UNIT – 8 – IONIC EQUILIBRIUM

II. Answer the following questions:

1. What are Lewis acids and bases? Give two example for each. [MAR-20, AUG-22]

Lewis acid: A Lewis acid is a positive ion (or) an electron deficient molecule.

Eg.: BF_3, $AlCl_3$, BeF_2.

Lewis base: A Lewis base is a anion (or) neutral molecule with at least one pair of electrons.

Eg.: NH_3, R-NH_2, F^-, Cl^-.

2. Discuss the Lowry – Bronsted concept of acids and bases. [PTA3, HY22, MAR23, SUT24]

According to their **Lowry – Bronsted Theory (Proton Theory)** concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton from other substance. In other words, an acid is a proton donor and a base is a proton acceptor.

When hydrogen chloride is dissolved in water, it donates a proton to the later. Thus, HCl behaves as an acid and H_2O is base. The proton transfer from the acid to base can be represented as

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

When ammonia is dissolved in water, it accepts a proton from water. In this case, ammonia (NH_3) acts as a base and H_2O is acid. The reaction is represented as

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

Let us consider the reverse reaction in the following equilibrium

$$\underset{\text{Proton donar (acid)}}{HCl} + \underset{\text{Proton acceptor (Base)}}{H_2O} \rightleftharpoons \underset{\text{Proton donar (acid)}}{H_3O^+} + \underset{\text{Proton acceptor (Base)}}{Cl^-}$$

H_3O^+ donates a proton to Cl^- to form HCl i.e., the products also behave as acid and base.

In general, Lowry – Bronsted (acid – base) reaction is represented as

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

The species that remains after the donation of a proton is a base ($Base_1$) and is called the conjugate base of the Bronsted acid ($Acid_1$). In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.

Conjugate acid - base pair

$$\underset{\text{Proton donar (acid)}}{HCl} + \underset{\text{Proton acceptor (Base)}}{H_2O} \rightleftharpoons \underset{\text{Proton donar (acid)}}{H_3O^+} + \underset{\text{Proton acceptor (Base)}}{Cl^-}$$

Conjugate acid - base pair

HCl and Cl^-, H_2O and H_3O^+ are two conjugate acid – base pairs. i.e., Cl^- is the conjugate base of the acid HCl . (or) HCl is conjugate acid of Cl^-. Similarly H_3O^+ is the conjugate acid of H_2O.

3. Indentify the conjugate acid base pair for the following reaction in aqueous solution

i) $HS^-_{(aq)} + HF \rightleftharpoons F^-_{(aq)} + H_2S_{(aq)}$ **[SRT-22]** **ii)** $HPO_4^{2-} + SO_3^{2-} \rightleftharpoons PO_4^{3-} + HSO_3^-$

iii) $NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$ **[SRT-22]**

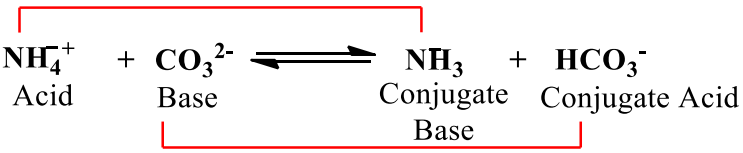
(i)

$$\underset{\text{Base}}{HS^-_{(aq)}} + \underset{\text{Acid}}{HF} \rightleftharpoons \underset{\text{Conjugate Base}}{F^-_{(aq)}} + \underset{\text{Conjugate Acid}}{H_2S_{(aq)}}$$

(ii)

$$\underset{\text{Acid}}{HPO_4^{2-}} + \underset{\text{Base}}{SO_3^{2-}} \rightleftharpoons \underset{\text{Conjugate Base}}{PO_4^{3-}} + \underset{\text{Conjugate Acid}}{HSO_3^-}$$

(iii)



4. Account for the acidic nature of $HClO_4$ in terms of Bronsted – Lowry theory, identify its conjugate base.

$$HClO_4 \rightleftharpoons H^+ + ClO_4^-$$

- According to Lowry – Bronsted concept, a strong acid has weak conjugate base and a weak acid has a strong conjugate base.
- Let us consider the stabilities of the conjugate bases ClO_4^-, ClO_3^-, ClO_2^- and ClO^- formed from these acid $HClO_4$, $HClO_3$, $HClO_2$, HOCl respectively.
- These anions are stabilized to greater extent, it has lesser attraction for proton and therefore, will behave as weak base. Consequently, the corresponding acid will be strongest because weak conjugate base has strong acid and strong conjugate base has weak acid.
- The charge stabilization mercases in the order, $ClO^- < ClO_2^- < ClO_3^- < ClO_4^-$.
- This means ClO_4^- will have maximum stability and therefore will have a minimum attraction for W. Thus ClO_4^- will be weakest base and its conjugate acid $HClO_4$ is the strongest acid.
- ClO_4^- is the conjugate base of the acid $HClO_4$.

5. When aqueous ammonia is added to $CuSO_4$ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, $[Cu(H_2O)_4]_{(aq)}^{2+} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}{}_{(aq)}$, among H_2O and NH_3 Which is stronger Lewis base.

$$\mathbf{[Cu(H_2O)_4]_{(aq)}^{2+} + 4NH_{3(aq)} \rightleftharpoons [Cu(NH_3)_4]^{2+}{}_{(aq)} + 4H_2O}$$

- Nitrogen less electronegative than oxygen and donates its lone pair of electrons readily. Hence NH_3 is a stronger Lewis base.
- If a batter Lewis base (ligand) is available, a Lewis acid (central metal ion) will react (ligand exchange reaction).
- In this reaction H_2O is exchanged with NH_3.
- The Lewis acid Cu^{2+} exchange the Lewis base H_2O with better Lewis base NH_3 to form $[Cu(NH_3)_4]^{2+}$.
- Hence NH_3 is a stronger Lewis base than H_2O in this reaction.

6. The concentration of hydroxide ion in a water sample is found to be 2.5×10^{-6} M. Identify the nature of the solution.

$[OH^-] = 2.5 \times 10^{-6}$M

pOH $= -\log[OH^-] = -\log(2.5 \times 10^{-6}) = -\log(2.5) + (-\log(10^{-6})) = -0.3979 + 6$

pOH $= 5.6021$

pH + pOH = 14 $\Rightarrow$ pH = 14 – pOH $= 14 - 5.6021 =$ **8.3979**

$\therefore$pH is 8.3979 (greater than 7). So, the solution is **basic**.

7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas at 25°C to get a solution with $[H_3O^+] = 4 \times 10^{-5}$ M. Is the solution neutral (or) acidic (or) basic.

$[H_3O^+] = 4 \times 10^{-5}$M

$pH = -\log_{10}[H_3O^+] = -\log(4 \times 10^{-5}) = -\log(4) + (-\log(10^{-5})) = -0.6021 + 5 =$ **4.3979**

since pH is less than 7, the solution is **acidic**.

8. Calculate the pH of 0.04 M HNO_3 Solution.

Concentration of HNO_3 = Normality = Molarity× Basicity = 0.04M × 1 = 0.04M = 4×10^{-2} M;

$pH = -\log_{10}[H_3O^+] = -\log(4 \times 10^{-2}) = -\log(4) + (-\log(10^{-2})) = -0.6021 + 2 =$ **1.3979**

$\therefore$pH = **1.40**

9. Define solubility product. [PTA-1, HY-19, SUT-24, MAR-25]

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

$$K_{sp} = [X^{n+}]^m\ [Y^{m-}]^n$$

10.Define ionic product of water. Give its value at room temperature. [PTA-5, SEP-20, QY-24, SRT-25]

Ionic product of water (kW) is given by the product of concentration of hydronium (H_3O^+) and hydroxide (OH^-) ion.

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

$$K_{eq} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

Since water is a solvent and is taken in excess, change in concentration due to dissociation is negligible.

$\therefore K_{eq} = [H_2O]^2 = [H_3O^+]\ [OH^-] = kW$

At 298K (25°C) $kW = 1 \times 10^{-14}\ mol^2dm^{-6}$.

11.Explain common ion effect with an example. [PTA-4, JUN-20, QY-22,24, MAY-22,24]

When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid is suppressed further. For example, the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case, CH_3COOH and CH_3COONa have the common ion, CH_3COO^-

Eg: Acetic acid is a weak acid. It is not completely dissociated in aqueous solution and hence the following equilibrium exists.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

However, the added salt, sodium acetate, completely dissociates to produce Na^+ and CH_3COO^- ion. $CH_3COONa_{(aq)} \rightarrow Na^+_{(aq)} + CH_3COO^-_{(aq)}$

Hence, the overall concentration of CH_3COO^- is increased, and the acid dissociation equilibrium is disturbed. We know from Le chatelier's principle that when a stress is applied to a system at equilibrium, the system adjusts itself to nullify the effect produced by that stress. So, inorder to maintain the equilibrium, the excess CH_3COO^- ions combines with H^+ ions to produce much more unionized CH_3COOH i.e, the equilibrium will shift towards the left. In other words, the dissociation of CH_3COOH is suppressed. Thus, the dissociation of a weak acid (CH_3COOH) is suppressed in the presence of a salt (CH_3COONa) containing an ion common to the weak electrolyte. It is called the common ion effect.

12.Derive an expression for Ostwald's dilution law. [PTA-1&3, JUN-20, QY,HY,SRT-22, APR-23, SUT-24]

Ostwald's dilution law relates the dissociation constant of the weak acid (K_a) with its degree of dissociation (α) and the concentration (c). Degree of dissociation (α) is the fraction of the total number of moles of a substance that dissociates at equilibrium.

$$\alpha = \frac{Number\ of\ moles\ dissociated}{Total\ no\ of\ moles}$$

We shall derive an expression for ostwald's law by considering a weak acid, i.e. acetic acid (CH_3COOH). The dissociation of acetic acid can be represented as

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

The dissociation constant of acetic acid is, $Ka = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]}$ --------**(1)**

	CH_3COOH	H^+	CH_3COO^-
Initial number of moles	1	-	-
Degree of dissociation of CH_3COOH	α	-	-
Number of moles at equilibrium	1 – α	α	α
Equilibrium concentration	(1 – α)C	αC	αC

Substituting the equilibrium concentration in equation (1)

$$K_a = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C} = \frac{\alpha^2 C}{1-\alpha} \qquad \text{--------(2)}$$

We know that weak acid dissociates only to a very small extent. Compared to one, α is so small and hence in the denominator (1 – α) ≈ 1. The above expression (2) now becomes,

$K_a = \alpha^2 C$; $\Rightarrow \alpha^2 = \frac{K_a}{C}$; $\Rightarrow \alpha = \sqrt{\frac{K_a}{C}}$

13.Define pH. [MAY-22, SUT-24, MAR-25]

The term pH is derived from the French word *'Purissance de hydrogene'* meaning, the power of hydrogen. pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$\mathbf{pH = - \log_{10}[H_3O^+]}$$

14.Calculate the pH of 1.5×10^{-3} M solution of $Ba(OH)_2$.

$$Ba(OH)_2 \rightarrow Ba^{2+} + 2OH^-$$
$$\mathbf{1.5 \times 10^{-3} M} \qquad \mathbf{2 \times 1.5 \times 10^{-3} M}$$

$[OH^-] = 3 \times 10^{-3}$M [∵ pH + pOH = 14]

pH = 14 – pOH

pH = 14 – (- log$[OH^-]$) = 14 + log$[OH^-]$ = 14 + log(3×10^{-3}) = 14 + log3 + log10^{-3}

pH = 14 + 0.4771 – 3 = 11 + 0.4771 = 11.4771 ≈ 11.48. ∴ **pH = 11.48**

15.50ml of 0.05M HNO_3 is added to 50ml of 0.025M KOH. Calculate the pH of the resultant solution. [GMQ-19]

Number of moles $HNO_3 = 0.05 \times 50 \times 10^{-3} = 2.5 \times 10^{-3}$

Number of moles $KOH = 0.025 \times 50 \times 10^{-3} = 1.25 \times 10^{-3}$

Number of moles HNO_3 after mixing = $(2.5 \times 10^{-3}) – (1.25 \times 10^{-3}) = 1.25 \times 10^{-3}$

∴ concentration of $HNO_3 = \frac{Number\ of\ moles\ of\ HNO_3}{Volume\ in\ litre}$

After mixing, total volume = 100ml = 100×10^{-3}L

∴ $[H^+] = \frac{1.25 \times 10^{-3}\ moles}{100 \times 10^{-3} L} = 1.25 \times 10^{-2}$mol L^{-1}

pH = -log $[H^+]$ = -log (1.25×10^{-2}) = -log(1.25) – log(10^{-2}) = -0.0969 + 2 = **1.9031**

16.The K_a value for HCN is 10^{-9}. What is the pH of 0.4M HCN solution? [PTA-5]

$K_a = 10^{-9}$; C = 0.4M; pH = -log$[H^+]$;

$[H^+] = \sqrt{K_a \times C} = \sqrt{10^{-9} \times 0.4} = \sqrt{10^{-10} \times 4} = 2 \times 10^{-5}$

∴ pH = -log $[H^+]$ = -log (2×10^{-5}) = -log(2) – log(10^{-5}) = -0.3010 + 5 = **4.699**

17.Calculate the extent of hydrolysis and the pH of 0.1 M ammonium acetate Given that $K_a = K_b = 1.8 \times 10^{-5}$.

$h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}} = \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 1.8 \times 10^{-5}}} = \sqrt{\frac{1 \times 10^{-4}}{1.8 \times 1.8}} = \sqrt{0.3086 \times 10^{-4}} = 0.5555 \times 10^{-2}$

∵ $K_a = K_b$; $\Rightarrow pK_a = pK_b$; $\Rightarrow pK_w = 14$;

$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b = \frac{1}{2}pK_w + 0 = \frac{1}{2} \times 14 = 7.$ **∴pH = 7**

18.Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base. [FRT-25]

Consider the reactions between a strong acid, HCl, and a weak base, NH_4OH, to produce a salt, NH_4Cl, and water.

$$HCl_{(aq)} + NH_4OH_{(aq)} \rightleftharpoons NH_4Cl_{(aq)} + H_2O_{(l)}$$
$$NH_4Cl_{(aq)} \rightarrow NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$$

NH_4^+ is a strong conjugate acid of the weak base $NH_4OH$and it has a tendency to react with OH^- from water to produce unionised NH_4OH shown below.

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_4OH_{(aq)} + H^+{}_{(aq)}$$

There is no such tendency shown by Cl^- and therefore $[H^+] > [OH^-]$; the solution is acidic and the pH is less than 7.

As discussed in the salt hydrolysis of strong base and weak acid. In this case also, we can establish a relationship between the K_h and K_b as

$$K_h.K_b = K_w \qquad \Rightarrow K_h = \frac{K_w}{K_b}$$

Let us calculate the K_h value in terms of degree of hydrolysis (h) and the concentration of salt

$K_h = h^2C$ and $[H^+] = \sqrt{K_h.C} = \sqrt{\frac{K_w}{K_b}.C}$

$pH = -\log[H^+] = -\log\left(\frac{K_w.C}{K_b}\right)^{\frac{1}{2}} = -\frac{1}{2}\log K_w - \frac{1}{2}\log C + \frac{1}{2}\log K_b = \mathbf{7 - \frac{1}{2}pK_b - \frac{1}{2}\log C}$

19.Solubility product of Ag_2CrO_4 is 1×10^{-12}. What is the solubility of Ag_2CrO_4 in 0.01M $AgNO_3$ solution?

Given: $K_{sp} = 1 \times 10^{-12}$;

Solubility: $Ag_2CrO_4 \rightleftharpoons 2Ag^+ + CrO_4^{2-}$; ***Concentration:*** $AgNO_3 \rightarrow Ag^+ + NO_3^-$;

S **2S** **S** **0.01M** **0.01M** **0.01M**

$[Ag^+] = 0.01 + 2s$ {$\because$ 0.01>>2s, so, 2s can be neglected}

$\therefore$ So, $[Ag^+] = 0.01$; $\Rightarrow [CrO_4^{2-}] = S$;

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

$1 \times 10^{-12} = (1 \times 10^{-2})^2 (S)$; $\Rightarrow S = \frac{1 \times 10^{-12}}{(1 \times 10^{-2})^2} = \frac{1 \times 10^{-12}}{1 \times 10^{-4}} = 1 \times 10^{-12} \times 10^{+4} = \mathbf{1 \times 10^{-12}M}$

20.Write the expression for the solubility product of $Ca_3(PO_4)_2$. [SRT-22]

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

s **3s** **2s**

$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2 = (3s)^3 (2s)^2 = 27s^3 \times 4s^2 = \mathbf{108s^5}$

21.A saturated solution, prepared by dissolving $CaF_{2(s)}$ in water, has $[Ca^{2+}] = 3.3 \times 10^{-4}$ M. What is the K_{sp} of CaF_2?

$CaF_{2(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2F^-{}_{(aq)}$

3.3×10^{-4}M **$2\times3.3\times10^{-4}$M**

$K_{sp} = [Ca^{2+}][F^-]^2 = (3.3\times10^{-4})(2\times3.3\times10^{-4})^2 = 3.3\times6.6\times6.6\times10^{-4}\times10^{-8} = 143.748 \times 10^{-12}$

$\mathbf{K_{sp} = 1.44 \times 10^{-10}}$

22.K_{sp} of AgCl is 1.8×10^{-10}. Calculate molar solubility in 1 M $AgNO_3$.

$AgCl_{(s)} \rightleftharpoons Ag^+{}_{(aq)} + Cl^-{}_{(aq)}$

x = solubility of AgCl in 1M $AgNO_3$

$AgNO_{3(aq)} \rightleftharpoons Ag^+{}_{(aq)} + NO_3^-{}_{(aq)}$

1M **1M**

$[Ag^+] = x + 1 \approx 1M$ ($\because x << 1$) $\Rightarrow [Cl^-] = x$

$K_{sp} = [Ag^+][Cl^-]$; $\Rightarrow 1.8 \times 10^{-10} = (1)(x)$; $\Rightarrow \mathbf{x = 1.8 \times 10^{-10}}$

23.A particular saturated solution of silver chromate Ag_2CrO_4 has $[Ag^+] = 5 \times 10^{-5}$ and $[CrO_4^{2-}] = 4.4 \times 10^{-4}$ M. What is the value of K_{sp} for Ag_2CrO_4?

$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}] = (5 \times 10^{-5})^2 (4.4 \times 10^{-4}) =$ **1.1×10^{-12}**

24.Write the expression for the solubility product of Hg_2Cl_2. [HY-24]

$Hg_2Cl_2 \rightleftharpoons Hg_2^{2+} + 2Cl^-$

S S 2S

$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (S)(2S)^2 = (S)(4S^2) =$ **$4S^3$**.

25.K_{sp} of Ag_2CrO_4 is 1.1×10^{-12}. What is solubility of Ag_2CrO_4 in 0.1M K_2CrO_4. [GMQ19]

$Ag_2CrO_{4(s)} \rightleftharpoons 2Ag^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$

x **2*x*** ***x***

x is the solubility of Ag_2CrO_4 in 0.1M K_2CrO_4

$K_2CrO_{4(s)} \rightleftharpoons 2K^+_{(aq)} + CrO_4^{2-}{}_{(aq)}$

0.1M 2(0.1M) 0.1M

$[CrO_4^{2-}] = (x + 0.1) \approx 0.1$ $[\because x << 0.1]$

$K_{sp} = [Ag^+]^2[CrO_4^{2-}]$; $1.1 \times 10^{-12} = (2x)^2 (0.1) = 0.4x^2$

$x^2 = \frac{1.1 \times 10^{-12}}{0.4}$; $\Rightarrow x = \sqrt{\frac{1.1 \times 10^{-12}}{0.4}} = \sqrt{2.75 \times 10^{-12}} =$ **1.65×10^{-6}M**

26.Will a precipitate be formed when 0.150 L of 0.1M $Pb(NO_3)_2$ and 0.100 L of 0.2 M NaCl are mixed? K_{sp} ($PbCl_2$) = 1.2×10^{-5}.

When two are more solution are mixed, the resulting concentrations are different from the original.

Total volume = 0.250L

$Pb(NO_3)_2 \rightleftharpoons Pb^{2+} + 2NO_3^-$

0.1M 0.1M 0.2M

Number of moles, Pb^{2+} = molarity × Volume of the solution in litre = 0.1 × 0.5

$[Pb^{2+}]_{mix} = \frac{0.1 \times 0.15}{0.25} = 0.06M$

$NaCl \rightleftharpoons Na^+ + Cl^-$

0.2M 0.2M 0.2M

Number of moles, Cl^- = molarity × Volume of the solution in litre = 0.2 × 0.1

$[Cl^-]_{mix} = \frac{0.2 \times 0.1}{0.25} = 0.08M$

Precipitation of $PbCl_{2(s)}$ occurs if $[Pb^{2+}][Cl^-]^2 > K_{sp}$

$[Pb^{2+}][Cl^-]^2 = (0.06)(0.08)^2 =$ **3.84×10^{-4}**

Since ionic product $[Pb^{2+}][Cl^-]^2 > K_{sp}$ is precipitated.

27.K_{sp} of $Al(OH)_3$ is 1×10^{-15} M. At what pH does 1.0×10^{-3} M Al^{3+} precipitate on the addition of buffer of NH_4Cl and NH_4OH solution?

$Al(OH)_3 \rightleftharpoons Al^{3+}_{(aq)} + 3OH^-_{(aq)}$

$K_{sp} = [Al^{3+}][OH^-]^3$

$Al(OH)_3$ Precipitates when, $[Al^{3+}][OH^-]^3 > K_{sp}$; $\Rightarrow [1 \times 10^{-3}][OH^-]^3 > 1 \times 10^{-15}$;

$[OH^-]^3 > 1 \times 10^{-15} \times 1 \times 10^{+3}$; $\Rightarrow [OH^-]^3 > 1 \times 10^{-12}$; $\Rightarrow [OH^-] \geq 1 \times 10^{-4}$ M

$pOH = -\log_{10}[OH^-] = -\log_{10}(1 \times 10^{-4}) = 4$

$pH + pOH = 14$

$pH = 14 - pOH$

$pH = 14 - 4 =$ **10**

Thus, $Al(OH)_3$ precipitates at a pH of 10.

EVALUATE YOURSELF

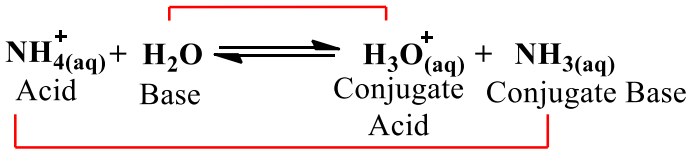
1. Classify the following as acid (or) base using Arrhenius Concept (i) HNO_3, (ii) $Ba(OH)_2$, (iii) H_3PO_4 and (iv) CH_3COOH.

Acid: (i) HNO_3, (ii) H_3PO_4 and (iii) CH_3COOH.

Base: (i) $Ba(OH)_2$

2. Write a balanced equation for the dissociation of the following in water and identify the conjugate acid-base pairs. (i) NH_4^+ , (ii) H_2SO_4 , (iii) CH_3COOH

(i)



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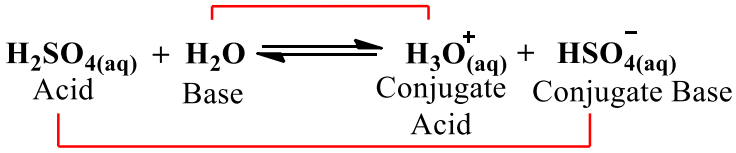

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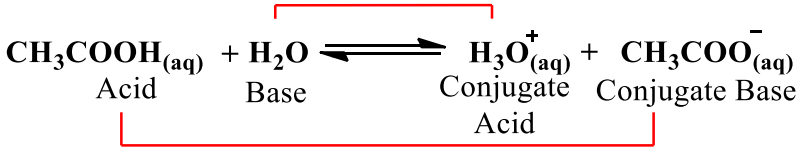


3. Identify the Lewis acid and the Lewis base in the following reactions,

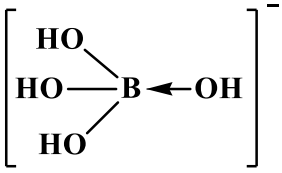
(i) $CaO + CO_2 \rightarrow CaCO_3$

(ii) $CH_3\text{-}O\text{-}CH_3 + AlCl_3 \rightarrow$

(i) CaO – Lewis base; CO_2 – Lewis acid

(ii) $H_3C\text{-}O\text{-}CH_3$ – Lewis base; $AlCl_3$ – Lewis acid

4. H_3BO_3 accepts OH^- ion from water as shown below, $H_3BO_{3(aq)} + H_2O_{(l)} \rightleftharpoons B(OH)_4^- + H^+$, predict the nature of H_3BO_3 using Lewis concept.



; electron pair acceptor – Lewis acid

5. At a particular temperature, the K_w of a neutral solution was equal to 4×10^{-14}. Calculate the concentration of $[H_3O^+]$ and $[OH^-]$.

Given solution is neutral, $\therefore [H_3O^+] = [OH^-]$

Let $[H_3O^+] = x$; then $[OH^-] = x$

$K_w = [H_3O^+][OH^-]$; $\Rightarrow 4 \times 10^{-14} = x \cdot x$; $\Rightarrow x^2 = 4 \times 10^{-14}$

$x = \sqrt{4 \times 10^{-14}} = \mathbf{2 \times 10^{-7}}$

6. (a) Calculate pH of 10^{-8} M H_2SO_4 [QY-23]

(b) Calculate the concentration of hydrogen ion in moles per litre of a solution whose pH is 5.4 [QY-22, SRT-24]

(c) Calculate the pH of an aqueous solution obtained by mixing 50ml of 0.2M HCl with 50ml 0.1M NaOH.

(a) $H_2SO_4 \overset{H_2O}{\rightleftharpoons} 2H_3O^+ + SO_4^{2-}$

$\quad 10^{-8}M \qquad 2\times10^{-8}M \qquad 10^{-8}M$

In this case the concentration of H_2SO_4 is very low and hence $[H_3O^+]$ from water cannot be neglected.

$\therefore [H_3O^+] = 2 \times 10^{-8}$ (from H_2SO_4) + 10^{-7} (from water) = $(2\times10^{-8}) + (10\times10^{-8}) = (2+10)\times10^{-8}$

$\therefore [H_3O^+] = 12 \times 10^{-8} = 1.2 \times 10^{-7}$

$pH = -\log_{10}[H_3O^+] = -\log_{10}(1.2 \times 10^{-7}) = (-\log(1.2)) + (-\log(10^{-7})) = -0.0791 + 7 = \mathbf{6.9209}$

(b) pH of the solution = 5.4

$[H_3O^+]$ = antilog of (-pH) = antilog of (-5.4) = 0.000003981 = $\mathbf{3.981 \times 10^{-6}\ mol\ dm^{-3}}$

(c) No. of moles of HCl = $0.2 \times 50 \times 10^{-3} = 10 \times 10^{-3}$

No. of moles of NaOH = $0.1 \times 50 \times 10^{-3} = 5 \times 10^{-3}$

No. of moles of HCl after mixing = $(10 \times 10^{-3}) - (5 \times 10^{-3}) = 5 \times 10^{-3}$

After mixing total volume = 100ml

$\therefore$ Concentration of HCl in moles per litre = $\frac{5 \times 10^{-3}\ mol}{100 \times 10^{-3}\ L} = 5 \times 10^{-2}$; $[H_3O^+] = \mathbf{5 \times 10^{-2} M}$

$pH = -\log(5 \times 10^{-2}) = -\log(5) + (-\log(10^{-2})) = -0.6990 + 2 = \mathbf{1.30}$

7. K_b for NH_4OH is 1.8×10^{-5}. Calculate the percentage of ionisation of 0.06M ammonium hydroxide solution.

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.8 \times 10^{-5}}{6 \times 10^{-2}}} = \sqrt{3 \times 10^{-4}} = 1.732 \times 10^{-2} = \frac{1.732}{100} = \mathbf{1.732\%}$$

8. (a) Explain the buffer action in a basic buffer containing equimolar ammonium hydroxide and ammonium chloride.

(b) Calculate the pH of a buffer solution consisting of 0.4M CH_3COOH and 0.4M CH_3COONa. What is the change in the pH after adding 0.01 mol of HCl to 500ml of the above buffer solution? Assume that the addition of HCl causes negligible change in the volume. (Given: Ka = 1.8×10^{-5})

(a) Dissociation of buffer components: $NH_4OH_{(aq)} \rightleftharpoons NH_4^+{}_{(aq)} + OH^-{}_{(aq)}$

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

Addition of H^+: The added H+ ions are neutralized by NH_4OH and there is no appreciable decrease in pH.

$NH_4OH_{(aq)} + H^+ \rightarrow NH_4^+{}_{(aq)} + H_2O_{(l)}$

Addition of OH^-: $NH_4^+{}_{(aq)} + OH^-{}_{(aq)} \rightarrow NH_4OH_{(aq)}$

The added OH^- ions react with NH_4^+ to produce unionized NH_4OH. Since NH_4OH is a weak base, there is no appreciable increase in pH.

(b) pH of buffer:

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H^+{}_{(aq)}$

0.4 – α **α** **α**

$CH_3COONa_{(aq)} \rightarrow CH_3COO^-{}_{(aq)} + Na^+{}_{(aq)}$

0.4 **α** **α**

$[CH_3COOH] = 0.4 - \alpha \simeq 0.4$; $[CH_3COO^-] = 0.4 + \alpha \simeq 0.4$

$[H^+] = \frac{K_a\,[CH_3COOH]}{[CH_3COO^-]} = \frac{K_a \times 0.4}{0.4} = K_a = 1.8 \times 10^{-5}$; $\therefore \mathbf{[H^+] = 1.8 \times 10^{-5}}$

$pH = -\log_{10}[H^+] = -\log(1.8 \times 10^{-5}) = -\log(1.8) + (-\log(10^{-5})) = -0.2553 + 5 = \mathbf{4.74}$

Addition of 0.01 mol HCL to 500ml of buffer added $[H^+] = \frac{0.01 mol}{500 ml} = \frac{0.01\ mol}{\frac{1}{2} L} = 0.02M$

$CH_3COOH_{(aq)} \rightleftharpoons CH_3COO^-{}_{(aq)} + H^+{}_{(aq)}$

0.4 – α **α** **α**

$CH_3COONa_{(aq)} \rightarrow CH_3COO^-{}_{(aq)} + Na^+{}_{(aq)}$

0.4 **0.4** **0.4**

$CH_3COO^- + HCl \rightarrow CH_3COOH + Cl^-$

0.02 **0.02** **0.02** **0.02**

$[CH_3COOH] = 0.4 - \alpha + 0.02 = 0.42 - \alpha \simeq 0.42$

$[CH_3COO^-] = 0.4 + \alpha - 0.02 = 0.38 + \alpha \simeq 0.38$

$[H^+] = \frac{(1.8 \times 10^{-5})(0.42)}{(0.38)}$ = **1.99×10^{-5}**

pH = $-\log_{10}[H^+] = -\log(1.99 \times 10^{-5}) = -\log(1.99) + (-\log(10^{-5})) = -0.30 + 5 =$ **4.70**

9. (a) How can you prepare a buffer solution of pH 9. You are provided with 0.1M NH_4OH solution and ammonium chloride crystals. (Given: pK_b for NH_4OH is 4.7 at 25°C)

(b) What volume of 0.6M sodium formate solution is required to prepare a buffer solution of pH 4.0 by mixing it with 100ml of 0.8M formic acid. (Given: pK_a for formic acid is 3.75)

(a) We know that, pH + pOH = 14 ; ⇒ pOH = 14 – pH = 14-9 = **5**;

$pOH = pK_b + \log\frac{[salt]}{[base]}$; ⇒ $5 = 4.7 + \log\frac{[NH_4Cl]}{[NH_4OH]}$; ⇒ $0.3 = \log\frac{[NH_4Cl]}{0.1}$;

$\frac{[NH_4Cl]}{0.1}$ = antilog of (0.3) ; ⇒ $[NH_4Cl] = 0.1M \times 1.995 = 0.1995M =$ **0.2M**

Amount of NH_4Cl required to prepare 1 litre 0.2M solution = Strength of NH_4Cl × molar mass of NH_4Cl

$= 0.2 \times 53.5 =$ **10.70g**

10.70g ammonium chloride is dissolved in water and the solution is made up to one litre to get 0.2M solution. On mixing equal volume of the given NH_4Cl solution and the prepared NH_4Cl solution will give a buffer solution with solution will give a buffer solution with required pH value (pH = 9).

(b) [sodium formate] = number of moles of HCOONa = $0.6 \times V \times 10^{-3}$

[formic acid] = number of moles of HCOOH = $0.8 \times 100 \times 10^{-3} = 80 \times 10^{-3}$

$pH = pK_a + \log\frac{[salt]}{[acid]}$; ⇒ $4 = 3.75 + \log\frac{[sodium\ formate]}{[formic\ acid]}$;

$4 = 3.75 + \log\frac{0.6V \times 10^{-3}}{80 \times 10^{-3}}$; ⇒ $4 - 3.75 = \log\frac{0.6V}{80}$; ⇒ $0.25 = \log\frac{0.6V}{80}$;

Antilog of 0.25 = $\frac{0.6V}{80}$; ⇒ $1.778 = \frac{0.6V}{80}$; ⇒ $0.6V = 1.778 \times 80 = 142.4$;

$V = \frac{142.4}{0.6} =$ **237.33 ml**

10. Calculate the, (i) hydrolysis constant, (ii) degree of hydrolysis and (iii) pH of 0.05M sodium carbonate solution (pK_a for HCO_3^- is 10.26)

Sodium carbonate is a salt of weak acid, H_2CO_3 and a strong base, NaOH, and hence the solution is alkaline due to hydrolysis.

$Na_2CO_{3(aq)} \rightarrow 2Na^+_{(aq)} + CO_3^{2-}{}_{(aq)}$

$CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HCO_3^-{}_{(aq)} + OH^-_{(aq)}$

$-\log K_a = pK_a = 10.26$; ⇒ i.e., K_a = antilog of $(-pK_a)$ = antilog of (-10.26)

K_a = antilog of (-11 + 0.74) = **5.5×10^{-11}** [antilog of 0.74 = 5.49 ≃ 5.5]

(i) $h = \sqrt{\frac{K_w}{K_a \times C}} = \sqrt{\frac{1 \times 10^{-14}}{5.5 \times 10^{-11} \times 0.05}} = 6.03 \times 10^{-2}$

$h = 6.03 \times 10^{-2}$

(ii) $K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{5.5 \times 10^{-11}} = 1.8 \times 10^{-4}$

$K_h = 1.8 \times 10^{-4}$

(iii) pH of solution:

$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2} = 7 + \frac{10.26}{2} + \frac{\log 0.05}{2} = 7 + 5.13 - 0.65 = 11.4795 \simeq 11.48$

pH = 11.48

GOVERNMENT EXAM QUESTION PAPER

1. What are buffer solutions? Explain their types with examples. [PTA1, HY19, JUN20, JUL22, SEP22]

Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid. This buffer solution resists drastic changes in its pH upon addition of a small quantities of acids (or) bases, and this ability is called buffer action.

Basic buffer solution : a solution containing a weak base and its salt.

Example : Solution containing NH_4OH and NH_4Cl

2. Derive the relation between pH and pOH. [PTA-1, HY-19]

A relation between pH and pOH can be established using their following definitions

$pH = -\log_{10}[H_3O^+]$ ----------(1)

$pOH = -\log_{10}[OH^-]$ ----------(2)

Adding Eq.No (1) & (2)

$pH + pOH = -\log_{10}[H_3O^+] - \log_{10}[OH^-] = -(\log_{10}[H_3O^+] + \log_{10}[OH^-])$

$pH + pOH = -(\log_{10}[H_3O^+][OH^-])$----------(3)

$\because K_w = [H_3O^+][OH^-]$ ----------(4)

$pH + pOH = -\log K_w = pK_w$ $[\because pK_w = -\log K_w]$

At 25°C $Kw = 1 \times 10^{-14}$

$pK_w = -\log(1 \times 10^{-14}) = -\log(1) + (-\log(10^{-14})) = 0 + 14 = 14$

$pH + pOH = pK_w$; $\Rightarrow \therefore$ **pH + pOH = 14**

3. What are Buffer index (β)? [PTA-2, MAR-24]

Buffer index is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(pH)}$$

here, **dB** = number of gram equivalents of acid / base added to one litre of buffer solution.

d(pH) = The change in the pH after the addition of acid / base.

4. Calculate the pH of 0.01M CH_3COONa solution (pK_a for CH_3COOH is 4.74) [SEP-20]

Given pKa = 4.74; concentration of solution = 0.1M;

$pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2} = 7 + \frac{4.74}{2} + \frac{\log 0.1}{2} = 7 + 2.37 - 0.5 =$ **8.87**

5. State Ostwald's dilution law. [AUG-21]

Ostwald's dilution law relates the dissociation constant of the weak acid (Ka) with its degree of dissociation (α) and the concentration (c). Degree of dissociation (α) is the fraction of the total number of moles of a substance that dissociates at equilibrium.

$$\alpha = \frac{Number\ of\ moles\ dissociated}{total\ number\ of\ moles}$$

6. What are the Limitation of Arrhenius concept? [MAY-22, QY-24]

- Arrhenius theory does not explain the behaviour of acids and bases in non aqueous solvents such as acetone, Tetrahydrofuran etc...
- This theory does not account for the basicity of the substances like ammonia (NH_3) which do not possess hydroxyl group.

7. What is Henderson equation? [MAR-20, FRT-25]

The concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution i.e.,

$[H_3O^+] = K_a \frac{[acid]_{eq}}{[base]_{eq}}$; $\Rightarrow$ For a basic buffer $pOH = pK_b + \log\frac{[salt]}{[base]}$

8. Calculate the concentration of [OH^-] in a fruit juice which contains 2×10^{-3}M [H_3O^+] ion. Identify the nature of the solution. [SRT-22]

Given that $H_3O^+ = 2 \times 10^{-3}$M

$K_w = [H_3O^+][OH^-]$; $\Rightarrow \therefore [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1 \times 10^{-14}}{2 \times 10^{-3}} = \mathbf{5 \times 10^{-12}M}$ $[2 \times 10^{-3} >> 5 \times 10^{-12}]$

i.e., $[H_3O^+] >> [OH^-]$, hence the juice is acidic in nature.

9. Derive Henderson-Hasselbalch equation. [GMQ-19, MAR-20, QY-24]

- The concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution i.e.,

$$[H_3O^+] = K_a \frac{[acid]_{eq}}{[base]_{eq}} ;$$

- The weak acid is dissociated only to a small extent. Moreover, due to common ion effect, the dissociation is further suppressed and hence the equilibrium concentration of the acid is nearly equal to the initial concentration of the unionised acid. Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of the added salt.

$$[H_3O^+] = K_a \frac{[acid]}{[salt]}$$

- Here [acid] and [salt] represent the initial concentration of the acid and salt, respectively used to prepare the buffer solution Taking logarithm on both sides of the equation

$$\log[H_3O^+] = \log K_a + \log\frac{[acid]}{[salt]}$$

reverse the sign on both sides $-\log[H_3O^+] = -\log K_a - \log\frac{[acid]}{[salt]}$

We know that, $pH = -\log[H_3O^+]$ and $pK_a = -\log K_a$

$pH = pK_a - \log\frac{[acid]}{[salt]}$; $\Rightarrow pH = pK_a + \log\frac{[salt]}{[acid]}$

similarly for a basic buffer, $\Rightarrow pOH = pK_b + \log\frac{[salt]}{[base]}$

10. Write the pH value of the following substance: (a) vinegar, (b) black coffee, (c) backing soda and (d) soapy water. [MAR-20]

(a) vinegar = 2, (b) black coffee = 5, (c) baking soda = 9 and (d) soapy water = 12

11. Classify the following into Lewis acids and Lewis bases. (a) BF_3, (b) CO_2, (c) MgO and CH_3^- [SEP-20]

Lewis acid: BF_3, CO_2 **Lewis base:** MgO, CH_3^-

12. Find the pH of a buffer solution containing 0.20 mole per litre sodium acetate and 0.81 mole per litre acetic acid. K_a for acetic acid is 1.8×10^{-5}. [AUG-21]

Given that $K_a = 1.8 \times 10^{-5}$

$pK_a = -\log K_a = -\log(1.8 \times 10^{-5}) = -\log(1.8) + (-\log(10^{-5})) = -0.26 + 5 = \mathbf{4.74}$

$pH = pK_a + \log\frac{[salt]}{[acid]} = 4.74 + \log\left(\frac{0.20}{0.18}\right) = 4.74 + \log\left(\frac{10}{9}\right) = 4.74 + \log 10 - \log 9$

$pH = 4.74 + 1 - 0.95 = 5.74 - 0.95 = \mathbf{4.79}$

13. (i) Write the nature of solution and possibility of precipitation for the following conditions. Ionic product > K_{sp}, ionic product < K_{sp}, and ionic product = K_{sp}.
(ii) Give an example for acid buffer solution. What is the equation to find the pH of an acid buffer solution? [SRT-22]

(i) Relationship between ionic product and solubility product (K_{sp})

(1) Ionic product > K_{sp}, precipitation will occur and the solution is super saturated.

(2) Ionic product < K_{sp} , no precipitation and the solution is unsaturated.

(3) Ionic product = K_{sp} , equilibrium exist and the solution is saturated.

(ii) Acidic buffer solution: a solution containing a weak acid and its salt.

Example: solution containing acetic acid and sodium acetate.

Equation to find the pH of an acid buffer solution.

14.What do you mean by salt hydrolysis? [PTA-5]

Salt hydrolysis is the reaction of the cation or the anion or both the ions of the salt with water to produce either acidic or basic solution.

15.How solubility product is determined from molar solubility? [PTA-2]

The maximum number of moles of solute that can be dissolved in one litre of the solution. For solute X_mY_n,

$$X_mY_{n(s)} \rightleftharpoons mX^{n+}_{(aq)} + nY^{m-}_{(aq)}$$

From the above stoichiometrically balanced equation we have come to know that 1 mole of $X_mY_{n(s)}$ dissociated to furnish 'm' moles of X^{n+} and 'n' moles of Y^{m-} if 's' is molar solubility X_mY_n then

$[X^{n+}] = ms$ and $[Y^{m-}] = ns$

$\therefore K_{sp} = [X^{n+}]^m[Y^{m-}]^n = (ms)^m(ns)^n = \mathbf{(m)^m(n)^n(s)^{m+n}}$

16.Explain the buffer action in a acidic buffer containing equimolar acetic acid and sodium acetate? [QY-22]

Let us explain the buffer action in a solution containing CH3COOH and CH3COONa. The dissociation of the buffer components occurs as below.

$$CH_3COOH_{(aq)} \rightleftharpoons H^+_{(aq)} + CH_3COO^-_{(aq)}$$

$$CH_3COONa_{(aq)} \xrightarrow{H_2O_{(l)}} Na^+_{(aq)} + CH_3COO^-_{(aq)}$$

If an acid is added to this mixture, it will be consumed by the conjugate base CH_3COO^- to form the un-dissociated weak acid i.e., the increase in the concentration of H+ does not reduce the pH significantly.

$$H^+_{(aq)} + CH_3COO^-_{(aq)} \rightarrow CH_3COOH_{(aq)}$$

If a base is added, it will be neutralized by H_3O^+, and the acetic acid is dissociated to maintain the equilibrium. Hence the pH is not significantly altered.

$$OH^-_{(aq)} + H_3O^+_{(aq)} \rightarrow H_2O_{(l)}$$

$$CH_3COOH_{(aq)} \overset{H_2O_{(l)}}{\rightleftharpoons} H^+_{(aq)} + CH_3COO^-_{(aq)} + H_3O^+_{(aq)}$$

$$OH^-_{(aq)} + CH_3COOH_{(aq)} \rightarrow CH_3COO^-_{(aq)} + H_2O_{(l)}$$

17.What is buffer capacity? [QY-22]

The buffering ability of a solution can be measured in terms of buffer capacity. Vanslyke introduced a quantity called buffer index, β, as a quantitative measure of the buffer capacity. It is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\boldsymbol{\beta = \frac{dB}{d(pH)}}$$

here, **dB** = number of gram equivalents of acid / base added to one litre of buffer solution.

d(pH) = The change in the pH after the addition of acid / base.

18.Calculate the pH of 0.1M CH_3COOH solution. Dissociation constant of acetic acid is 1.8×10^{-5} [MAR-25]

pH = - log[H] For weak acids,

$[H^+] = \sqrt{K_a \times C} = \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3}$ M

pH = - log (1.34×10^{-3}) = 3 – log1.34 = 3 – 0.1271 = 2.8729 ≈ **2.87**

19.A Solution of 0.10M of a weak electrolyte is found to be dissociated to the extent of 1.20% at 25°C. Find the dissociation constant of acid. [SUT-24]

Given that $\alpha = 1.20\% = \frac{1.20}{100} = 1.2 \times 10^{-2}$

$\mathbf{K_a = \alpha^2 C} = (1.2 \times 10^{-2})^2 (0.1) = 1.44 \times 10^{-4} \times 10^{-1} = \mathbf{1.44 \times 10^{-5}}$

20.Give any two differences between Lewis acid and Lewis base? [FRT-25]

Lewis acids	Lewis bases
Electron deficient molecules such as BF_3,$AlCl_3$,BeF_2 etc...	Molecules with one (or) more lone pairs of electrons. NH_3,H_2O,R-O-H,R-O-R, R - NH_2
All metal ions Examples: Fe^{2+},Fe^{3+},Cr^{3+},Cu^{2+} etc...	All anions F^-,Cl^-,CN^-,SCN^-,SO_4^{2-} etc...
Molecules that contain a polar double bond Examples : SO_2,CO_2,SO_3 etc...	Molecules that contain carbon – carbon multiple bond Examples: $CH_2{=}CH_2$,$CH \equiv CH$ etc...
Molecules in which the central atom can expand its octet due to the availability of empty d – orbitals Example: SiF_4,SF_4,$FeCl_3$ etc..	All metal oxides CaO,MgO,Na_2O etc...
Carbonium ion $(CH_3)_3C^+$	Carbanion CH_3^-