Chemical Equilibrium:-

Formulas:-

- $\boxed{K_c = \frac{K_f}{K_r}} = \frac{\text{Rate constant for forward Rx}}{\text{Rate constant for backward Rx}}$

- $\boxed{K_c = \frac{[\text{products}]}{[\text{Reactants}]}}$

As, $A + B \underset{K_r}{\overset{K_f}{\rightleftharpoons}} C + D$

- $\boxed{R_f = K_f[A][B]}$

- $\boxed{R_r = K_r[C][D]}$

- $\boxed{K_p = K_c(RT)^{\Delta n}}$

If ratio is greater than K_c

$\boxed{\frac{[\text{products}]}{[\text{Reactants}]} > K_c}$

Reverse Reaction will occur to attain equilibrium.

If ratio is less than K_c

$\boxed{\frac{[\text{products}]}{[\text{Reactants}]} < K_c}$

Reaction will proceed in forward direction.

If ratio is equal to K_c

$\boxed{K_c = \frac{[\text{products}]}{[\text{Reactants}]}}$

Reaction is at equilibrium

- $\boxed{K_w = [H^+][OH^-]} = 10^{-14}$ at 25°c

- $\boxed{K_c = \frac{[H^+][OH^-]}{[H_2O]}} = 1.8 \times 10^{-16}$ mol·dm^{-3}

- $\boxed{PH = -\log[H^+]}$

- $\boxed{POH = -\log[OH^-]}$

- $\boxed{PK_w = PH + POH = 14}$

- $\boxed{K_a \propto \frac{1}{PK_a}}$ $\boxed{K_a \propto \text{acidic strength}}$

- $\boxed{K_b \propto \frac{1}{PK_b}}$

- $\boxed{\% \text{ ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100}$

- $\boxed{PK_a = -\log K_a}$

- $\boxed{PK_b = -\log K_b}$

- $\boxed{PK_a + PK_b = 14}$ at 25°c

- $\boxed{K_a \propto \frac{1}{K_b}}$

- Acidic Buffers $\boxed{PH = PK_a + \log \frac{[Salt]}{[Acid]}}$

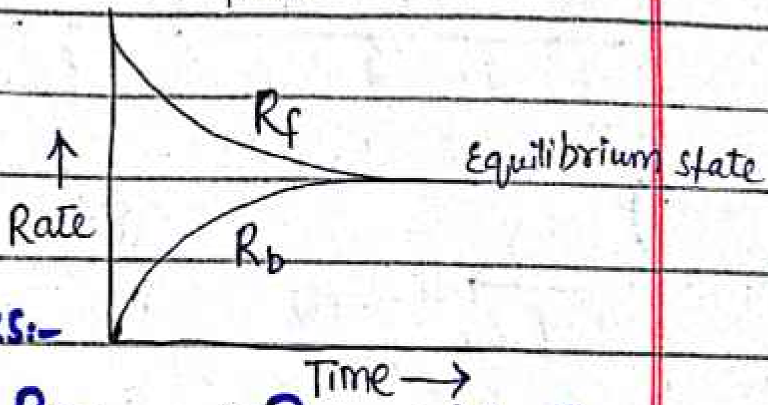
- Basic Buffers $\boxed{POH = PK_b + \log \frac{[salt]}{[base]}}$

Chemical equilibrium:-

"A chemical reaction in which products of a reaction can react to form the original reactants under the same set of conditions"

- represented by double arrow ($\rightleftharpoons$)
- Never undergo completion
- Usually carried out in close vessel.

$$N_{2(g)} + 3H_{2(g)} \underset{\text{high pressure}}{\overset{Fe/450^\circ C}{\rightleftharpoons}} 2NH_{3(g)}.$$



Types of Rxs:-

Irreversible Rxs.	Reversible Rxs.
Reactions which occur in one direction and gets completed.	Reactions occur in both directions (forward/backward) and never be completed.
change in free energy is negative i.e ($\Delta G<0$)	Change in free energy is (ΔG) zero.
e.g $NH_4NO_2 \xrightarrow{\Delta} N_2 + 2H_2O$ $2KClO_3 \xrightarrow{\Delta} 2KCl + 3O_2$	e.g. $N_2 + O_2 \leftrightarrow 2NO$ $3Fe + 4H_2O \leftrightarrow Fe_3O_4 + 4H_2$

Equilibrium State and Chemical energy changes

At equilibrium ΔG is equal to zero and we have

$$\Delta G = \Delta H - T\Delta S$$

$\because \Delta G = 0$

$$\boxed{\Delta H = T\Delta S}$$

→ Equilibrium

physical equilibrium

"(when equilibrium exists between same chemical species)."

e.g. $H_2O_{(s)} \xleftrightarrow[1atm]{0°C} H_2O_{(l)}$

Ice Water

Chemical equilibrium

"(when equilibrium exists between different chemical species)".

e.g

$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$

$CaCO_{3(s)} = CaO_{(s)} + CO_{2(g)}$

Homogeneous chemical equilibrium

"If a chemical equilibrium has only one phase"

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

Heterogeneous chemical equilibrium

If a chemical equilibrium has more than one phase"

$3Fe_{(s)} + 4H_2O_{(l)} \rightleftharpoons Fe_3O_{4(s)} + 4H_{2(g)}$

Some features of chemical equilibrium:-

- Here the rate of forward.Rx = Rate of backward. Rx.
- It is dynamic in nature means reaction will not cease but keep going on both directions with equal rates.
- Equilibrium can be attained from either side.
- Equilibrium state remains unaffected by the presence of catalyst. But it helps to attein this state rapidly

Law of Mass Action:

- ↳ proposed by 'Guldberg and Wage' (1864)
- "According to this law, the rate of chemical reaction is directly proportional to the product of the active masses of the reacting substances"

$$A + B \underset{K_r}{\overset{K_f}{\rightleftharpoons}} C + D$$

Active mass/Molar concentration:-

It means conc. of the reactant expressed in moles per litre or the pressure of a reacting gas in atmosphere.

- It is denoted by [] symbol.

Note • Active mass of pure solid or a pure liquid is assumed to be one.

- Its unit is $mol.lit^{-1}$.

Note • At constant temperature

$$\boxed{\text{Partial pressure} \propto \text{Active mass}}$$

Equilibrium Constant:- "It is the ratio of rate of forward and backward reaction at a particular temperature"

(or) "It ratio of active masses of reactants to that of active masses of products at a particular temperature."

- It is denoted by K_c or K_p.

Note

Completion of Reaction $\propto K_c$
Stability of Reaction $\propto \frac{1}{K_c}$
Stability of product $\propto K_c$

Factors influencing Equilibrium constant

→ **Kc doesnot depend upon**

- concentration of reactants and products
- pressure
- presence of catalyst
- presence of inert material
- The direction from which equilibrium has been set up.

→ **Kc depends upon**

- Temperature

- Temperature
  - (i) For exothermic Rx:
    ↳ K_p decrease with increase of temperature since K_f decrease $\left(K_p = \frac{K_f}{K_b}\right)$
  - (ii) For endothermic Rx: K_p increase with increase of temperature since K_f increase.
- The mode of representing the Rx.
- Stoichiometric representation of Rx
- Nature of reactant or product.

Units of K:

$$\boxed{K_c = (\text{mol}/\text{lit})^{\Delta n}}$$

$$\boxed{K_p = (\text{atm})^{\Delta n}}$$

Relation b/w Kp and Kc

$$\boxed{K_p = K_c (RT)^{\Delta n}}$$

Relation b/w Kp and Kc for different types of Rxs:-

- $\Delta n = 0$ $K_p = K_c$

here, Kp and Kc has no units.

$(\leftrightarrow)$ or $(\rightleftharpoons)$

$$N + O_2 \longleftrightarrow 2NO$$

- $\Delta n = +ve$ $K_p > K_c$

$$PCl_5 \longleftrightarrow PCl_3 + Cl_2$$

- $\Delta n = -ve$ $K_c > K_p$

$$2SO_2 + O_2 \longleftrightarrow 2SO_3$$

⇒ Kc and Kp expressions for HI-formation after calculations are

$$H_2 + I_2 \rightleftharpoons 2HI$$

t=0 a mole b mole 0 mole

t=eq. (a−x) mole (b−x) mole (2x) mole

$$\therefore K_c = \frac{4x^2}{(a-x)(b-x)}$$

$$\therefore K_p = \frac{4x^2}{(a-x)(b-x)}$$

Degree of dissociation:

It is the ratio of number of molecules dissociated at equilibrium to initial number of molecules.

→ denoted by (α)

→ LE-Chateliers principle:-

"If a stress is applied to a system at equilibrium, the system acts in such a way so as to nulify, as far as possible, the effect of that stress."

• Effect of concentration:

- An increase in concentration of reactants favours forward Rx.
- An increase in conc. of product favours backward Rx

• **Effect of pressure:-** By increasing the pressure, equilibrium shifts in the direction in which there is decrease in volume or less number of molecules and vice versa.

Effect of temperature.

- Increase in temperature favours the forwards reaction in the endothermic Rx. (ΔH = +Ve)
- Decrease in temperature favours the forward reaction in the exothermic Rx (ΔH = -Ve)

Effect of catalyst on equilibrium constant:-

catalyst doesnot affect the equilibrium position but reduces the time to attain equilibrium by increasing the rate in both directions, and by lowering the energy of activation.

→Applications of Le Chatelier's principle:-

1- On physical Equilibrium:-

(i) Ice - water system (Melting of ice)

$$Ice \leftrightarrow water - heat \quad (\Delta H = +Ve)$$

- endothermic process
- decrease of volume occur

- favourable conditions for melting are high temperature and high pressure.

(ii) Water - Steam System (Evaporation of water)

Water ⟷ Steam - heat ($\Delta H = +ve$)

- endothermic process
- increase of volume occur.
- favourable conditions for evaporation are high temperature and low pressure.

(iii) Solubility of gases and liquids.

When a gas dissolves in a liquid, there is a decrease in its volume so an increase in pressure will favour dissociation of a gas in liquid. i.e Solubility of a gas is directly proportional to partial pressure of the gas (**Henry's law**).

→ On opening carbonated water bottle CO_2 comes out as its pressure decreases.

(iv) Effect of Temperature on Solubility:-

- Exothermic Substances are like (CaO, $Ca(OH)_2$, KOH) are more soluble in cold water than in hot water i.e. low temperature favours their solubility.

- Endothermic Substances like (sugar, urea) are more soluble in hot water than cold water. i.e high temperatures favours their solubility.

(v) Effect of pressure on boiling point:

On increasing pressure boiling point increases as vapour pressure decreases.

(vi) Effect of pressure on Melting point:-

$$\text{Solid}(V_1) \rightleftharpoons \text{liquid}(V_2)$$

→ If $V_1 > V_2$ melting is favoured

by increase of pressure so melting point decreases for such solids.

⇒ If $V_1 < V_2$ melting is favoured by lower pressure so melting point increases for such solids.

Note:-

- Conversion of a solid into liquid, liquid into gas is favoured by high temperature in most of the cases.
- Melting of solids is accomplised by increase of volume so low pressure favours their melting, while high pressure favours solidification.

2- On Chemical Equilibrium:-

(i) formation of Nitric Oxide:-

$$N_{2(g)} + O_{2(g)} \longleftrightarrow 2NO_{(g)} \quad -43200 \text{ calories}$$

Hence, favourable conditions for

formation of NO are more concentration of N_2, O_2 constant pressure. (as $n_p = n_r$) and high temperature (as it is endothermic)

(ii) formation of Ammonia:

$$N_{2(g)} + 3H_{2(g)} \longleftrightarrow 2NH_{3(g)} + 22400\,cal.$$

Faveurable conditions for NH_3 formation are more concentration of N_2, H_2 high pressure (as $n_p < n_r$) and low temperature (as it is exothermic).

⇒ Haber's process:

- German Chemist F. Haber in 1933 first developed the ammonia synthesis process.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \quad \Delta H = -92.4\,kJ$$

- Optimum conditions are for this
  - Temperature (400°C) or (673K)
  - pressure 200 - 300 atm
  - catalyst (pieces of iron catalyst embadded in a fused mixture of MgO, Al_2O_3, SiO_2)

Ionic product of water:-

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$H_2O \rightleftharpoons H^+ + OH^-$$

$$\boxed{K_c = \frac{[H^+][OH^-]}{[H_2O]}} = 1.8 \times 10^{-16} \text{ moles dm}^{-3}$$

$$\boxed{K_w = [H^+][OH^-]} = 10^{-14} \text{ at } 25°C$$

$$\boxed{K_w \propto Temp.}$$

$$\boxed{PK_w \propto \frac{1}{Temp}}$$

$$\boxed{K_w \propto \frac{1}{PK_w}}$$

⇒ Sorenson (1909) a danish biochemist introduced the terms PH and POH

PH: "The negative log of hydrogen ion concentration."

POH:

"The negative log of hydroxide ion concentration"

Relationship of $[H_3O^+]$, $[OH^-]$, pH and pOH

	$[H_3O^+]$	pH	$[OH^-]$	pOH
Basic	1×10^{-14}	14.0	1×10	0.0
	1×10^{-13}	13.0	1×10^{-1}	1.0
	1×10^{-12}	12.0	1×10^{-2}	2.0
	1×10^{-11}	11.0	1×10^{-3}	3.0
	1×10^{-10}	10.0	1×10^{-4}	4.0
	1×10^{-9}	9.0	1×10^{-5}	5.0
	1×10^{-8}	8.0	1×10^{-6}	6.0
Neutral	1×10^{-7}	7.0	1×10^{-7}	7.0

Acidic	1×10^{-6}	6.0	1×10^{-8}	8.0
	1×10^{-5}	5.0	1×10^{-9}	9.0
	1×10^{-4}	4.0	1×10^{-10}	10.0
	1×10^{-3}	3.0	1×10^{-11}	11.0
	1×10^{-2}	2.0	1×10^{-12}	12.0
	1×10^{-1}	1.0	1×10^{-13}	13.0
	1×10^{0}	0.0	1×10^{-14}	14.0

Approximate pH and pOH of some common materials at 25°C

Material	pH	pOH	Material	pH	pOH
1.0 M HCl	0.1	13.9	bread	5.5	8.5
0.1 M HCl	1.1	12.9	potatoes	5.8	8.2
0.1 M CH_3COOH	2.9	11.10	rainwater	6.2	7.8
gastric juice	2.0	12,00	milk	6.5	7.5
lemons	2.3	11.7	saliva	6.5-6.9	7.5-7.1
vinegar	2.8	11.2	pure water	7.0	7.00
soft drinks	3.0	11.00	eggs	7.8	6.2
apples	3.1	10.9	0.1 M $NaHCO_3$	8.4	5.6
grapefruit	3.1	10.9	sea water	8.5	5.5
oranges	3.5	10.5	milk of magnesia	10.5	3.5
tomatoes	4.2	9.8	0.1 M NH_3	11.1	2.9
cherries	3.6	10.4	0.05 M Na_2CO_3	11.6	2.4
bananas	4.6	9.4	0.1 M NaOH	13.0	1.00

PH range $0 \longrightarrow 14$ at $25^\circ C$

For neutral Solution PH = 7

For acidic solution PH less than 7

For Basic Solution PH more than 7

Note: (i) If Ka is less than 10^{-3}

→ Then the acid will be weak

- CH_3COOH Ka = 1.85×10^{-5} weak acid
- H_2S Ka = 1.0×10^{-7} weak acid
- H_2O Ka = 1.85×10^{-16} very weak acid

(ii) If Ka = 1 to 10^{-3}

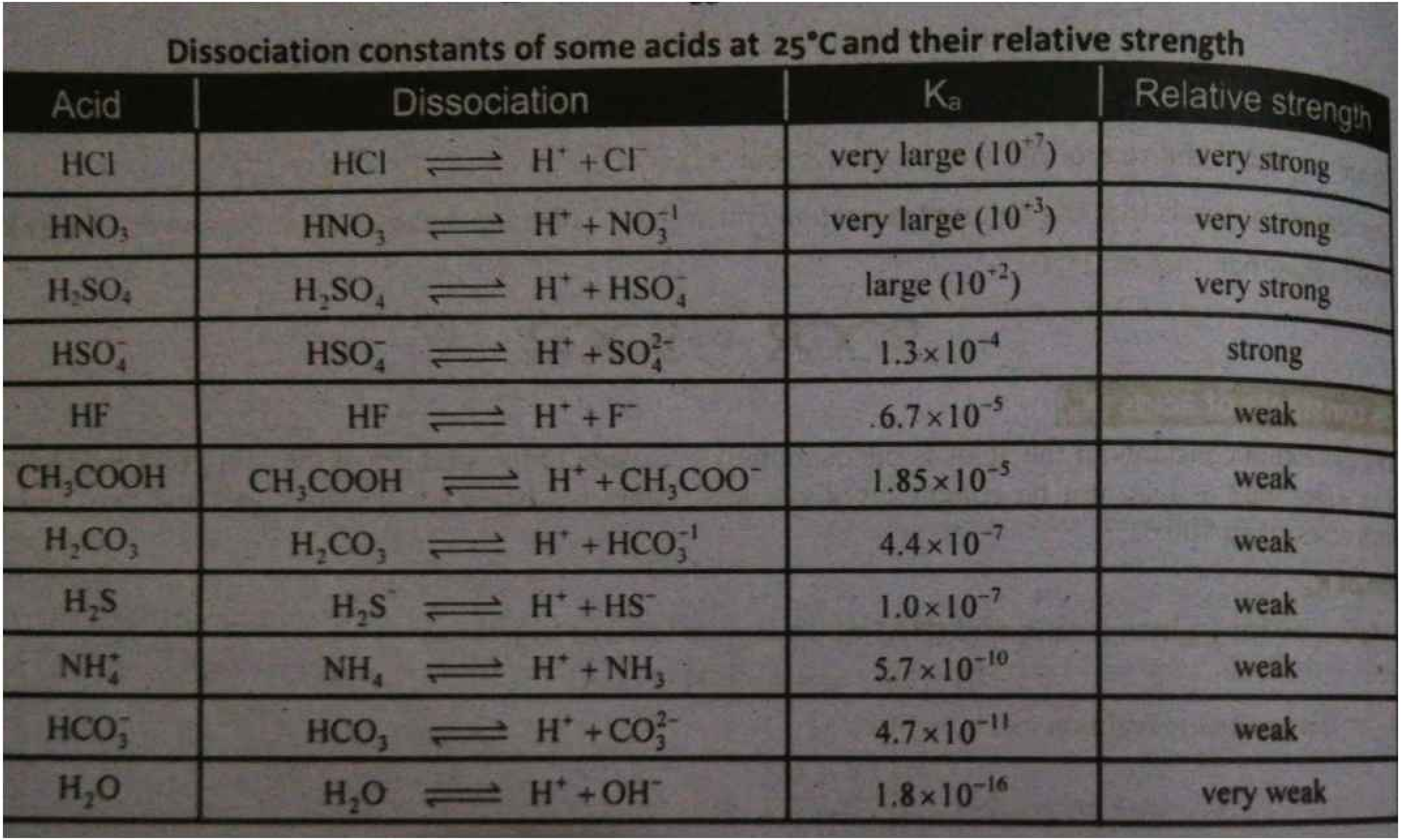
then the acid will be moderately strong.

(iii) If Ka>1

→ Then the acid will be strong.

- HCl Ka = 10^{7} very strong acid
- HNO_3 Ka = 10^{3} "
- H_2SO_4 Ka = 10^{2} "

⇒ The %age Ionization of weak acid depends upon the extent of dilution of their aqueous solutions.



Dissociation constants of some acids at 25°C and their relative strength

Acid	Dissociation	K_a	Relative strength
HCl	$HCl \rightleftharpoons H^+ + Cl^-$	very large (10^{+7})	very strong
HNO_3	$HNO_3 \rightleftharpoons H^+ + NO_3^{-1}$	very large (10^{+3})	very strong
H_2SO_4	$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$	large (10^{+2})	very strong
HSO_4^-	$HSO_4^- \rightleftharpoons H^+ + SO_4^{2-}$	1.3×10^{-4}	strong
HF	$HF \rightleftharpoons H^+ + F^-$	6.7×10^{-5}	weak
CH_3COOH	$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$	1.85×10^{-5}	weak
H_2CO_3	$H_2CO_3 \rightleftharpoons H^+ + HCO_3^{-1}$	4.4×10^{-7}	weak
H_2S	$H_2S^- \rightleftharpoons H^+ + HS^-$	1.0×10^{-7}	weak
NH_4^+	$NH_4 \rightleftharpoons H^+ + NH_3$	5.7×10^{-10}	weak
HCO_3^-	$HCO_3 \rightleftharpoons H^+ + CO_3^{2-}$	4.7×10^{-11}	weak
H_2O	$H_2O \rightleftharpoons H^+ + OH^-$	1.8×10^{-16}	very weak

PKa:

The negative log of dissociation Constant of acid (Ka)

$$\boxed{PKa = -\log Ka}$$

$$\boxed{PKa \propto \frac{1}{Ka}}$$

Lowry Bronsted acid and base concept:-

↳ proposed by J.M Lowry and J.W Bronsted in 1923.

Acid: Those species which donate or have tendency to donate proton [H^+].

$$\underset{\text{Acid}}{HCl} + \underset{\text{base}}{H_2O} \overset{H^+}{\rightleftharpoons} H_3O^+ + Cl^-$$

Base: Those species which accepts or have tendency to accept proton (H^+)

$$\underset{\text{Base}}{NH_3} + \underset{\text{Acid}}{H_2O} \overset{H^+}{\rightleftharpoons} NH_4^+ + OH^-$$

Conjugate acid-base pair:-

When a weak acid or a weak base is dissolved in water, the conjugate acid-base pair is formed.

- $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
  Acid base conjugate base conjugate Acid.

→ Conjugate base of a very weak acid is relatively very strong base and vice versa.

$$\boxed{K_a \propto \frac{1}{K_b}}$$

Common ion Effect:-

"The suppression of ionization of a weak electrolyte by adding a common ion from outside"

Buffer Solutions:- "Those solutions which resists the change in their PH when a small amount of an acid or a base is added to them."

- **Acidic buffer** formed by mixing weak acid and salt of it with strong base. (PH less than 7)

  e.g: $CH_3COOH + CH_3COONa$

- **Basic buffers** formed by mixing weak base and a salt of it with strong acid (PH more than 7)

  e.g: $NH_4OH + NH_4Cl$

Henderson's equation:

(i) for acidic buffers: This equation shows that two factors evidently govern the PH of a buffer solution

(i) PKa of acid used.

(ii) Ratio of conc. of the salt and the acid.

$$PH = PK_a + \log \frac{[Salt]}{[Acid]}$$

(ii) for basic buffers:

$$POH = PK_b + \log \frac{[Salt]}{[Base]}$$

Note:- For equal conc. of salt and base in case of basic buffer.

$$POH = PK_b$$

Buffer capacity:-

"The capability of a buffer solution to resist the change in its PH when a small amount of acid or a base is added in it".

Solubility product:- (Ksp)

"The product of equilibrium conc. of ions raised to an exponent equal to the coefficient of the balanced equation at given temperature is called solubility product."

↳ Applications

① Determination of Ksp from Solubility

- Ksp = Ionic product → saturation
- Ksp > Ionic product → unsaturation
- Ksp < Ionic product → super saturation

② Determination of solubility from Ksp.