Ch-7 (Part: 2) Acids, Bases, pH and Buffer

1. Ionic Equilibrium: The equilibrium established between the unionized molecules and the ions in the solution of weak electrolytes is called ionic equilibrium. e.g.

$$CH3\ COOH \Leftrightarrow CH3COO^{-} + H^{+}$$

2. Electrolytes: Chemical substances which can conduct electricity in their aqueous state or in molten state are called electrolytes. The conduction of current through electrolyte is due to the movement of ions.

Strong Electrolytes: Electrolytes which dissociate almost completely into constituent ions in aqueous solution are known as strong electrolytes. e.g. all salts (except $HgCl_2$, $CdBr_2$), mineral acids like HCl, H2SO$_4$, HNO_3 etc) and bases like NaOH, KOH etc.

Weak Electrolytes: Electrolytes which dissociate to a lesser extent in aqueous solution are called weak electrolyte. All organic acids (except sulphonic acids) and bases like NH_3, NH_4OH, amines etc.

3. Degree of Ionisation or Degree of Dissociation (α): It is the fraction of the total number of molecules which ionise (dissociate) into constituent ions.

α = (number of molecules ionised or dissociated/total number of molecules taken)

For strong electrolytes, α = 1

For weak electrolytes**,** α < 1

Values of the degree of dissociation (ex) depends upon the following factors-

1) Nature of solute 2) Nature of solvent

3) Concentration 4) Temperature

4. Arrhenius Concept of Acids and Bases: According to Arrhenius, an acid is a compound that releases H^+ ions or hydronium ions (H_3O^+) in water and a base is a compound that releases OH^- ions in water. For example, HCl is an Arrhenius acid and NaOH is an Arrhenius base.

$$HCl\ (aq) \rightarrow H^{+}\ (aq) + Cl^{-}\ (aq)$$

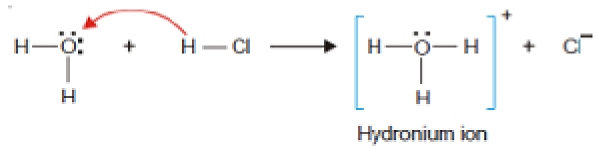
$$HCl\ (aq) + H_2O\ (l) \Leftrightarrow H_3O^{+}\ (aq) + Cl^{-}\ (aq)$$

$$NaOH\ (aq) \rightarrow OH^{-}\ (aq) + Na^{+}\ (aq)$$

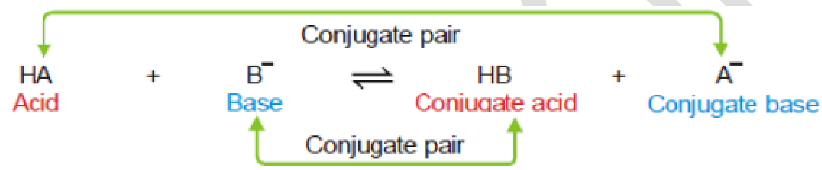
Drawback of Arrhenius Concept: Arrhenius theory fails to explain the acidic and basic behaviour in non-aqueous solutions. It cannot explain the acidic character of $A1Cl_3$, BF_3 and basic character of NH_3, PH_3, etc.

5. Bronsted-Lowry Concept of Acids and Bases: Acid is a chemical substance that can donate a proton (H+) to some other substance and a base is a chemical substance that can accept a proton from other substance. Thus, an acid is a proton donor (protongenic) and a base is proton acceptor (protophilic).

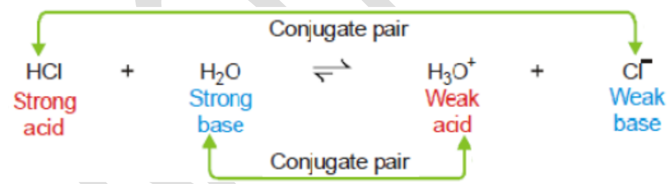
For example Reaction of HCl gas with water molecules, HCl donates a proton to a water molecule to produce hydronium ion so according to this concept HCl gas is a Bronsted acid and water that accepts a proton is a Bronsted base.



Conjugate Acid-Base pairs: In an acid-base reaction the acid (HA) gives up its proton (H^+) and produces a new base (A^-). The new base that is related to the original acid is called a conjugate (meaning related) base. Similarly the original base (B^-) after accepting a proton (H^+) gives a new acid (HB) which is called a conjugate acid.
The acid (HA) and the conjugate base (A^-) that are related to each other by donating and accepting a single proton, are said to constitute a conjugate Acid-Base pair.



Strength of Bronsted acids and bases: Strong acid has weak conjugate base and weak acid has strong conjugate base. For example



Amphoteric or amphiprotic or ampholytes substance: Those substance which acts as an acid as well as a base, e.g. water acts as base with HCl and an acid with NH_3.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \longrightarrow \underset{\text{acid}}{H_3O^+} + \underset{\text{base}}{Cl^-}$$

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \longrightarrow \underset{\text{acid}}{NH_4^+} + \underset{\text{base}}{OH^-}$$

Some other examples of amphoteric substances are as follows-

$$H_2S \xleftarrow{+H^+} HS^- \xrightarrow{-H^+} S^{2-}$$

$$H_2CO_3 \xleftarrow{+H^+} HCO_3^- \xrightarrow{-H^+} CO_3^{2-}$$

$$HPO_4^- \xleftarrow{+H^+} HPO_4^{2-} \xrightarrow{-H^+} PO_4^{3-}$$

6. Lewis Concept of Acids and Bases:

Lewis acid is a chemical substance which can accept a pair of electrons, e.g.

- Molecules with incomplete octet of central atom like $AlCl_3$, $BeCl_2$, $MgCl_2$, etc.
- Simple cations like Ag^+, Na^+ etc.
- Molecules in which the central atom has vacant d-orbital, e.g.,SF_4, $SnC1_4$ PF_3 etc.

Lewis base is a chemical substance which can donate a pair of electrons. e.g.

- Neutral molecules containing lone pairs like NH_3, RNH_2, ROH etc.
- Negatively charged species like CN, Cl, OH, etc.
- In coordination complexes, the ligands act as Lewis base.

Limitations of Lewis Concept:

- It does not explain the behaviour of protonic acids such as HCl, H_2SO_4, HNO_3 etc.
- It does not predict the magnitude of relative strength of acids and bases.
- All Bronsted-Lowry's acids are Lewis acids while acids need not be Bronsted-Lowry's acids.

7. The Ionization Constant of Water (Kw) and Its Ionic product: The Ionic constant of Water, Kw, is the equilibrium constant for the reaction in which water undergoes an acid-base reaction with itself. That is, water is behaving simultaneously as both an acid and a base. The following equation describes the reaction of water with itself called autoprotolysis.

$$\underset{\text{acid}}{H_2O\ (l)} + \underset{\text{base}}{H_2O\ (l)} \Longleftrightarrow \underset{\text{conjugate acid}}{H_3O^+(aq)} + \underset{\text{conjugate base}}{OH^-(aq)}$$

The equilibrium constant for this reaction can be written as:

$Kc = [H_3O^+]\ [OH^-]\ /\ [H_2O]\ [H_2O]$

While in pure liquid water, $[H_2O]$ is a constant value, then

$Kc\ [H_2O]\ [H_2O] = [H_3O^+]\ [OH^-]$

Since the term Kc $[H_2O]$ $[H_2O]$ is a constant, let it be symbolized by Kw, so:

$Kw = [H_3O^+]\ [OH^-]$

This constant, Kw, is called the water auto protolysis constant or water auto ionization constant.

The value of Kw is determined by experiment and it gets 1.011×10^{-14} at 25 °C. Generally, a value of 1.00 x 10¯14 is used. The value of Kw increases with increase in temperature.

Hence, both $[H_3O^+]$ and $[OH^-]$ are equal to 1.00×10^{-7} M in pure water. We can distinguish acidic, neutral and basic aqueous solution by the relative values of the H_3O^+ and OH^- concentrations, like as

Acidic: $[H_3O^+] > [OH^-]$

Neutral: $[H_3O^+] = [OH^-]$

Basic: $[H_3O^+] < [OH^-]$

8. The pH Scale: pH is defined as the negative logarithm of hydrogen ion concentration.

$$pH = -\log [H^+] \quad \text{or} \quad [H^+] = 10^{-pH}$$

Similarly, negative logarithm of hydroxyl ion concentration is pOH.

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

We know,

$$Kw = [H^+][OH^-] = 1 \times 10^{-14} \text{ (at 298K)}$$

$$-\log Kw = -\log [H^+] - \log [OH^-] = 14$$

$$pKw = pH + pOH = 14 \text{ (at 298 K)}$$

pH of solution is accurately measured by pH meter or emf method or roughly by pH paper or indicator paper. The Ph scale at 298K can be show as follows-

H^+	1	10^{-1}	10^{-2}	10^{-3}	10^{-4}	10^{-5}	10^{-6}	10^{-7}	10^{-8}	10^{-9}	10^{-10}	10^{-11}	10^{-12}	10^{-13}	10^{-14}
pH	0	1	2	3	4	5	6	7	8	9	10	11	12	13	14

← Acidic character increases — Neutral — Basic character increases →

9. Ionization or Dissociation Constant of Weak Acid: Let us consider the dissociation of weak acid (HX) as

$$HX (aq) \Leftrightarrow H^+ (aq) + X^- (aq)$$

In a weak acid, there is partial ionization of HX in to their ions. The equilibrium constant for acid ionization is called acid ionization constant and it is represented by Ka. It can be expressed in terms of molar concentration as following-

$$Ka = \frac{[H^+][X^-]}{[HX]}$$

If 'c' is initial concentration of undissociated acid and 'α' is degree of ionization of acid i.e. the extent to which the acid ionizes. The equilibrium can be expressed by

	$HX (aq)$	$\Leftrightarrow H^+ (aq)$	$+ X^- (aq)$
Initial Concentration	c	0	0
Change in Concentration	$-c\alpha$	$+c\alpha$	$+c\alpha$
Equilibrium Concentration	$c - c\alpha$	$c\alpha$	$c\alpha$

Using the these notation we can be written the equilibrium constant for weak acid as follows,

$$Ka = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

The pH scale for the hydrogen ion concentration can be extended for weak acid then we get

$$pKa = -\log [Ka]$$

10. Ionization or Dissociation Constant of Weak Base: Let us consider the dissociation of weak base (MOH) as

$$MOH\ (aq) \Leftrightarrow M^+\ (aq) + OH^-\ (aq)$$

In a weak base, there is partial ionization of MOH in to their ions. The equilibrium constant for base ionization is called base ionization constant and it is represented by K_b. It can be expressed in terms of molar concentration as following-

$$K_b = \frac{[M^+]\,[OH^-]}{[MOH]}$$

If 'c' is initial concentration of undissociated base and 'α' is degree of ionization of base i.e. the extent to which the base ionizes. The equilibrium can be expressed by

	$MOH\ (aq)$ $\Leftrightarrow$	$M^+\ (aq)$ +	$OH^-\ (aq)$
Initial Concentration	c	0	0
Change in Concentration	$-\ c\alpha$	$+\ c\alpha$	$+c\alpha$
Equilibrium Concentration	$c - c\alpha$	$c\alpha$	$c\alpha$

Using the these notation we can be written the equilibrium constant for weak base as follows,

$$K_b = \frac{c^2\alpha^2}{c\,(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

The pH scale for the hydrogen ion concentration can be extended for weak base then we get

$$pK_b = -\log\,[K_b]$$

11. Relation b/w Ka and Kb:

$$K_w = K_a \times K_b = 10^{-14}\ \text{(at 298K)}$$

$$pk_w = pk_a + pk_b = 14\ \text{(at 298K)}$$

12. Dissociation constant for polyprotic acids and bases: For a tribasic acid,

$$H_3PO_4 \overset{K_{a_1}}{\Leftrightarrow} H^+ + H_2PO_4^-$$

$$H_2PO_4^- \overset{K_{a_2}}{\Leftrightarrow} H^+ + HPO_4^{-2}$$

$$HPO_4^{-2} \overset{K_{a_3}}{\Leftrightarrow} H^+ + PO_4^{-3}$$

The overall dissociation constant (K_a) is given as

$$K_a = K_{a1} + K_{a2} + K_{a3}$$

Where, K_{a1}, K_{a2} and K_{a3} are the first, second and third ionization constant for respectively acid. Similarly for dibasic acid like H_2SO_4, have two ionization constant. Higher order ionization constant value are smaller than lower order due to more difficult to remove a proton from a negative ion due to electrostatic forces like as $K_{a1} > K_{a2} > K_{a3}$

13. Factors affecting acid strength:

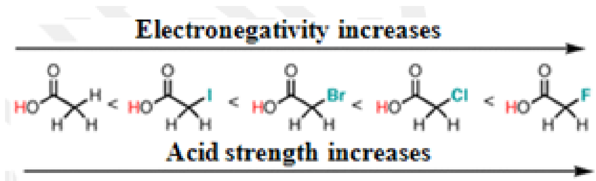
1) Charge: Acidity increases with increases positive charge on an atom–

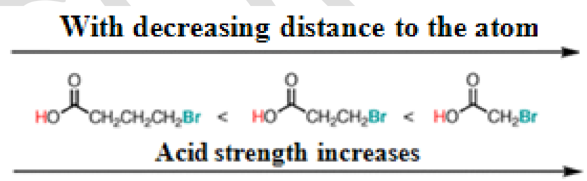
$$OH^- < H_2O < H_3O^+$$
$$\longrightarrow$$
$$NH_2^- < NH_3 < NH_4^+$$

2) The Role of the Atom:

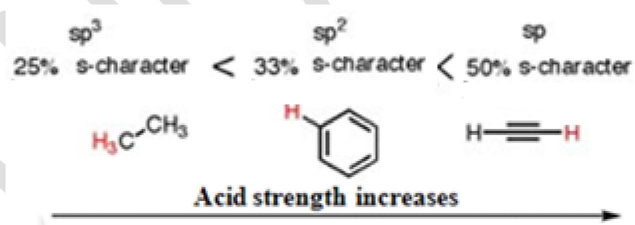
- Across the periodic table, acidity increases with increasing the electronegativity like $CH_4 < NH_3 < H_2O < HF$
- But down the periodic table acidity increases with increases size like $HF < HCl < HBr < HI$
- So similarly H_2S is stronger acid than H_2O, it can show as $H_2O < H_2S$

3) Electronegativity and Inductive effects: Electronegative atoms can draw negative charge toward themselves, which can lead to considerable stabilization of conjugate bases. Electron withdrawing group can increase acidity of a nearby atom, which increases with increases electronegativity and increase with decreasing distance to the atom. For examples:

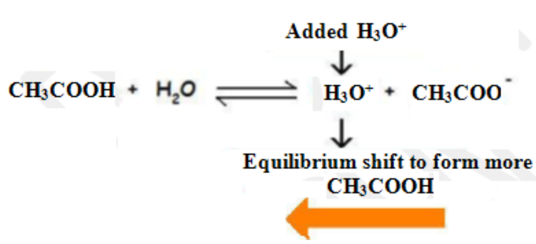




4) Orbitals: The more s character in the orbital, the closer the electrons will be to the nucleus, and the lower in energy (= stable) so the higher the s- character of a bond to hydrogen, the more acidic it will be like as



14. Common ion effect: The common ion effect suppresses the ionization of a weak acid or weak base by adding more of an ion that is a product of this equilibrium. For example, the common ion effect of H_3O^+ on the ionization of acetic acid.



When a strong acid supply the H_3O^+ the equilibrium shift to form more acetic acid so we can say that common ion effect is a phenomenon based on the Le Chatelier's principal.

15. Hydrolysis of salts and the pH of their solutions: Salt is a compound formed by neutralization reaction between an acid and a base. They generally ionize in water furnishing cations and anions. The cations or anions formed during ionization of salts either exist as hydrated ions in aqueous solutions or interact with water to regenerate the acids and bases. The process of interaction between cations or anions of salts and water is known as hydrolysis of salts. On the basis of hydrolysis, salts are divided into three categories:
Acidic salts, Basic salts and Neutral salts
Let us discuss hydrolysis of salts of the following types:
1) Salts of strong acid and strong base (Neutral Salt): Salts formed by the neutralization of strong acid and strong base are neutral in nature as the bonds in the salt solution will not break apart. They generally get hydrated but do not hydrolyse. Therefore, such salts are generally known as neutral salts. For example: NaCl
2) Salts of weak acid and strong base (Basic Salts): Salts formed by the neutralization of weak acid and strong base are basic in nature. For example: CH_3COONa

$$CH_3COONa\ (aq) \rightarrow CH_3COO^-\ (aq) + Na^+\ (aq)$$

Acetate ion formed undergoes hydrolysis to form acetic acid and OH^- ions.

$$CH_3COO^-\ (aq) + H_2O \leftrightharpoons CH_3COOH\ (aq) + OH^-\ (aq)$$

As we know acetic acid is a weak acid, it remains unionized in the soln. This results in an increase in concentration of OH^- ions which makes the soln alkaline. pH of the soln is greater than 7.
3) Salts of strong acid and weak base (Acidic Salts): Salts formed by the neutralization of strong acid and weak base are acidic in nature. For example: NH_4Cl

$$NH_4Cl\ (aq) \rightarrow Cl^-\ (aq) + NH_4^+\ (aq)$$

Ammonium ion formed undergoes hydrolysis to form ammonium hydroxide and H^+ ions.

$$NH_4^+\ (aq) + H2O \leftrightharpoons NH_4OH\ (aq) + H^+\ (aq)$$

As we know ammonium hydroxide is a weak base, it remains unionized in the solution. This results in an increase in concentration of H^+ ions which makes the solution acidic. pH of such solutions is less than7.
4) Salts of weak acid and weak base: Salts formed by the neutralization of weak acid and weak base are acidic, basic or neutral depending on the nature of acids and bases involved. For example: CH3COONH4. General mechanism for the hydrolysis of ions formed from these salts:

$$CH_3COO^- + NH_4^+ + H2O \leftrightharpoons CH_3COOH + NH_4OH$$

Degree of hydrolysis in such cases is independent of concentration of solution and pH of such solutions is given by:

$$pH = 7 + 1/2\ (pK_a - pK_b)$$

Hence, we can say that the pH of a solution can be less than 7 or greater than 7 depending on the values of pKa and pKb.

16. Buffer Solution: A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base. In other words, a buffer solution resists (or buffers) a change in its pH. That is, we can add a small amount of an acid or base to a buffer solution and the pH will change very little.

Types of Buffer Solution: Two common types of buffer solutions are:

1) Acidic Buffers: A mixture of weak acid and its salt with a strong base. e.g, CH_3COOH + CH_3COONa. Buffer system present in blood is H_2CO_3 + $NaHCO_3$.

2) Basic Buffers: A mixture of weak base and its salt with a strong acid. e.g., NH_4OH + NH_4Cl.

How to buffer solution work: It is explain by example of a common buffer system consisting of solution of acetic acid and sodium acetate (CH_3COOH/CH_3COONa).

$$CH_3COOH \rightarrow CH_3COO^- (aq) + H^+ (aq)$$
$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$

Since the salt is completely ionized, it provides the common ions CH_3COO^- in excess. The common ion effect suppresses the ionization of acetic acid. This reduces the concentration of H^+ ions which means that pH of the solution is raised. The buffer solution maintains fairly constant pH and the changes in pH could be described as marginal.

17. Solubility Equilibria of sparingly soluble salts: The solubility of ionic solids in water differs to a great extent. On the basis of solubility, we can classify the salts into three main categories:

1) Soluble: The salts which are soluble and there solubility > 0.1 M

2) Slightly soluble: The salts which are slightly soluble and there solubility is b/w 0.01M & 0.1M

3) Sparingly soluble: The salts which are sparingly soluble and there solubility < 0.01 M

Let us consider the equilibrium between the sparingly soluble salts and its saturated solutions. There are many compounds such as lead chloride ($PbCl_2$), silver chloride (AgCl) etc. which are very slightly soluble in water. These substances are called sparingly soluble salts.

18. Solubility product constant: When sparingly soluble salts are dissolved in water, equilibrium is established between the undissolved solid salt and ions of the dissolved salt. For example: For a sparingly soluble compound like AgCl, the following equilibrium occurs between the undissolved solid salts and the silver and chloride ions in the saturated solution:

$$AgCl (s) \rightleftharpoons Ag^+ (aq) + Cl^- (aq)$$

Applying the law of chemical equilibrium, we will get:

$$K = [Ag^+] [Cl^-] / [AgCl]$$

$$K \times [AgCl] = [Ag^+] [Cl^-]$$

The concentration of the pure solid substance remains constant. Therefore, the concentration of solid AgCl in the solid state i.e. [AgCl] is constant at a particular temperature, so

$$K \times \text{constant} = K_{sp} = [Ag^+][Cl^-]$$

Where Ksp is known as solubility product constant.

Generally, if the sparingly soluble salt, Ax By is in equilibrium with saturated solution of its ions, then

$$A_x B_y = x A^{y+} + y B^{x-}$$

Where A^{y+} and B^{x-} denote the positive and negative ions respectively and x and y represent the number of these ions in the formula of the electrolyte.

The solubility product expression is:

$$K_{sp} = [A^{y+}]^x [B^{x-}]^y$$

Hence, the solubility product constant of a salt at a given temperature is equal to the product of the concentrations of its ions in the saturated solution, with each concentration term raised to the power to the number of ions produced on dissociation of one mole of the substance or in other words Product of the molar concentrations of the ions in a saturated solution, each concentration term raised to the power equal to the no. of ions produced.

Application of Solubility Product Constant:

1) The concept Product of Ksp helps in predicting the formation of precipitate. In general if

- Ionic product < Ksp, no precipitate (ppt) is formed.
- Ionic product > Ksp, precipitate (ppt) is formed.

2) In predicting the solubility of a sparingly soluble salt

$$A_x B_y = x A^{y+} + y B^{x-}$$
$$\quad\quad\quad xS \quad\quad yS$$

$$K_{sp} = (xS)^x (yS)^y$$

$$K_{sp} = x^x y^y S^{x+y}$$

knowing the values of Ksp, x and y, the solubility (S) of the salt can be Computed.

For salt of type AB: $Ksp = S^2$

For salt of type AB_2: $Ksp = 4S^3$

For salt of type AB_3: $Ksp = 27S^4$

Important Formulas

1) $pH = -\log[H^+]$ or $[H^+] = 10^{-pH}$ or $[H^+] = \text{antilog}(-pH)$

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

3) $Kw = [H^+][OH^-] = 10^{-14}$ (at 298K)

4) $pKw = pH + pOH = 14$ (at 298 K)

5)

	$HX (aq) \Leftrightarrow H^+ (aq) + X^- (aq)$		
Initial Concentration	c	0	0
Change in Concentration	$-c\alpha$	$+c\alpha$	$+c\alpha$
Equilibrium Concentration	$c - c\alpha$	$c\alpha$	$c\alpha$

$$Ka = \frac{c^2\alpha^2}{c(1-\alpha)} = \frac{c\alpha^2}{1-\alpha}$$

'c' is initial concentration of undissociated acid or base and 'α' is degree of ionization

6) $pKa = -\log[Ka]$

$pK_b = -\log[K_b]$

7) $K_w = K_a \times K_b = 10^{-14}$ (at 298K)

8) $pk_w = pk_a + pk_b = 14$ (at 298K)

9) $\% \text{Dissociation} = \frac{[HA]_{\text{dissociated}}}{[HA]_{\text{initial}}}$

10) $pH = 7 + 1/2\,(pK_a - pK_b)$

11) Ksp (Solubility product constant):

$$A_x B_y = x A^{y+} + y B^{x-}$$
$$\quad xS \qquad yS$$
$$K_{sp} = (xS)^x (yS)^y$$

Knowing the values of Ksp, the solubility (S) of the salt can be calculated.

For salt of type AB: $Ksp = S^2$

For salt of type AB_2: $Ksp = 4S^3$

For salt of type AB_3: $Ksp = 27S^4$