

Ionic Equilibrium



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Equilibrium Constant For Ionic Equilibrium

Ionic equilibrium involve ions in aqueous solutions

Only K_c is considered

Note : no meaning of K_p

Different
notation

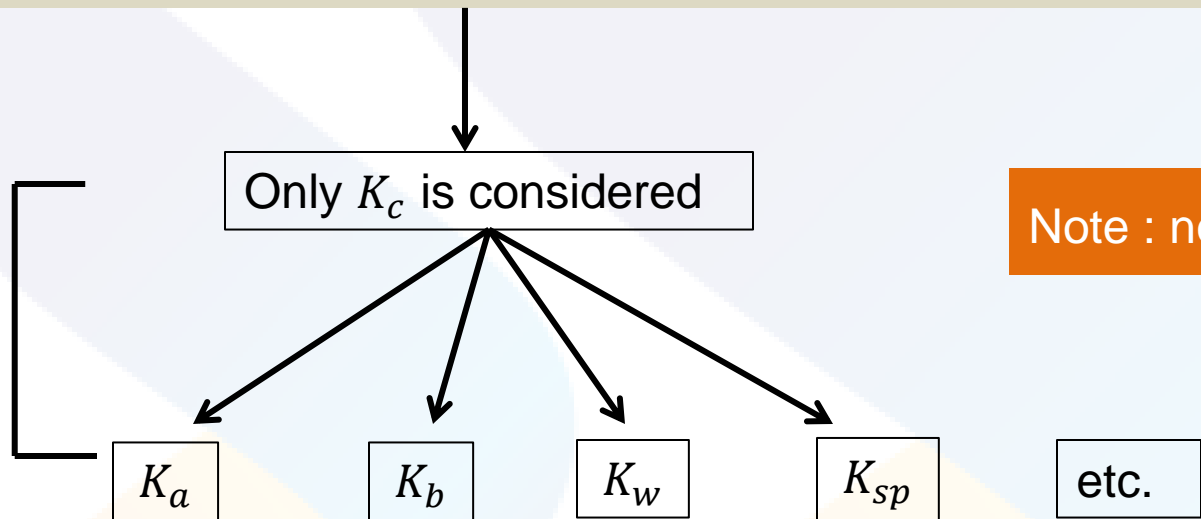
K_a

K_b

K_w

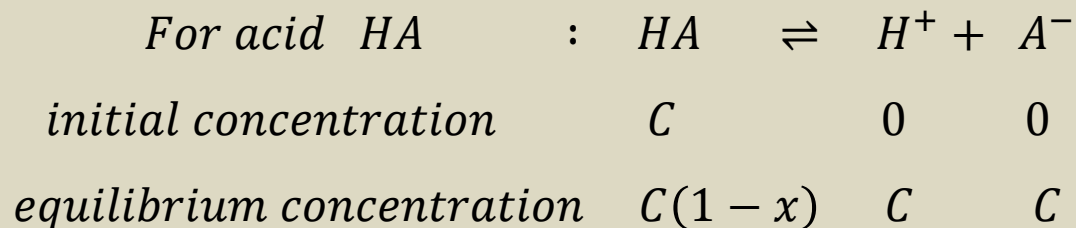
K_{sp}

etc.

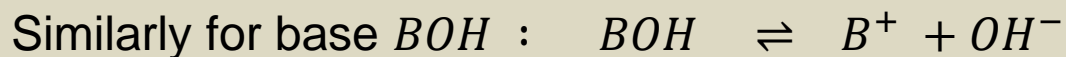




Relative Strengths



$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{cx^2}{1-x}$$



$$K_b = \frac{cx^2}{1-x}$$

K_a and K_b depends only on temperature

Greater the value of K_a ,& K_b greater is strength of acid & base respectively



Arrhenius Acids and Bases

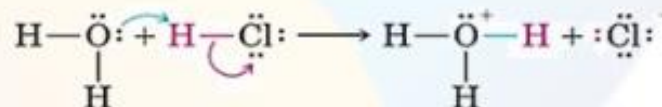
Acid: Produces H_3O^+ ions in aqueous solution

Base: Produces OH^- ions in aqueous solution

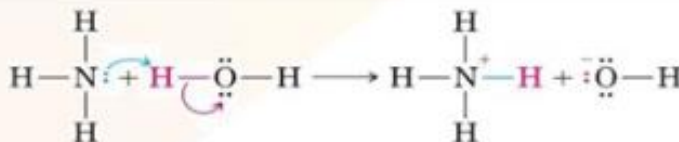
H^+ reacts immediately with a water molecule to give a hydronium ion.



When **ACIDS** dissolve in water, they **react with water** to give hydronium ion and chloride ion



When **BASES** dissolve in water, **ions separate** (ions become hydrated), produce OH^- ions





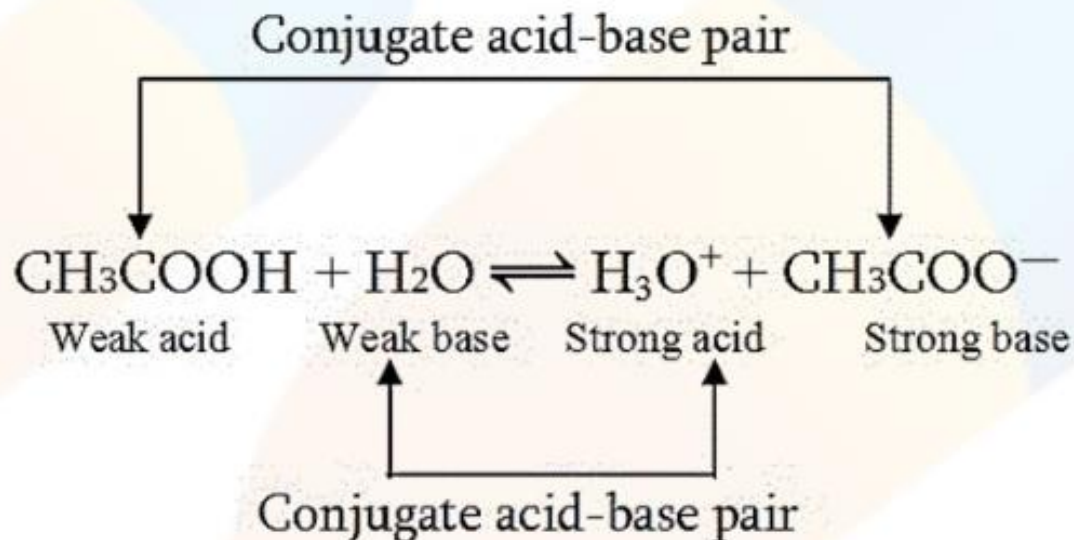
Bronsted-Lowry Acids and bases

Acid: A proton donor

Base: A proton acceptor

Acid-base reaction: A proton-transfer reaction

- Conjugate acid-base pair: Any pair of molecules or ions that can be interconverted by transfer of a proton





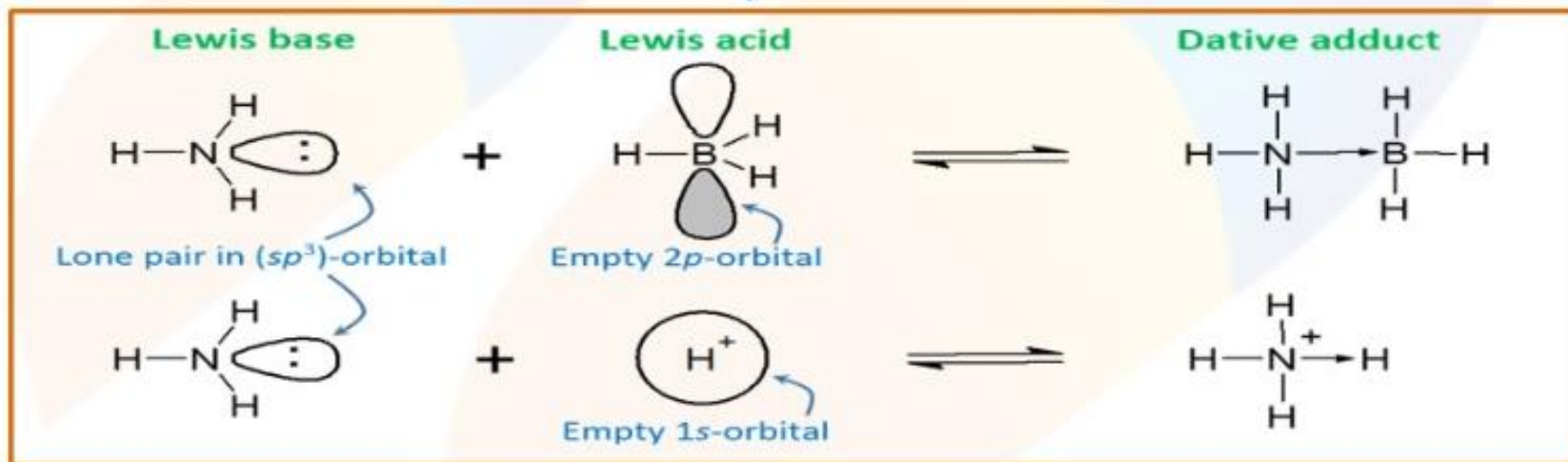
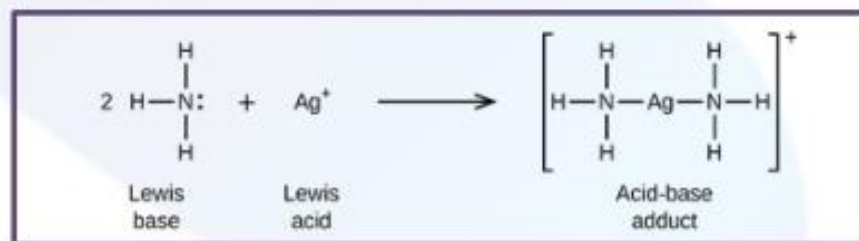
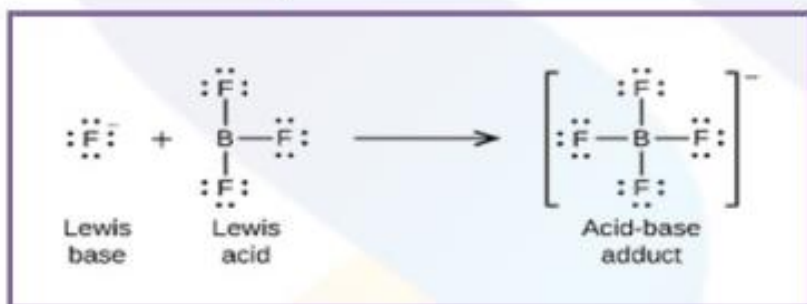
Lewis Acids and Bases

Acid: An electron pair acceptor



Base: An electron pair donor

□ Lewis acid + Lewis base \leftrightarrow Adduct (Coordination compound)





Expression of Strengths of Acids And Bases (pK)

$$pK_a = -\log K_a$$

$$pK_a + pK_b = pK_w$$

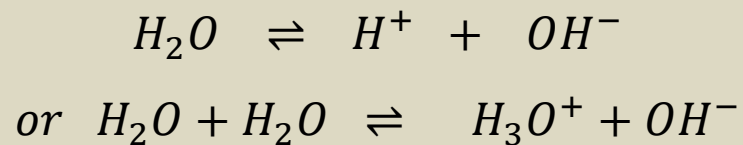
$$pK_w = 14 \text{ at } 25^\circ\text{C}$$

Strength of a base is expressed in terms of pK_a of its conjugate acid

Higher the pK_a value lower the acid strength and therefore higher the base strength



Ionic Product of Water (K_w)



$$K = \frac{[H^+][OH^-]}{[H_2O]}$$

Note that $[H_2O]$ may be taken as constant

$$\Rightarrow K \times [H_2O] = [H^+][OH^-]$$

Or

$$K_w = [H^+][OH^-]$$

$$= 10^{-14} (\text{mole/L})^2 \text{ at } 25^\circ\text{C}$$

Note that K_w increases with increase in temperature



pH And pOH

$$pH = -\log[H^+] = \log \frac{1}{[H^+]}$$

$$pOH = -\log[OH^-]$$

pH scale determines the concentration of H^+ in the solution

Note that since at a given temperature K_w is constant addition of H^+ ions will reduce OH^- ions and vice versa



$$pH + pOH = pK_w = 14$$

For a natural solution at 25°C

$$pH = -\log 10^{-7} = 7$$

Solution is acidic if $pH < 7$ i.e. $[H^+] > 10^{-7}$

pH can be zero or negative and in that case $[H^+]$ is replaced by activities of H^+



pH of Buffer Solution

Weak acid and its salt

$$[H^+] = K_a \frac{[acid]}{[salt]}$$

$$pH = pK_a + \log \left(\frac{\text{moles of salt}}{\text{moles of acid}} \right)$$

Better as buffer for $pH < 7$

Weak base and its salt

$$pOH = pK_b + \log \left(\frac{\text{moles of salt}}{\text{moles of base}} \right)$$

Better as buffers for $pH > 7$

Note: buffer solution maintain their pH value on slight changes in $[salt]$ or $[acid]/[base]$



Buffer Capacity

$$\text{buffer capacity} = \frac{\text{number of moles of acid/alkali added per litre}}{\text{change in pH}}$$

For maximum buffer capacity



$$\frac{[\text{salt}]}{[\text{acid}]} \quad \text{or} \quad \frac{[\text{salt}]}{[\text{base}]} = 1$$

$$\text{i.e. } K_a \approx [H^+] \quad \text{or} \quad K_b \approx [OH^-]$$

Buffer solution has lost its usefulness when one component of buffer pair is less than about 10% of other



Hydrolysis of Salt

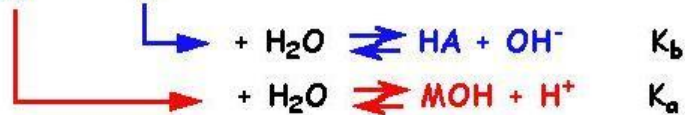
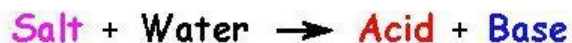
Phenomenon of interaction of cations of a salt with OH^- ions and anions with H^+ ions

Note that : resulting solution after hydrolysis may be acidic , basic or even natural

Hydrolysis is an endothermic process

Note that : salts of strong acids and strong bases do not undergo hydrolysis

Salt hydrolysis is the reverse of neutralization



$K_a = K_b$ the solution is neutral

$K_a > K_b$ the solution is acidic

$K_a < K_b$ the solution is basic



Hydrolysis of Salts of Weak Acids And Strong Bases

$$K_h = \frac{K_w}{K_a}$$

→ K_h is the hydrolysis constant

Degree of hydrolysis (x) of salts

a is initial moles of salt

$$K_h = \frac{K_w}{K_a} = \frac{ax^2}{1-x}$$

$\approx ax^2$ (if x is very small)

x should be neglected only when it is less than 5% (i.e. 0.05)

And

$$pH = \frac{1}{2}(pK_w + pK_a + \log a)$$

Note: above expression are valid for univalent salt



Hydrolysis of Salt of Weak Bases And Strong Acids

$$K_h = \frac{K_w}{K_a}$$

x is degree of dissociation of base

$$K_h = \frac{ax^2}{1-x}$$

$$\approx ax^2 \quad (\text{if } x \text{ is very small})$$



a is initial moles of salt

$$pH = \frac{1}{2}(pK_w - pK_b - \log a)$$

Note that : above expression are valid for univalent salts



Hydrolysis Of Salts Of Weak Acids And Weak Bases

$$K_h = \frac{K_w}{K_a \times K_b}$$

Degree of dissociation of acid and base

Assumed same for both and = x

$$K_h = \frac{x^2}{(1-x)^2}$$

$$\approx x^2 \quad (\text{if } x \text{ is very small i.e. } < 5\%)$$

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

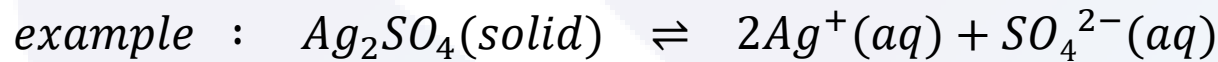
Note that if $K_a = K_b$ resulting solution is natural

Note that : the expressions above are valid for univalent salts



Solubility Product (K_{sp})

K_{sp} comes in picture for a saturated solution of sparingly soluble salt



At equilibrium

$$K(\text{equilibrium constant}) = \frac{[Ag^+]^2 [SO_4^{2-}]}{[Ag_2SO_4]}$$

Note that for solid $[] = 1$



$$K_{sp} = [Ag^+]^2 [SO_4]^{2-}$$

Note that : at a given salt K_{sp} is constant at a given temperature irrespective of source from which ions originate



Ionic Product And K_{sp}

Ionic product in the reaction quotient for a solution of sparingly soluble salt



= product of concentration of ions raised to their stoichiometric coefficients

If Ionic Product



$> K_{sp}$, the solution **gets precipitated**

$= K_{sp}$, the solution is **just saturated**

$< K_{sp}$, the solution is **not saturated**



Ostwald Theory of Indicator

An indicator is usually weak acid or weak base and used to determine end point in a titration

NOTE: Indicator change their color within a certain pH range which is due to shifting of indicator equilibrium

example : HPh (indicator colorless) $\rightleftharpoons H^+ + Ph^-$ (pink)

$$K_{In}(\text{indicator constant}) = \frac{[H^+][Ph^-]}{[HPh]}$$

When $[Ph^-] = [HPh]$ i.e. for natural color

$$K_{In} = [H^+]$$



$$pK_{In} = pH$$



Degree of Ionization or Degree of Dissociation (α)

It is the fraction of the total number of molecules which ionize (dissociate) into constituent ions.

For strong electrolytes
 $\alpha = 1$

For weak electrolytes
 $\alpha < 1$

Ostwald's Dilution Law

The degree of dissociation (α) of weak electrolyte is inversely proportional to the square root of the molar concentration of the solution.

$$K = \frac{C\alpha^2}{1 - \alpha}$$

If α is very small $1 - \alpha = K_a = C\alpha^2$

$$\text{or } \alpha = \sqrt{\frac{K_a}{C}}$$

$$= \alpha \propto \frac{1}{\sqrt{C}}$$

Here K is dissociation constant and C is molar concentration of the solution.

