# Fundamental of Soil Science (SAC-111)

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# pH, Complexation and Solubility Equilibria

*Since so many analytical procedures involve solution chemistry an understanding of the principles is essential*

# pH, Complexation and Solubility Equilibria

- Definitions
- Equilibrium constants
- Equilibria in analytical reactions
- Solvents in analytical chemistry
- Acid-base equilibria
- Solubility equilibria

# Definitions

- Acid

  A species which donates protons in a reaction or accepts electrons

- Base

  A species which accepts protons in a reaction or donates electrons

# Definitions

- Complex

  A compound which is formed in a complexation reaction between two or more species which are capable of independent existence

- Ligand

  A species with at least one basic site which can participate in complex formation

# Definitions

- **Strong Electrolyte**

  A compound which is almost completely dissociated in solution

- **Weak Electrolyte**

  A compound which remains significantly undissociated in solution
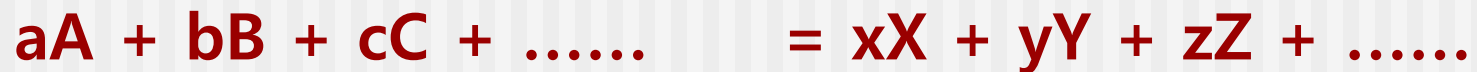
# Definitions

- 'p' Notation

$$pX = -\log_{10}X$$

- Used for convenience in handling quantities which vary in magnitude through many powers of ten

[$H_3O^+$ concentration of an aqueous solution may vary from 10 mol $dm^{-3}$ to $10^{-14}$ mol $dm^{-3}$. Expressed in the 'p' notation, this becomes pH = -1 to pH = 14]

# Equilibrium Constants

An equation may be written for a generalized reaction

**aA + bB + cC + ……    = xX + yY + zZ + ……**

[a, b, c, x, y, z are numbers indicating its stoichiometry]

The position of equilibrium is expressed by the thermodynamic equilibrium constant $K_e$ which is defined by

$$K_e = \frac{[X]^x \ [Y]^y \ [Z]^z \ ......}{[A]^a \ [B]^b \ [C]^c \ ......}$$

The square brackets refer to the activity of the component
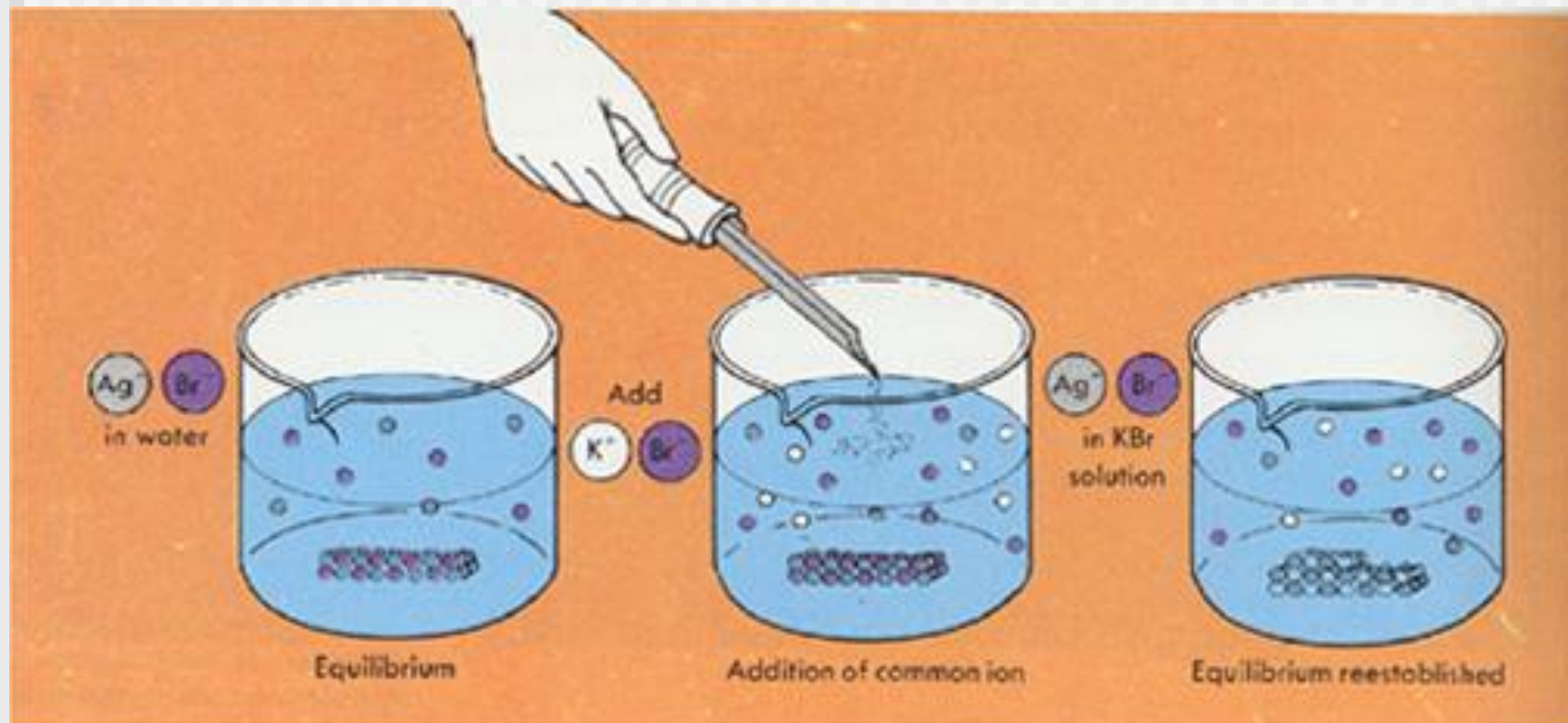
# Equilibria in Analytical Reactions

- Often it may be necessary to shift the position of equilibrium in a reaction to obtain larger quantities of desired product

- One widely used method of achieving a shift is removal of one of the products from the system

[by distillation or precipitation]
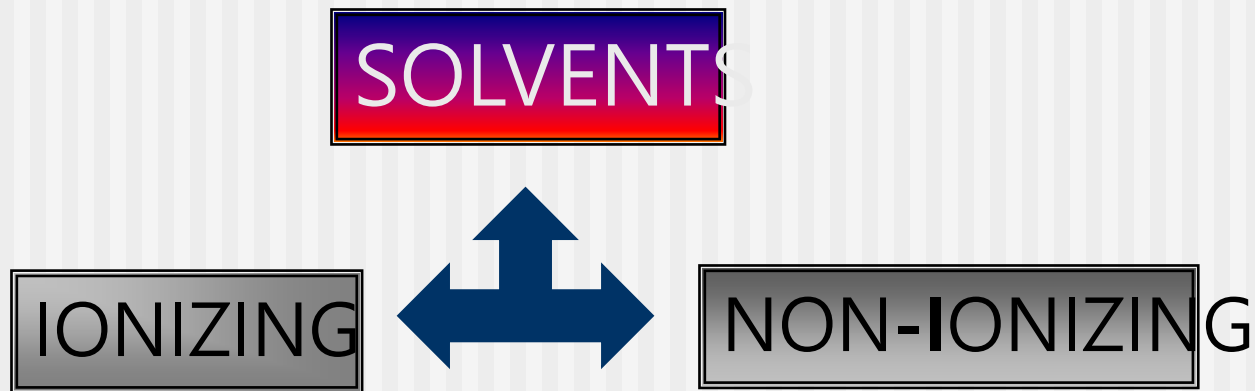
# Equilibria in Analytical Reactions

- In these circumstances to maintain $K_e$ the reactants will be steadily converted to products until one or all are exhausted
- Alternative approach uses an excess of the reagent which in most cases causes a shift towards the products of the reaction -
  this is the "**common ion effect**"

Ag⁺  Br  
in water

Add  
K⁺  Br

Ag⁺  Br  
in KBr  
solution

Equilibrium

Addition of common ion

Equilibrium reestablished

# Solvents in Analytical Chemistry

SOLVENTS

IONIZING ⟷ NON-IONIZING

Promote ionization of a solute

Do not promote ionization

As always, such divisions are not entirely satisfactory

# Some Typical Solvents

| Ionizing | Intermediate | Non-ionizing |
|---|---|---|
| Water<br>HCl acid<br>Acetic acid<br>Ammonia<br>$SO_2$<br>Amines | Alcohols containing up to 4 carbon atoms | Chloroform<br>Hexane<br>Benzene<br>Ethers<br>Esters |

# Ionizing Solvents

- Some ionizing solvents are of major importance in analytical chemistry, others of peripheral interest
- Subdivided into **protonic solvents** [water and the common acids] &
- **Non-protonic solvents** [$SO_2$ and $BrF_3$]
- Ionizing solvents have one property in common, **self ionization**, reflecting their ability to produce ionization of a solute
- Equilibrium constants for these reactions are known as "**self-ionization constants**"

# Some Self-ionizing Equilibria

| | | |
|---|---|---|
| $2H_2O$ | = | $H_3O^+ + OH^-$ |
| $2CH_3COOH$ | = | $CH_3COOH_2^+ + CH_3COO^-$ |
| $2HCl$ | = | $H_2Cl^+ + Cl^-$ |
| $2NH_3$ | = | $NH_4^+ + NH_2^-$ |
| $2RNH_2$ | = | $RNH_3^+ + RNH^-$ |

# Non-ionizing Solvents

- Major uses of non-ionizing solvents in chemical analysis are two-fold

- May simply provode a media for dissolution & reaction of covalent materials

- Or, may play a [more active part](#) in a chemical process

# Non-ionizing Solvents

- $O_2$-containing organic solvents can be used to effect solvent extraction of metal ions from acid aqueous solutions

$$\begin{array}{c} R \\ \diagdown \\ R \diagup \end{array} O: \longrightarrow H^+$$
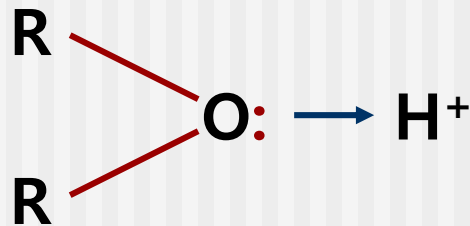
- Lone pair of electrons of O atom forms a dative bond with proton followed by the extraction of the metal ion as an association complex

# Acid – Base Equilibria

- Lowry-Bronsted concept provides basis for interpretation of reactions in protonic solvents
- This is summarized by the generalized equilibrium:

$$\textbf{AH} + \textbf{B} = \textbf{A}^- + \textbf{BH}^+$$

AH = Acid, B = Base for forward reaction

$A^-$ = Conjugate base, $BH^+$ = Conjugate acid for the reverse reaction

# Acid − Base Equilibria

- Dissociation of a typical acid in water may be represented by:

$$\textbf{AH} + \textbf{H}_2\textbf{O} = \textbf{A}^- + \textbf{H}_3\textbf{O}^+$$

Water acts as a base and $H_3O^+$ as conjugate acid

$$AH + H_2O = A^- + H_3O^+$$

The equilibrium constant $K_a$ known as "**acid dissociation constant**" is given by

$$K_a = \frac{[A^-][H_3O^+]}{[AH][H_2O]}$$

In the case of a base a parallel treatment may be used in which the water acts as an acid

$$B + H_2O = BH^+ + OH^-$$

and $K_b$, the "**base dissociation constant**", is given by

$$K_b = \frac{[BH^+][OH^-]}{[B][H_2O]}$$

If the concentrations are expressed in mol dm$^{-3}$, $K_a$ and $K_b$ have the same units

# Solubility Equilibria

- Solubility of solids in liquids an important process for an analyst, who frequently uses dissolution as a primary step in an analysis or uses precipitation as a separation procedure
- Dissolution of a solid in a liquid is favored by entropy change
- However, it is necessary to supply energy in order to break up the lattice
  [For ionic solids this may be several hundred kj per mole]

# Solubility Equilibria

- After break up of lattice, solute species are dispersed within the solvent, requiring further energy and producing some weakening of solvent-solvent interactions
- Energy needed to bring about this change can only be supplied by the solvation of the solute species

# Solubility Equilibria

- The solvation energy may be in the range $-400$ to $-4000$ kj mol$^{-1}$ for aqueous systems containing ionic solids
- Non-ionizing solvents have much lower ability to produce solvation & insufficient energy is available to break up lattices & produce a solution

# Solubility Equilibria

- Solvent-solute interactions between an ionizing solvent and a covalent solid are small, but may be large enough to overcome the low lattice energy for many solids, although their solubility will still be very low as a result of the associated nature of the solvent

# Solubility Equilibria

- Dissolution equilibrium for an ionic compound AB may be summarized by:

**AB (solid) + Solvent = A$^+$ (solv) + B$^-$ (solv)**

# Solubility Products

Solubility of a sparingly soluble salt is expressed by the equilibrium constant for the reaction, for e.g.

$$K_e = \frac{[A^+][B^-]}{[AB][S]^n}$$

Both [AB] and [S] are unchanged in solubility reactions of sparingly soluble salts, hence the above equation may be rewritten as

$$K_{sp} = [A^+][B^-]$$

$K_{sp}$, known as **solubility product**, is widely used as a measure of the solubility of sparingly soluble salts

**Raising temperature will increase $K_{sp}$ together with the solubility of the solid**

# Have a good day!

## Next Lecture
Theory of Indicators