Ionic Equilibrium

Types of Substances

Substances can be classified into following two types, viz., non-eletrolytes and electrolytes.

Non-electrolytes

They do not conduct electricity in molten state or aqueous solution, for ex. solution of sugar, urea, glucose, glycerine.

Electrolytes

They conduct electricity in molten state or aqueous solution, for ex. NaCl. Electrolytes can be further divided into following types:

Strong electrolytes These get strongly ionized in water, hence they exhibit high conduction, for example, strong acids like HCl, H_2 SO_4 , HNO_3 , strong bases like KOH, NaOH and salt of strong acid or strong base like NaCl, CH_3 COONa, NH_4 X.

Concept Ladder

In the solid state, electrolytes are bad conductors of electricity, they become good conductors either in the molten state or in a solution.

Weak electrolytes They show less conduction as they are less strongly ionized in water, for ex., weak acids like HCN, CH_3COOH, H_3PO_4, H_2CO_3, weak bases like NH4OH and their salts like NH_2CN, CH_3COONH_4.

Rack your Brain

Does human body also have electrolytes? If yes, then what is their role?

Arrhenius Theory

It is also called as dissociation of electrolytes theory or introduction of ionic theory. The main postulates of this theory are:

- Electrolytes on dissolving in a solvent, ionize into ions.

$$AB \xrightleftharpoons[H_2O]{\text{Solvent}} A^+ + B^-$$

Ions

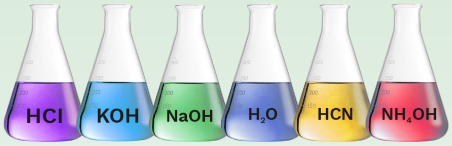
[Ionization]

- Ionization process is reversible and the ionization constant (K) is given as

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

IONIC EQUILIBRIUM

IONIC CONDUCTORS OR ELECTROLYTES



Conductors in which the current passes through them due to the presence of free ions are called Ionic Conductors or Electrolytes or Electrolytic conductors. Ionic conductors are further divided into two types on the basis of their strengths.

STRONG ELECTROLYTES

- Those substance which almost completely ionise into ions in their aqueous solution are called strong electrolytes.
- Degree of ionisation(a) for strong electrolyte is equal to 1.

WEAK ELECTROLYTES

- Those substances which ionise to a small extent in their aqueous solution are known weak electrolytes.
- Degree of ionisation for weak electrolytes is less than 1.

Concept Of Electrolyte

Strong Electrolyte	Weak Electrolyte
$A^+B^- \rightarrow A^+ + B^-$ $C \quad 0 \quad 0$ $0 \quad C \quad C$	$AB \rightleftharpoons A^+ + B^-$ $C \quad 0 \quad 0$ $C(1-\alpha) \quad C\alpha \quad C\alpha$
$\alpha = 1$	$\alpha < 1$
No equilibrium	Equilibrium
Irreversible	Reversible

Ostwald's Dilution Law

According to Ostwald, the degree of dissociation (α) of a weak electrolyte is inversely proportional to the square root of the molar concentration of the solution.

$$K = \frac{C\alpha^2}{1-\alpha}$$

If α is very small $1-\alpha \approx 1 \Rightarrow K_a = C\alpha^2$

$$\text{or } \alpha = \sqrt{\frac{K_a}{C}} \Rightarrow \alpha \propto \frac{1}{\sqrt{C}}$$

Here, K_a is dissociation constant and C is molar concentration of the solution.

DEGREE OF IONISATION OR DEGREE OF DISSOCIATION

- It is the fraction of the total number of molecules which ionise (dissociate) into constituent ions.
- $\alpha = \dfrac{\text{number of molecules ionised or dissociated}}{\text{total numbers of molecules taken}}$
- Values of the degree of dissociation (α) depends upon the following factors

Nature of solute · Nature of solvent · Concentration · Temperature

- The discharging of ions are always in equivalent amount, it is independent of their their relative speeds during electrolysis.
- Ions act like molecules towards depressing the freezing point, elevating the boiling point,
- lowering osmotic pressure and vapour pressure.

Evidence in Support of Ionic Theory

- X-ray diffraction method gives information about presence of ions in solid electrolytes.
- Ions obey Ohm’s law (I = E/R)
- Ionic reactions, for example,

$$AgNO_3 + NaCl \longrightarrow Ag^{+}Cl^{-} \downarrow + Na^{+}NO_3^{-}$$

- Color of some solutions is due to the presence of ions, for ex. $CuSO_4$ solution is blue due to Cu^{2+}.

Concept Ladder

The process of ionisatino is reversible for weak electrolytes.

Degree of ionization

It is denoted by α and is defined as the range to which ionization of an electrolyte takes place in a solvent.

$$\alpha = \frac{\text{Number of molecules dissociated}}{\text{Total number of molecules}}$$

Degree of ionization or α depends on:

- Nature of solute and solvent. For weak electrolytes α is less than that for strong electrolytes.
- α represents a dielectric constant of solvent it is directly proportional to the ionization of electrolyte in it.
- ● The degree of dissociation for weak electrolyte is directly proportional to dilution, i.e., α is maximum at infinite dilution.
- $\alpha \propto \frac{1}{\text{Concentration}}$
- $\alpha \propto$ Temperature

Rack your Brain

Is there any difference between ionisation and dissociation?

Concept Ladder

The degree of dissociation of an electrolyte is assumed to be unity at infinite dilution, i.e., $\alpha = 1$ at infinite dilution.

Ostwald Dilution Law

- This law states the law of mass action for dilute solutions and weak electrolytes and it gives the relationship between the dissociation of weak electrolytes.
- It is not applicable for highly concentrated or solutions strong electrolytes. Consider a weak electrolyte AB in V litres of a solution.

	$AB \rightleftharpoons$	$A^+ +$	B^-
Initial moles	1	0	0
Moles at equilibrium	$1-\alpha$	α	α
Concentration at Equilibrium	$(1-\alpha)/V$	(α/V)	(α/V)

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

$$K = \frac{(\alpha/V)\times(\alpha/V)}{(1-\alpha)/V}$$

$$\text{So, } K = \frac{\alpha^2/V^2}{(1-\alpha)/V} = \frac{\alpha^2}{(1-\alpha)/V}$$

$$\text{As } 1 >>> \alpha \qquad \text{so } (1-\alpha) = 1$$

$$K = \frac{\alpha^2}{V} \text{ or } \alpha^2 = KV \qquad \text{or } \alpha = \sqrt{KV}$$

$$\alpha = \sqrt{V}$$

Hence, degree of dissociation is directly proportional to the square root of its dilution at constant temperature.

- If C is the concentration then

$$AB \rightleftharpoons A^+ + B^-$$

$$C(1-\alpha) \qquad C\alpha \quad C\alpha$$

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

$$K = C\ \alpha^2 \text{ or } \alpha^2 = K/C$$

$$\alpha = \sqrt{(K/C)}$$

$$\text{that is, } \alpha \propto \sqrt{(1/C)}$$

Hence, degree of dissociation is inversely proportional to the square root of its concentration at constant temperature.

Rack your Brain

What is the value of degree of dissociaiton for a strong electrolyte?

Concept Ladder

Smaller the value of K_a or K_b, weaker will be the electrolyte.

Rack your Brain

Can the approximation of (1 - α) ~ 1 be applied when α is 10%?

- $\alpha = \dfrac{\lambda_V}{\lambda_\infty}$ or $\dfrac{\Lambda_V}{\Lambda_\infty}$

  Here λ_∞ or Λ_∞ is equivalent conductivity at infinity dilution where as λ_v or Λ_v is equivalent conductivity at V dilution.
- $\lambda_V = K_V \times V$

  Here K_v = Specific conductivity

  V = Volume of solution in litres
- $\lambda_\infty = \lambda_c + \lambda_\alpha$

  Here λ_c and λ_α are the ionic mobilities of cation and anion respectively.

Common Ion Effect

The value of degree of dissociation will be decreased for a weak electrolyte on adding a strong electrolyte containing a common ion.

- The concentration of the uncommon ion of the weak electrolyte decreases due to common ion effect.

Examples:

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

$NH_4Cl \rightleftharpoons NH_4^+ + Cl^-$

Common ion

Here the value of α for NH_4OH will be decreased by NH_4Cl.

(2) $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$

$CH_3COONa \rightleftharpoons CH_3COO^- + Na^+$

Common ion

Here CH_3COONa decreases the value of α for CH_3COOH because equilibrium shifts in backword direction.

- Due to common ion effect solubility of a partially soluble salt decreases, for ex. presence of KCl or $AgNO_3$, decreases the solubility of AgCl in H_2O.
- By addition of NaCl salting out of soap.
- Purification of NaCl by passing HCl gas.

Previous Year's Questions

The molar solubility of CaF_2 (K_{sp} = 5.3×10^{-11}) in 0.1 M solution of NaF will be

[NEET-2019]

(1) 5.3×10^{-11} mol L^{-1}

(2) 5.3×10^{-8} mol L^{-1}

(3) 5.3×10^{-9} mol L^{-1}

(4) 5.3×10^{-10} mol L^{-1}

Concept Ladder

Degree of dissociation of a weak electrolyte gets suppressed by the addiiton of a strong electrolyte containing same ion.

Previous Year's Questions

Consider the nitration of benzene using mixed conc. H_2SO_4 and HNO_3. If a large amount of $KHSO_4$ is added to the mixture, the rate of nitration will be

[NEET-2016]

(1) slower	(2) unchanged
(3) doubled	(4) faster

Isohydirc Solution

Isohydric solution in the solution which contains same conc. of common ions.

Ionic Product Of Water

It is the product of the molar conc. of H^+ or H_3O^+ and OH^- ions. It is denoted by K_w.

$$H_2O + H_2O \rightleftharpoons H_3^+O + OH^-$$

$K_w = [H_3O^+] . [OH^-]$
or $[H^+]. [OH^-]$

Here K_w = Ionic product of water

- $K_w = K_a . K_b$
- $pK_w = -\log_{10} K_w$
- $K_w = K_a \times K_b$
- $pK_w = pK_a + pK_b$
- At 25°C, $K_w = 1 \times 10^{-14}$
  $pK_w = 14$
- With increase in temp. the value of K_w increases, for example, at 98°C Kw is 1×10^{-12}.

pH Scale

- It was introduced by Sorenson, for measurement of acidity or basicity of the given solution.
- pH stands for potentiel de-H^+ or conc. of H^+. It is given by

$$[H^+] = 10^{-pH}$$

$$pH = -\log_{10} [H^+]$$

pH of aqueous solution is equal to –ve logarithm of $H^+(H^+_3O)$ concentration in mole/ litre.

$$pH = \log_{10} \frac{1}{[H^+]}$$

Rack your Brain

How common ion effect can be explained using Le Chatelier Principle?

Concept Ladder

Pure water is a weak electrolyte, it undergoes self ionisation which is also known as autoprotolysis.

Rack your Brain

How dissociation constant of water is different from ionic product of water?

pH of weak acid

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

$$\begin{array}{lll} 1 & 0 & 0 \\ C(1-x) & Cx & Cx \end{array}$$

$K = Cx^2$

$x = \sqrt{K_a / C}$

$[H^+] = Cx = C\sqrt{(K_a / C)} \approx \sqrt{(K_a . C)}$

$pH = -\log_{10} Cx$

$pH = -\log_{10} \sqrt{(K_a . C)}$

Here C = Molar concentration of acid

x = degree of dissociation

K_a = Dissociation constant of acid

pH of weak base

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

$$\begin{array}{lll} 1 & 0 & 0 \\ (1-x) & Cx & Cx \end{array}$$

$[OH^-] = Cx = \sqrt{(K_b . c)}$

$pOH = -\log_{10} Cx$

$pOH = -\log_{10} \sqrt{(K_b . C)}$

Here K_b = Dissociation constant of the base

pOH

$[OH^-] = 10^{-pOH}$

$pOH = -\log_{10}[OH^-] \text{ or } \dfrac{1}{\log_{10}[OH^-]}$

$pH + pOH = 14$

$pH + pOH = pK_w$

$pK_a = -\log_{10} K_a$

$pK_a \propto \dfrac{1}{K_a} \propto \dfrac{1}{\text{Acidic strength}}$

Concept Ladder

The pH of a mixture of two weak acids can be obtained as :

$$pH = \sqrt{K_{a1} \times c_1 + K_{a2} \times C_2}$$

Rack your Brain

A stronger acid will have ______ value of pH.

Concept Ladder

pH of strong acid or base does not depend upon temperature. pH of weak acid decreases with increase in temperature, due to increase in ionization. pH of weak base increases with increase in temperature, due to increase in ionization or $[OH^-]$ ion concentration.

- A weak acid consist high value of pK_a.
- A weak base consist high value of pK_b.

pH Value and Nature of a Solution

- For $[H^+] > 10^{-7}$,value of pH is less than 7 and the solution is acidic.
- For $[H^+] = 10^{-7}$, value of pH is 7 and the solution
- is neutral.
- For $[H^+] < 10^{-7}$, value of pH is more than 7 and the solution is basic.

pH Range of Some Substances

Substance	pH range
Gastric juice	1–3.0
Soft drink	2–4.0
Lemon	2.2–3.4
Vinegar	2.2–2.4
Urine	4.8–8.4
Milk	6.3–6.6
Saliva	6.5–7.5
Blood	7.3–7.5
Sea water	8.5
Tears	7.4

Limitations of pH scale

- pH value of a solution does not instantaneously give us an idea of the relative strength of the solution.
- pH is zero for 1N solution of strong acid.
- pH is negative for concentrations 2N, 3N, 10N of strong acids.
- At higher concentrations, in place of pH, **Hammelt acidity functions** are used.

Previous Year's Questions

The pH of 0.01 M NaOH (aq) solution will be –

[NEET-2019]

(1) 7.01
(2) 2
(3) 12
(4) 9

Previous Year's Questions

pH of a saturated solution of $Ca(OH)_2$ is 9. The solubility product (K_{sp}) of $Ca(OH)_2$ is :

[NEET-2019]

(1) 0.5×10^{-10}
(2) 0.5×10^{-15}
(3) 0.25×10^{-10}
(4) 0.125×10^{-15}

Buffer Solution

- Buffer solution is the solution in which there is no change in pH takes place even on adding small amount of strong base or a acid.
- It is also known as reserve acidity or basicity of the solution, this action of resisting change in value of pH is known as buffer action.

Features

- Buffer solution has a definite pH, that is a definite reserve basicity or acidity.
- There is no change in pH for a long period of time.
- There is no change in pH on dilution.
- There is slight change in pH (unnoticeable) on adding small quantity of a strong base or acid.

Buffer Capacity

Buffer capacity is the ratio of no. of moles of the acid or base added in 1 L of the solution, so as to change its pH by unity. It is denoted by

$$\varphi.\varphi = \frac{\text{Number of moles of acid / base added to 1 L of solution}}{\text{Change in pH}}$$

Types of Buffer Solutions

1. **Acidic buffer:** The solution of a weak acid & its salt with a strong base is termed as acidic budffer. For example,
   - $CH_3COOH + CH_3COONa$
   - Phthalic acid + potassium phthalate
   - Boric acid + borax $H_2CO_3 + NaHCO_3$
   - Citric acid + sodium citrate
2. **Basic buffer:** The solution of a weak base and it salt with a strong acid is termed as basic buffer. For example,
   - $NH_4OH + NH_4Cl$
   - Glycerine + Glycerine hydrogen chloride.
3. **Ampholytes:** The compounds containing both acidic and basic groups and therefore, exist as zwitter ions at a certain pH (isoelectric

Previous Year's Questions

Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value?

[AIPMT-2012]

(1) $BaCl_2$ (2) $AlCl_3$
(3) LiCl (4) $BeCl_2$

Previous Year's Questions

What is the pH of the resulting solution when equal volumes of 0.1 M NaOH and 0.01 M HCl are mixed?

[NEET-2015]

(1) 12.65 (2) 2.0
(3) 7.0 (4) 1.04

point). Hence, amino Acids and proteins also act like a buffer solution.

4. 4. A mixture of normal salt and acidic salt of a polybasic acid. For ex,
   Na_2HPO_4 + Na_3PO_4
5. Salt of weak base and weak acid (in H_2O).For example, CH_3COONH_4 , NH_4CN

Uses of Buffer solutions

- For finding the pH value of unknown solution by using an indicator.
- $NH_4Cl + NH_4OH$ and $(NH_4)_2CO_3$ buffer solutions precipitates carbonates of group V elements of periodic table.
- CH_3COOH and CH_3COONa buffer is used to remove PO_4^{-3} in qualitative inorganic analysis after IInd group.
- CH_3COOH and CH_3 COONa buffer is used to precipitate $PbCrO_4$ quantitatively in gravimetric analysis.
- They are also used in dye, printing ink,paper, dairy product.

Solubility And Solubility Product

Solubility

- It is denoted by ‘s’ and is expressed in mole per litre or gram per litre. It is the weight of solute in grams, present in 100 mL of solvent.

$$\text{Solubility (s)} \propto \frac{1}{\text{Concentration of common ions or number of common ions}}$$

Solubility increases due to complex ion formation. For ex. the solubility of AgCl in H_2O, in presence of $AgNO_3$.

Here, AgCl is more soluble in NH_3, due to formation of complex.

$$AgCl + 2NH_3 \longrightarrow Ag(NH_3)_2Cl$$

Due to formation of complex compound (Nesseler’s reagent) $HgCl_2$ is more soluble in KI.

Previous Year’s Questions

Buffer solutions have constant acidity and alkalinity because

[AIPMT-2012]

(1) these give unionised acid or base or base on reaction with added acid or alkali

(2) acids and alkalies in these solutions are shielded from attack by other ions

(3) they have large excess of H^+ or OH^- ions

(4) they have fixed value of pH

Rack your Brain

When [Salt] = [Acid], i.e., pH = pKa for acidic buffer, and thus buffer has its maximum capacity. What would be the conditions for a basic buffer?

Concept Ladder

A buffer must contain two components to work a weak acid that reacts with added base a weak base that reacts with added acid.

$$HgI_2 + 2KI \longrightarrow K_2HgI_4$$

In the analysis of IInd group elements, As_2S_3 , Sb_2S_3, SnS, are soluble in $(NH_4)_2S$ due to complex ion formation.

$$SnS + S^{-2} \longrightarrow SnS_2^{-2}$$
$$Sb_2S_3 + 3S^{-2} \longrightarrow 2SbS_3^{-3}$$
$$As_2S_5 + 2S^{-2} \longrightarrow 2AsS_4^{-3}$$

Simultaneous solubility The solubility of a solution of 2 electrolytes containing common ions are known as simultaneous solubility.

Ex.amples are:

1. $CaF_2 + SrF_2$
2. AgBr + AgSCN
3. $MgF_2 + CaF_2$

Solubility Product

In a saturated solution, the product of the molar concentrations of ions of an electrolyte at a particular temperature is known as solubility product. It is denoted by K_{sp} or S.

For a binary electrolyte AB

$$\underset{\text{Solid}}{AB} \rightleftharpoons \underset{\text{Un-ionized}}{AB} \rightleftharpoons A^+ + B^-$$

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

$$\text{or } K.[AB] = [A^+][B^-]$$

$$K_{sp} = [A^+][B^-] \text{ (At constant temperature)}$$

General representation

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

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

Examples:

1. $CaF_2 \rightleftharpoons Ca^{+2} + 2F^-$

$$K_{sp} = [Ca^{+2}][F^-]^2$$

Previous Year's Questions

Which will make basic buffer :

[NEET-2019]

(1) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH

(2) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH

(3) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH

(4) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH

Concept Ladder

At the saturated stage, the quantity of the solute dissolved is always constant for the given amount of a particular solvent at a definite temperature and this is known as the solubility of solute.

Rack your Brain

What happens to the solubility of a sparingly soluble salt on the addiiton of a common ion?

2. $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{-2}$

$K_{sp} = [Ag^+]^2[CrO_4^{-2}]$

Relation Between Solubility (s) and Solubility Product (K_{sp})

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x}$$

a	0	0
a – s	x s	y s

$K_{sp} = (x\,s)^x\ (y\,s)^y$

or

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

If α is given :

$K_{sp} = x^x\,y^y\,(\alpha\,s)^{x+y}$

For example, $Cu_2Cl_2 \rightleftharpoons \underset{2s}{2Cu^+} + \underset{2s}{2Cl^-}$

So $K_{sp} = 2^2\,2^2\,(s)^{2+2} = 16\,s^4$

$Fe(OH)_3 \rightleftharpoons \underset{s}{Fe^{+3}} + \underset{3s}{3OH^-}$

$K_{sp} = 1^1\,3^3\,(s)^{1+3} = 27\,s^4$

$Al_2(SO_4)_3 \rightleftharpoons \underset{2s}{2Al^{+3}} + \underset{3s}{3SO_4^{-2}}$

$K_{sp} = 2^2\,3^3\,(s)^{2+3} = 108\,s^5$

$Na_3Li_3(AlF_6)_2 \rightleftharpoons 3Na^+ + 3Li^{+3} + 2AlF_6^{-3}$

$K_{sp} = 3^3\,3^3\,2^2\,(s)^{3+3+2} = 2916\,s^8$

Solubility Product and Precipitation

- If $K_{sp} \approx$ ionic product, solution is saturated, & for precipitation, more solute to be added.
- If ionic product > K_{sp}, solution is super saturated, & therefore gets easily precipitated.
- If ionic product < K_{sp}, solution is unsaturated & therefore no precipitation takes place.

Previous Year's Questions

Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol^{-1} solubility product of $Ag_2C_2O_4$ is

[NEET-2017]

(1) 2.42×10^{-8}
(2) 2.66×10^{-12}
(3) 4.5×10^{-11}
(4) 5.3×10^{-12}

Concept Ladder

Solubility product is defined as the product of concentrations of the ions raised to a power equal to the number of times, the ions occur in the equation representing the dissociaiotn of the when the solution is saturated.

Rack your Brain

What is teh difference between ionic product and solubility product?

Salt Hydrolysis

- Salt hydrolysis is the ionic interaction between ions of the salt and water causes acidity or basicity in aqueous solution, when a salt is added to water.
- Cationic hyrolysis is interaction of cation and anionic hydrolysis is interaction of anion.
- Hydrolysis is an endothermic process and is reverse of neutralization.
- If neutralization constant is Kn and hydrolysis constant is K_h, then $K_n = 1/K_h$.
- A solution of the salt of weak base and strong acid is acidic and for it $pH < 7$ or $[H^+] > 10^{-7}$, for ex. $FeCl_3$ (salt of a strong acid + weak base). Here, the solution is involves cationic hydrolysis and acidic in nature.
- A solution of the salt of weak acid and strong base is basic and for it, $pH > 7$ or $[H^+] < 10^{-7}$, for ex. KCN (salt of a weal acid + strong base). Here, the solution involves anionic hydrolysis and is basic in nature.
- A solution of the salt of weak base and a weak acid is :
  1. Basic, if $K_a < K_b$
  2. Acidic, if $K_a > K_b$
  3. Neutral, if $K_a = K_b$ is neutral
- CH_3COONH_4 (salt of a weak base + weak acid) Here, the solution involves both anionic and cationic hydrolysis and is neutral in nature.
- The solution of salt of strong base & strong acid is neutral or $pH = 7$ or $[H^+] = 10^{-7}$
- A salt of a strong acid and base can never be hydrolyzed.

  However, ions are hydrated, for ex. K_2SO_4 (salt of a strong acid + strong base).

Previous Year's Questions

Find out the solubility of $Ni(OH)_2$ is 0.1 M NaOH. Given that the ionic product of $Ni(OH)_2$ is 2×10^{-15}

[NEET-2020]

(1) 2×10^{-8} M
(2) 1×10^{-13} M
(3) 1×10^{8} M
(4) 2×10^{-13} M

Concept Ladder

The net effect of dissolveing a salt (which undergoes hydrolysis) is to break up the water molecules (hydrolysis) to produce a weak acid or weak base or both and thus, phenomenon is always endothermic.

Rack your Brain

During the hydrolysis of NH_4Cl, which ion will undergo hydrolysis?

Various Expressions for K_h, h and pH for Different Type of Salts

1. For the salt of weak acid & strong base like KCN,

$$K_h = \frac{K_w}{K_a}$$

$$h = \sqrt{(K_h / C)}$$

$$h = \sqrt{(K_w / K_a . C)}$$

$$pH = \frac{1}{2}[pK_w + pK_a + \log\ C]$$

$$pOH = \frac{1}{2}[pK_w - pk_a - \log\ C]$$

2. For the salt of strong acid & weak base like $FeCl_3$,

$$K_h = \frac{K_w}{K_a}$$

$$h = \sqrt{(K_h / C)}$$

$$h = \sqrt{(K_w / K_b . C)}$$

$$pH = \frac{1}{2}[pK_w + pK_b + \log\ C]$$

3. For the salt of weak acid & weak base like CH_3COONH_4,

$$K_h = \frac{K_w}{K_aK_b}$$

$$h = \sqrt{(K_w / K_aK_b)}$$

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

Acid and Base

Arrhenius Concept of Acid and Base

According to Arrhenius concept, "H^+ ion donor in H_2O are acids and OH^- ion donor in H_2O are bases."

Previous Year's Questions

The ionisation constant of ammonium hydroxide is 1.77 × 10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is

[AIPMT]

(1) 5.65 × 10^{-10}
(2) 6.50 × 10^{-12}
(3) 5.65 × 10^{-13}
(4) 5.65 × 10^{-12}

Concept Ladder

The pH of the salt of W.A. and W.B. is independent of its concentration.

Rack your Brain

How the degree of hydrolysis of salts of weak acids and weak bases changes with dilution?

SALT HYDROLYSIS

Hydrolysis is defined as the process in which a salt reacts with water to give back the acid and the base. It is reverse of neutralisation.

Salt + Water → **Acid + Base**

Salt hydrolysis is an endothermic reaction therefore on increasing the temperature, the extent of hydrolysis increases.

Hydrolysis at a Glance

Salt	Nature	Degree	Hydrolysis Constant	pH
Strong Acid + Strong Base ($NaCl$)	Neutral	No Hydrolysis	–	–
Weak Acid + Strong Base (CH_3COONa)	Base	$h = \sqrt{\frac{K_w}{CK_a}}$	$K_h = \frac{K_w}{K_a}$	$pH = \frac{[pK_w + pK_a + \log C]}{2}$
Strong Acid + Weak Base (NH_4Cl)	Acidic	$h = \sqrt{\frac{K_w}{CK_b}}$	$K_h = \frac{K_w}{K_b}$	$pH = \frac{[pK_w - pK_b - \log C]}{2}$
Weak Acid + Weak Base (CH_3COONH_4)	–	$h = \sqrt{\frac{K_w}{(K_a \times K_b)}}$	$K_h = \frac{K_w}{K_a\,K_b}$	$pH = \frac{[pK_w + pK_a - pK_b]}{2}$

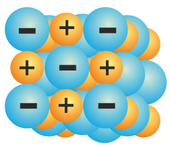
Solution

Basic Solution (Na_2CO_3)
↙ NaOH Strong Base
↘ H_2CO_3 Weak Acid

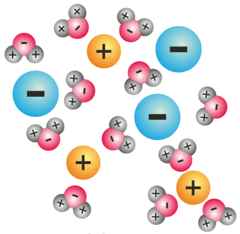
Neutral Solution (Na_2SO_4)
↙ NaOH Strong Base
↘ H_2SO_4 Strong Acid

Acidic Solution (NH_4NO_3)
↙ NH_3 Weak Base
↘ HNO_3 Strong Acid

NaCl crystal structure



+ Sodium (Na)
– Chlorine (Cl)



NaCl in water

Use of Hydrolysis in the "Real World"

Life processes require energy for processes like respiration, muscle contraction, distribution of hormone etc. The energy that is converted from food, is stored into ATP molecules (Adenosine Triphosphate). To release the energy stored in the bonds of ATP molecules, hydrolysis must occur to break a phosphate group of an ATP molecule, thus releasing energy from the bonds. ATP now becomes ADP (Adenosine Diphosphate) by losing a phosphate group through hydrolysis.

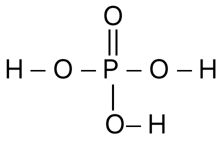
Acid

- $HA + H_2O \longrightarrow A^- + H_3O^+$

  where H_3O^+ hydronium ion or hydrated proton.
- Due to presence of H-bonding, H_2O can accept H^+ to form hydronium ion (H_3O^+). For example, [$H_5O^+_2$, $H_7O^+_3$]
- H^+ can hold H_2O molecule by H-bond, as it has high heat of hydration. For ex. H_2SO_4, HNO_3, HX.
- H_3O^+ has sp^3 hybridization and has trigonal pyramidal shape.
- The Number of H^+ ions donated = Basicity or protosity of the acid.

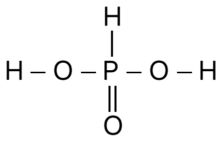
Examples:

1. H_3PO_4 (tribasic)



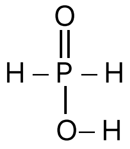
$$H-O-\underset{\underset{O-H}{|}}{\overset{\overset{O}{||}}{P}}-O-H$$

2. H_3PO_3 (dibasic)



$$H-O-\underset{\underset{O}{||}}{\overset{\overset{H}{|}}{P}}-O-H$$

3. H_3PO_2 (mono basic)



$$H-\underset{\underset{O-H}{|}}{\overset{\overset{O}{||}}{P}}-H$$

Base

$B.OH + H_2O \longrightarrow B^+ + H_3O_2^- \,[\text{or}\, H_5O_3^-]$

For example, NaOH, KOH.

Strength of Acid and Base

1. Acidic strength $\propto K_a$

   K_a = Dissociation constant of the acid

Concept Ladder

$H_2PO_2^-$ and HPO_3^{2-} are only bronsted bases. As H_3PO_2 and H_3PO_3 are monobasic and dibasic acid respectively, they can release only one and two H^+ ions respectively.

Rack your Brain

Why water is amphoteric in nature?

Concept Ladder

The neutralization of an acid and base is basically a neutralization reaction between H^+ and OH^- ions.

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

2. Base strength ∝ K_b

   K_b = Dissociation constant of the base
3. Relative strength $= \sqrt{(K_1 / K_2)}$

$$H_3PO_4 \xrightleftharpoons{K_1} H_2PO_4^- + H^+ \text{ or } H_3O^+$$

$$H_2PO_4^- \xrightleftharpoons{K_2} HPO_4^{-2} + H^+$$

$$HPO_4^- \xrightleftharpoons{K_3} PO_4^{-3} + H^+$$

   $H_3PO_4 > H_2PO_4^- > HPO_4^{-2}$ is the correct acidic strength order of $K_1 > K_2 > K_3$
4. With development of negative charge, the removal of H^+ becomes more and more difficult so acidic nature decreases.

Bronsted Lowery Concept or Proton Concept

Acid

Acids are proton or H^+ donor.

$$\underset{\text{Acid}}{HA} \longrightarrow \underset{\text{Conjugate base}}{A^-} + H^+$$

$$\text{For example, } HA \longrightarrow H^+ + \underset{\text{Conjugate base}}{X^-}$$

$$\underset{\text{Acid}}{H_2SO_4} \longrightarrow H^+ + \underset{\text{Conjugate base}}{HSO_4^-}$$

$$HNO_3 \longrightarrow H^+ + NO_3^-$$

Base

Bases are proton or H^+ acceptor

$$\text{Base} + \underset{\text{Proton given by acid}}{H^+} \longrightarrow \underset{\text{Conjugate Acid}}{(\text{Base H})} +$$

$$\text{For example, } \underset{\text{Base}}{OH^-} + H^+ \longrightarrow \underset{\text{Conjugate Acid}}{H_2O}$$

Amphoteric or Ampholyte Substances

Amphoteric substances can donate or accept H^+ or proton, hence they can behave both like an acid as well as base.

Examples:

1. $$\underset{\text{Conjugate acid}}{NH_4^+} \xleftarrow{+H+} \underset{\text{Ampholyte}}{NH_3} \xrightarrow{-H^+} \underset{\text{Conjugate base}}{NH_2^-}$$

2. $$\underset{\text{Conjugate acid}}{H_3O^+} \xleftarrow{+H^+} \underset{\text{Ampholyte}}{H_2O} \xrightarrow{-H^+} \underset{\text{Conjugate base}}{OH^-}$$

Concept Ladder

The fundamental concept of Bronsted Lowry Concept is that when an acid & a base react with each other, the acid forms its conjugate base, & the base forms its conjugate acid by exchange of a proton.

Rack your Brain

Which is neither an acid nor a base according to Arrhenius concept?

H_3PO_4, HCl, NH_3, KOH

Previous Year's Questions

Boric acid is an acid because its molecule

[NEET-2016]

(1) Contians replaceable H^+ ion

(2) gives up a proton

(3) accepts OH^- from water releasing proton

(4) combines with proton from water molecule

Some other examples are HSO_4^- , HCO_3^-, $H_2PO_4^-$, HPO_4^{2-}, $H_2PO_3^-$, HS^- and $HC_2O_4^-$

Lewis Concept of Acid and Base

Lewis acids: The species which can accept lone pair of electrons due to defficiency of electron are termed as Lewis acids. The species which act as Lewis acids are as follows:

1. Cations

   $-\underset{|}{C^+}-, NO_2^+, X^+$ (Halonium ion)

2. Electron deficient central atoms

   $$\underset{\underset{4}{\downarrow}}{BeX_2},\ \underset{\underset{6}{\downarrow}}{BX_3},\ \underset{\underset{6}{\downarrow}}{FeX_3},\ \underset{\underset{6}{\downarrow}}{AlX_3},\ \underset{\underset{4}{\downarrow}}{SnCl_2},\ \underset{\underset{4}{\downarrow}}{ZnCl_2}$$

3. Central atom having multiple bonds

   O=C=O, O=S=O, S=C=S, SO_3

4. When central atom of a molecule has vacant d-orbital then it can have more than 8 electrons, i.e., octet state can be expand and molecule can behave as a Lewis acid. For example,

   (a) $\underset{\text{Lewis acid}}{PX_5} + X^- \longrightarrow \underset{\text{Lewis base}}{PX_6^-}$

   (b) $\underset{\text{Lewis acid}}{SiX_4} + 2X^- \longrightarrow \underset{\text{Lewis base}}{SiX_6^{-2}}$

- Some other examples of Lewis acids are: PX_3, SnX_4, GeX_4 , SF_4 , $TeCl_4$, SeF_4
- Elements with an electron sextet (for example O, S)

Strength of Lewis Acid

1. Lewis acid strength ∝ Electronegativity difference

Example:

$$\xrightarrow[\text{Acidic nature increases}]{AlF_3\ \ AlCl_3\ \ AlBr_3\ \ AlI_3}$$

2. In case of boron halide (BX_3)

   BI_3 > BBr_3 > BCl_3 > BF_3

   No back bonding — less back bonding — Maximum back bonding

Concept Ladder

All arrhenius acids are also Bronsted acids but all arrhenius bases are not Bronsted bases.

This is because an arrhenius acid is a substance which can give a H^+ ion whereas a Bronsted acid is a substance which can donate a proton which is also a H^+ ion.

Rack your Brain

What is conjugate acid and base for NH_3?

Previous Year's Questions

Conjugate base for Bronsted acids H_2O and HF are :

[NEET-2019]

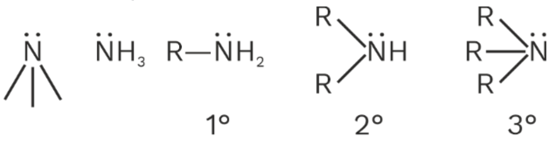
(1) H_3O^+ and H_2F^+, respectively
(2) OH^- and H_2F^+, respectively
(3) H_3O^+ and F^-, respectively
(4) OH^- and F^-, respectively

3. In BF_3, electron pairs is shifted from fluorine back to boron atom. Due to small size and more electron density ($2p^5$) of F-atom, there is more e^-—e^- repulsion. Whereas in case of B, the atom size is large and 2p orbital is almost vacant.
4. 4. The strength of some Lewis acids is given below in their decreasing order as:
   BX_3 , AlX_3 , FeX_3 , GaX_3 , SbX_5 , InX_3 , SnX_4 , AsX_5, ZnX_2 , HgX_2

Lewis bases The species which can donate lone pair of electrons are termed as Lewis bases.

- Any anion or molecule central atom with lone pair of electrons and with octet state, as it can donate its lone pair hence it is a Lewis base.

  For example, OH^-, X^-



$\ddot{\text{P}}\text{H}_3$ H—$\underset{\cdot\cdot}{\ddot{\text{O}}}$—H R—$\underset{\cdot\cdot}{\ddot{\text{O}}}$—H R—$\underset{\cdot\cdot}{\ddot{\text{O}}}$—R

Some of the multiple bonded molecules which form complexes with transition metals are as CO, NO, C_2H_4.

Strength of Lewis Base

$$\text{Lewis base} \propto \frac{1}{\text{Electronegativity difference}}$$

$NH_3 > NI_3 > NBr_3 > NCl_3 > NF_3$

Least electronegativity difference

Factors Affecting Acidic Strength

Effect of electronegativity difference

- Acidic strength is directly proportional to Electronegativity difference

1. $HF > H_2O > NH_3 > CH_4$
   As electronegativity of F > O > N > C.
   $HNO_3 > H_2CO_3 > H_3BO_3$
   As electronegativity of N > C > B.

Concept Ladder

The term nucleophile and electrophile are more or less inter changable with lewis bases and lewis acids respectivley.

Rack your Brain

Write name of some convinental amines which behaves as lewis bases?

Previous Year's Questions

Which of the folloiwng oxides is not expected to react with sodium hydroxide?

[NEET-2009]

(1) B_2O_3 (2) CaO
(3) SiO_2 (4) BeO

2. $HClO > HBrO > HIO$ $HClO_3 > HBrO_3 > HIO_3$
   The above order is due the electronegativity order of $Cl > Br > I$.
3. Acidic strength is directly proportional to the size of central atom or ease of removal of H^+
   $HF < HCl < HBr < HI$
   $H_2O < H_2S < H_2Se$
   $NH_3 < PH_3 < AsH_3 < SbH_3$
4. Strength of oxyacid's ∝ Oxidation number of central atom.

   (a) $\xrightarrow[\text{Increasing order of acidic nature}]{HO\overset{+1}{X} < H\overset{+3}{X}O_2 < HX\overset{+5}{O}_3 < HX\overset{+7}{O}_4}$

   (b) $N^{-3}H_3 < H_2N_2^{+1}O_2 < HN^{+3}O_2 < HN^{+5}O_3$

Effects of a solvent on acidic strength Levelling effect is a solvent which also effects acidic strength.
For example,

1. *CH_3COOH*
   (a) CH_3COOH behaves like a strong acid in liquid ammonia as but as a weak acid in water, as ammonia has a greater tendency to accept H^+ than water. For example,

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{base}}}{CH_3COO^-} + \underset{\substack{\text{Conjugate}\\\text{acid}}}{H_3O^+}$$

$$\underset{\text{Acid}}{CH_3COOH} + \underset{\text{Base}}{NH_3} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{base}}}{CH_3COO^-} + \underset{\substack{\text{Conjugate}\\\text{acid}}}{NH_4^+}$$

- CH_3COOH is weaker acid than HF it behaves like a base.

$$\underset{\text{Base}}{CH_3COOH} + \underset{\text{Acid}}{HF} \rightleftharpoons \underset{\substack{\text{Conjugate}\\\text{acid}}}{CH_3COO^+H_2} + \underset{\substack{\text{Conjugate}\\\text{base}}}{F^-}$$

2. *HNO_3*
   Nitric acid is a strong acid in H_2O but acts as a base in HF as it is weaker acid than CH_3COOH.
3. *$HClO_4$*
   $HClO_4$ (being strongest acid) behaves as a weak acid in HF.

Concept Ladder

All Lewis bases are also Bronsted bases but all Bronsted acids may not be Lewis acids. This is because a substance that is capable of giving an electron pair has the tendency to accept a proton.

Rack your Brain

Why CO acts as a Lewis acid?

Previous Year's Questions

Which of the following fluoro-compounds is most likely to behave as a lewis base?

[NEET-2016]

(1) BF_3 (2) PF_3
(3) CF_4 (4) SiF_4

Corresponding Conjugate Bases in Increasing Order of Acidic Strength

A strong acid has weak conjugate base.

ClO_4^-, ClO_3^-, I^-, H_2O, NO_3^-, F^-, SO_4^{2-}, $H_2PO^-_4$, $HCOO^-$, CH_3COO^-, HCO_3^-, HS^-, NH_3, CN^-, $C_6H_5\ O^-$, OH^-, OR^-, $C^- \equiv CH$, NH_2^-, $CH^- = CH_2$, CH^-_3, $C^-_2H_5$, $C^-_6H_{11}$

Nature of Oxides

Lux–flood concept

- An acidic oxide takes up O while a basic oxide gives up O.

Example:

$$\underset{\text{Basic}}{CaO} + \underset{\text{Acid}}{CO_2} \longrightarrow \underset{\text{Acidic}}{CaCO_3}$$

$$6Na_2O + P_4O_{10} \longrightarrow 4Na_3PO_4$$

- A basic oxide produces a base while an acidic oxide produces an acid with water.

Example:

$$\underset{\text{Acidic}}{SO_3} + H_2O \longrightarrow H_2SO_4$$

$$\underset{\text{Basic}}{Na_2O} + H_2O \longrightarrow 2NaOH$$

Some Acidic Oxides

Cl_2O_7, P_4O_{10}, SO_2, CO_2, SiO_2, SO_3, N_2O_3, B_2O_3, CrO_3, WO_3, MoO_3, Mn_2O_7h.

Some Basic Oxides

M_2O (here M = IA metal), MO (Here M = IIA metal), ZrO_2, Sc_2O_3, TiO_2.

Some Amphoteric Oxides

BeO, CrO, Al_2O_3, Sb_2O_3, SnO, PbO, ZnO, Cr_2O_3.

Acid–Base Indicators

- Acid–base indicators are those weak organic acids or bases which shows a sharp colour change at the end point of a titration.
- These indicators exhibit different colours in acidic and basic medium. For ex. methyl orange shows red colour in acidic medium while shows yellow colour in basic medium.

Rack your Brain

Write value of pH for litmus paper when it has (i) red color, (ii) blue color?

Concept Ladder

Greater the value of

$HClO_4$, $HClO_3$, HI, H_2SO_4, HBr, HCl, H_3O^+, HNO_3, HF, HSO_4^-, H_3PO_4, HCOOH, CH_3COOH, $H_2\ CO_3$, H_2S, NH_4^+, HCN, C_6H_5OH, H_2O, R–OH, $HC\equiv CH$, NH_3, $H_2C=CH_2$, CH_4, C_2H_6, C_6H_{12}

- Due to sharp change of pH at the end point of an acid–base titration, colour of indicator changes.
- pH range is the pH value range between lower & upper limit at which the colour of indicator changes.
- This pH range depends upon the concentration and nature of acid and base used in the titration. For example, phenolphthalein or methyl orange or methyl red indicator can be used for strong acid versus strong base in the titration range.
- For titration between strong base with a weak acid phenolphthalein is used, but it does not work in the titration of a strong acid with a weak base.
- While titrating a strong acid with a base, both methyl orange and methyl red can be used.
- There is no suitable indicator in the titration of a weak acid with weak base, as change in pH is not sharp at the end point.
- A universal indicator is formed after mixing several indicators in a definite proportion, which shows characteristics colours at different values of pH.
- A sharp change in colour occurs when benzoid form changes into quinoid form.
- Acid is present in slight excess at the end point in acid–base titration.
- The ratio of $[In^-]/[HIn]$ determines the colour of an indicator.

Hard and Soft Acids & Bases (HSAB Principle)

The property to retain valence electrons very strongly is termed as hardness. According to this concept, hard and soft bases or acids are described as follows:

Hard acids Acceptor atom has high charge, is of small sized, and has no electron. For example, BF_3, $AlCl_3$, H^+, Li^+, Na^+, Be^{2+}, Mg^{2+}, Al^{3+}, Cr^{3+}, Fe^{3+}.

Concept Ladder

An indicator changes colour when the concentration of hydrogne ion (in mol per litre) in the solution is equal to the dissociation ocnstant of the indicator, i.e., indicator is 50% dissociated.

Rack your Brain

Why phenolphthalein is not a suitable indicator for titrating a weak base against strong acid?

Concept Ladder

In acid -base titrations right before the equivalence point there is a sharp increase in pH.

pH steadies itself around the midpoint because the solutions at this point in the curve are buffer solutions, which means that adding small increments of a strong base will only barely change the p.

ACID-BASE INDICATORS

Acid-Base indicators are organic substances which have one colour in acid solution while an altogether different colour in alkaline solution.

THEORIES OF ACID-BASE INDICATORS

OSTWALD'S THEORY (1891)

According to this theory:

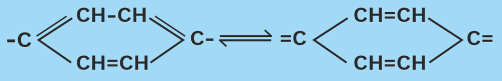
- Acid- base indicators are weak organic acids or bases.
- They have different colours in ionised and non-ionised states.
- The colour of the indicator depends on the relative proportion of the unionised indicator molecules and its ions.

$$\underset{\text{one colour}}{HIn} \rightleftharpoons \underset{\text{(Different colour)}}{H^{+} + In^{-}}$$

MODERN QUINOID THEORY

Main postulates of this theory are:

- The indicators used in acid-alkali titrations are aromatic organic compounds which are equilibrium mixtures of at least two tautomeric forms, ordinarily one form is benzenoid while the other is quinoid.
- The two forms have different colours. The quinoid form is usually deeper in colour than the benzenoid form. Out of these one form exists in acidic solution while other in alkaline solution.
- Change in pH causes the transition of benzenoid form to quinoid form and vice versa and consequently a change in colour. This theory explains the action of phenolphthalein, methyl orange and other acid base indicators.



Benzenoid from
(Lighter colour)

Quinoid form
(deeper colour)

CHOICE OF INDICATORS

Nature of Titration	pH Jump at the Equivalence point	Suitable Indicator
Strong Acid and Strong Base	4-10	Any Indicator (Methyl orange, Methyl red, Phenophthalein, Bromo thymol blue etc.)
Weak Acid and Strong Base	6.5-10	Phenophthalein, thymol blue, thymolphthalein
Strong Acid and Weak Base	4-7.5	Methyl orange, Methyl red, Bromocresol green
Weak Acid and Weak Base	6.5-7.5	No Indicator is suitable

Soft acids Acceptor atom has a low charge and is of large sized, and possesses electrons. For example, Cu^+, Pb^{2+}, Cd^{2+}, Hg^{2+}, Ag^+.

Hard bases These can hold electrons strongly and are Lewis bases. For example, R–OH, H_2O, NH_3, RNH_2, RO^-, OH^-, F^-.

Soft bases From these type of Lewis bases electron can be easily removed. For example, R^-, R_2S, CN^-, RS^-, I^-, CO.

Rack your Brain

What is point of inflection?

Acid Base Titrations

S.No.	Type of titration	Example	pH change at the end point
1	Strong acid–weak base	0.1 M HCl and 0.1 M NH_4OH	4–6.3
2	Strong base–weak acid	0.1 M NaOH and 0.1 M CH_3COOH	7.7–9.7
3	Weak acid– weak base	0.1 M CH_3COOH and 0.1 M NH_4OH	-
4	Strong acid–strong base	0.1 M HCl and 0.1 M NaOH	5.5–8.5

Some Indicators & Their Colour Changes with the Respective pH Range

Indicator	Colour in acidic medium	Colour in basic medium	pH range
Phenolphthalein	Colourless	Pink	8.2–10
Thymol blue	Yellow	Blue	8–9.6
Phenol red	Yellow	Red	6.8–8.4
Methyl red	Red	Yellow	4.2–6.3
Methyl orange	Red	Yellow	3.1–4.4

Important formula

Degree of Ionization

$$\alpha = \frac{\text{Number of molecules dissociate}}{\text{Total number of molecules}}$$

Ostwald dilution law

For a binary weak electrolyte

$$K = \frac{\alpha^2}{V} \text{ or } \alpha^2 = KV \text{ or } \alpha = \sqrt{(KV)}$$

- If ‘C’ is the concentration, then

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

  $$K = C\ \alpha^2 \text{ or } \alpha^2 = K / C$$

  $$\alpha^2 = (K/\,C)$$

  $$\alpha = \frac{\lambda_V}{\lambda_{\_}} \text{or} \frac{\wedge_V}{\wedge_{\_}}$$

- λ_∞ or Λ_∞ is equivalent conductivity at infinite dilution. Where λ_v or Λ_v is equivalent conductivity at V dilution.
- $\lambda_v = K_v \times V$

  Here K_v = specific conductivity

  V = Volume of solution at V.
- $\lambda_\infty = \lambda_c + \lambda_\alpha$

  Here λ_α and λ_c are ionic mobilities of cations and anions.

Ionic product of water

- $K_w = K_a \times K_b$
- $pK_w = pK_a + pK_b$

pH scale

- $[H^+] = 10^{-pH}$
- $pH = -\log_{10} [H^+]$
- $pH = \log_{10} \frac{1}{[H^+]}$

pOH

$[OH^-] = 10^{-OH}$

$pOH = -\log[OH^-]$ or $\dfrac{1}{\log[OH^-]}$

Solubility product

$K_{sp} = [A^+][B^-]$ (At constant temperature)

$A_x\,B_y \rightleftharpoons xA^{+y} + YB^{-x}$

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

Relation between solubility (s) & solubility product (K_{sp})

$$K_{sp} = (x\ s)^x\ .\ (y\ s)^y$$

or

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

Degree of hydrolysis

$$h = \frac{\text{Number of moles of salt hydrolyzed}}{\text{Total moles of the salt taken}}$$

Various expressions for h, K_h and pH for different types of salts

For salt of weak base and strong acid (KCN)

$$K_h = \frac{K_w}{K_a}$$

$$h = \sqrt{(K_h / C)}$$

$$h = \sqrt{(K_w / K_a\ .C)}$$

$$pH = \frac{1}{2}[pK_w + pK_a + \log\ C]$$

$$pOH = \frac{1}{2}[pK_w - pK_a - \log\ C]$$

For salt of strong acid & weak base ($FeCl_3$)

$$K_h = \frac{K_w}{K_b}$$

$$h = \sqrt{(K_h / C)}$$

$$h = \sqrt{(K_w / K_b \, . C)}$$

$$pH = \frac{1}{2}[pK_w - pK_b - \log \; C]$$

For salt of weak acid & weak base

$$K_h = \frac{K_w}{K_b K_b}$$

$$h = \sqrt{(K_w / K_a \, .K_b)}$$

$$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$$

Q.1 In the reaction of BeF_2 with $2F^-$ to form BeF_4^{2-}, which reactant is the Lewis acid and which is the Lewis basie?

A.1 BeF_2 is the Lewis acid it can accept lone pair of electrons from $:\ddot{\underset{\cdot\cdot}{F}}^{-}$, and F^- is the Lewis base.

Q.2 Aniline ($C_6H_5NH_2$) is an weak organic base acid in aqueous solution Suggest a solvent in which aniline would become a strong base.

A.2 A solvent is needed which has appreciable stronger acid properties than H_2O; one such solvent is liquid acetic acid (CH_3COOH).

Q.3 Calculate the concentration of hydrogen ion in the acidic solution with pH = 4.3

A.3 $pH = -\log[H_3O^+]$

$\log[H_3O^+] = -4.3 = -4-0.3 + 1-1$

$= \bar{5}.7$

$\therefore [H_3O^+] = \text{Antilog}\,(\bar{5}.7)$

$= 5 \times 10^{-5}\ M = 0.5 \times 10^{-4}\ M$

Q.4 Calculate the concentration of OH in the solution of base with pH = 12.301.

A.4 $pH = 12.301$

$pOH = 14 - 12.301 = 1.699$

$pOH = -\log[\bar{O}H] = 1.699$

$\therefore \log[\bar{O}H] = 1.699 = -1 - 0.699 + 1 - 1$

$= \bar{2}.301$

$\therefore [\bar{O}H] = \text{Antilog}\,(\bar{2}.301)$

$= 2 \times 10^{-2}\ M = 0.2 \times 10^{-1}\ M$

Q.5 What amount of H_2SO_4 must be dissolved in 500 mL of soltuion to have a pH of 2.15?

A.5 pH = 2.15

$-\log[H^+] = 2.15$

$\log [H^+] = 2.15 = -2 - 0.15 + 1 - 1 = \bar{3}.85$

$[H^+] = \text{Antilog}\,(\bar{3}.85) = 7 \times 10^{-3}$ N

Strength of H_2SO_4 (g L^{-1}) = N × Ew

$$\left(\text{Ew of } H_2SO_4 = \frac{98}{2} = 49\right)$$

$= 7 \times 10^{-3} \times 49 = 0.343$ g L^{-1}

$= \frac{0.343 \times 500\,\text{mL}}{1000\,\text{mL}} = 0.171$ g

Q.6 Calculate the pH of solution made by two solution having pH = 1.5 and 2.5

A.6 The two pH values differ by one unit.

Approximate final $pH = \frac{(1.5 + 2.5)}{2} = 2$

Actual final pH = 2.0 - 0.24 = 1.76

Q.7 Calculate the pH of solution made by Three solution having pH = 2, 4 and 6.

A.7 Here also, the three pH value do not different by one unit so calculate the pH directly.

$$\left[H^+\right]_{\text{total}} = \left(\frac{10^{-2} + 10^{-4} + 10^{-6}}{3}\right) = \frac{10^{-2}}{3}\left(1 + 10^{-2} + 10^{-4}\right)\left(\text{Neglect } 10^{-2} \text{ and } 10^{-4}\right) = \frac{10^{-2}}{3}$$

$$pH = -\log\left[\frac{10^{-2}}{3}\right]$$

$$pH = -\log 10^{-2} + \log 3$$

$$pH = 2.48$$

Q.8 Calculate the Ionic constant of the conjugate acid of NH_3.(Given $K_b = 1.77 \times 10^{-5}$)

A.8 Ionic constant of conjugate acid $\left(NH_4^+\right)$

$$K_a = \frac{K_w}{K_b} = \frac{10^{-14}}{1.77 \times 10^{-5}} = 5.64 \times 10^{-10}$$

Q.9 What is the pH of the solution when 100 mL of 0.1 M HCl is mixed with 100 mL of 0.1 M CH_3COOH?

A.9 The diluted HCl is 0.1 M so that pH = 1.00.

With added strong acid present, the concentration of H^+ ions from ionisation of weak acid (CH_3COOH) is insignificant.

Q.10 Find the concentration of H^+, HCO_3^-, and CO_3^{-2} in a 0.01 M solution of carbonic acid if the pH of solution is 4.18. ($K_1 = 4.45 \times 10^{-7}$, $K_2 = 4.69 \times 10^{-11}$)

A.10 Given, pH = 4.18 = -log[H^+]

$\therefore$ [H^+] = 6.61×10^{-5} mol L^{-1}

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$K_1 = \frac{\left[H^+\right]\left[HCO_3^-\right]}{\left[H_2CO_3\right]}$$

$$\text{or } 4.45 \times 10^{-7} = \frac{\left[6.61 \times 10^{-5}\right]\left[HCO_3^-\right]}{[0.01]}$$

$$\text{or } \left[HCO_3^-\right] = 6.73 \times 10^{-5} \text{mol L}^{-1}$$

Again for dissociation of HCO_3^-, we have

$$\left[HCO_3^-\right] \rightleftharpoons H^+ + CO_2^{2-}$$

$$K_2 = \frac{\left[H^+\right]\left[CO_3^{2-}\right]}{\left[HCO_3^-\right]}$$

$$\text{or } 4.69 \times 10^{-11} = \frac{\left[6.61 \times 10^{-5}\right]\left[CO_3^{2-}\right]}{\left[6.73 \times 10^{-5}\right]}$$

$$\left[CO_3^{2-}\right] = 4.78 \times 10^{-11} \text{mol L}^{-1}$$

Q.11 Calculate the pH of a solution made by mixing 0.1 M NH_3 and 0.1 M $(NH_4)_2SO_4$. (pK_b of NH_3 = 4.76)

A.11 It is a basic buffer.

$[\text{Base}] = [NH_3] = 0.1\ \text{M}$

$[\text{Salt}] = [(NH_4)_2SO_4] = 0.1 \times 2 = 0.2\ \text{M}$

$$\left[(NH_4)_2\,SO_4 \rightarrow 2\overset{+}{N}H_4 + SO_4^{2-}\right]$$

$$\text{pOH} = pK_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= 4.76 + \log\frac{0.2\text{M}}{0.1\text{M}}$$

$$= 4.76 + \log 2$$

$$= 4.76 + 0.3 = 5.06$$

$$\therefore \quad \text{pH} = 14 - 5.03 = 8.94$$

Q.12 How many moles of HCl can be added to 1.0 L of solution of 0.1 M NH_3 and 0.1 M NH_4Cl without changing pOH by more than one unit? (pK_b of NH_3 = 4.75)

A.12 Proceed as above in part (a). Rule (BAB). In basic buffer (B), on adding a strong acid (A), the concentration of weak base (B) decreases and salt increases.

On adding the strong acid, pH decreases and pOH increases.

New pOH = 4.75 + 1 = 5.75.

$$\therefore 5.75 = 4.75 + \log\left[\frac{0.1+x}{0.1-x}\right]$$

$$5.75 - 4.75 = \log\left[\frac{0.1+x}{0.1-x}\right]$$

$$1 = \log\left[\frac{0.1+x}{0.1-x}\right]$$

Taking antilong both sides

$$10 = \frac{0.1+x}{0.1-x}$$

$$1 - 10x = 0.1 + x$$

$$11x = 0.9 \Rightarrow x = \frac{0.9}{11} = 0.082\,\text{mol.}$$

$$x = 0.082\ \text{mol} = 0.082\,\text{M}\,(V = 1\text{L})$$

Q.13 Calculate the degree of hydrolysis and pH of 0.02 M ammonium cyanide (NH_4CN) at 298K. (K_a of HCN = 4.99×10^{-9}, K_b for NH_4OH = 1.77×10^{-5})

A.13

$$K_h = \frac{10^{-14}}{4.99 \times 10^{-9} \times 1.77 \times 10^{-5}} = 1.132$$

It can be seen that hydrolysis constant (K_h) is not small, and for calculating h, the equation used is

$$h = \frac{\sqrt{K_h}}{1+\sqrt{K_h}} = \frac{\sqrt{1.132}}{1+\sqrt{1.132}} = \frac{1.06}{1+1.06} = \frac{1.06}{2.06} = 0.51$$

Using the formula

$$\begin{aligned} pH &= pK_a - \log(h) + \log(1-h) \\ &= -\log\left(4.99 \times 10^{-10}\right) - \log(0.51) + \log(1-0.51) \\ &= 9.30 \end{aligned}$$

Q.14 Arrange the following bases in order of decreasing basicity:
S^{2-}, CH_3COO^-, CN^-, NH_3, F^-

A.14 Stronger the acid, weaker its conjugate base and vice versa.

First arrange them in decreasing acidic character.

$HF > CH_3COOH > NH_4^+ > HCN > HS^-$

Therefore, the decreasing order of basic character

$S^{2-} > SN^- > NH_3 > CHCOO^- > F^-$

Q.15 Arrange the following 0.1M solutions in order of increasing pH:
H_2CO_3, KBr, HI, NH_3, KCN, NaOH, NH_4Br

A.15 Stronger the acid, less is the pH, stronger the base, high is the pH. Increasing order of pH:

$HI < H_2CO_3 < NH_4Br < KBr < NH_3 < KCN < NaOH$

Q.16 Calculate the pH at which an acid indicator with $K_a = 1.0 \times 10^{-5}$ changes colour when the indicator is 1.00×10^{-3}M.

A.16 The point at which acid and conjugate base forms of acid indicator are present in equal concentration is known as the midpoint of the colour change range of an indicator, hence

$$K_{ind} = \frac{\left[H_3O^+\right]\left[In^-\right]}{[HIn]} = \left[H_3O^+\right] = 1.0 \times 10^{-5}$$

and pH = 5.00

Q.17 At what pH will a 1.0×10^{-3} M solution of an indicator with $K_b = 1.0 \times 10^{-10}$ changes colour?

A.17 The indicator changes colour when the conjugates are equal to concentration.

$$K_{ind} = \frac{[HIn]\left[\overset{-}{O}H\right]}{[HIn]} = \left[\overset{-}{O}H\right] = 1.0 \times 10^{-10}$$

thus $pOH = 10.00$ and $pH = 4.00$

Q.18 Calculate the pH at which an indicator with $pK_b = 4$ changes colour.

A.18

$$In^- + H_2O \rightleftharpoons HIn + \overset{-}{O}H$$

At the colour change, $\left[In^-\right] = [HIn]$

$$K_b = \frac{\left[\overset{-}{O}H\right][HIn]}{\left[In^-\right]} = 1.0 \times 10^{-4} = \left[\overset{-}{O}H\right]$$

and pOH = 4.0

$\therefore$ pH = 10.00

Q.19 Determine the solubility of AgCl.

A.19 For AgCl, K_{sp} = 1.8 × 10^{-10}, hence

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

$$K_{sp} = \left[Ag^+\right]\left[Cl^-\right]$$

$$K_{sp} = S^2M^2$$

i. $S/M = \left(1.8 \times 10^{-10}\right)^{1/2} = 1.34 \times 10^{-5}$.

$\left[Ag^+\right] = \left[Cl^-\right]; S = 1.34 \times 10^{-5}\,mol\,L^{-1}$

ii. S of AgCl in $gL^{-1} = 1.34 \times 10^{-5} \times 143.35g\ mol^{-1}$

$= 1.92 \times 10^{-3}\,gL^{-1}$

Q.20 Let the solubilities of AgBr in water and in 0.01M $CaBr_2$, 0.01 M KBr, and 0.05M $AgNO_3$ be S_1, S_2, S_3 and S_4 respectively. Give the decreasing order of the solutbilitys.

A.20 i. $AgBr + H_2O \longrightarrow Ag^+(aq) + Br^-(aq)$ ....(s_1)

ii. AgBr in 0.01 M $CaBr_2$ ....(s_2)

$\left[Br^-\right]$ added = 0.01 × 2 = 0.02 M

iii. AgBr in 0.01 M KBr ....(s_3)

$\left[Br^-\right]$ added = 0.01 M

iv. AgBr in 0.05 M $AgNO_3$ ....(s_4)

$\left[Ag^+\right]$ added = 0.05 M

Since both Br^- ions and Ag^+ ions act as common ions, so larger the concentration of Br^- or Ag^+ ion added, more is the suppression of ionissation of Agbr and hence less will the solubility of AgBr.

Therefore, the decreasing solubility order:

$S_1 > S_3 > S_2 > S_4$

Q.21 A solution contains 0.01 M each of $CaCl_2$ and $SrCl_2$. A 0.005M solution of SO_4^{2-} is slowly added the given solution. (a) If H_2SO_4 is containuously added, determien when will other salt be precipitated?

A.21 Now, If SO_4^{2-} ions are continuously added, at some instant, its concentration will become equal to that minimum required for precipitating out Ca^{2+} ions. Hence $CaSO_4$ will start precipitating if,

$[SO_4^{2-}] = 1.3 \times 10^{-2}$ M.

Q.22 The solubility of silver benozate (PhCOOAg) in H_2O and in solution of pH = 4, 5, and 6 are S_1, S_2, S_3 and S_4, respectively. Given the decreasing order of their solubilities.

A.22 Solubility of a salt of W_A increases with the increase in $[H^+]$ or increases at lower pH. Thus, decreasing order of solubility is

$S_2 > S_3 > S_4 > S_1$

Q.23 Explain why CoS is more soluble than predicted by the K_b.

A.23 Not all the sulphide which dissolves remains as S^{2-}, most of it hydrolyses.

$$S^{2-} + H_2O \rightleftharpoons HS^- + OH$$

Q.24 Explain why CuS is more soluble than predicated by the K_{sp}.

A.24 The S^{2-} hydrolyses extensively. The amount which dissolves and the amount which exists as S^{2-} in solution are very different.

Q.25 The solubility of CuS in pure water at 25°C is 3.3×10^{-4}g L^{-1}. Calculate K_{sp} of CuS. The accurate value of K_{sp} of Cus was found to be 8.5×10^{-36} at 25°C

A.25 $$CuS \longrightarrow Cu^{2+} + S^{2-}$$

$$S = \frac{3.3 \times 10^{-4}\,g\,L^{-1}}{95.6\,g\ mol^{-1}} = 3.5 \times 10^{-6} M$$

$$\text{Apparent } K_{sp} = \left(3.5 \times 10^{-6}\right)^2 = 1.2 \times 10^{-11}.$$

Q.26 Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNiC. Calculate its percent dissociation in a solution which contains 0.10 moles of nicotinic acid per 2.0 L of solution.

A.26 Given,

$$\begin{array}{lcccc} \text{HNiC} & \rightleftharpoons & H^+ & + & \text{NiC}^- \\ 1 & & 0 & & 0 \\ 1-\alpha & & \alpha & & \alpha \end{array}$$

Also,

$$C = 0.1/2 = 5\times10^{-2}\,\text{mol}\,L^{-1},\ K_a = 1.4\times10^{-5}$$

$$\therefore \quad K_a = \frac{C\alpha^2}{(1-\alpha)} = C\alpha^2$$

$$\alpha = \sqrt{K_a/C} = \sqrt{\frac{1.4\times10^{-5}}{5\times10^{-2}}} = 1.67\times10^{-2} \text{ or } 1.67\%$$

Q.27 For the indicator 'HIn' the ratio $(\text{Ind}^-)/(\text{HIn})$ is 7.0 at pH of 4.3. What is K_{eq} for the indicator?

A.27 $\text{pH} = 4.3, \left[H^+\right] = 5.0\times10^{-5}\,M$

$$\text{HIn} \rightleftharpoons H^+ + \text{In}^-$$

$$K_{eq} = \frac{\left[H^+\right]\left[\text{In}^-\right]}{[\text{HIn}]}$$

$$= \left(5.0\times10^{-5}\right)(7.0) = 3.5\times10^{-4}\,M$$

Q.28 Determine $\left[OH^-\right]$ of a 0.050 M solution of ammonia to which sufficient NH_4Cl has been added to make the total $\left[NH_4^+\right]$ equal to 0.1 M.

A.28 $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

$$K_b = \frac{\left[NH_4^+\right]\left[OH^-\right]}{\left[NH_3\right]} = \frac{(0.1)x}{(0.050)} = 1.8\times10^{-5}$$

thus

$$x = \left[OH^-\right] = 9.0\times10^{-6}$$

Chapter Summary

1. Based on Ingold concept, an electrophile is an acid whereas a nucleophile is a base.
   For ex. $AlCl_3$ is an acid and NH_3 is a base.
2. In the reaction $I_2 + I^- \longrightarrow I_3^-$, the Lewis base is I^-.
3. $\underset{\text{Acid}}{[Fe(H_2O)_6]^{3+}} + \underset{\text{Base}}{H_2O} \longrightarrow \underset{\text{Conjugate base}}{[Fe(H_2O)_5\,OH]^{2+}} + \underset{\text{Conjugate acid}}{H_3O^+}$
4. $\underset{\text{Base}}{[Zn(H_2O)_5\,OH]^{2+}} + \underset{\text{Acid}}{H_3O^+} \longrightarrow \underset{\text{Conjugate acid}}{[Fe(H_2O)_6\,O]^{3+}} + \underset{\text{Conjugate base}}{H_2O^+}$
5. Salt hydrolysis is the reaction of a anion or cation with H_2O accompanied by cleavage of O–H bond.
6. A change of even 0.2 unit in pH of blood causes death also.
7. $H_2CO_3 + NaHCO_3$ is the buffer system present in blood.
8. In case of strong acid with 10^{-8}M concentration pH is 6.95 and in case of strong base with same concⁿ pH is 7.0414.

   (H^+) from $H_2O = 1 \times 10^{-7}$

   (H^+) from acid $= 1 \times 10^{-8}$

   Net $(H^+) = 1.1 \times 10^{-7}$

   $pH = -\log [1.1 \times 10^{-7}] = 6.95$

   Similarly, for base [O– H] Net $= 1.1 \times 10^{-8}$

   $pOH = 6.95$

   $pH = 14 - 6.95 = 7.05$