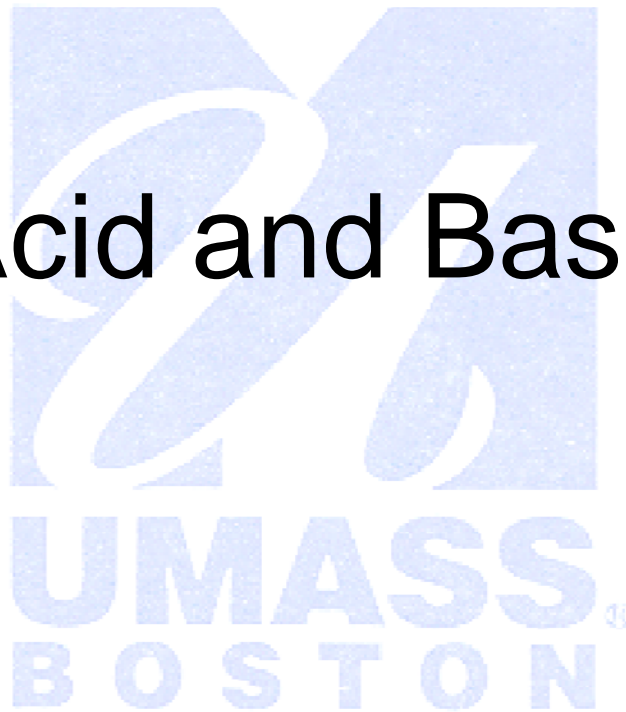


Acid and Base



pH of strong acid or base

- $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$
 $\text{pH} = -\log [\text{H}^+] = -\log [\text{HCl}]$ since HCl is completely dissociated.
- $\text{KOH} \rightarrow \text{K}^+ + \text{OH}^-$
 $\text{pH} = -\log [\text{H}^+] = -\log\{K_w/[\text{OH}]\} = -\log\{K_w/[\text{KOH}]\}$
- However, if the concentration of strong acid or base is low close 10^{-7} , then the dissociation of H_2O has to be taken into consideration

Example of low concentration of strong base

- What is the pH of 1.0×10^{-8} M of KOH?

Charge balance in the solution:

$$[\text{K}^+] + [\text{H}^+] = [\text{OH}^-]$$

since the KOH is totally dissociated in the solution $[\text{K}^+] = 1.0 \times 10^{-8}$ M

$$\text{so, } [\text{OH}^-] = 1.0 \times 10^{-8} + [\text{H}^+]$$

$$K_w = [\text{H}^+][\text{OH}^-] \Rightarrow [\text{OH}^-] = K_w / [\text{H}^+]$$

$$[\text{H}^+] = 9.6 \times 10^{-8} \text{ M, pH} = 7.02$$

Weak acid and base

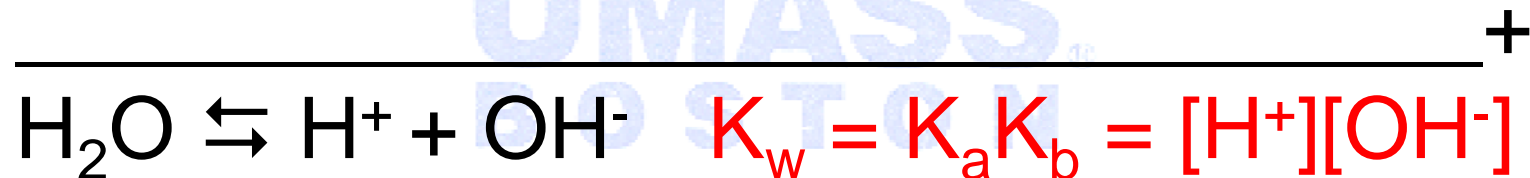
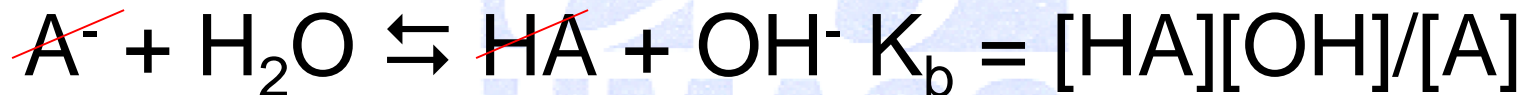
- A weak acid or base is NOT fully dissociated in the solution
 - Acid dissociation constant
 $HA \rightleftharpoons H^+ + A^-$, $K_a = [H^+][A^-]/[HA]$
 - Base hydrolysis (: reaction with water) constant
 $B + H_2O \rightleftharpoons BH^+ + OH^-$, $K_b = [BH^+][OH^-]/[B]$
 - HA and A^- ; BH^+ and B are conjugate.
- $pK_a = -\log K_a$; $pK_b = -\log K_b$;

Weak acid and base

- Fraction of dissociation: the fraction of the weak acid become dissociated:

$$\alpha = [A^-]/F$$

- Relation between K_a and K_b of conjugate



Judgments for the approximation

- Making a educated judgments for the approximation is going to be the key part of solving the analytical equations.
- Even for a weak acid, if the concentration is not too low, $[H^+]$ from the dissociation of water can be ignored, so $[H^+] \approx [A^-] = x$
 $K_a = [H^+][A^-]/[HA] = x^2/(F-x)$
- Is the approximation justified: say $F=0.05$; $K_a = 1.07 \times 10^{-3}$ (o-hydroxybenzoic) $\Rightarrow [H^+] = 6.80 \times 10^{-3} \text{ M}$, which is significant higher than the H from water dissociation
- One more step: if K_a is very low, than $x \ll F$ than
 $K_a = [H^+][A^-]/[HA] = x^2/(F-x) \approx x^2/F$
e.g. $K_a = 1.58 \times 10^{-10}$ (Trimethylammonium chloride),
 $F=0.1$
 $K_a = x^2/(F-x) \Rightarrow \underline{x=3.97 \times 10^{-6} \text{ M}} \ll \text{than } F=0.1$
so $K_a = x^2/F$ can be used, if we do, $x=3.97 \times 10^{-6} \text{ M}$, exactly the same

Treatment of weak base

- Similar to the treatment of weak acid



$$K_b = [BH^+][OH^-]/[B]$$

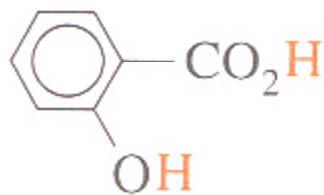
assume $[OH^-] \approx [BH^+] = x$; then

$$K_b = x^2/(F-x)$$

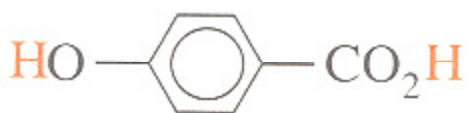
- Fraction of association (hydrolysis):

$$\alpha = [BH^+]/F$$

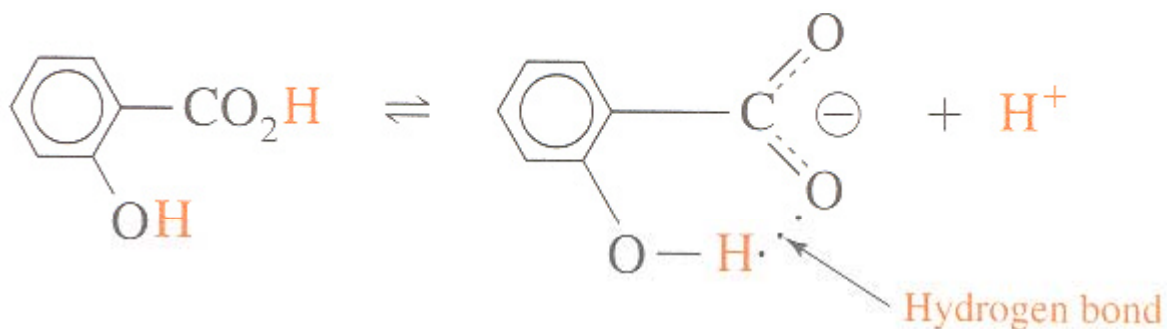
Example of ortho- and para-hydrobenzoic acids



o-Hydroxybenzoic acid
(salicylic acid)
 $pK_a = 2.97$

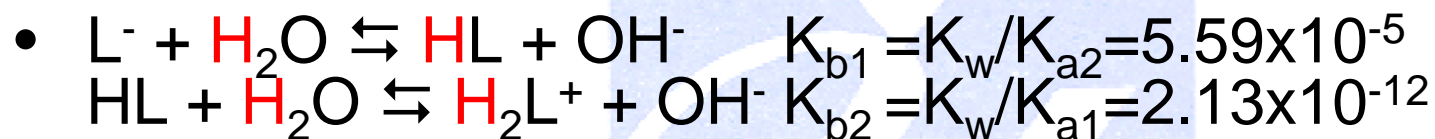


p-Hydroxybenzoic acid
 $pK_a = 4.58$



Hydrolysis of weak base

- Hydrolysis: the reaction of anything with water (dissolve 0.05 M L⁻ in water).



$$K_{b2} \ll K_{b1},$$

So HL will hardly *hydrolyze*, thus L⁻ can be treated as monobasic species, $K_b \approx K_{b1} = 5.59 \times 10^{-5}$.



$$\begin{array}{ccc} 0.050 - X & X & X \end{array}$$

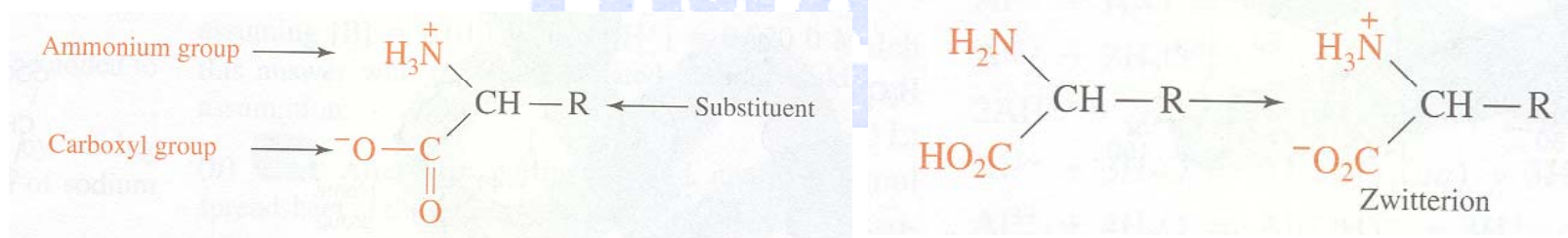
$$K_b = x^2/(0.050 - x) \Rightarrow x = [OH^-] = 1.64 \times 10^{-3} \text{ M}$$

$$[H^+] = K_w/[OH^-] = 6.08 \times 10^{-12} \text{ M} \Rightarrow \text{pH} = 11.22$$

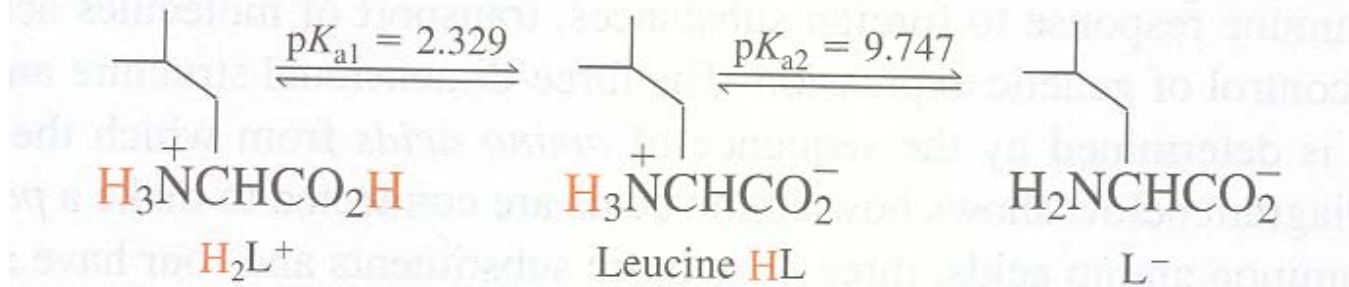
Polyprotic Acid and base

- Can donate (acid) or accept (base) more than one protons.
- Diprotic, triprotic...

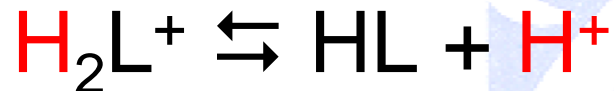
amino acid



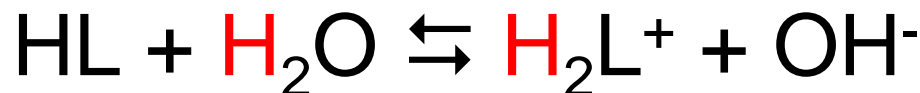
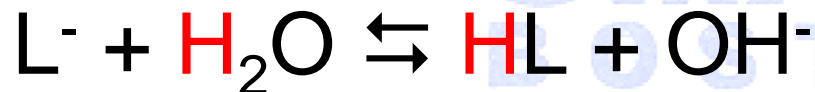
Diprotic acid and base (amino acid)



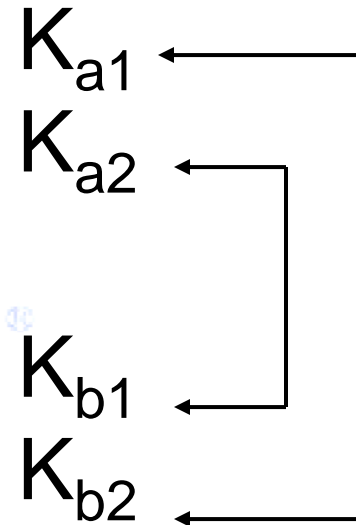
- Diprotic acid:



- Diprotic base



$$K_{\text{a}1} K_{\text{b}2} = K_{\text{w}} ; K_{\text{a}2} K_{\text{b}1} = K_{\text{w}}$$



Dissociation of diprotic acid



Making a educated judgments for the approximation is going to be the key part of solving the analytical equations

Assumption:

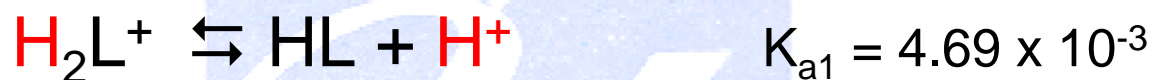
since $K_{a1} \gg K_{a2}$

so the dissociation of HL is insignificant comparing with the dissociation of H_2L^+

Let prove the assumption is reasonable!

Dissociation of diprotic acid

- Dissolve 0.05 H_2L^+ in water



Initial	0.05	0	0
end	0.05-x	x	x

Assumption 1: K_{a2} can be ignored.

Assumption 2: K_w can be ignored..

$$K_{a1} = \frac{x^2}{(0.05-x)} = 4.69 \times 10^{-3} \Rightarrow x = 1.31 \times 10^{-2} \text{ M} = [HL] = [H^+]$$



Can x be ignored?

$$\text{pH} = 1.88$$

Dissociation of diprotic acid

- How about



$$\frac{1.3 \times 10^{-2}}{1.3 \times 10^{-2}} \quad x \quad 1.3 \times 10^{-2}$$

$$K_{a2} = 1.3 \times 10^{-2} x / 1.3 \times 10^{-2} \Rightarrow x = K_{a2} = 1.79 \times 10^{-10} \text{ M}$$

Fraction of dissociation:

$$1^{\text{st}} 0.013 / 0.05 = 26\% ; 2^{\text{nd}} 1.79 \times 10^{-10} / 0.013 = 1.37 \times 10^{-6}\%$$

Assumption:

since $K_{a1} \gg K_{a2}$

so the dissociation of HL is insignificant comparing with the dissociation of H_2L^+

IS REASONABLE

Is the number right?

Dissociation of diprotic acid

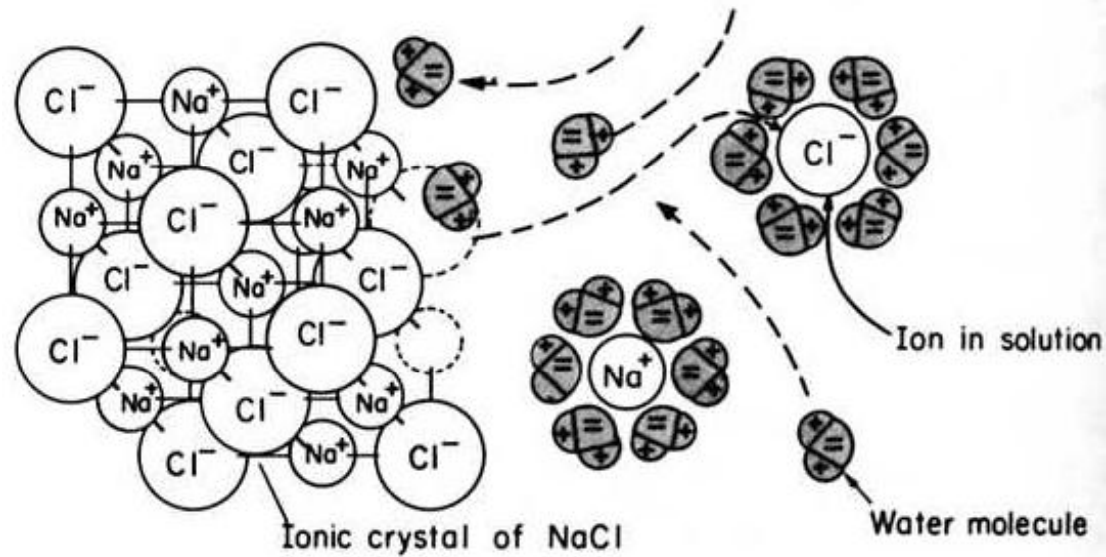
- For most of diprotic acids, K_{a1} is sufficiently large than K_{a2} , so the solution of a diprotic acid behaves like a monoprotic acid, $K_a \approx K_{a1}$
- $[L] \approx K_{a2}$

UMASS
BOSTON



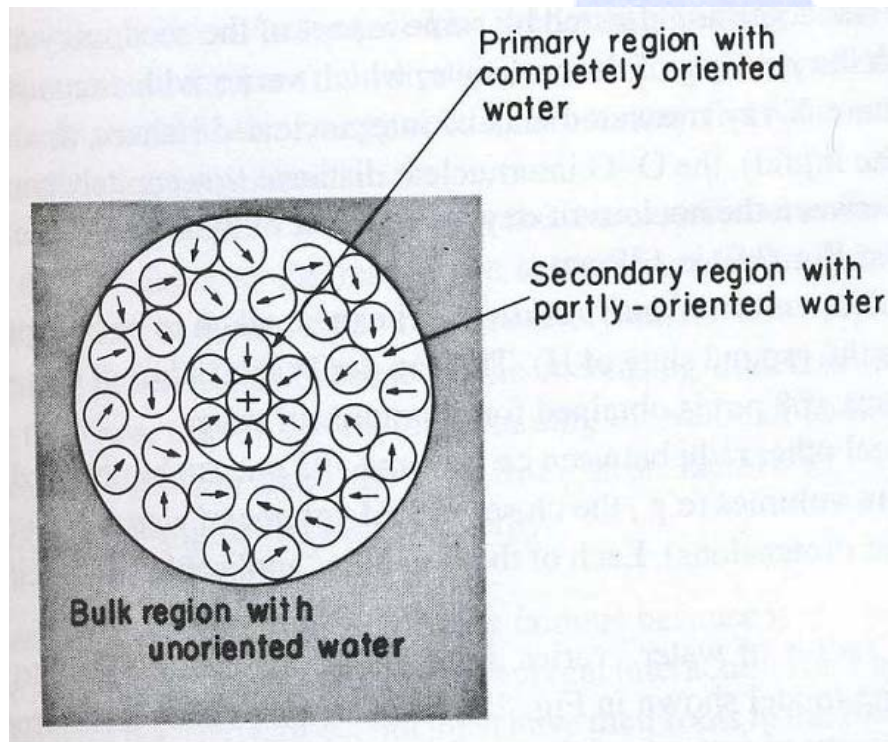
Activity

- How the salt becomes dissolved



Activity

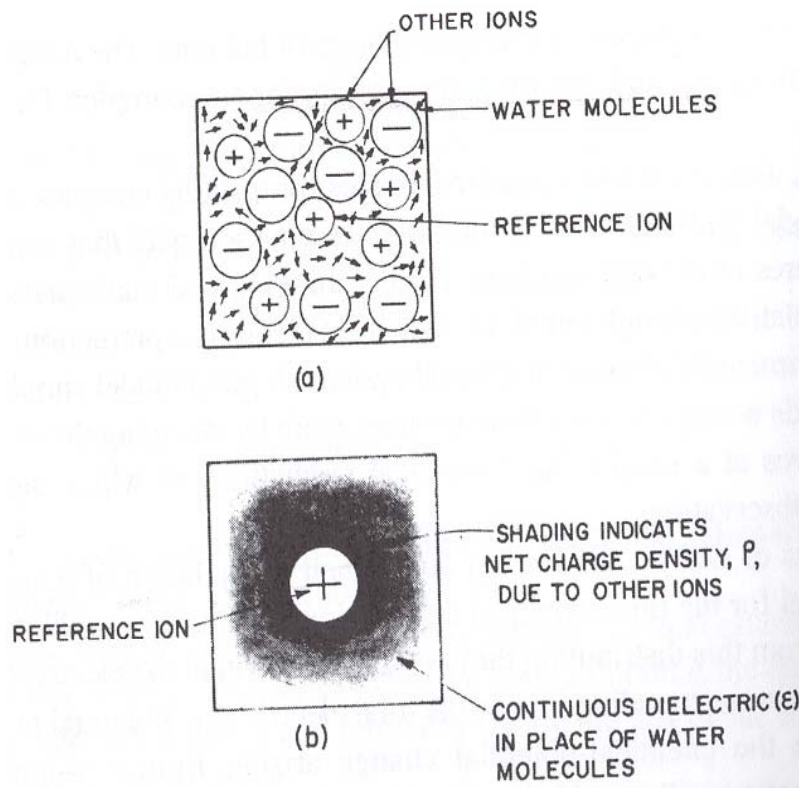
- The picture of ion in solution: Hydration shell



- The dissolved ion will interact with solvent e.g. water dipole. The ion-dipole force will immobilize the solvent dipole around it to a hydrated ion, the ion is surrounded by the shell, the whole cluster move together as a single kinetic entity. The region can be sharply defined
- Primary region: solvent dipoles are well completely oriented
Secondary region: solvent dipoles are partially oriented. The region cannot be sharply defined.

Activity

- Ionic Cloud theory – Hydrated Radius



- Select on ion as *reference ion or central ion*.

- Only the central ion is given the individuality of a discrete charge

- Water molecules are treated as a continuous dielectric medium.

- The ions, except the central ion are treated as continuous distribution of charge – Charge Cloud.

- Hydrated radius is the effective radius of the ion plus the hydration shell

Activity

- The rate of migration of ion in an electric field depends on the hydrated radius

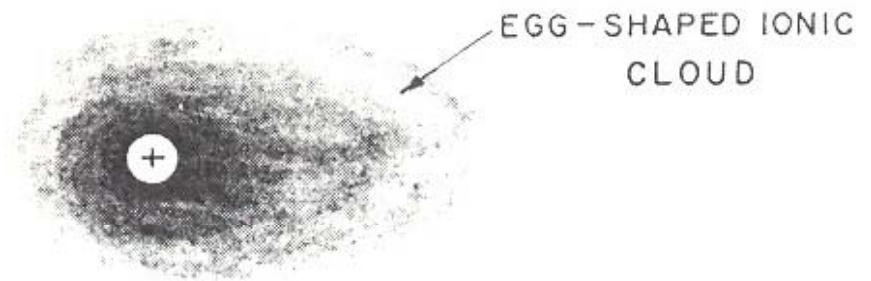
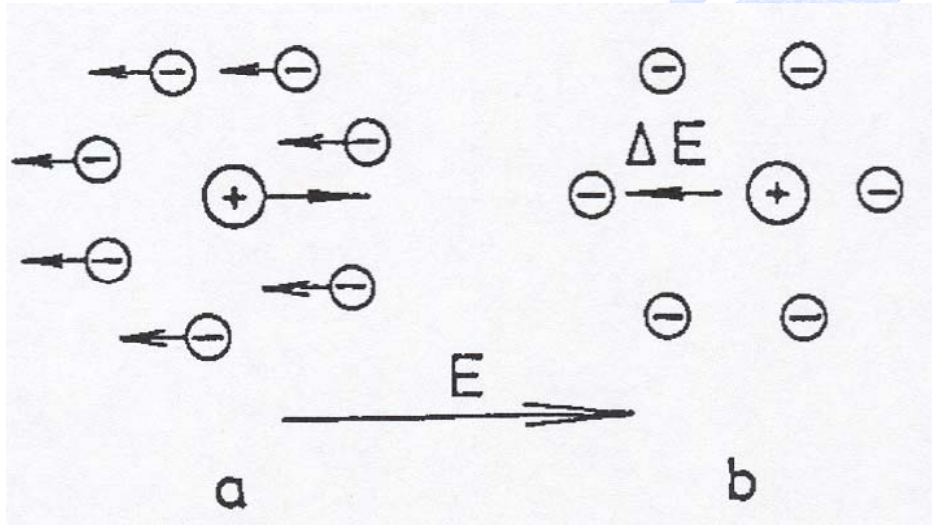


Fig. 4.81. The egg-shaped ionic cloud around a moving central ion.

Ionic Strength

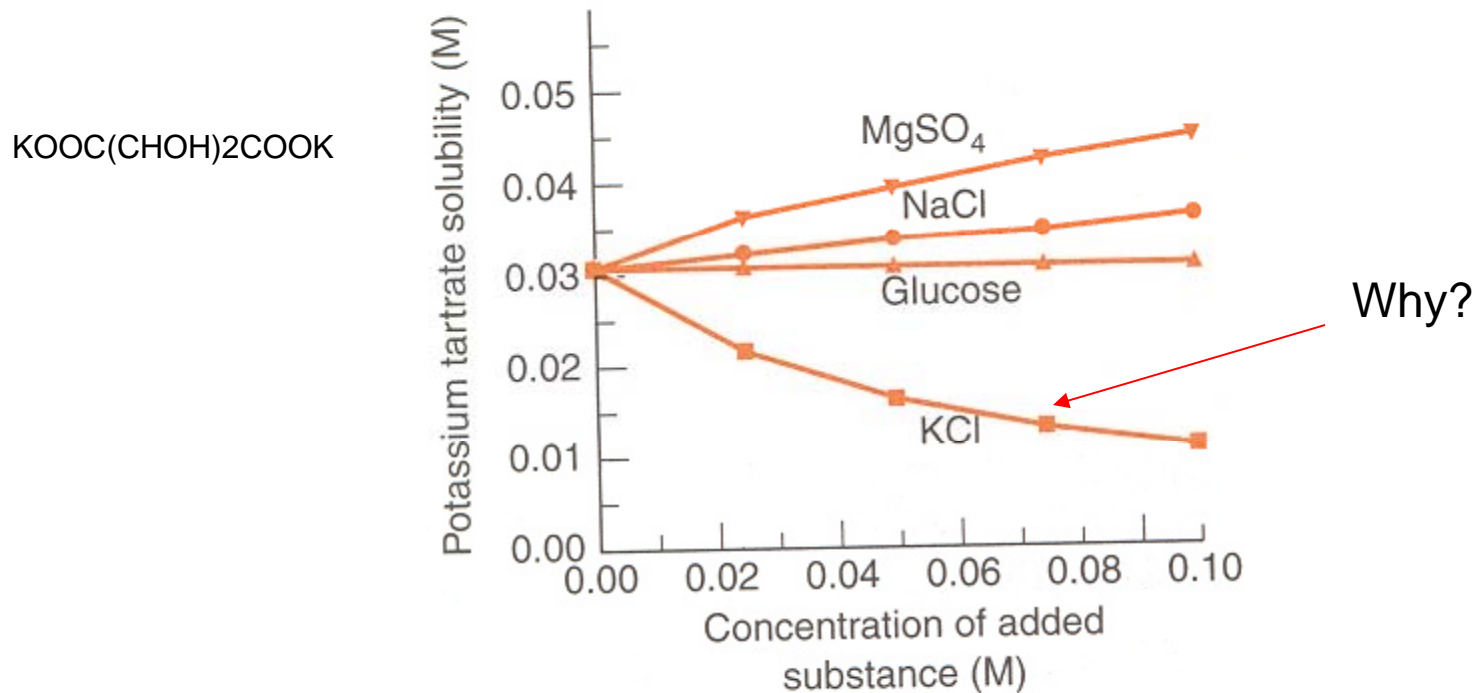
- Ionic Strength: the measure of the total concentration of **ions (charges)** in the solution:

$$\mu = \frac{1}{2}(C_1Z_1^2 + C_2Z_2^2 + \dots) = \frac{1}{2}\sum C_i Z_i^2$$

- The greater the ionic strength of a solution, the higher the charge in the ionic atmosphere (hydrated shell), each hydrated ion contains less net charge and there is less attraction between any particular cation and anion.

Impact of ionic strength to the solubility of salt

- Addition of an “inert” salt increase the solubility of an ionic compound



Activity

- Since the ions in the solution are hydrated complexes rather than the simple bare ions, “effective concentration” is no longer the same as the regular concentration. The “effective concentration” which taking into the consideration of ionic strength is called activity:

$$\alpha = [A] \gamma_A$$

γ_A : activity coefficient

Activity coefficient

- Extended Debye Hückel Equation

$$\log \gamma = \frac{-0.51z^2 \sqrt{\mu}}{1 + (\alpha \sqrt{\mu} / 305)} \quad (\text{at } 25^\circ \text{C})$$

α : effective hydrated radius
(picometers 10^{-12}m)

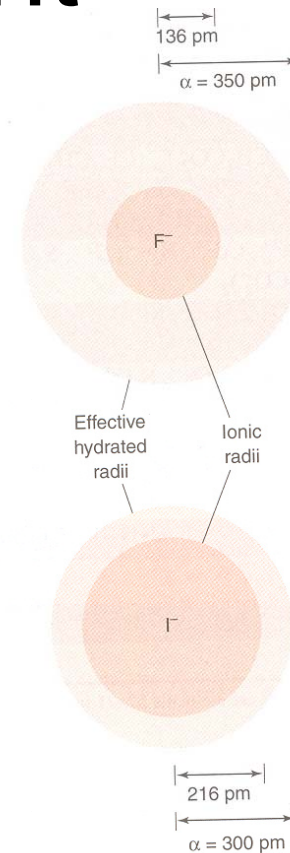
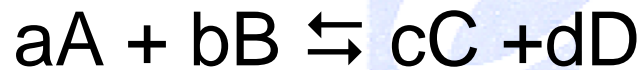


Figure 8-4 Ionic and hydrated radii of fluoride and iodide. The *smaller* F⁻ ion binds water molecules more tightly than does I⁻, so F⁻ has the *larger* hydrated radius.

Activity coefficient

- Activity coefficient measures the deviation of behavior from ideality, $\gamma=1$, ideal behavior $\alpha = [A]$
- Equilibrium constant should use activity to replace concentration



$$K = \frac{\alpha_C^c \alpha_D^d}{\alpha_A^a \alpha_B^b} = \frac{[C]^c \gamma_C^c [D]^d \gamma_D^d}{[A]^a \gamma_A^a [B]^b \gamma_B^b}$$

Effect of Ionic strength, ion charge, and ion size on activity coefficient

- Ionic strength increase, the activity coefficient decrease.
- The charge on the ion increase, departure of its activity coefficient from unity increase.
- The smaller the hydrated radius of the ion, the more important activity effects become.

