

pH, Complexation and Solubility Equilibria

Basic concepts of Laboratory Techniques (PGS 504)

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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

[H₃O⁺ 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



[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

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

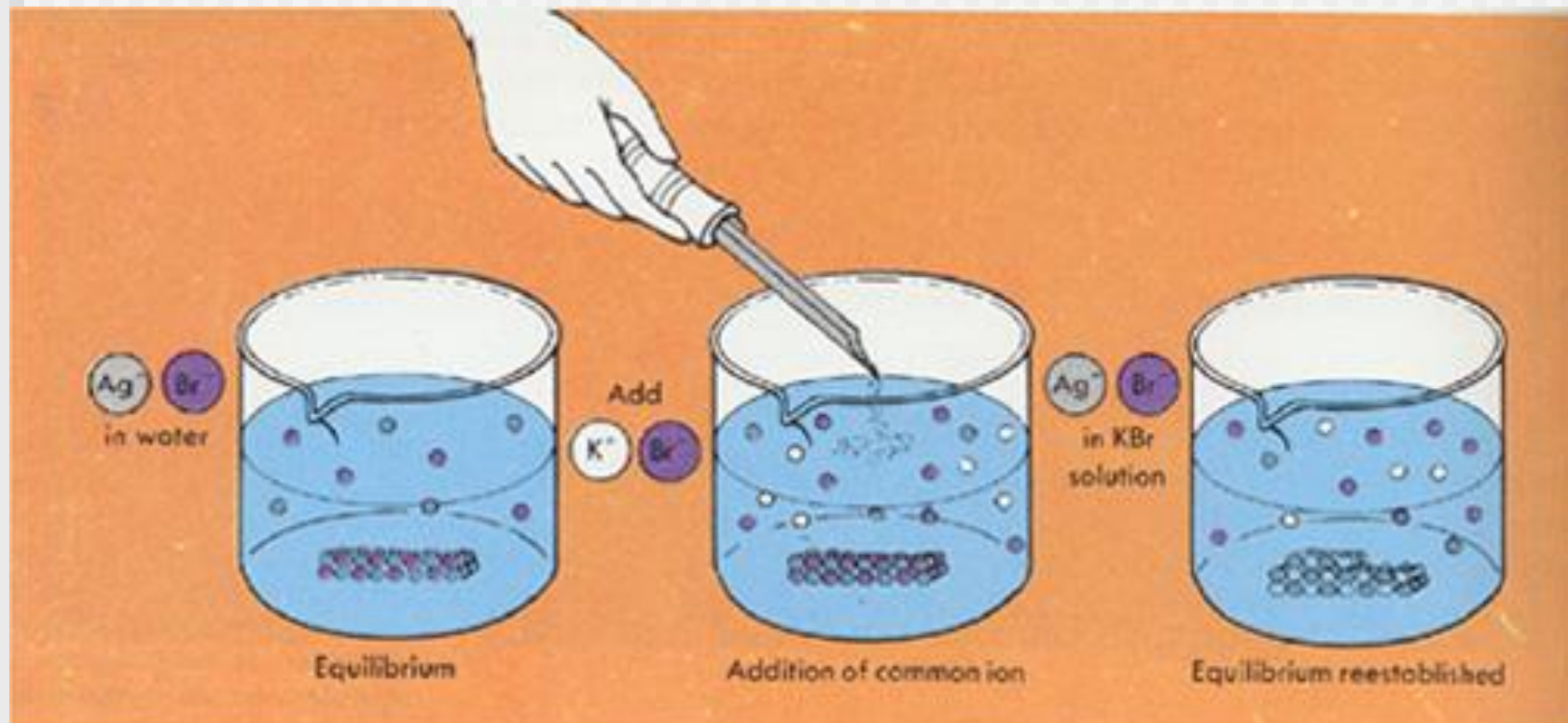
The square brackets refer to the activity of the component

Equilibria in Analytical Reactions

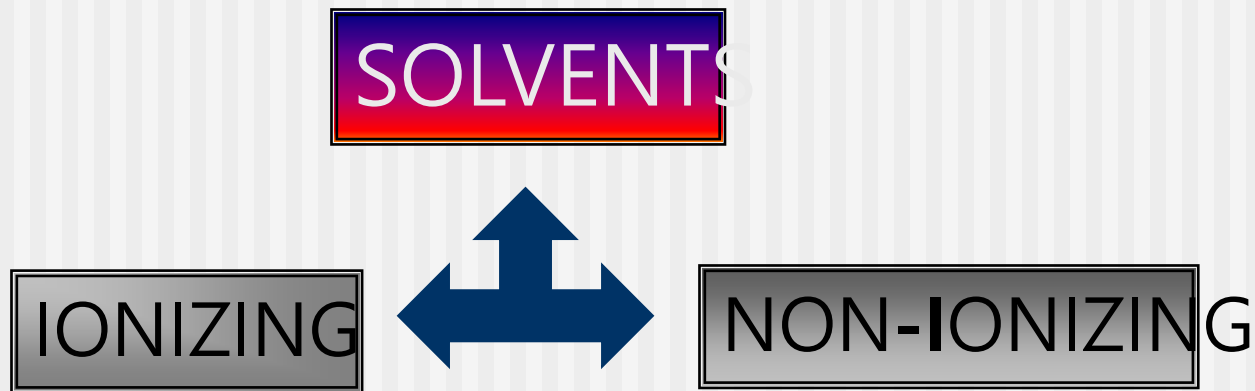
- Often it may be necessary to shift the position of equilibrium in a reaction to obtain larger quantities of desired product
- One widely used method of achieving a shift is removal of one of the products from the system
[by distillation or precipitation]

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**”



Solvents in Analytical Chemistry



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 HCl acid Acetic acid Ammonia SO ₂ Amines	Alcohols containing up to 4 carbon atoms	Chloroform Hexane Benzene Ethers 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

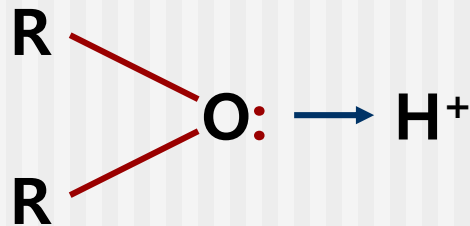
$2\text{H}_2\text{O}$	=	$\text{H}_3\text{O}^+ + \text{OH}^-$
$2\text{CH}_3\text{COOH}$	=	$\text{CH}_3\text{COOH}_2^+ + \text{CH}_3\text{COO}^-$
2HCl	=	$\text{H}_2\text{Cl}^+ + \text{Cl}^-$
2NH_3	=	$\text{NH}_4^+ + \text{NH}_2^-$
2RNH_2	=	$\text{RNH}_3^+ + \text{RNH}^-$

Non-ionizing Solvents

- Major uses of non-ionizing solvents in chemical analysis are two-fold
- May simply provide a media for dissolution & reaction of covalent materials
- Or, may play a more active part in a chemical process

Non-ionizing Solvents

- O₂-containing organic solvents can be used to effect solvent extraction of metal ions from acid aqueous solutions



- 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:



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:



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



The equilibrium constant K_a known as “**acid dissociation constant**” is given by

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{AH}][\text{H}_2\text{O}]}$$

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



and K_b , the “**base dissociation constant**”, is given by

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}][\text{H}_2\text{O}]}$$

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:



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