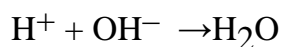


Chemical Equilibrium - 3

ACIDS-BASES: theories of acids & bases, K_W and P_H

1. Arrhenius theory

- i. According to this 'An acid ionises in aqueous solution producing hydrogen ions and A base ionises in aq solution producing hydroxyl ions'.
- ii. The degree of ionisation of an acid or a base is a measure of its strength.
- iii. Since strong acids and strong bases ionise to a greater extent in water, their aqueous solutions are good conductors.
- iv. According to Arrhenius theory neutralisation is the reaction between hydrogen ions and hydroxyl ions to form water



Limitations to Arrhenius theory

- i. Arrhenius Theory explains the behaviour of acids and bases in aqueous solutions only.
- ii. It fails to explain the behaviour of acids and bases in non-aqueous media.
It failed to explain the basic nature of NH_3 and acidic nature of CO_2 , SO_2 etc.

2. The number of replaceable hydrogen atoms present in one molecule of an acid is called its basicity or proticity.

E.g. For HCl , basicity is 1

For H_2SO_4 , basicity is 2

For H_3PO_4 , basicity is 3

3. The number of $-OH$ groups present in one molecule of a base is called its acidity.

E.g. For $NaOH$, KOH , NH_4OH etc acidity is 1

For $Mg(OH)_2$, $Ca(OH)_2$, $Ba(OH)_2$ etc acidity is 2

4. When a polybasic acid (or polyprotic acid) is partially neutralised, an acid salt is formed. An acid salt contains some replaceable hydrogen atoms, and have reaction with bases.

E.g. NaHCO_3 , NaHSO_4 , NaH_2PO_4 etc.

5. When a polybasic acid is completely neutralised, a normal salt is formed.

E.g. Na_2SO_4 , Na_3PO_4 etc.,

6. All monobasic acids form neutral salts only.

7. If the acidity of a base is n , it can form 'n' types of salts of which

Number of acidic salts = $n-1$;

Number of neutral salts = 1

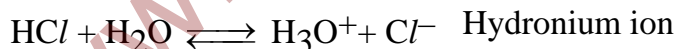
For example H_3PO_4 , basicity is 3. Hence it forms two acidic and one neutral salt.

8. Bronsted -Lowry Theory:

- According to this 'an acid is a proton donor and a base is a proton acceptor'.
- The reaction between an acid and a base is complementary. Proton transfer always takes place from acid to base. This proton transfer is called neutralisation.

Ex. When hydrogen chloride is dissolved in water, HCl donates proton and H_2O accepts proton. HCl is acid and H_2O is base.

The Bronsted-Lowry reaction is represented as:



- According to Lowry and Bronsted, neutralisation involves the transfer of a proton from the acid to the base resulting in the formation of a conjugate base and acid pair. A neutralisation reaction contains two conjugate acid – base pairs

Acid - Proton = Conjugate base

Base + Proton = Conjugate acid

If the acid is strong, its conjugate base is weak and vice versa.

A reaction most likely to proceed in the direction of formation of weak conjugate acid & bases

E.g. $\text{HCl} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{Cl}^-$ reaction favours in forward direction

- iv. Ions like HCO_3^- , HSO_4^- , H_2PO_4^- , etc., can lose and also gain protons. Hence they can behave as Bronsted acids as well as Bronsted bases and they are amphoteric or amphiprotic.
- v. Bronsted acids or bases are molecular, cationic or anionic.
- vi. Bronsted theory explains the behaviour of acids and bases in both aqueous and non aqueous solvents. It explains the behaviour of NH_3 as base

Limitations to Bronsted theory

- i. Bronsted theory failed to explain the acidic nature of electron deficient molecules like BCl_3 , AlCl_3 , BF_3 etc.
- ii. Proton donation and acceptance happens only in the presence of another substance.
9. In the case of hydracids of a family, the acidic strength increases with an increase in the atomic number of the element.

E.g.: in VIA group hydrides $\text{H}_2\text{Te} > \text{H}_2\text{Se} > \text{H}_2\text{S} > \text{H}_2\text{O}$

in VIIA group hydrides $\text{HI} > \text{HBr} > \text{HCl} \gg \text{HF}$

10. In the case of oxyacids of a family, the acidic strength decreases with an increase in the atomic weight of the central atom.

In VI group acidic strengths are in the order $\text{H}_2\text{SO}_4 > \text{H}_2\text{SeO}_4 > \text{H}_2\text{TeO}_4$

11. When the same element forms a number of oxyacids, with an increase in the oxidation number of the element, the acidic strength increases.

Eg: In the case of oxyacids of chlorine, the acidic strength is

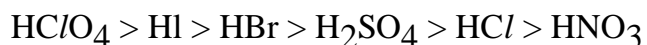
$\text{HClO}_4 > \text{HClO}_3 > \text{HClO}_2 > \text{HClO}$

12. Nature and strength of substances depend on the nature of the solvent involved.

Ex. Pure and dry HCl is not an acid. It does not turn blue litmus red. Similarly a solution of HCl in benzene is not an acid.

13. A weak acid behaves as a strong acid in the presence of a strong base and a weak base behaves as a strong base in strong acid.
14. Strength of all strong acids is equal when taken in their aqueous solution. It is known as levelling effect. To compare the relative strengths of strong acids, a weak proton acceptor like acetic acid is used as solvent.

The strengths of strong acids are compared in acetic acid, their strengths are in the order.



To compare the relative strengths of strong bases, a weak base like NH_3 is used as solvent.

15. Lewis Theory

a) According to 'A base is an electron pair donor or a nucleophile an acid is an electron pair acceptor or an electrophile' and neutralisation involves the formation of a coordinate covalent bond between an acid and a base.

b) Types of Lewis Bases

i. All anions like Cl^- , Br^- , I^- , NH_2^- , F^- , SCN^- , OH^- are Lewis bases

ii. Molecules with one (or) more lone pair of electrons on the central atom are Lewis bases

E.g. H_2O , NH_3 , $R-OH$, $R-NH_2$, ROR , R_2NH , R_3N , C_5H_5N , CO , NO

iii. Molecules with multiple bonds like, $CH\equiv CH$, $CH_2 = CH_2$ are Lewis bases.

c) Types of Lewis acids

i . Cations like Ag^+ , Co^{3+} , Fe^{2+} , Fe^{3+} , Cu^{2+} are Lewis acids

ii .Molecules whose central atom has an incomplete octet with an empty orbital like

BF_3 , BCl_3 , BBr_3 , AlCl_3 are Lewis acids

iii. Compounds in which the central atom has available d-orbital and may expand its octet

E.g.: SiF_4 , SnCl_4 , SF_4 , TeF_4 , FeCl_3 , SCl_4 , SnCl_2

iv. Molecules having multiple bonds between atoms of dissimilar electro negativities

E.g.: CO_2 , SO_2 , SO_3 , NO_2 , Cl_2O_7 , P_4O_{10}

v. Elements with electron sextet in valance shell also act as Lewis acids.

E.g.: O and S ,Species like SO_2 , SF_4 , SCl_4 , PCl_3 etc can act both as Lewis acid and Lewis base.

d) In complex compounds

i) All ligands are Lewis bases

ii) All central ions are Lewis acids

iii) All complex compounds are Lewis salts.

iv) Formation of complex compound is neutralisation.

Limitations to Lewis Theory

i. This theory failed to explain the relative strength of acids and bases.

ii. It failed to explain the acidic nature of protonic acids.

iii. It failed to explain the catalytic nature of proton

iv. Acid-base reactions are instantaneous but formation of dative bond is a slow process. All acid-base reactions do not involve dative bond formation

16. All Bronsted bases are Lewis bases.

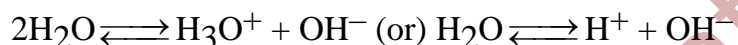
E.g. NH_3 , Cl^- , Br^- , OH^- , BF_4^- are both Bronsted bases and also Lewis bases, as they have lone pairs and accept H^+ ion.

17. All Lewis acids need not be Bronsted acids.

E.g. SO_2 , Cu^{2+} , Fe^{3+} etc are only Lewis acids but not Bronsted acids. As they have vacant orbitals to accept lone pair of electrons but do not contain H to donate H^+ ion.

18. Ionic Product of Water

i. Water undergoes self-ionisation and the following equilibrium exists



ii. In water or in any aqueous solution the product $[\text{H}^+][\text{OH}^-]$ is a constant at a given temperature and is known as the ionic product of water K_w .

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

At 298K, $K_w = 10^{-14} \text{ mole}^2/\text{lit}^2$.

iii. As temperature increases the value of K_w also increases.

iv. For water, dissociation constant $K_a = K_w / \text{molarity of water}$

[Molarity of water = $1000/18$ moles/lit]

v. With an increase in temperature the degree of ionisation of water increases then

a) K_w , $[\text{H}^+]$, $[\text{OH}^-]$ are increased

b), pH and pOH are decreased but water remains neutral.

vi. In pure water or in a neutral solution.

$$[\text{H}^+] = [\text{OH}^-] = 10^{-7} \text{ mole/lit at } 25^\circ\text{C}$$

For an acidic solution; $[H^+] > [OH^-]$ or $[H^+] > 10^{-7}$ mole/lit or $[OH^-] < 10^{-7}$ mole/lit at $25^\circ C$

For an alkaline solution; $[H^+] < [OH^-]$ or $[H^+] < 10^{-7}$ and $[OH^-] > 10^{-7}$ mole/lit $25^\circ C$

19. **pH scale:** pH scale is applicable to dilute aqueous solutions whose concentration is $10^{-14} N$ to $1 N$ at $25^\circ C$.

i. $pH = -\log [H^+] = \log 1/[H^+]$

ii. Similarly $pOH = -\log [OH^-] = \log 1/[OH^-]$

$$pK_a = -\log_{10}[K_a], pK_b = -\log_{10}[K_b] \text{ and } pK_w = -\log_{10}[K_w]$$

For an aqueous solution; $pH + pOH = pK_w = 14$ at $25^\circ C$

iii. For strong acids, $[H^+] = \text{Normality of acid}$

For strong bases $[OH^-] = \text{Normality of base}$

iv. When two strong acids are mixed, $[H^+] = \frac{N_1 V_1 + N_2 V_2}{(V_1 + V_2)}$

v. When two strong bases are mixed, $[OH^-] = \frac{N_1 V_1 + N_2 V_2}{(V_1 + V_2)}$

vi. When a strong acid and a strong base is mixed

a. If $N_a V_a = N_b V_b$; solution is neutral, $pH = 7$

b. If $N_a V_a > N_b V_b$; solution is acidic, $pH < 7$,

$$[H^+] = \frac{N_a V_a - N_b V_b}{(V_a + V_b)(\text{or}) V_f}$$

c. If $N_a V_a < N_b V_b$; solution is basic, $pH > 7$,

$$[OH^-] = \frac{N_b V_b - N_a V_a}{(V_a + V_b)(\text{or}) V_f}$$

vii. When a strong acid is diluted 'n' times, the pH increases by $\log n$ units but it cannot

increase beyond 7.

E.g. If HCl solution of $P^H=3$ is diluted by 100times, the P^H of resulting solution is 5.

$$[\text{As } \log 100 = 2, P^H = 3 + 2 = 5]$$

viii. When a strong base is diluted n times, the P^H decreases by $\log n$ units but it cannot decrease beyond 7.

20. In the case of a weak acid or weak base.

$$[\text{H}^+] = C \alpha = \sqrt{K_a \cdot C}, \quad P^H = -\frac{1}{2}[\log K_a + \log C]$$

$$[\text{OH}^-] = C\alpha = \sqrt{K_b \cdot C}, \quad P^{\text{OH}} = -\frac{1}{2}\log K_b - \frac{1}{2}\log C \quad \text{and } P^H = 14 - P^{\text{OH}}$$

21. As ionic equilibrium is set up only in the case of weak electrolytes, Ostwald's dilution law is applicable only to weak electrolytes.

22. According to Ostwald's dilution law, for a weak electrolyte, the dissociation constant

is given by, $K_a = \frac{C\alpha^2}{1-\alpha}$ If α is very small, Then $K_a = C \alpha^2$

Where 'C' is the concentration of the electrolyte. α Is The Degree of Dissociation

The fraction of the total amount of an electrolyte which dissociates into ions is called the degree of dissociation (α)

$$\text{i.e. } \alpha = \frac{\text{No. of molecules dissociated}}{\text{No. of molecules present in the solution}}$$

23. For weak acids and weak bases α is very small while for strong acids and strong bases α is nearly equal to unity.

24. Ostwald theory fails in the case of strong electrolytes.

25. K_a is the measure of the strength of the acid. Larger the value of K_a , the stronger is the acid.

Lower the value of P^{K_a} , higher is the strength of the acid.

26. If the ionisation constants of two weak acids are K_{a1} and K_{a2} , then

$$\frac{\text{Strength of acid}_1}{\text{Strength of acid}_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$$

27. Higher the value of K_b , lower is the value of P^{K_b} , then higher is the strength of the base.
28. For a conjugate acid base pair, K_a and K_b are related as $K_a \cdot K_b = K_w$
29. P^{K_a} , P^{K_b} and P^{K_w} are related as, $P^{K_a} + P^{K_b} = P^{K_w}$
30. In case of weak electrolytes, the extent of ionisation depends up on the concentration of the solution and temperature. As the temperature increases or as the concentration of the solution decreases or as the dilution increases then the degree of dissociation (α) increases.