Environmental Chemistry

Part 3 Hydrospheric Chemistry

3.3 Adsorption and Reaction at Surfaces

Adsorption and Reaction at Surfaces

PHYSISORPTION	CHEMISORPTION
weak, long range bonding **van der waals interactions (e.g. london dispersion, dipole-dipole)..**	**strong, short range bonding** **chemical bonding involving orbital overlap and charge transfer.**
not surface specific **physisorption takes place between all molecules on any surface providing the temperature is low enough.**	**surface specific** **e.g. chemisorption of hydrogen takes place on transition metals but not on gold or mercury.**
$DH_{ads} = 5 \ldots.. 50 \text{ kJ mol}^{-1}$	**$DH_{ads} = 50 \ldots.. 500 \text{ kJ mol}^{-1}$**
Non activated with equilibrium achieved relatively quickly. Increasing temperature always reduces surface coverage.	**Can be activated, in which case equilibrium can be slow and increasing temperature can favour adsorption.**
No surface reactions.	**Surface reactions may take place:-Dissociation, reconstruction, catalysis.**
multilayer adsorption **bet isotherm used to model adsorption equilibrium.**	**monolayer adsorption** **langmuir isotherm used to model adsorption equilibrium..**

Adsorption

Studies involving the behaviour between solutes & surfaces in solution .

The process occurs naturally in the environment.(Sediments & Soils)

A method of the removal of contaminants from gases & liquids using adsorbents primarily activated charcoal.

adsorption isotherm(吸附等温线)

The nature of the surface and the compound determine it ability to be adsorb.

Charged Compounds $\longrightarrow$ Charged surface

Nonpolar Compounds $\longrightarrow$ Non polar surfaces

The state which describes the equilibria existing between absorbate, absorbent, solute and solvent at constant temperature is an adsorption **isotherm.**

Adsorption(Major isotherms)

Langmuir's adsorption Isotherm(L型)

Freundlich adsorption Isotherm(F型)

（包含HENY ADSORPTION(H型)）

BET adsorption Isotherm

Adsorption

The degree of a compound can be measured and the extent of adsorption θ expressed as a fraction.
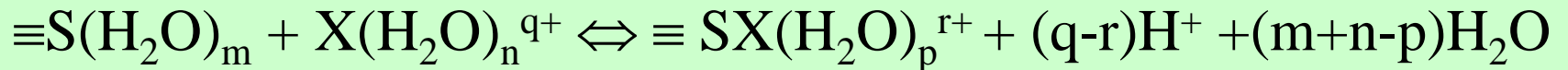
$$\theta = \frac{\text{Number of adsorption sites Occupied (V)}}{\text{Number of adsorption sites available } (V_\infty)}$$

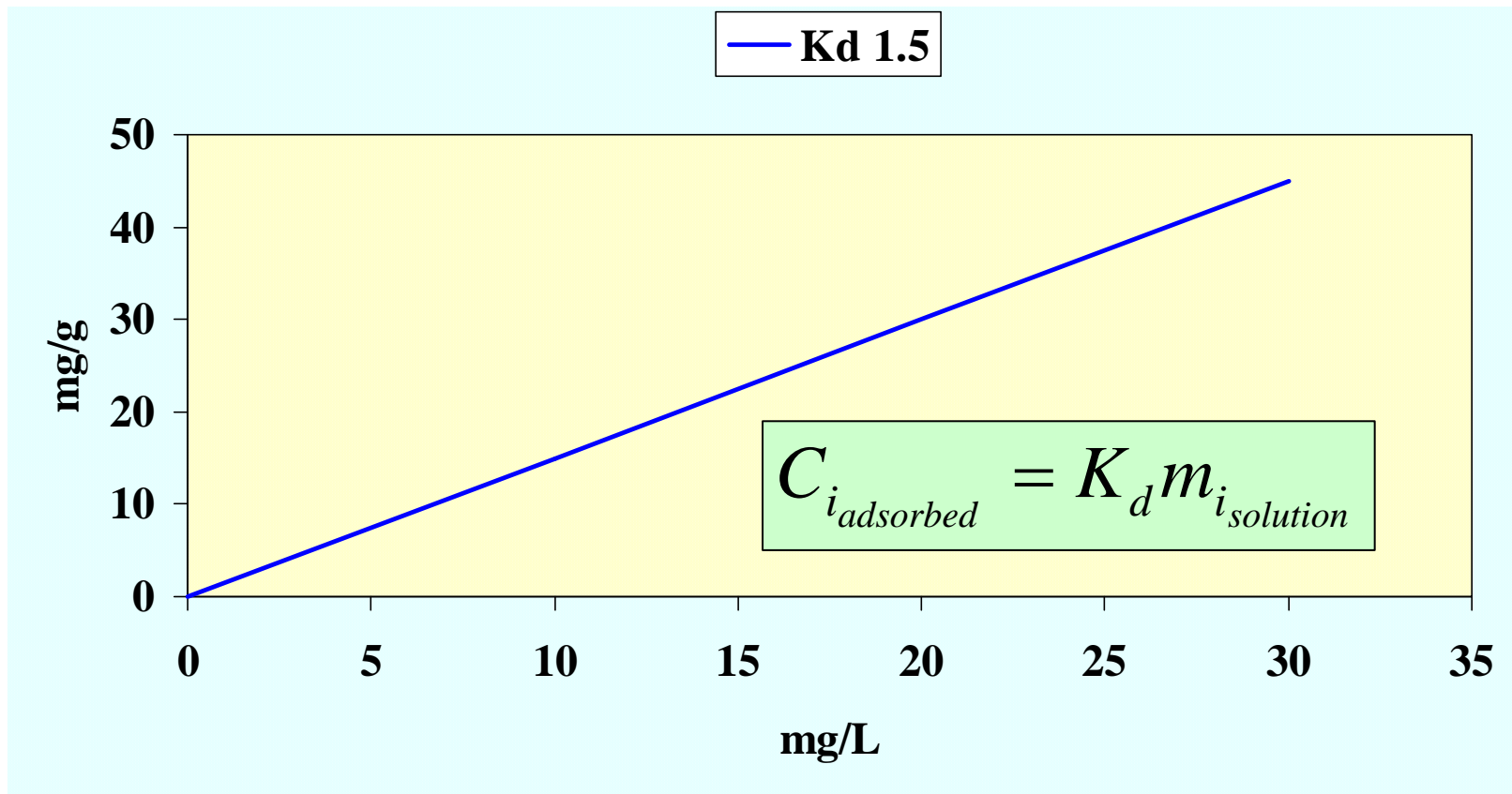(V_∞) = the volume of monolayer coverage

Types of Adsorption

$$\equiv S(H_2O)_m + X(H_2O)_n{}^{q+} \Leftrightarrow \equiv SX(H_2O)_p{}^{r+} + (q-r)H^+ + (m+n-p)H_2O$$

- Physical adsorption - van der Waals forces
- Electrostatic adsorption - electric charge
- Chemical adsorption - bond to solid

Linear Distribution Coefficient
（H$_{\text{ENRY}}$型）

$$C_{i_{adsorbed}} = K_d m_{i_{solution}}$$

G (或q)= kC

Adsorption
(Freundlich Adsorption Isotherm)

Freundlich Adsorption Isotherm Follows the relationship

$$G \ (或 q) = kC^{1/n}$$

The constants can be determined by

$$\log_{10} q = \log_{10} k + \ 1/n \ \log_{10} C$$

Important in determining the removal capability and effectiveness of activated carbon in removing compounds.
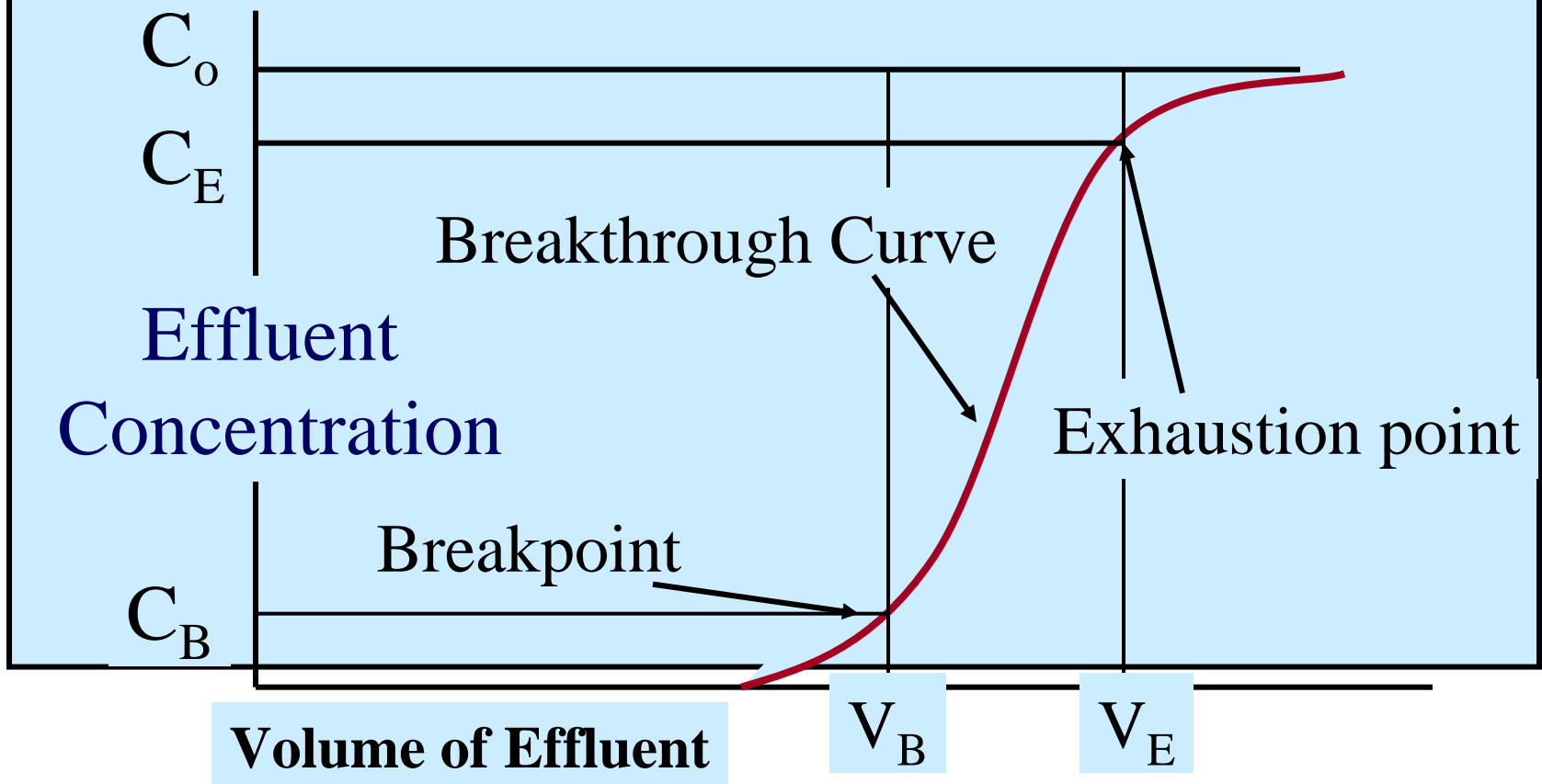
- **Adsorption (Freundlich Isotherm)**
- **Priority Pollutant   k   1/n**
- Chlordane氯丹   245   0.38
- Dieldrin 狄氏剂   606   0.51
- DDE   232   0.37
- DDT dichloro-diphenyl-trichloroethane 322   0.50
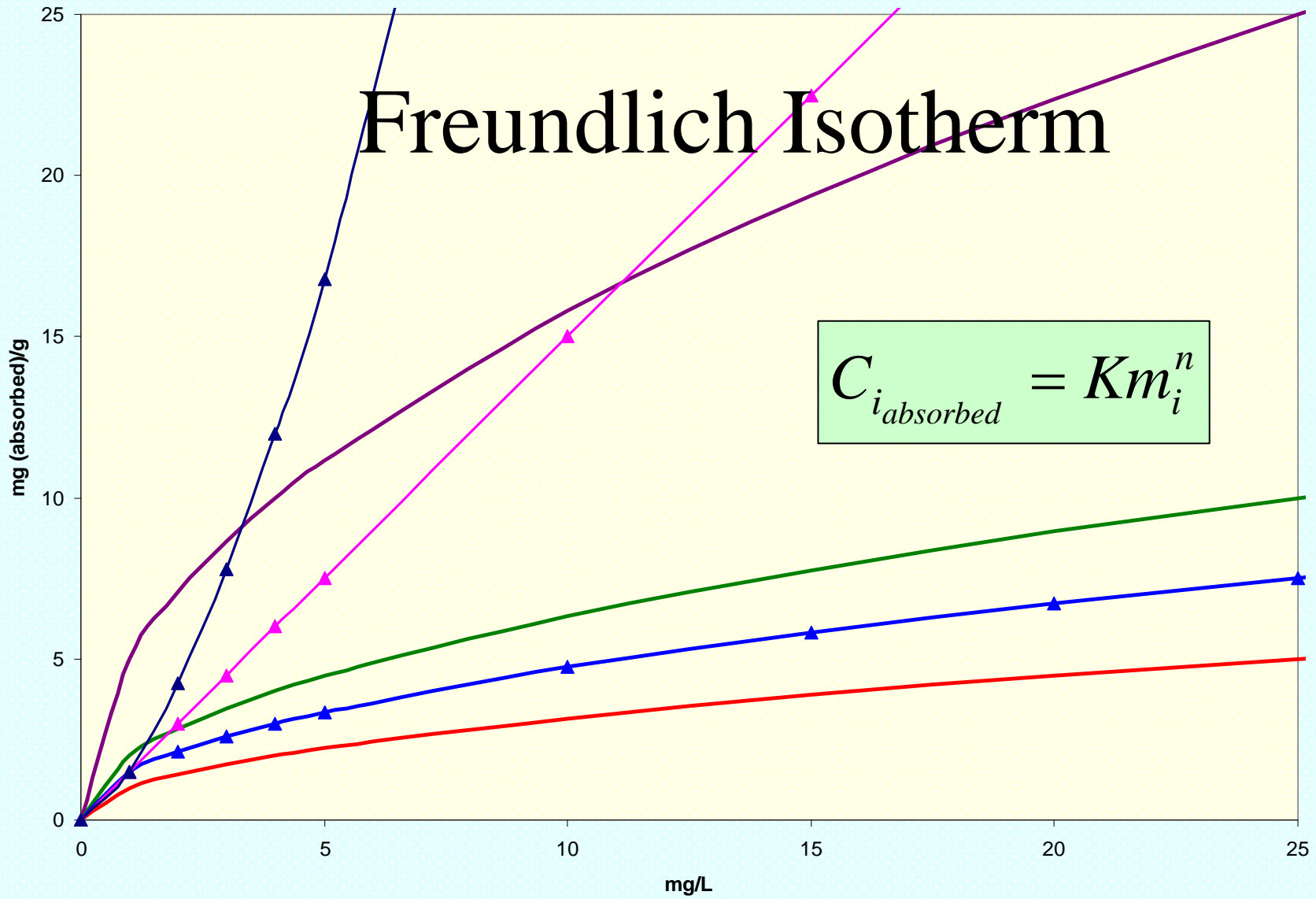- Lindane   256   0.49

Adsorption (Fixed Bed Absorber).

C_o

C_E

Effluent
Concentration

Breakthrough Curve

Exhaustion point

Breakpoint

C_B

V_B V_E

Volume of Effluent

Freundlich Isotherm

$$C_{i_{absorbed}} = K m_i^n$$

Legend: 0.5 - 5 | 0.5 - 2 | 0.5 - 1.5 | 0.5 - 1 | 1 - 1,5 | 1.5 - 1.5
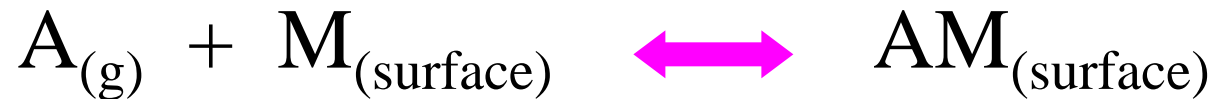
mg (absorbed)/g

mg/L

n and K

Adsorption
(Langmuir Adsorption Isotherm等温线)

Simplest isotherm assumes

(1) Only monolayer adsorption

(2) All sites are the same & surface is uniform

(3) The ability to adsorb at a site is independent of the occupation of neighbouring sites

$$A_{(g)} \ + \ M_{(surface)} \ \longleftrightarrow \ AM_{(surface)}$$

Langmuir Isotherm

An isotherm describes the dependence of volume, concentration , or in the case of a surface, coverage **Q**, on pressure **p** at constant temperature **T at equilibrium**.

$$Q = [f(p)]^T$$

In the equilibrium between the gas phase and the adsorbed phase, LeChatelier's Principle predicts that at constant temperature **an increase in pressure will increase the number of molecules adsorbed on the surface** since the volume occupied by the molecules at the surface (per mole) is smaller.

This can, however, reach a limiting value. The number of molecules adsorbed at any pressure **p** will also depend on the strength of the adsorbate bond to the surface.

p

Θ
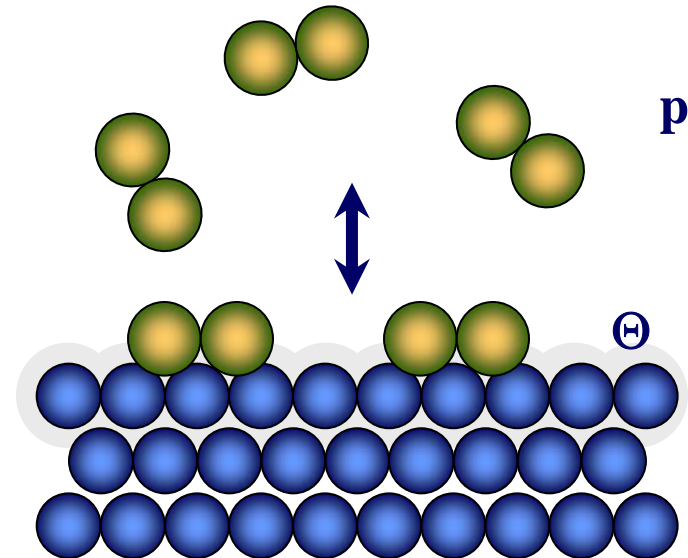
Langmuir Isotherm

Langmuir's "checkerboard" model of chemisorption assumes that a surface is composed of a finite number of equivalent adsorption sites.

So the maximum coverage is obtained when all sites are filled. The coverage Θ is expressed in terms of the the number of molecules adsorbed in relation to the number of available sites. i.e. When all sites are filled, $\Theta = 1$.

Consider the equilibrium:

$$A_{gas} \xrightleftharpoons[k_{des}]{} A_{adsorbed}$$

p

Θ
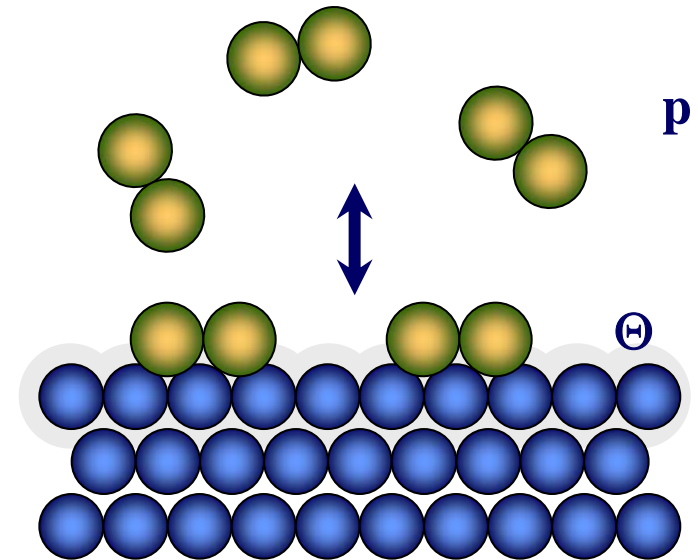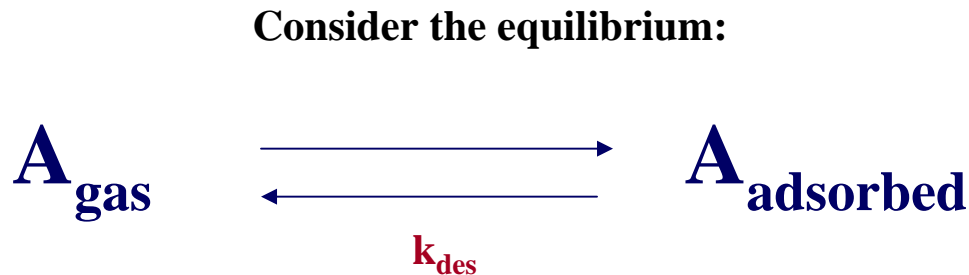
Rate of desorption proportional to:

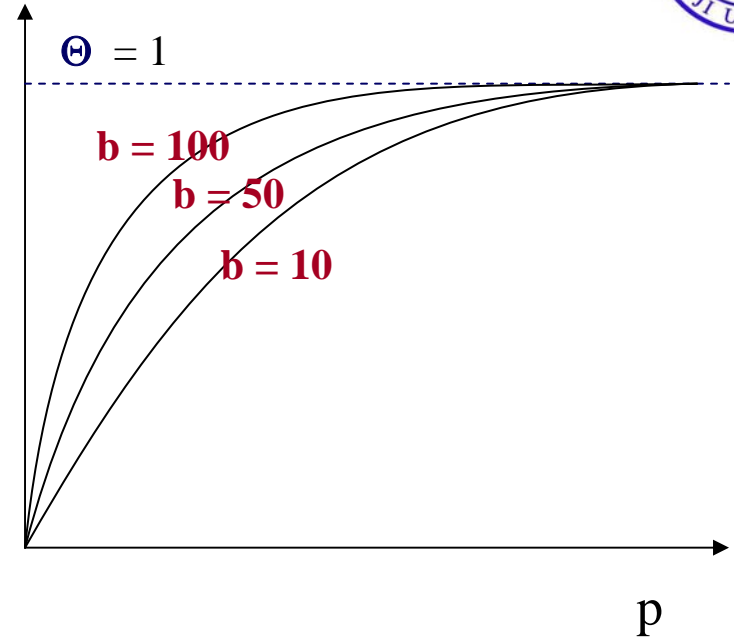1) the fraction of surface covered by adsorbate Θ .

i.e **rate of desorption = $k_{des} \, \Theta$**

At equilibrium

Rate of adsorption = Rate of desorption

$$K_{ads}\, p\, (1 - \Theta) = k_{des}\, \Theta$$

$$\Theta$$

If we write $b = k_{ads} / k_{des}$

$$\Theta = 1$$

b = 100

b = 50

b = 10

p

$$\Theta = bp / (1+bp) \quad \ldots\ldots\ldots\ldots \text{ The Langmuir Isotherm}$$

Since $b = k_{ads} / k_{des}$, this is the same as an equilibrium constant K

And since ln $K = -\Delta G/RT$ one can write:

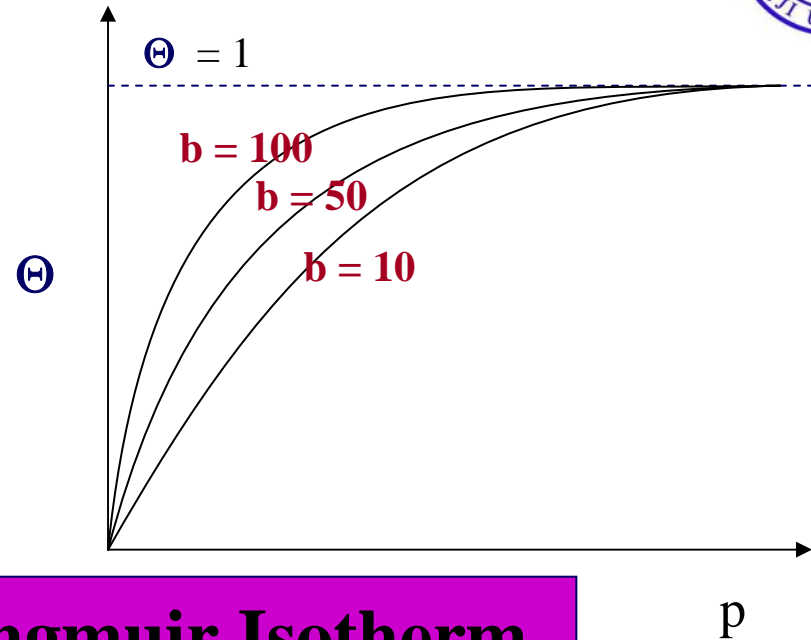**$b = \exp(-DG/RT)$, i.e b reflects the strength of the adsorbate bond to the surface.**

At equilibrium

Rate of adsorption = Rate of desorption

$$K_{ads} \, p \, (1 - \Theta) = k_{des} \, \Theta$$

Θ

If we write $b = k_{ads} / k_{des}$

$\Theta = 1$

b = 100
b = 50
b = 10

p

$$\Theta = bp / (1+bp) \quad \text{... The Langmuir Isotherm}$$

$$\Theta = K \, p / (1+K \, p) \text{ The Langmuir Isotherm}$$

The equation above can be linearised for testing of experimental data by inversion ;

Since $\quad \Theta = n_{ads} / n_{max}$

$$p / n_{ads} = 1 / b \, n_{max} + p / n_{max}$$

The equation above can be linearised for testing of experimental data by inversion ;

- Since $\quad Q = n_{ads} / n_{max}$

- $p / n_{ads} = 1 / b\, n_{max} + p / n_{max}$

$G = n_{ads} \quad G^0 = n_{max} \quad p = c$

- $1 / G = 1 / G^0 + 1 /(K\, G^0) * 1 / c$

Adsorption(Langmuir's Adsorption Isotherm)

Can also be expressed as

$$q/q_m = k_b C/(1 + k_b C)$$
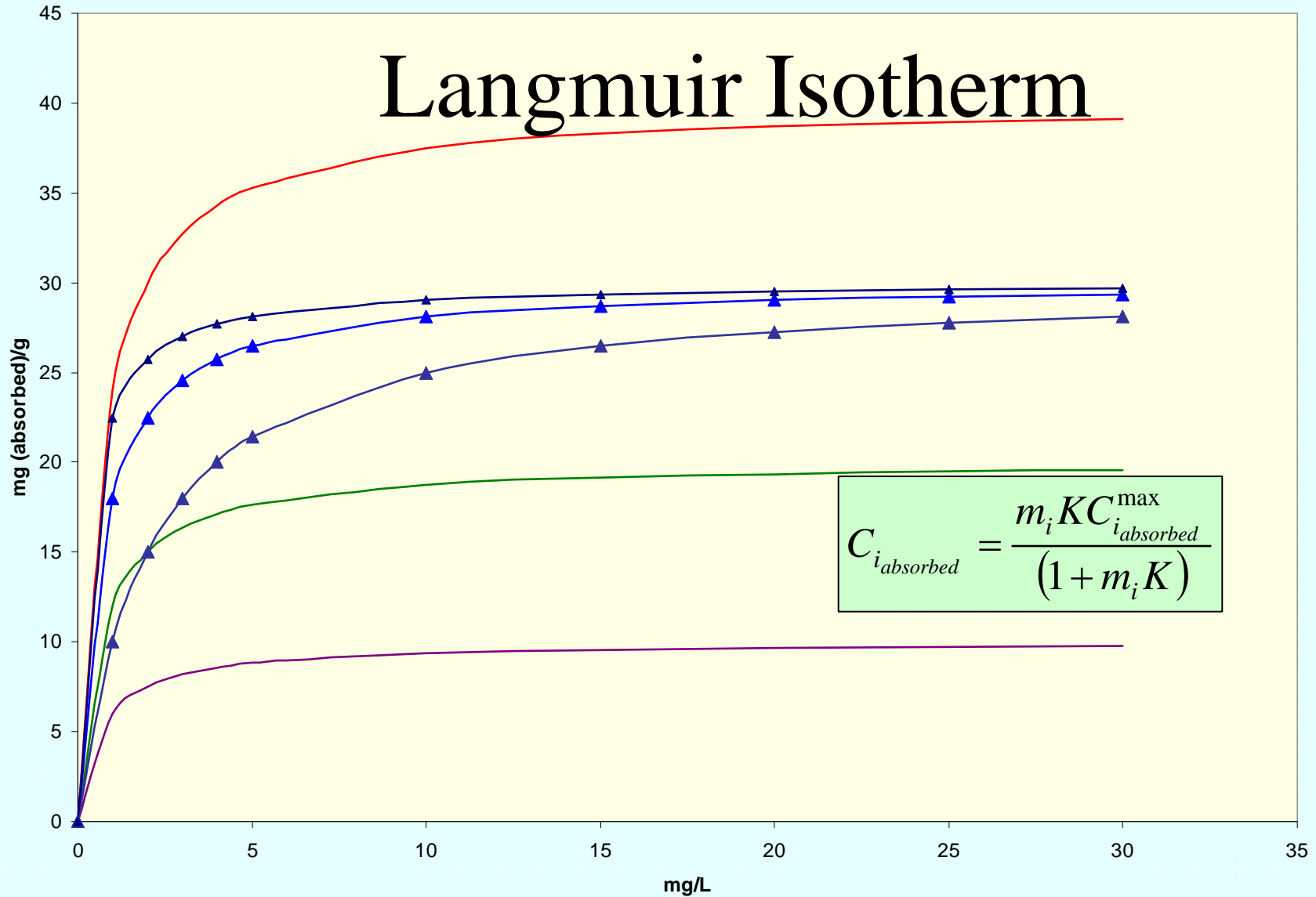
q_m = max no moles adsorbed / mass adsorbent

q = number of moles adsorbed / mass of adsorbent

k_b = constant related to enthalpy of adsorption

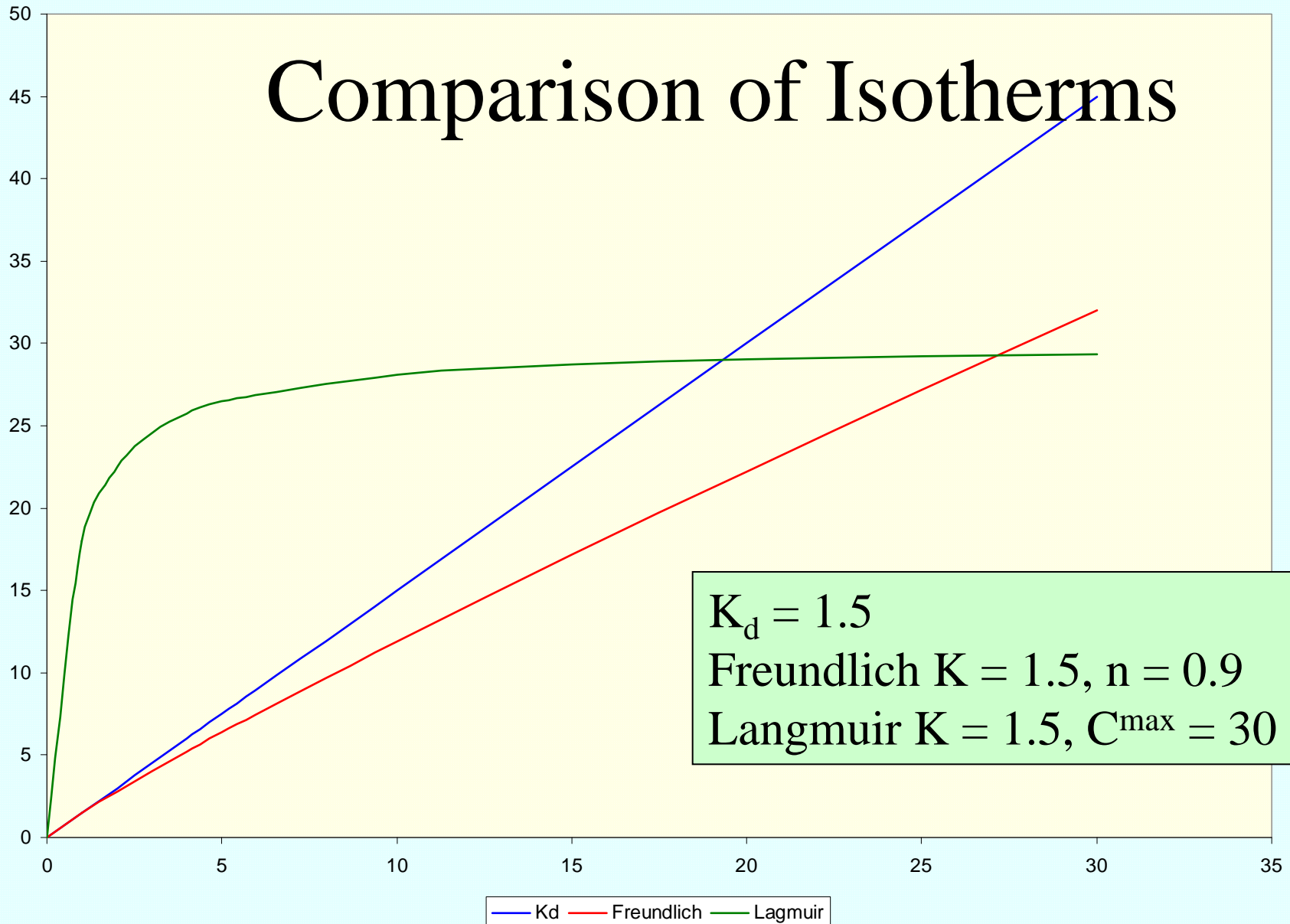C = solution concentration at equilibrium

Langmuir Isotherm

$$C_{i_{absorbed}} = \frac{m_i K C_{i_{absorbed}}^{\max}}{(1 + m_i K)}$$

mg (absorbed)/g

mg/L

— 10,1.5 — 20,1.5 ▲ 30,1.5 — 40,1.5 ▲ 30,0.5 ▲ 30,3

Comparison of Isotherms

$K_d = 1.5$
Freundlich $K = 1.5$, $n = 0.9$
Langmuir $K = 1.5$, $C^{max} = 30$

Kd — Freundlich — Lagmuir

ZPC - Isoelectric Point
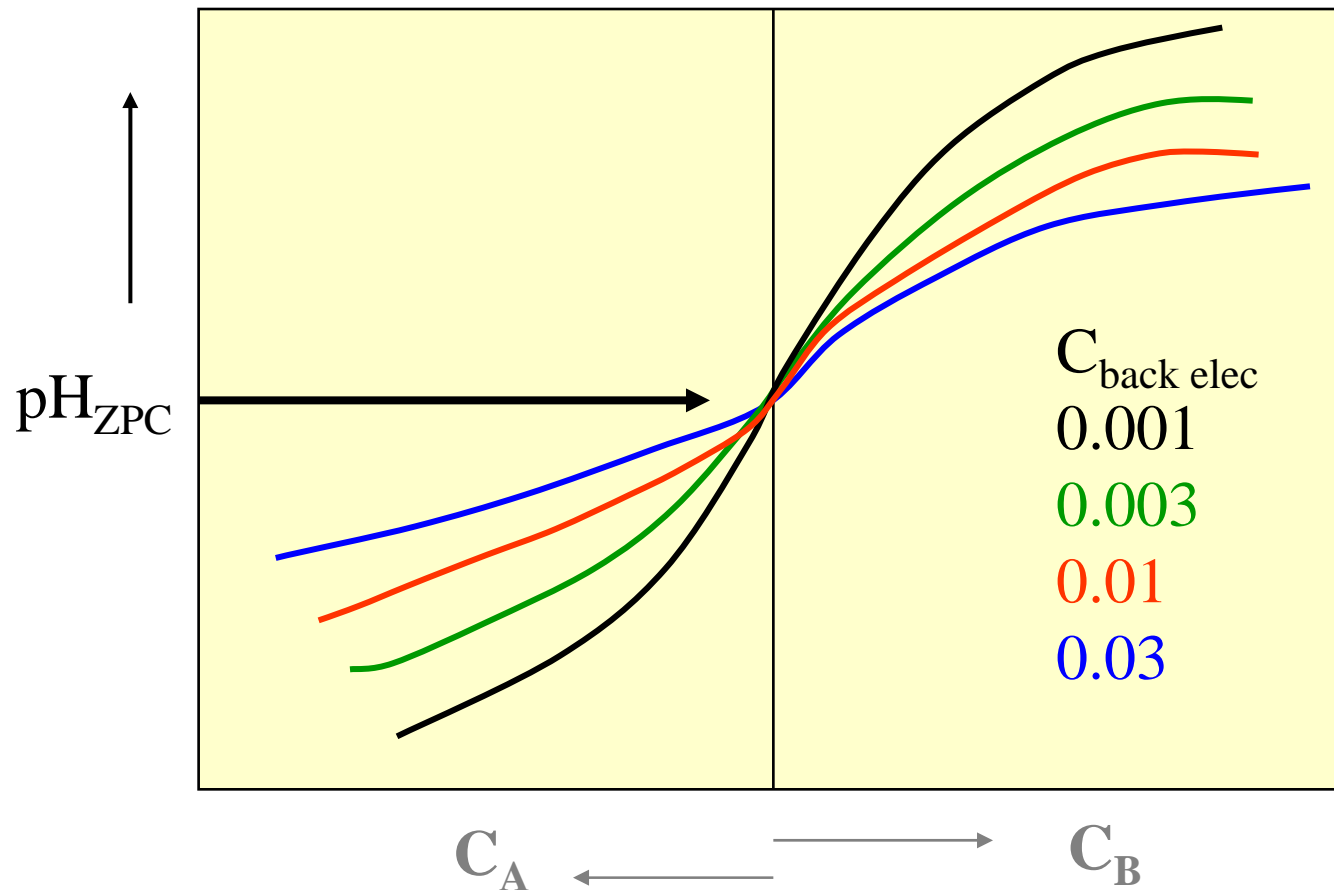
Typical Isoelectric Points

Substance	pH_{ZPC}	Substance	pH_{ZPC}
Quartz	1-3	Kaolinite	$\leq$2 - 4.6
SiO_2 gel	3.5	Montmor.	$\leq$2 - 3
Feldspars	6 - 7	Gibbsite	~9
Hematite	4.2 - 6.9	β-MnO_2	4.6 - 7.3
Goethite	6 - 9	δ-MnO_2	1.5 - 2.8

Cation and Anion Adsorption
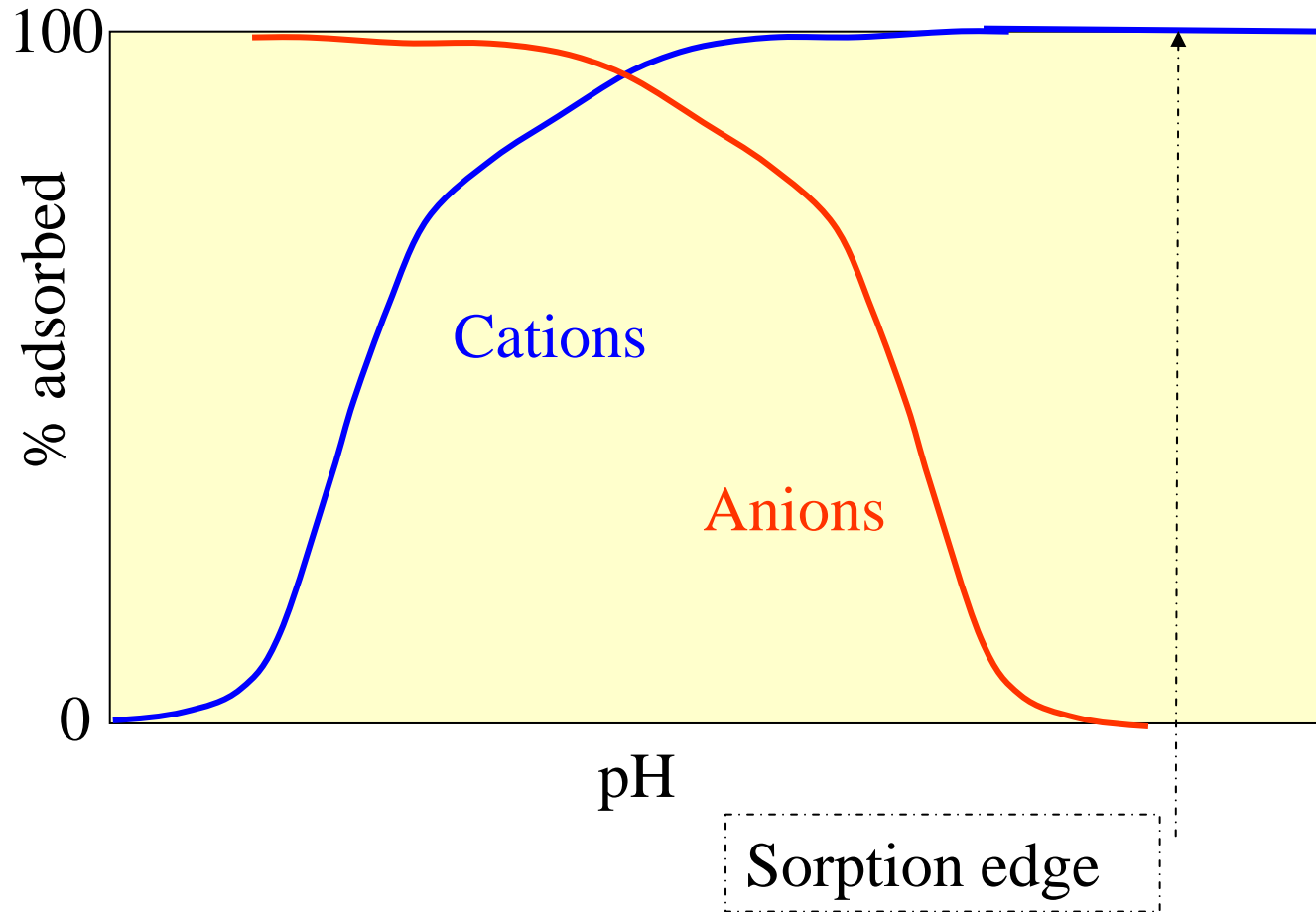
Electrostatic Adsorption Models

- Sorbing surface contains functional groups that react with sorbing solutes to form surface complexes

- Surface complexing can be described my mass-action equations (K) corrected for electrostatic effects

Electrostatic Adsorption Models

- Surface charge σ and electrical potential Ψ are consequences of chemical reactions involving the surface groups

- Binding constants are empirical parameters related to the intrinsic thermodynamic constants by the activity coefficient of the surface species.