By- SHAILENDRA SHUKLA SIR

Common Ion Effect

"When a strong electrolyte containing common ion is added to the solution of a weak electrolyte, the degree of dissociation of weak electrolyte gets suppressed. This effect is called common ion effect."

For example, when aqueous solution of CH_3COONa (strong electrolyte) is added to the aqueous solution of CH_3COOH (weak electrolyte), the degree of dissociation of CH_3COOH gets decreased due to common ion effect.

$$\underset{\text{Weak electrolyte}}{CH_3COOH\ (aq)} \rightleftharpoons \boxed{CH_3COO^-\ (aq)} + H^+\ (aq)$$

$$\underset{\text{Strong electrolyte}}{CH_3COONa\ (aq)} \rightleftharpoons \boxed{CH_3COO^-\ (aq)} + Na^+\ (aq)$$

Common ion

Here, CH_3COOH being a weak electrolyte remains very feebly ionised in its aqueous solution at equilibrium. When aqueous solution of CH_3COONa is added to this solution, the concentration of CH_3COO^- ions gets increased at the equilibrium of CH_3COOH. Hence, following Le- Chatelier's principle, the equilibrium shifts in backward direction i.e. CH_3COO^- ions combine with H^+ ions to form un-dissociated CH_3COOH molecules. Thus, degree of dissociation of CH_3COOH gets decreased.

Similarly, when aqueous solution of strong electrolyte NH_4Cl is added to the aqueous solution of weak electrolyte NH_4OH, the degree of dissociation of NH_4OH gets decreased due to common ion effect.

$$\underset{\text{Weak electrolyte}}{NH_4OH\ (aq)} \rightleftharpoons \boxed{NH_4^+\ (aq)} + OH^-\ (aq)$$

$$\underset{\text{Strong electrolyte}}{NH_4Cl\ (aq)} \rightleftharpoons \boxed{NH_4^+\ (aq)} + Cl^-\ (aq)$$

Common ion

Buffer solutions

"Such solutions whose acidity and alkalinity remains reserved and therefore, their pH value does not change on adding small amount of any strong acid or base, are called buffer solutions."

Buffer solutions are of following two types-

(1)Acidic buffer solutions- These are the equimolar mixture of a weak acid and its salt with a strong base. For example,

(i) CH_3COOH + CH_3COONa

(ii) H_2CO_3 + $NaHCO_3$ (Buffer solution found in blood)

CHEMISTRYTOPPERSCOMPETITION.COM

(iii) Boric acid + Borax
(iv) Citric acid + Sodium citrate

(2)Basic Buffer Solutions- These are the equimolar mixture of a weak base and its salt with a strong acid. For example,
(i) $NH_4OH + NH_4Cl$
(ii) $NH_4OH + NH_4NO_3$

Buffer action of Buffer solutions- The mechanism by which a buffer solution resists its pH change on addition of a strong acid or a strong base is called buffer action of the buffer solution.

Buffer action of an acidic buffer solution can be explained by talking the example of the buffer solution of acetic acid and sodium acetate.

Here, CH_3COOH being a weak electrolyte, is very feebly dissociated in its aqueous solution. When aqueous solution of CH_3COONa (strong electrolyte) is added, its degree of dissociation gets decreased further due to common ion effect.

$$\underset{\text{Weak electrolyte}}{CH_3COOH\ (aq)} \rightleftharpoons \boxed{CH_3COO^-\ (aq)} + H^+\ (aq)$$

$$\underset{\text{Strong electrolyte}}{CH_3COONa\ (aq)} \rightleftharpoons \boxed{CH_3COO^-\ (aq)} + Na^+\ (aq)$$

Common ion

Now, this mixture behaves like buffer solution. When small amount of any strong acid such as HCl is added to this solution, the H^+ ions furnished by HCl get combined with CH_3COO^- ions of solution to form almost un-dissociated CH_3COOH molecules.

$$HCl\ (aq) \rightleftharpoons H^+\ (aq) + Cl^-\ (aq)$$

$$\underset{\text{(Buffer solution)}}{H^+\ (aq) + CH_3COO^-\ (aq)} \rightleftharpoons \underset{\text{(Almost un-dissociated)}}{CH_3COOH\ (aq)}$$

Thus, H^+ ion concentration in solution remains almost unchanged and therefore, the p^H value of the solution remains almost unchanged.

On the other hand, if small amount of a strong base such as NaOH is added to this solution, the OH^- ions furnished by NaOH get combined with H^+ ions of solution to form almost un-dissociated H_2O molecules.

$$NaOH\ (aq) \rightleftharpoons Na^+\ (aq) + OH^-\ (aq)$$

$$\underset{\text{(Buffer solution)}}{OH^-\ (aq) + H^+\ (aq)} \rightleftharpoons \underset{\text{(Almost un-dissociated)}}{H_2O\ (l)}$$

CHEMISTRYFORCOMPETITION.COM

Here, decrease in H^+ ion concentration of the solution is compensated by more dissociation of CH_3COOH. Thus, H^+ ion concentration in solution remains unchanged and therefore, the p^H value of the solution remains unchanged.

Buffer action of Basic Buffer solutions- Buffer action of a basic buffer solution can be explained by talking the example of the buffer solution of NH_4OH and NH_4Cl.

Here, NH_4OH being a weak electrolyte, is very feebly dissociated in its aqueous solution. When aqueous solution of NH_4Cl (strong electrolyte) is added, its degree of dissociation gets decreased further due to common ion effect.

$$\underset{\text{Weak electrolyte}}{NH_4OH\ (aq)} \rightleftharpoons \boxed{NH_4^+\ (aq)} + OH^-\ (aq)$$

$$\underset{\text{Strong electrolyte}}{NH_4Cl\ (aq)} \rightleftharpoons \boxed{NH_4^+\ (aq)} + Cl^-\ (aq)$$

Common ion

Now, this mixture behaves like buffer solution. When small amount of a strong acid such as HCl is added to this solution, the H^+ ions furnished by HCl get combined with OH^- ions of the buffer solution to form almost un-dissociated H_2O molecules.

$$HCl\ (aq) \rightleftharpoons H^+\ (aq) + Cl^-\ (aq)$$

$$\underset{\text{(Buffer solution)}}{H^+\ (aq) + OH^-\ (aq)} \rightleftharpoons \underset{\text{(Almost un-dissociated)}}{H_2O\ (l)}$$

Here, decrease in OH^- ion concentration of the solution is compensated by more dissociation of NH_4OH. Thus, OH^- ion concentration in solution remains unchanged and therefore, the p^H value of the solution remains unchanged.

On the other hand, if small amount of a strong base such as NaOH is added to this solution, the OH^- ions furnished by NaOH get combined with NH_4^+ ions of solution to form almost un-dissociated NH_4OH molecules.

$$NaOH\ (aq) \rightleftharpoons Na^+\ (aq) + OH^-\ (aq)$$

$$OH^-\ (aq) + NH_4^+\ (aq) \rightleftharpoons H_2O\ (l)$$

Thus, OH^- ion concentration in solution remains almost unchanged and therefore, the p^H value of the solution remains almost unchanged.

CHEMISTRYFORCOMPETITION.COM

Salt Hydrolysis-

"The reactions in which a salt reacts with water to produce acidity or alkalinity is called salt hydrolysis."

For example, due to salt hydrolysis, the aqueous solution of NH_4Cl is acidic in nature.

$$H_2O\ (l) \rightleftharpoons H^+ + OH^-$$

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

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$HCl + NH_4OH$$

(Almost completely dissociated) (Very feebly dissociated)

Here, due to more dissociation of HCl, the aqueous solution of NH_4Cl is acidic in nature.

(a)Salt Hydrolysis of the salts of strong acids and weak bases-

Aqueous solutions of the salts of strong acids and weak bases (e.g. NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, $CuSO_4$, $FeCl_3$, $AlCl_3$ etc.) are acidic in nature due to cationic salt hydrolysis.

For example, due to salt hydrolysis, the aqueous solution of $CuSO_4$ is acidic in nature.

$$2H_2O\ (l) \rightleftharpoons 2H^+ + 2OH^-$$

$$CuSO_4\ (aq) \rightleftharpoons SO_4^{2-}\ (aq) + Cu^{2+}\ (aq)$$

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$H_2SO_4 + Cu(OH)_2$$

(Almost completely dissociated) (Very feebly dissociated)

Here, due to more dissociation of H_2SO_4, the aqueous solution of $CuSO_4$ is acidic in nature.

(b)Salt Hydrolysis of the salts of weak acids and strong bases-

Aqueous solutions of the salts of weak acids and strong bases (e.g. CH_3COONa, CH_3COOK, Na_2CO_3, K_2CO_3, NaCN, KCN etc.) are basic in nature due to anionic salt hydrolysis.

For example, due to anionic salt hydrolysis, the aqueous solution of CH_3COONa is basic in nature.

$$H_2O\ (l) \rightleftharpoons H^+ + OH^-$$

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

$$\downarrow\uparrow \qquad\qquad \downarrow\uparrow$$

$$CH_3COOH + NaOH$$

(Very feebly dissociated) (Almost completely dissociated)

CHEMISTRYFORCOMPETITION.COM

Here, due to more dissociation of NaOH, the aqueous solution of CH_3COONa is basic in nature.

(c)Salt Hydrolysis of the salts of weak acids and weak bases- Aqueous solutions of the salts of weak acids and weak bases (e.g. CH_3COONH_4, $(NH_4)_2CO_3$, NH_4CN etc.) are almost neutral in nature due to salt hydrolysis.

For example, due to salt hydrolysis, the aqueous solution of CH_3COONH_4 is almost neutral in nature.

$$\begin{array}{rcl} H_2O\ (l) & \rightleftharpoons & H^+ + OH^- \\ CH_3COONH_4\ (aq) & \rightleftharpoons & CH_3COO^-\ (aq) + NH_4^+\ (aq) \\ & & \downarrow\uparrow \qquad\qquad \downarrow\uparrow \\ & & CH_3COOH + NH_4OH \end{array}$$

(Very feebly dissociated) (Very feebly dissociated)

Here, due to slightly more dissociation of NH_4OH, the aqueous solution of CH_3COONH_4 is slightly basic in nature.

Similarly, due to salt hydrolysis, the aqueous solution of $(NH_4)_2CO_3$ is almost neutral in nature.

$$\begin{array}{rcl} 2H_2O\ (l) & \rightleftharpoons & 2H^+ + 2OH^- \\ (NH_4)_2CO_3\ (aq) & \rightleftharpoons & CO_3^{2-}\ (aq) + 2NH_4^+\ (aq) \\ & & \downarrow\uparrow \qquad\qquad \downarrow\uparrow \\ & & H_2CO_3 + 2NH_4OH \end{array}$$

(Very feebly dissociated) (Very feebly dissociated)

Here, due to slightly more dissociation of H_2CO_3, the aqueous solution of $(NH_4)_2CO_3$ is slightly acidic in nature.

- Aqueous solutions of the salts of strong acids and strong bases (e.g. NaCl, KCl, Na_2SO_4, K_2SO_4, $NaNO_3$, KNO_3, Na_2SO_4, K_2SO_4 etc.) are completely neutral. Hence, these salts are not considered to be hydrolysed.

Solubility Product- Let a sparingly soluble binary salt AB ionises in its aqueous solution to establish following equilibrium-

$$AB\ (s) \rightleftharpoons A^+(aq) + B^-\ (aq)$$

Applying law of mass action, dissociation constant,

$$K = \frac{[A^+(aq)]\,[B^-(aq)]}{AB(s)}$$

or $$K \times [AB(s)] = [A^+(aq)]\,[B^-(aq)]$$

or $$[A^+(aq)]\,[B^-(aq)] = K_{sp}$$

Where, K_{sp} is a new constant called solubility product of the salt.

CHEMISTRY FOR COMPETITION.COM

Thus, "At constant temperature, in saturated solution of a sparingly soluble salt, the product of the molar concentration of its ions is constant, which is called the solubility product of the salt."

For example,

(i) For AgCl -

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

Here, $K_{sp} = [Ag^{+}(aq)]\,[Cl^{-}(aq)]$

(ii) For $BaCl_2$ -

$$BaCl_2\,(s) \rightleftharpoons Ba^{2+}(aq) + 2Cl^{-}(aq)$$

Here, $K_{sp} = [Ba^{2+}(aq)]\,[Cl^{-}(aq)]^2$

(iii) For $Ca_3(PO_4)_2$ -

$$Ca_3(PO_4)_2\,(s) \rightleftharpoons 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

Here, $K_{sp} = [Ca^{2+}(aq)]^3\,[PO_4^{3-}(aq)]^2$

(iv) For a salt of type A_xB_y -

$$A_xB_y\,(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$

Here, $K_{sp} = [A^{y+}(aq)]^x\,[B^{x-}(aq)]^y$

Relation between solubility (s) and solubility product (K_{sp})-

(a) For binary salts of type AB

Let, the solubility of a binary salt of type AB (e.g. AgCl, AgBr, $BaSO_4$ etc.) is s mol/l. Then,

$$AB\,(s) \rightleftharpoons A^{+}(aq) + B^{-}(aq)$$
$$s\ mol/l \qquad s\ mol/l \quad s\ mol/l$$

Here, $K_{sp} = [A^{+}(aq)]\,[B^{-}(aq)]$

or $K_{sp} = s \times s$

or $K_{sp} = s^2$

or $s = \sqrt{K_{sp}}$

Thus, the solubility of a binary salt is equal to the square root of its solubility product.

(b) For ternary salts of type AB_2

Let, the solubility of a ternary salt of type AB_2 (e.g. $BaCl_2$, Ag_2SO_4 etc.) is s mol/l. Then,

$$AB_2\,(s) \rightleftharpoons A^{2+}(aq) + 2B^{-}(aq)$$
$$s\ mol/l \qquad s\ mol/l \quad 2s\ mol/l$$

Here, $K_{sp} = [A^{2+}(aq)]\,[B^{-}(aq)]^2$

or $K_{sp} = s \times (2s)^2$

CHEMISTRYFORCOMPETITION.COM

or $K_{sp} = 4s^3$

or $s = \sqrt[3]{\frac{K_{sp}}{4}}$

(c) For quaternary salts of type AB_3

Let, the solubility of a quaternary salt of type AB_3 (e.g. $AlCl_3$, $(NH_4)_3PO_4$ etc.) is s mol/l. Then,

$$AB_3\,(s) \rightleftharpoons A^{3+}(aq) + 3B^-(aq)$$
$$s \text{ mol/l} \qquad s \text{ mol/l} \qquad 3s \text{ mol/l}$$

Here, $K_{sp} = [A^{3+}(aq)]\,[B^-(aq)]^3$

or $K_{sp} = s \times (3s)^3$

or $K_{sp} = 27s^4$

or $s = \sqrt[4]{\frac{K_{sp}}{27}}$

(d) For a salts of type A_xB_y

Let, the solubility of a salt of type A_xB_y is s mol/l. Then,

$$A_xB_y\,(s) \rightleftharpoons xA^{y+}(aq) + yB^{x-}(aq)$$
$$s \text{ mol/l} \qquad xs \text{ mol/l} \qquad ys \text{ mol/l}$$

Here, $K_{sp} = [A^{y+}(aq)]^x\,[B^{x-}(aq)]^y$

or $K_{sp} = (xs)^x \times (ys)^y$

or $K_{sp} = x^x y^y s^{(x+y)}$

or $s = \sqrt[(x+Y)]{\frac{K_{sp}}{x^x y^y}}$

Theory of Precipitation

(1) If ionic product of a substance is lesser than its solubility product, the solution is unsaturated and no precipitation occurs.

(2) If ionic product of a substance is equal to its solubility product, the solution is saturated, but here also no precipitation occurs.

(3) If its ionic product of a substance exceeds its solubility product, then the substance gets precipitated.

Thus, the precipitation of a substance occurs only when its ionic product exceeds its solubility product. This is called the theory of Precipitation.

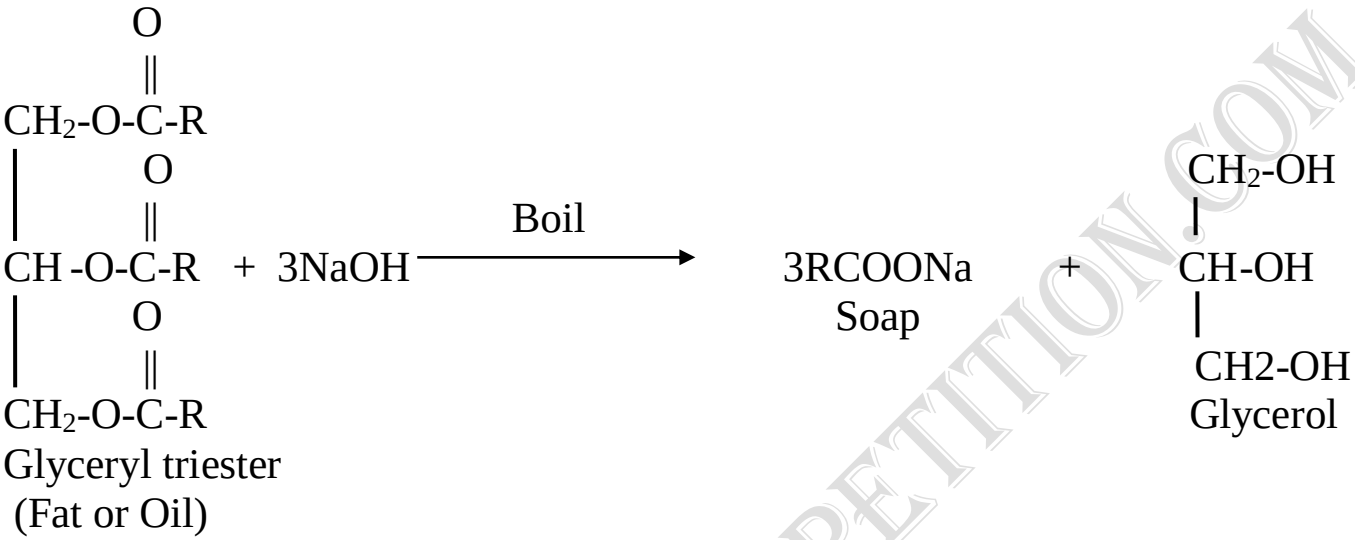
Applications of Theory of Precipitation

(a)Salting out of Soap- The sodium or potassium salts of higher fatty acids such as stearic acid ($C_{17}H_{35}COOH$), palmitic acid($C_{15}H_{31}COOH$), oleic acid

CHEMISTRYFORCOMPETITION.COM

($C_{17}H_{33}COOH$) etc. are called soap. For example, Sodium stearate ($C_{17}H_{35}COONa$), Sodium palmitate ($C_{15}H_{31}COONa$), Sodium oleate ($C_{17}H_{33}COONa$) etc.

Soap is prepared by hydrolysis of the fat or oils with alkalies. Fat or oils contain triglycerides of higher fatty acids and on hydrolysis with alkalies give soap.



Here, since soap is sparingly soluble in water, major quantity of soap gets precipitated and is filtered off. The supernatent liquid thus obtained is saturated solution of soap and is called sweet water.

From sweet water, the residual soap is precipitated by adding salt (NaCl). This process is called salting out of the soap.

Since, sweet water is saturated solution of soap, for this solution,

$$K_{sp} = [RCOO^-(aq)]\,[Na^+(aq)]$$

When NaCl is added to sweet water, NaCl being a strong electrolyte ionises completely to give high concentration of Na^+ and Cl^- ions. Thus, ionic product of soap exceeds its solubility product and therefore, the soap gets precipitated.

(b) Purification of Common salt- Common salt obtained from sea water contains a number of soluble impurities. For purification, it is first dissolved in water to form its saturated solution. In this solution, the ionic product of NaCl is equal to its solubility product.

$$[Na^+(aq)]\,[Cl^-(aq)] = K_{sp}$$

Now HCl gas is passed through this solution which being strong electrolyte ionises almost completely give high concentration of H^+ and Cl^- ions. Thus, ionic product of Common salt exceeds its solubility product and therefore, it gets precipitated.

CHEMISTRY FOR COMPETITION.COM

Here, ionic product of impurities remains lesser than their solubility product. Hence, they do not precipitate but remain left in solution.

(c) Applications in Analytical Chemistry-

(I) Precipitation of Ist group Radicals- Ist group Radicals (Ag^+, Cu_2^{2+}, Pb^{2+}, Hg_2^{2+} etc. are precipitated as their chlorides by adding dilute HCl to the original solution. In fact, solubility product of chlorides of these radicals is relatively lesser, so that, on adding dilute HCl, the ionic product of their chlorides exceeds their solubility product. Hence, they get precipitated.

Here, chlorides of other radicals, if present are also formed but they don't precipitate because, the solubility products of the chlorides of these radicals are relatively higher and therefore, their ionic products do not exceed to their solubility products. Hence, they remain left in solution.

(2)Precipitation of IInd group Radicals- IInd group Radicals (Hg^{2+}, Pb^{2+}, Cu^{2+}, Cd^{2+}, Bi^{3+}, As^{3+} etc. are precipitated as their sulphides by passing H_2S gas in presence of dilute HCl.

In fact, solubility products of sulphides of these radicals are relatively lesser and therefore, they require lesser concentration of sulphide ions for their precipitation. Here, HCl decreases the degree of dissociation of H_2S due to common ion effect.

$$\underset{\text{Weak electrolyte}}{H_2S\ (aq)} \rightleftharpoons \boxed{2H^+\ (aq)} + S^{2-}\ (aq)$$

$$\underset{\text{Strong electrolyte}}{HCl\ (aq)} \rightarrow \boxed{H^+\ (aq)} + Cl^-\ (aq)$$

Common ion

Even at this decreased concentration of S^{2-} ions, the ionic products the sulphides IIIrd group radicals exceed to their solubility products. Hence, they get precipitated.

Here, sulphides of other radicals, if present are also formed, but they don't precipitate because, the solubility product of their sulphides is relatively higher and therefore, their ionic products do not exceed to their solubility products. Hence, they remain left in solution.

(3) Precipitation of the IIIrd group Radicals- IIInd group Radicals (Al^{3+}, Cr^{3+} and Fe^{3+} are precipitated as their hydroxides by adding NH_4OH in presence of NH_4Cl as group reagent.

In fact, solubility products of hydroxides of these radicals are relatively lesser and therefore, they require lesser concentration of hydroxide ions for their

CHEMISTRYFORCOMPETITION.COM

precipitation. Here, NH_4Cl decreases the degree of dissociation of NH_4OH due to common ion effect.

$$\underset{\text{Weak electrolyte}}{NH_4OH\ (aq)} \rightleftharpoons \boxed{NH_4^+\ (aq)} + OH^-\ (aq)$$

$$\underset{\text{Strong electrolyte}}{NH_4Cl\ (aq)} \rightarrow \boxed{NH_4^+\ (aq)} + Cl^-\ (aq)$$

Common ion

Even at this decreased concentration of OH^- ions, the ionic products the hydroxides these radicals exceed to their solubility products. Hence, they get precipitated.

Here, hydroxides of other radicals, if present are also formed but they don't precipitate because, the solubility products of hydroxides of these radicals are relatively higher and therefore, their ionic products do not exceed to their solubility products. Hence, they remain left in solution.

(4) Precipitation of the IVth group Radicals- IVnd group Radicals (Co^{2+}, Ni^{2+}, Mn^{2+} and Zn^{2+} are precipitated as their sulphides by passing H_2S gas in presence NH_4Cl and NH_4OH as group reagent.

In fact, solubility products of sulphides of these radicals are relatively higher and therefore, they require higher concentration of sulphide ions for their precipitation.

Here, NH_4OH removes H^+ furnished by H_2S and therefore, increases the degree of dissociation of H_2S furnishing more S^{2-} ions in solution.

$$\underset{\text{Weak electrolyte}}{H_2S\ (aq)} \rightleftharpoons 2H^+\ (aq) + S^{2-}\ (aq)$$

$$\underset{\text{Weak electrolyte}}{NH_4OH\ (aq)} \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$$

$$H^+\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l)$$

At this increased concentration of S^{2-} ions, the ionic products the sulphides these radicals exceed to their solubility products. Hence, they get precipitated.

Here, sulphides of Ba^{2+}, Sr^{2+} and Ca^{2+} if present are also formed but they don't precipitate because, the solubility products of sulphides of these radicals are relatively higher and therefore, their ionic products do not exceed to their solubility products. Hence, they remain left in solution.

(5) Precipitation of the Vth group Radicals- Vth group Radicals (Ba^{2+}, Sr^{2+} and Ca^{2+}) are precipitated as their carbonates by adding $(NH_4)_2CO_3$ in presence of NH_4OH and NH_4Cl as group reagent.

CHEMISTRYFORCOMPETITION.COM

In fact, solubility products of carbonates of these radicals are relatively lesser and therefore, they require lesserer concentration of carbonate ions for their precipitation. Here, NH_4Cl decreases the degree of dissociation of $(NH_4)_2CO_3$ due to common ion effect.

$$\underset{\text{Weak electrolyte}}{(NH_4)_2CO_3\,(aq)} \rightleftharpoons \boxed{2NH_4^+\,(aq)} + CO_3^{2-}\,(aq)$$

$$\underset{\text{Strong electrolyte}}{NH_4Cl\,(aq)} \rightarrow \boxed{NH_4^+\,(aq)} + Cl^-\,(aq)$$

Common ion

Even at this decreased concentration of CO_3^{2-} ions, the ionic products the carbonates of these radicals exceed to their solubility products. Hence, they get precipitated.

Here, carbonate of Mg^{2+}, if present is also formed but it does not precipitate because, the solubility product of magnesium carbonate is relatively higher and therefore, its ionic product does not exceed to the solubility product. Hence, it remains left in solution.

Acid-Base Equilibrium

(1) Arrhenius Concept of Acids and Bases-

According to this concept- "The substances which ionise in their aqueous solution to give hydrogen ion (H^+) are called acids, while those which ionise to give hydroxyl ion (OH^-) are called bases."

For example, substances like HCl, H_2SO_4, CH_3COOH etc. ionise in their aqueous solution to give hydrogen ion (H^+) are Arrhenius acids.

$$HCl\,(aq) \rightleftharpoons H^+(aq) + Cl^-(aq)$$

$$H_2SO_4\,(aq) \rightleftharpoons 2H^+(aq) + SO_4^{2-}(aq)$$

$$CH_3COOH\,(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$$

On the other hand, substances like NaOH, KOH, $Ca(OH)_2$ etc. ionise in their aqueous solution to give hydroxyl ion (OH^-) are Arrhenius bases.

$$NaOH\,(aq) \rightleftharpoons Na^+(aq) + OH^-(aq)$$

$$Ca(OH)_2\,(aq) \rightleftharpoons Ca^{2+}(aq) + 2OH^-(aq)$$

This concept successfully explains acid-base neutralisation reactions. According to this concept, in acid-base neutralisation reactions the H^+ ions of acids combine with OH^- ions of bases to form water while their remaining part combine together to form salt. For example,

$$\underset{\text{Acid}}{HCl\,(aq)} + \underset{\text{Base}}{NaOH\,(aq)} \rightleftharpoons \underset{\text{Salt}}{NaCl\,(aq)} + \underset{\text{Water}}{H_2O\,(l)}$$

CHEMISTRYFORCOMPETITION.COM

Limitations-

(i) This theory could not explain the acidic behaviour of the aqueous solution of salts like $AlCl_3$, $FeCl_3$, $CuSO_4$ etc. and basic behaviour of the aqueous solution of salts like CH_3COONa, Na_2CO_3, K_2CO_3 etc.

(ii) This theory could not explain the acidic behaviour of gaseous HCl.

(2) Bronsted and Lowry Concept of Acids and Bases

According to this concept- "The hydrogen containing substances which can give one or more protons (H^+) to other substances are called acids, while those which can take one or more protons from other substances are called bases."

For example, substances like HCl, H_2SO_4, CH_3COOH etc. can give one or more protons (H^+) to other substances are called Bronsted acids.

$$HCl \rightleftharpoons H^+ + Cl^-$$
$$H_2SO_4 \rightleftharpoons 2H^+ + SO_4^{2-}$$
$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$$

On the other hand, substances like NH_3, PH_3, $[C_5H_5NH]^+$ etc. can take one or more protons (H^+) from other substances are called Bronsted bases.

$$NH_3 + H^+ \rightleftharpoons NH_4^+$$
$$C_5H_5NH + H^+ \rightleftharpoons [C_5H_5NH]^+$$

There are certain substances, which can give one or more protons (H^+) to other substances or take one or more protons (H^+) from other substances depending upon conditions. Such substances are called Amphoteric substances. Water is the most common example of Amphoteric substance.

$$\underset{\text{Bronsted acid}}{HCl} + \underset{\text{Bronsted base}}{H_2O} \rightleftharpoons Cl^- + H_3O^+$$
$$\underset{\text{Bronsted acid}}{H_2O} + \underset{\text{Bronsted base}}{NH_3} \rightleftharpoons OH^- + NH_4^+$$

HSO_4^- and HCO_3^- are other examples of Amphoteric substances.

Conjugated acids and bases-

It is found that, the donation and acceptance of proton is a reversible process. If an acid removes a proton, its remaining part tends to take a proton to reform original acid i.e. it behaves like a base. For example,

$$\underset{\text{Acid}}{HCl} \rightleftharpoons \underset{\text{Proton}}{H^+} + \underset{\text{Base}}{Cl^-}$$
$$\underset{\text{Acid}}{CH_3COOH} \rightleftharpoons \underset{\text{Base}}{CH_3COO^-} + \underset{\text{Proton}}{H^+}$$

Similarly, if a base takes a proton, the new species formed tends to remove a proton to reform original base i.e. it behaves like an acid. For example,

CHEMISTRYFORCOMPETITION.COM

$NH_3 + H^+ \rightleftharpoons NH_4^+$

Base Proton Acid

$C_5H_5NH + H^+ \rightleftharpoons [C_5H_5NH]^+$

Base Proton Acid

"Such pairs of acids and bases which differ by only one proton and are inter-convertible by donation and acceptance of a proton are called conjugated acid-base pairs". For example,

$HCl \rightleftharpoons H^+ + Cl^-$

Acid Proton Conjugated base

$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

Acid Conjugated base Proton

$NH_3 + H^+ \rightleftharpoons NH_4^+$

Base Proton Conjugated acid

$C_5H_5NH + H^+ \rightleftharpoons [C_5H_5NH]^+$

Base Proton Conjugated acid

In order to get conjugated base of a Bronsted acid, a proton is removed from the acid. Thus,

Bronsted acid $\rightleftharpoons$ Proton + Conjugated base

For example,

$HCl \rightleftharpoons H^+ + Cl^-$

Acid Proton Conjugated base

$H_2SO_4 \rightleftharpoons H^+ + HSO_4^-$

Acid Proton Conjugated base

$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$

Acid Proton Conjugated base

On the other hand, in order to get conjugated acid of a Bronsted base, a proton is added to the base. Thus,

Bronsted base + Proton $\rightleftharpoons$ Conjugated acid

For example,

$NH_3 + H^+ \rightleftharpoons NH_4^+$

Base Proton Conjugated acid

$C_5H_5NH + H^+ \rightleftharpoons [C_5H_5NH]^+$

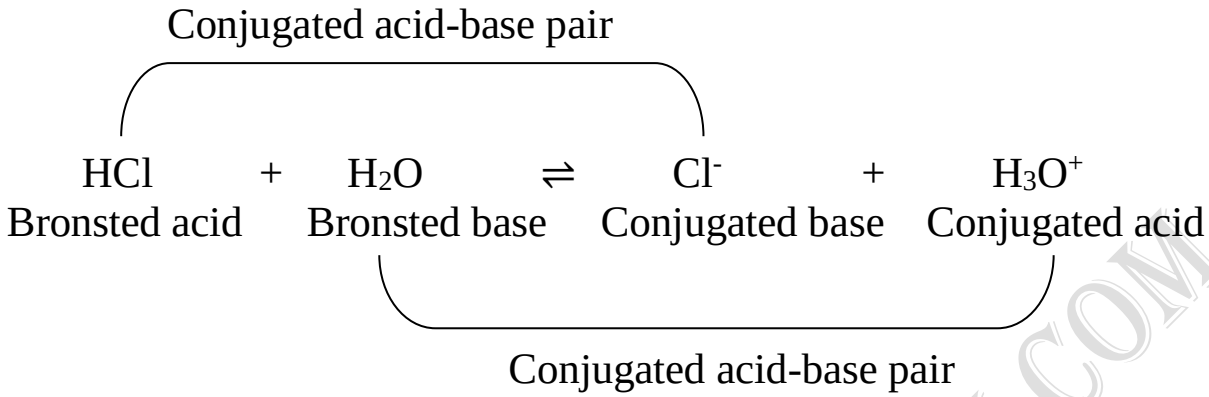
Base Proton Conjugated acid

$H_2O + H^+ \rightleftharpoons H_3O^+$

Base Proton Conjugated acid

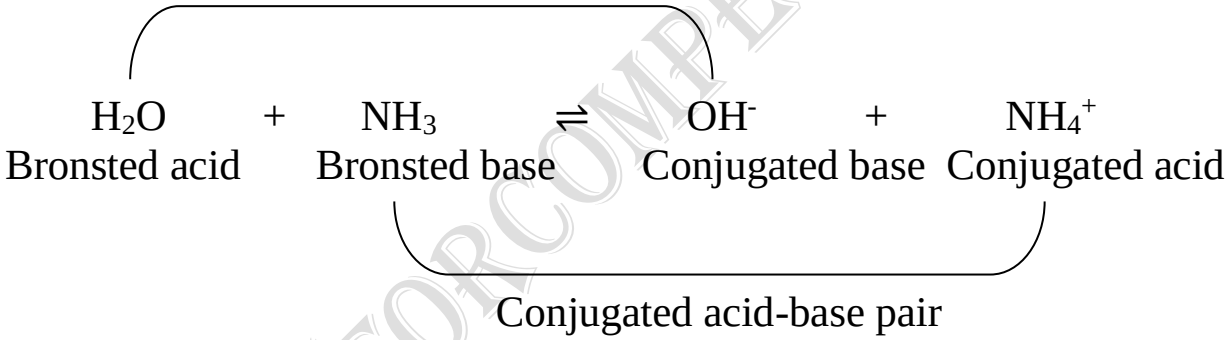
CHEMISTRYFORCOMPETITION.COM

An acid-base reaction involves two such pairs of conjugated acids and bases. For example, in following acid-base reaction-



Here, HCl behaves like Bronsted acid and gets converted into its conjugated base Cl^- by donating a proton to H_2O molecule. On the other hand, H_2O behaves like Bronsted base and gets converted into its conjugated acid H_3O^+ by gaining a proton from HCl.

Similarly, in following acid-base reaction-



Here, H_2O behaves like Bronsted acid and gets converted into its conjugated base OH^- by donating a proton to NH_3 molecule. On the other hand, NH_3 behaves like Bronsted base and gets converted into its conjugated acid NH_4^+ by gaining a proton from H_2O.

Relative Strength of Bronsted acids and Bases-

Acidic strength of Bronsted acids depends upon ease to which they ionize to give proton. The greater the ease to which an acid ionizes to give proton more is its acidic strength. For example, HCl, H_2SO_4, HNO_3, $HClO_4$ etc. ionize easily to give proton and behave like strong Bronsted acids. On the other hand, HCN, H_2CO_3, CH_3COOH etc. do not ionize easily to give proton and therefore, behave like weak Bronsted acids.

Basic strength of Bronsted bases depends upon their capacity to take proton. The greater the capacity of an acid to take proton, more is its basic strength. For example, ammonia, CN^-, CH_3COO^- etc. have very strong tendency to take proton and behave like strong Bronsted bases. On the other hand, Cl^-,

CHEMISTRYFORCOMPETITION.COM

NO_3^-, SO_4^{2-}, ClO_4^- etc. have very weak tendency to take proton and therefore, behave like weak Bronsted bases.

It has been found that, the conjugated base of a strong acid is a weak base, while that of a weak acid is a strong base. In the same way, conjugated acid of a strong base is a weak acid, while that of a weak base is a strong acid. For example,

HCl	+	H_2O	$\rightleftharpoons$	Cl^-	+	H_3O^+	
Strong acid		Weak base		Weak base		Strong acid	
CH_3COOH	+	NH_3	$\rightleftharpoons$	CH_3COO^-	+	NH_4^+	
Weak acid		Strong base		Strong base		Weak acid	

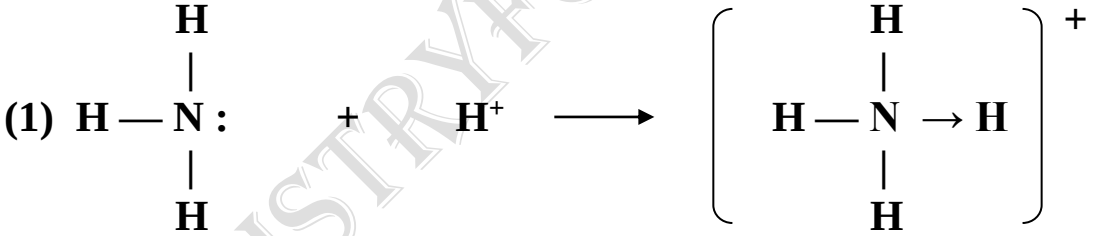
Lewis Concept of acids and bases (Electron pair donor-acceptor concept)

According to this concept, "Those substances which contain one or more lone pair of electrons and can donate it to other substances are called Lewis bases while the electron deficient substances which can gain one or more lone pair of electrons from Lewis bases are called Lewis acids."

Thus, Lewis bases are electron pair donor while acids are electron pair acceptor. Hence, this concept is also called electron pair donor-acceptor concept of acids and bases.

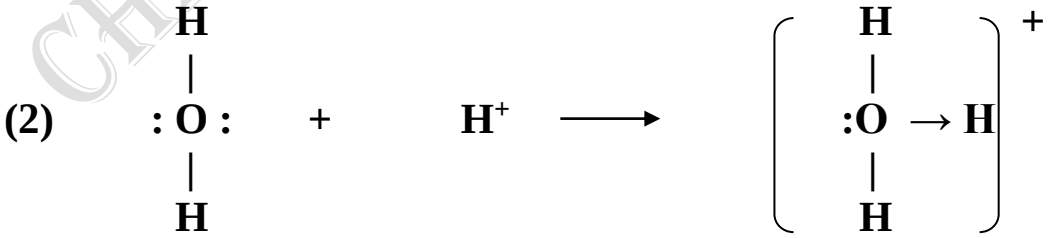
As per this concept, an acid-base reaction involves the the donation of a lone pair of electron by a Lewis base to a Lewis acid to form co-ordinate bond. For example,

(1)



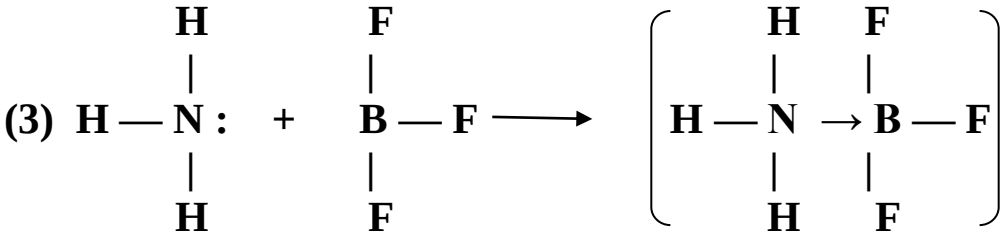
Ammonia (Lewis base) **Proton (Lewis acid)** **Ammonium ion**

(2)

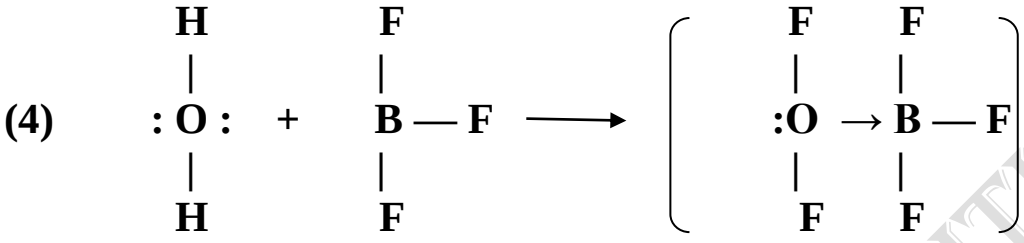


Water (Lewis base) **Proton (Lewis acid)** **Hydronium ion**

CHEMISTRYFORCOMPETITION.COM



Ammonia (Lewis base) **Boron trifluoride (Lewis acid)** **Addition compound**



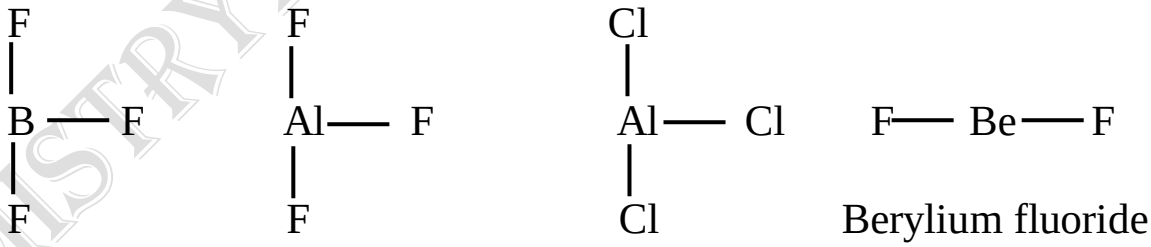
Water (Lewis base) **Boron trifluoride (Lewis acid)** **Addition compound**

Classification of Lewis Acids-

Lewis acids may be of following types-

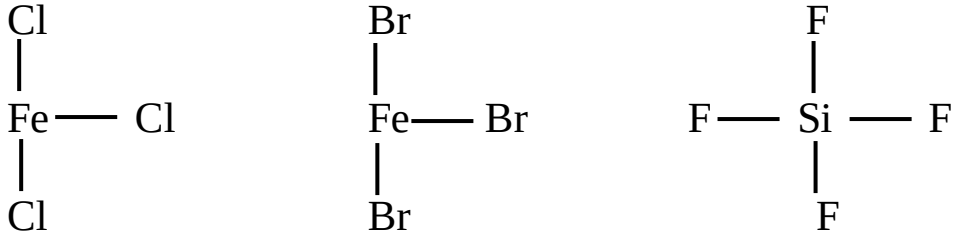
(1) All cations- H^+, Ag^+, Cu^{2+}, Fe^{3+}, Cl^+ (chloronium ion), Br^+ (Bromonium ion), I^+ (Iodinium ion), NO_2^+ (Nitronium ion), R^+ (Carbonium ion) etc.

(2) Neutral molecules containing electron deficient central atom-



Boron trifluoride Aluminium fluoride Aluminium chloride Berylium fluoride

(3) Neutral molecules having central atom with vacant d-orbitals-



Ferric chloride Ferric bromide Silicon tetrafluoride

CHEMISTRYFORCOMPETITION.COM

(4)Neutral molecules where atoms of different electronegativities remain bonded together by multiple bonds- For example,



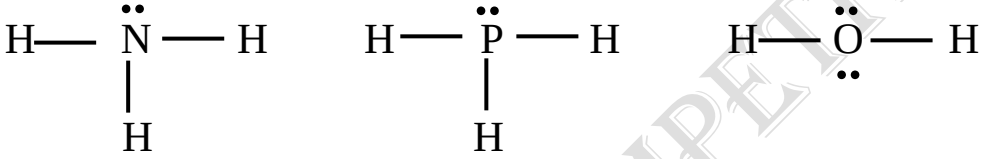
Carbon dioxide | Sulphur dioxide | Sulphur trioxide

Classification of Lewis Bases-

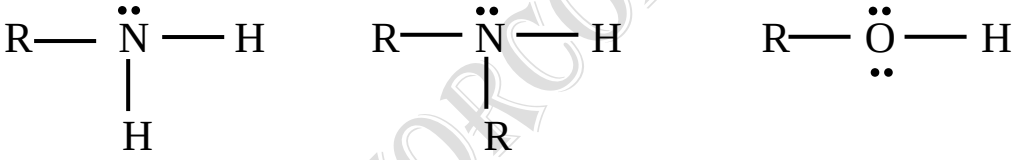
Lewis bases may be of following types-

(1) All anions- OH^-, CN^-, HSO_4^-, Cl^- (chloride ion), Br^- (Bromide ion), NO_2^- (Nitrite ion) etc.

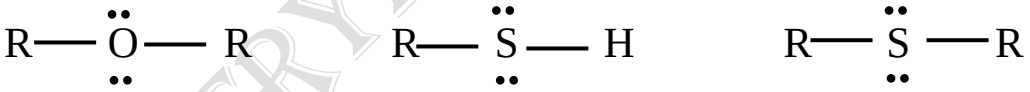
(2) Neutral molecules containing one or more lone pair of electrons on central atom-



Ammonia | Phosphine | Water



1^0 Amine | 2^0 Amine | Alcohol



Ether | Thio alcohol | Thio ether

Relative Strength of Lewis acids and Bases-

Basic strength of Lewis bases depends upon the availability of their lone pair of electrons for protonation. The greater the availability of lone pair of electrons for protonation, more is the basic strength of respective Lewis base. For example, ammonia is more basic than phosphine.

On the other hand, acidic strength of Lewis acids depends upon their tendency to take lone pair of electrons from a Lewis base. The greater the tendency of a Lewis acid to take lone pair of electrons from a Lewis base more is its acidic strength. For example, order of Lewis acid strength of boron halides is as under-

$$BF_3 < BCl_3 < BBr_3$$

CHEMISTRYFORCOMPETITION.COM