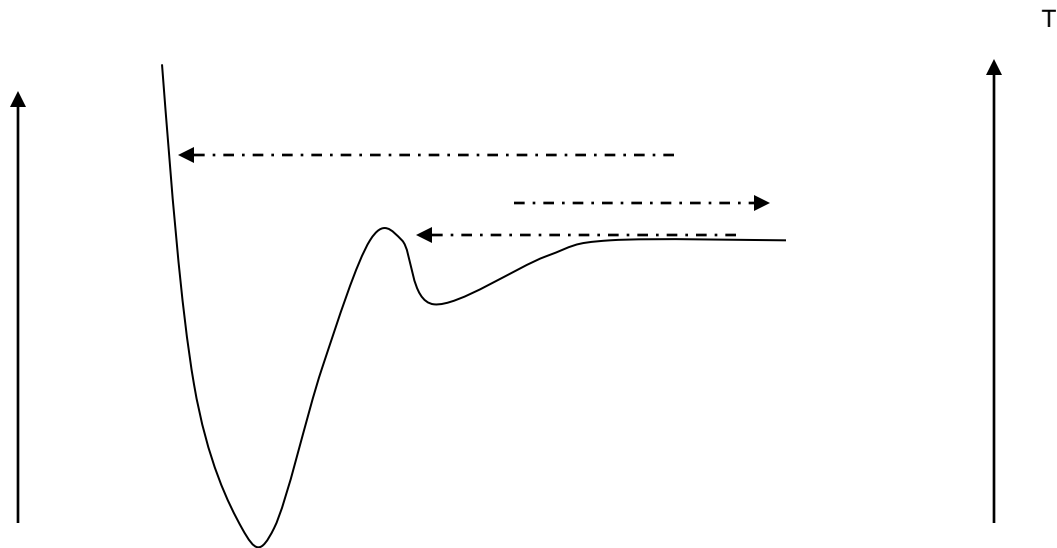
$$kd\Theta^2 = ka(1 - \Theta)^2 P$$

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

$$\Theta = \frac{(KP)^{1/2}}{1 + (KP)^{1/2}}$$

$$K = (k_a/k_d)^{1/2}$$

Adsorption and reaction



Adsorbed state