

### Factors affecting degree of dissociation or Ionisation of Electrolytes :-

1) Nature of electrolyte:- When ionizable parts of molecule of a substance are held more by covalent bonding than by electrovalent transfer of electrons, these are less prone to separate by ions. Such substances will be weak electrolytes.  $H_2S$ ,  $HCN$ ,  $Na_2CO_3$  are examples of this class of electrolytes. On the other hand salt like  $NaCl$ ,  $Ca(NO_3)_2$ , & bases like  $NaOH$ ,  $Ba(OH)_2$  in which transfer of electron seems to be more or less complete allow a very easy separation of ions under the dissolving influence of water & on this account belonging to class of strong electrolytes.

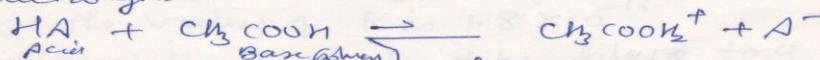
Acids like  $HCl$ ,  $HNO_3$ ,  $HClO_4$ , &  $H_2SO_4$ , though they are covalent molecules, acts as strong electrolytes in water on account of their strong tendencies to give up protons to water molecule forming  $H_3O^+$  ions & thus getting nearly completely ionised. In gaseous state or in solvents like benzene which are unable to accept protons, the ionisation of these acids is very low.

2) Nature of Solvent:- A solvent influences ionisation in following ways:

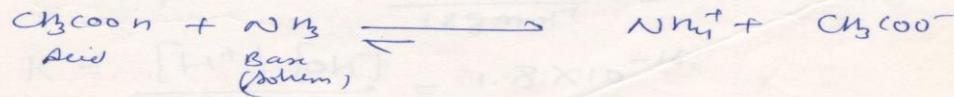
a) A solvent will tend to reduce the repulsion b/w ions by solvating them & thus more ionization can be expected in a solvent possessing greater solvating power for the involved ions.

b) Solvents of high dielectric constant reduce the force of attraction b/w charged particles & thus offer them a greater facility to remain apart. Water with its very high dielectric constant is a good medium for ionisation of substance.

c) Liquids like  $CH_3COOH$  or  $CH_3COONa$  also have protophilic (proton attacking) character, though much weaker than that of water. When strong acids like  $HCl$ ,  $HNO_3$ ,  $HClO_4$  or  $H_2SO_4$  are dissolved in such acids they are only partially ionised & behaves as weak electrolytes.



The strong protophilic nature of liquid ammonia greatly enhances the ionisation of acids like  $HCN$  &  $H_2SO_4$ ,  $CH_3COOH$  etc. as

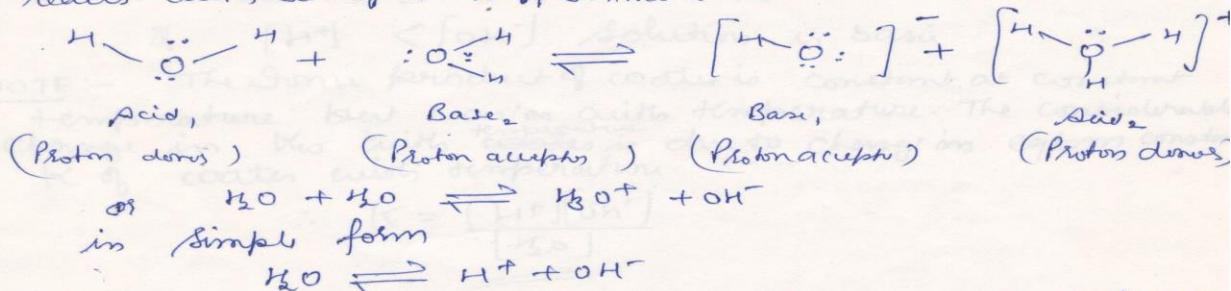


3) Conc. of solution:- Increasing the dilution of a solution increase degree of dissociation of electrolyte.

Temperature:- The degree of dissociation of an electrolyte increases with increasing the temperature.

5) Presence of other electrolyte :- Electrolytes with a common ion tend to reduce each others degree of dissociation but addition of electrolyte without a common ion may also change the degree of dissociation of original electrolyte.

Dissociation of water (Ionic Product of water):- The water is unique since it dissociates to form proton & hydroxyl ions.  
Water is an example of group of substances that are called amphotolyte or amphiprotic or amphoteric. An amphotolyte can donate as well accept a proton & hence can act as acid or base  
Since water behaves as an acid as well as base as well as base it reacts with itself or self ionizes as:



The Ionisation of water is a reversible process hence the law of chemical equilibrium can be applied to this eqn.

$$\therefore K_{\text{eq}} = \frac{[\text{H}^+] [\text{OH}^-]}{[\text{H}_2\text{O}]}$$

where  $K$  is Ionisation or dissociation constant of water  
at  $25^\circ\text{C}$  the value of  $K$  is  $1.8 \times 10^{-16}$

Since the dissociation of water takes place to a small extent. the conc. of undissociated water in dilute aqueous solution is nearly constant & equal to  $\frac{1000 \text{ g L}^{-1}}{18 \text{ g mol}^{-1}} = 55.5 \text{ mol L}^{-1}$

$$\therefore K = \frac{[\text{H}^+] [\text{OH}^-]}{55.5} = 1.8 \times 10^{-16}$$

Thus it is evident from above eqn that for dilute solution the product of conc of  $[\text{H}^+]$  &  $[\text{OH}^-]$  ions is ~~not~~ constant & is known as Ionic product of water which is generally

denoted by  $K_w$

$$\therefore K_w = [H^+][OH^-] = K \times 555$$

It should be noted that  $K_w$  is Ionic product of water & not the dissociation constant.

The value of  $K_w$  the Ionic product of water is determined to be  $1.0 \times 10^{-14}$  at  $25^\circ C$ .

It should be noted that

$$\therefore K_w = [H^+][OH^-] = 1.0 \times 10^{-14} \text{ mol}^2 \text{ L}^{-2}$$

It should be noted that often pure water dissociates, It gives equal conc. of  $H^+$  &  $OH^-$  ions. Thus in pure water

$$[H^+] = [OH^-] = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7} \text{ mol dm}^{-3}$$

Thus if  $[H^+] = [OH^-]$ , the solution is neutral

If  $[H^+] > [OH^-]$  solution is acidic

If  $[H^+] < [OH^-]$  solution is basic

NOTE:- The Ionic product of water is constant at constant temperature but varies with temperature. The considerable change in  $K_w$  with ~~temperature~~ is due to change in eqbm constant  $K$  of water with temperature

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

$$\text{Since } [H^+][OH^-] = 10^{-14}$$

taking -log on both sides

$$-\log[H^+] - \log[OH^-] = -\log 10^{-14}$$

$$pH + pOH = 14$$

Effect of temperature on pH :- Since pH scale has designed on the Ionic product  $K_w = [H^+][OH^-]$  of water & it has value  $10^{-14}$  at  $25^\circ C$ . On increasing the temperature the dissociation of water increases & the Ionic product of water will increase i.e. It will no longer remains  $10^{-14}$  at higher temperature & the value increased to higher temperature (say  $10^{-12}$ )

$$\text{Now } K_w = [H^+][OH^-] = 10^{-12} \quad [\text{higher temp}]$$

$$\therefore [H^+] = \sqrt{K_w} = \sqrt{10^{-12}} = 10^{-6} \text{ mol L}^{-1} \quad [\text{at higher temp}]$$

$$\text{But according to the definition of } pH = -\log[H^+] \\ \therefore pH \text{ at higher temp} = -\log(10^{-6}) = 6$$

As more & more  $H^+$  &  $OH^-$  will form on increasing temperature]

Thus at higher temperature

the solution will be acidic if  $\text{pH} < 6$

the solution will be basic if  $\text{pH} > 8$

& the solution will be neutral if  $\text{pH} = 6$

Hence we conclude that on increasing the temperature the pH of water does not change as the scale of pH get changed.

Hence water will remain neutral at any temperature as scale of pH will be different at different temperature.

$$\text{from } \text{P}_1 - 0.1 \times 0.1 = [\text{H}_3\text{O}] [\text{H}^+] = \omega_1$$

using  $\text{TB}$ , activities must ~~not~~  $\neq$  test before ~~at~~ below  $\text{TB}$   
~~water must be used up to the  $\text{TB}$  mark~~