

IONIC EQUILIBRIUM, P^H AND HYDROLYSIS

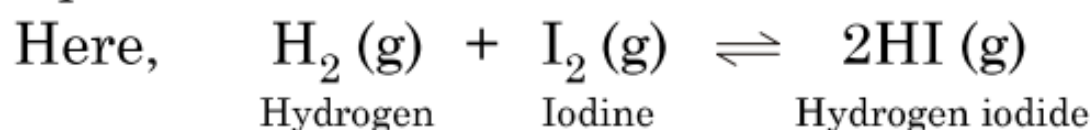
Physical Equilibrium

It is the equilibrium between the same chemical species in different phases. e.g.

- (i) Equilibrium between a liquid and its vapour.
- (ii) Equilibrium between a vapour and its saturated solution.

Homogeneous Equilibrium

A reversible reaction having all the species in same phase throughout, is called in homogeneous equilibrium.

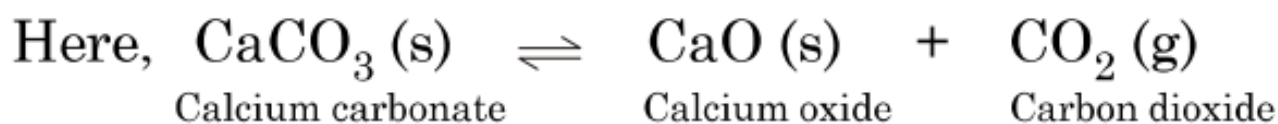


Here all reactants and products are gases.



Heterogeneous Equilibrium

A reversible reaction having its species in two or more phases, is called in heterogeneous equilibrium.



In this reaction CaCO_3 and CaO are solids, but CO_2 is a gas.

Ionic Equilibrium

A reversible reaction between species and its ions is called in ionic equilibrium.



Relationship between K_c and K_p

K_c = Equilibrium constant expressed in

K_p = Equilibrium constant expressed in pressures.

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

where R = $0.08206 \text{ litre atm K}^{-1} \text{ mol}^{-1}$.

T = absolute temperature.



Δn = number of moles of the gaseous products – number of moles of the gaseous reactants in the balanced equation.

Le-Chatelier Principle

It states that if some change is introduced in a system at equilibrium, the system proceeds in such a way that the effect of change is minimised.

Factors influencing equilibrium

- (i) Concentration of reactant or a product
- (ii) Reaction volume or applied pressure.
- (iii) Temperature

Electrolytes and non-electrolytes

Electrolyte: A compound whose aqueous solution or melt conducts electricity, is known as an electrolyte.

Non-electrolyte: A compound whose aqueous solution or melt does not conduct electricity, is known as a non-electrolyte.

Strong electrolyte: A substance which dissociates completely into its ions in an aqueous

solution and hence is a very good conductor of electricity, is known as strong electrolyte.

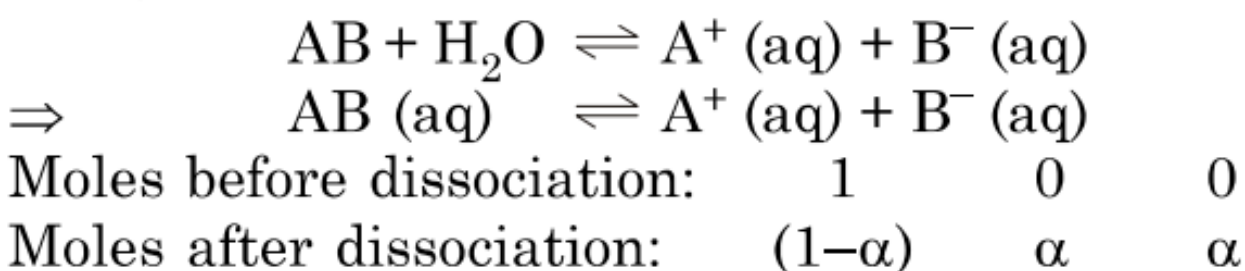
Weak electrolyte: A substance which dissociates to a small extent in an aqueous solution, is known as weak electrolyte.

Degree of dissociation or ionisation (α): Fraction of electrolyte that dissociates into its ions when it is dissolved in water, is known as its degree of dissociation or ionisation, α is 1 for strong electrolytes and less than one for weak electrolytes.

Ionisation Constant of a Weak Electrolyte

According to this law, for a weak electrolyte, the degree of ionisation is inversely proportional to the square root of its molar concentration. It can be proved as follows –

Here,



If C mol/litre is initial concentration of the electrolyte AB.

$$[AB] = C(1 - \alpha) \text{ mol/litre}$$

$$[A^+] = [B^-] = C\alpha \text{ mol/litre}$$

According to, law of equilibrium,

$$K = \frac{[A^+][B^-]}{[AB]}$$

$$= \frac{C\alpha \times C\alpha}{C(1 - \alpha)} = \frac{C\alpha^2}{1 - \alpha}$$

where K is ionisation constant for weak electrolytes. For weak electrolytes, $\alpha \ll 1$, so α can be neglected as compared to 1 i.e. $1 - \alpha \approx 1$.

$$\therefore K = C\alpha^2$$

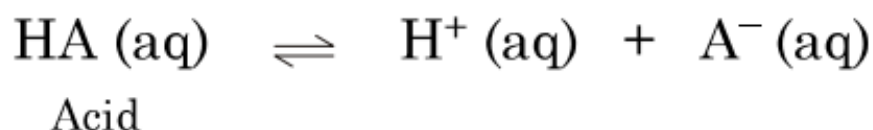
$$\Rightarrow \alpha = \sqrt{\frac{K}{C}}$$

Arrhenius Concept of Acids and Bases

Acid: An acid is a substance which contains hydrogen and which when dissolved into water gives hydrogen ions (H^+). The acid ionizes completely when dissolved in water, is called strong acid. An acid ionizes partially when dissolved in water, is called **weak acid**.

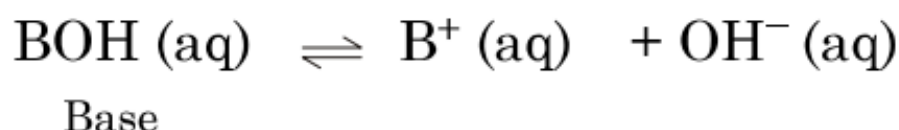


A **weak acid** solution contains unionized molecules in addition to ions. In general,

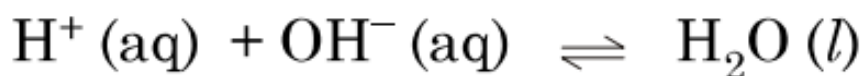


Base: A base is a substance which contains hydroxyl group and which when dissolved into water gives hydroxyl ions (OH^-).

A base that ionizes completely into its ions when dissolved in water, is called a **strong base**, and a base ionizes partially when dissolved in water is called a **weak base**. In general,



Neutralisation is the process in which hydrogen ions and hydroxyl ions combine to form unionized molecules of water.



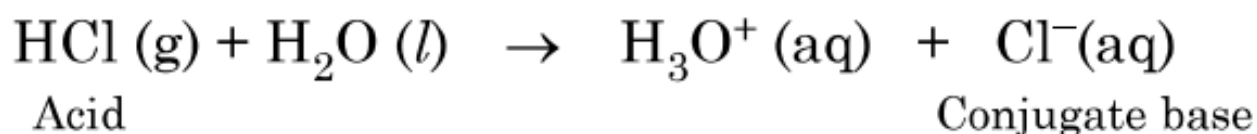
Bronsted-Lowry Concept of Acids and Bases

An **acid** is defined as a substance which has the tendency to give a proton (H^+).

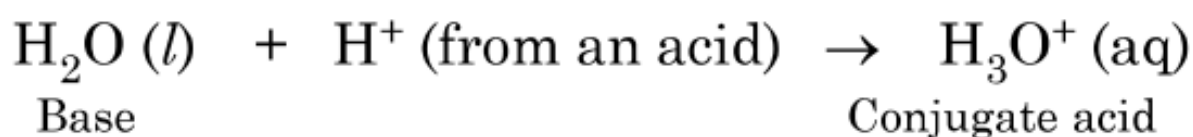


A **base** is defined as a substance which has a tendency to accept a proton (H^+).

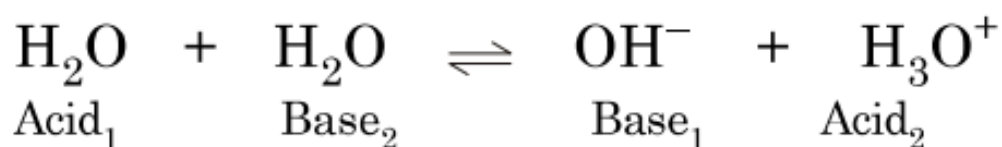
Conjugate base: The remainder part of an acid after donating a proton, is called conjugate base.



Conjugate acid: Base when accepts a proton released by an acid is called as conjugate acid.



Amphoterism: A particular can behave as an acid by donating a proton in one reaction and as a base in another by accepting a proton. Such a species is called as an amphoteric species. such as water.



Lewis Concept of Acids and Bases

Acid : An acid is a substance or an ion which is capable of accepting a pair of electrons and is called as Lewis acid.

Base : Base is a substance or an ion which is capable of donating an unshared pair of electrons and is called as Lewis base.



Types of Lewis Bases

- (i) *Neutral molecules* having at least one lone pair of electrons. e.g. NH_3 , R-NH_2 , $\text{R}_2\text{-NH}$, R-OH , H-OH etc.
- (ii) All negative ions like F^- , Cl^- , Br^- , OH^- , CN^- etc.

Types of Lewis Bases

- (i) Electron deficient compounds or molecules having a central atom with incomplete octet : e.g. BF_3 , AlCl_3 etc.
- (ii) Cations e.g. Ag^+ , Cu^{2+} , Fe^{3+} , etc.
- (iii) Molecules with multiple bonds between two atoms of different electronegativities e.g. CO_2 .
- (iv) Molecules whose central atoms has empty d-orbitals, e.g. SnCl_4 , SiF_4 , PF_5 , PCl_5 etc.

Some Important Results

1. $\text{pH} = -\log [\text{H}^+]$
2. $[\text{H}^+] = 10^{-\text{pH}}$
3. $\text{pOH} = -\log [\text{OH}^-]$
4. $\text{pK}_a = -\log K_a$
5. $\text{pK}_b = -\log K_b$

6. $p^{K_w} = -\log K_w$
7. P^H of acidic solution < 7
8. P^H of neutral solution $= 7$
9. P^H of basic solution > 7
10. $P^H + P^{OH} = p^{K_w} = 14$
11. K_w is called ionic product of water
 $= [H^+] [OH^-] = 10^{-14}$ at $25^\circ C$
 Thus in pure H_2O ; $[H^+] = [OH^-] = 10^{-7}$ molar
12. $K_h = \frac{K_w}{K_a}$, for hydrolysis of anion of weak acid

$K_h = \frac{K_w}{K_b}$, for hydrolysis of cation of weak base.

$K_h = \frac{K_w}{K_a \cdot K_b}$, for hydrolysis of weak acid-weak base salt.

where, K_h is hydrolysis constant, K_a is ionisation constant for an acid otherwise called acid dissociation constant and K_b is ionisation constant for a base otherwise called base dissociation constant.

13. **P^H of an acidic buffer solution and P^{OH} of an alkaline buffer solution.**

(a) Acidic Buffer : (Weak acid and its salt which is a strong electrolyte; e.g., CH₃COOH and CH₃COONa); in general, $H \rightleftharpoons HA^+ + A^-$

$$P^H = P^{K_a} + \log \frac{[A^-]}{[HA]} \quad (\text{Henderson's equation})$$

(b) Basic Buffer : (Weak base and its salt which is a strong electrolyte; e.g., NH₄OH and NH₄Cl) in general,

$$BOH \rightleftharpoons B^+ + OH^-, \quad P^{OH} = P^{K_b} + \log \frac{[B^-]}{[BOH]}$$