IONIC EQUILIBRIUM

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THEORY

Ionic equilibrium is the study of equilibrium in the reactions where formation of ions take place in aqueous solution.

1. ELECTROLYTES

Electrolytes are those compounds which on dissolving in polar solvents like water break into ions. The solution of electrolytes conducts electricity because of the presence of ions.

1.1. Classification of electrolytes

1.1.1 Electrolytes can be classified on the basis of their strength into two categories:

Strong electrolytes : Those electrolytes which easily break into ions and give almost complete dissociation. Eg. HCl, NaOH, NaCl, HNO_3, $HClO_4$, H_2SO_4, $CaCl_2$ etc

Weak electrolytes : Those electrolytes which dissociate partially. Eg. CH_3COOH, NH_4OH, HCN, $H_2C_2O_4$, and all organic acids and bases etc.

1.1.2 Electrolytes can be further classified on the basis of the kind of compound they are.

- **Acids**
- **Bases**
- **Salts**

1.2 Acids and Bases

The definition of acids and bases varies from theory to theory:

1.2.1 Arrhenius theory

This theory defines acids and bases from the perspective of water as a solvent.

Arrhenius acids: Those compounds which will increase H^+ ion concentration in water. Eg HCl, H_2SO_4, CH_3COOH etc

$$\mathbf{HA \leftrightarrow H^+ + A^-}$$

Arrehenius bases: Those compounds which will increase OH^- ion concentration in water. Eg. NaOH, $Ca(OH)_2$, NH_4OH etc

The major drawback of this theory is that the basis of all definitions is water.

$$\mathbf{BOH \leftrightarrow B^+ + OH^-}$$

1.2.2 Bronsted-Lowry concept

Acids : Those compounds which can transfer protons that is H^+ to other compounds

Bases: Those compounds which can accept protons.

That is, Bronsted acids are "proton donors" and Bronsted bases are "Proton acceptors".

HCl +	H_2O $\leftrightarrow$	H_3O^+ +	Cl^-
Acid-1	**Base-1**	**Acid-2**	**Base-2**

Conjugate Acid-Base pairs: Pairs which are separated by a proton and exhibit opposite behaviours in the two directions of the same reaction. Eg. In the above reaction HCl and Cl^- are conjugate acid-base pairs.

Note : In a conjugate pair if acid is strong the base is weak and vice-versa.

1.2.3 Lewis Concept

Acid: A compound which can accept a pair of electrons.

Base: is a compound which can transfer its lone pair of electrons.

Eg. $\mathbf{BF_3 + NH_3 \leftrightarrow H_3N \rightarrow BF_3}$

In the above reaction BF_3 is a lewis acid and NH_3 is a lewis base.

2. DISSOCIATION OF WEAK ACIDS AND BASES

$$\mathbf{HA \leftrightarrow H^+ + A^-}$$

$K_a = c\alpha^2/(1 - \alpha)$

K_a is called "ionisation constant" or the "Dissociation constant" of the acid.

For low dissociation : $1 - \alpha \approx 1$

$K_a = c\alpha^2$

$\Rightarrow \alpha = \sqrt{(K_a / C)}$ This expression will be valid only when $\alpha < 0.05\ (5\%)$

$[H^+] = c\alpha = \sqrt{cK_a} = [A^-]$

Similarly for a Weak base $K_a = c\alpha^2/(1 - \alpha)$

K_b is called "ionisation constant" or "dissociation constant" for the base.

$\alpha = \sqrt{(K_b / C}$ This expression will be valid only when $\alpha < 0.05\ (5\%)$

$[B^+] = [OH^-] = \sqrt{cK_b}$

Note :

α weak electrolytes increase on dilution

3. SELF-IONISATION OF WATER

$H_2O \leftrightarrow H^+ + OH^-$

$K_w = [H^+]\,[OH^-]$

K_w is called ionic product of water.

For pure water: $[H^+] = [OH^-]$

At 25° C we know that $[H^+][OH^-] = 10^{-14}$

$[H^+] = [OH^-] = \sqrt{K_w} = 10^{-7}\,M$

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

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

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

Note: K_w increases as temperature increases.

4. pH SCALE

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

$pH + pOH = pK_w = 14$ (at 25°)

At 25°C

$pH < 7$ Acidic

$pH > 7$ Basic

$pH = 7$ Neutral

5. MIXTURE OF TWO WEAK ACIDS

$[H^+] = (x + y) = \sqrt{c_1K_1 + c_2K_2}$

6. BUFFER SOLUTIONS

Solutions which can resist any change in pH on addition of small amount of acid or base.

Buffer solutions are of three types:

6.1 Acidic Buffer Eg.

$CH_3COOH + CH_3COONa$

Henderson-Hasselbalch equation

$pH = pK_a + \log\,[salt]/[acid]$

6.1.1 Buffer Range:

$pK_a - 1 \le pH \le pK_a + 1$

6.2 Basic Buffer Eg.

NH_4OH and NH_4Cl

$pOH = pK_b + \log\,[salt]/[base]$

6.2.1 Buffer range:

$pK_b - 1 \le pOH \le pK_b + 1$

6.3 Mixed Buffer Eg.

CH_3COONH_4

Note :

- pH of a buffer solution does not change on dilution.
- For any acid-conjugate base pair $K_a.K_b = K_w$

7. POLYPROTIC ACIDS

Those acids which can furnish more than one H^+ permolecule. Eg. H_2SO_4, H_2CO_3, H_3PO_4

For any polyprotic acid : $\mathbf{K_1 > K_2 > K_3}$ **....so on**

For dissociation of H_2A $\quad \mathbf{[A2^-] \approx K_2}$

i.e. The concentration of the second ion of a polyprotic acid is almost equal to the second dissociation constant.

8. SALT HYDROLYSIS

Depending on the nature of the parent acid and base there can be 4 type of salts:

8.1 Salt of strong acid and strong base (NaCl)

This type of salt do not get hydrolysed.

Neutral solution with pH = 7

8.2 Salt of weak acid and strong base (CH_3COONa)

This type of salt give acidic solution on hydrolysis.

$K_h = C\alpha_h^2 / (1 - \alpha_h) = K_w/K_a$; $pH = 7 + \frac{1}{2} pK_a - \frac{1}{2} \log C$

8.3 Salt of Strong acid and weak base (NH_4Cl)

This type of salt give basic solution on hydrolysis.

$K_h = C\alpha_h^2 / (1 - \alpha_h) = K_w/K_b$; $pH = 7 - \frac{1}{2} pK_b - \frac{1}{2} \log C$

8.4 Salt of weak acid and weak base (CH_3COONH_4)

This type of salt may give acidic,basic or neutral solution.

$K_h = \alpha_h^2 / (1 - \alpha_h)^2 = K_w/(K_a \times K_b)$; $pH = 7 + \frac{1}{2} pK_b - \frac{1}{2} pK_b$

9. SPARINGLY SOLUBLE SALTS & PRECIPITATION

When a salt is dissolved in water then it starts breaking into ions and after sometime the solubility process attains equilibrium.

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

$K_{sp} = [Ag^+]\,[Cl^-] = Q = I.P.$

$I.P. < K_{sp} \Rightarrow$ forward reaction, more salt can be dissolved

$I.P. = K_{sp} \Rightarrow$ saturation, no more salt can be dissolved

$I.P. > K_{sp} \Rightarrow$ backward reaction, precipitation of solid salt will take place

SOLVED EXAMPLES

Example - 1

Calculate the pH of the following solutions:

(a) 2g of TlOH dissolved in water to give 2 litre of the solution

(b) 0.3 g of $Ca(OH)_2$ dissolved in water to give 500 mL of the solution

(c) 0.3 g of NaOH dissolved in water to give 200 mL of the solution

(d) 1 mL of 13.6 M HCl is diluted with water to give 1 litre of the solution.

Sol. Molar conc. of TlOH $= \frac{2g}{(204+16+1)g\,mol^{-1}} \times \frac{1}{2L}$

$= 4.52 \times 10^{-3}\,M$

$\therefore \left[OH^-\right] = \left[TlOH\right] = 4.52 \times 10^{-3}\,M$

$\left[H^+\right] = 10^{-14}/(4.52 \times 10^{-3}) = 2.21 \times 10^{-12}\,M$

$pH = -\log(2.21 \times 10^{-12}) = 12 - (0.3424) = 11.66$

Molar conc. of $Ca(OH)_2 = \frac{0.3g}{(40+34)g\,mol^{-1}} \times \frac{1}{0.5L} = 8.11 \times 10^{-3}\,M$

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

$\therefore \left[OH^-\right] = 2\left[Ca(OH)_2\right] = 2 \times (8.11 \times 10^{-3})\,M$

$= 16.22 \times 10^{-3}\,M$

$pOH = -\log(16.22 \times 10^{-3}) = 3 - 1.2101 = 1.79$

$pH = 14 - 1.79 = 12.21$

(c) Molar conc. of NaOH

$= \frac{0.3g}{40g\,mol^{-1}} \times \frac{1}{0.2L} = 3.75 \times 10^{-2}\,M$

$\left[OH^-\right] = 3.75 \times 10^{-2}\,M$

$pOH = -\log(3.75 \times 10^{-2}) = 2 - 0.0574 = 1.43$

$\therefore pH = 14 - 1.43 = 12.57$

(d) $M_1V_1 = M_2V_2 \therefore 13.6M \times 1mL = M_2 \times 1000mL$

$\therefore M_2 = 1.36 \times 10^{-2}\,M$

$\left[H^+\right] = \left[HCl\right] = 1.36 \times 10^{-2}\,M.$

$pH = -\log(1.36 \times 10^{-2}) = 2 - 0.1335 = 1.87$

Example - 2

The degree of ionization of a 0.1 M bromoacetic acid solution is 0.132. Calculate the pH of the solution and the pK_a bromoacetic acid.

Sol. $CH_2(Br)COOH \rightleftharpoons CH_2(Br)COO^- + H^+$

Intial Conc	C	0	0
Conc at eqm	C − Cα	Cα	Cα

$K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \simeq C\alpha^2 = 0.1 \times (0.132)^2 = 1.74 \times 10^{-3}$

$pK_a = -\log(1.74 \times 10^{-3}) = 3 - 0.2405 = 2.76$

$\left[H^+\right] = C\alpha = 0.1 \times 0.132 = 1.32 \times 10^{-2}\,M$

$pH = -\log(1.32 \times 10^{-2}) = 2 - 0.1206 = 1.88$

Example - 3

The pH of 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Calculate the ionization constant and pK_b.

Sol. $Cod + H_2O \rightleftharpoons CodH^+ + OH^-$

$pH = 9.95 \therefore pOH = 14 - 9.95 = 4.05$ i.e.

$-\log\left[OH^-\right] = 4.05$

or $\log\left[OH^-\right] = -4.05 = \bar{5}.95$ or

$\left[OH^-\right] = 8.913 \times 10^{-5}\,M$

$K_b = \frac{\left[CodH^+\right]\left[OH^-\right]}{[Cod]} = \frac{\left[OH^-\right]^2}{[Cod]} = \frac{\left(8.91 \times 10^{-5}\right)^2}{5 \times 10^{-3}}$

$= 1.588 \times 10^{-6}$

$pK_b = -\log\left(1.588 \times 10^{-6}\right) = 6 - 0.1987 = 5.8$

Example - 4

Calculate the hydrogen ion concentration in the following biological fluids whose pH are given:

(a) Human muscle–fluid, 6.83

(b) Human stomach fluid, 1.2

(c) Human blood, 7.38

(d) Human saliva, 6.4

Sol. (a) $\log[H^+] = -pH = -6.83 = \bar{7}.17$

$\therefore [H^+] = \text{Antilog}\,\bar{7}.17 = 1.479\times10^{-7}\,M$

(b) $\log[H^+] = -pH = -1.2 = \bar{2}.8$

$\therefore [H^+] = \text{Antilog}\,\bar{2}.8 = 6.31\times10^{-2}\,M$

(c) $\log[H^+] = -pH = -7.38 = \bar{8}.62$

$\therefore [H^+] = \text{Antilog}\,\bar{8}.62 = 4.169\times10^{-8}\,M$

(d) $\log[H^+] = -pH = -6.4 = \bar{7}.60$

$\therefore [H^+] = \text{Antilog}\,\bar{7}.60 = 3.981\times10^{-7}\,M$

Example - 5

The pH of milk, black coffee, tomato juice, lemon juice and egg white are 6.8, 5.0, 4.2, 2.2 and 7.8 respectively. Calculate corresponding hydrogen ion concentration in each.

Sol. Similar to Q. 7.55 [Ans 1.5×10^{-7}M, 10^{-5}M, 6.31×10^{-3}M, 1.58×10^{-8} M]

Example - 6

If 0.561 g KOH is dissolved in water to give 200 mL of solution at 298 K, calculate the concentration of potassium hydrogen and hydroxyl ions. What is its pH?

Sol. $[KOH] = \frac{0.561}{56}\times\frac{1000}{200}M = 0.050M$

As $KOH \to K^+ + OH^-, \therefore [K^+] = [OH^-] = 0.05M$

$[H^+] = K_w/[OH^-] = 10^{-14}/0.05 = 10^{-14}/(5\times10^{-2})$

$= 2.0\times10^{-13}$ M.

$pH = -\log[H^+] = -\log(2.0\times10^{-13}) = 13 - 0.3010 = 12.699$

Example - 7

The solubility of $Sr(OH)_2$ at 298 K is 19.23 g/L of solution. Calculate the concentration of strontium and hydroxyl ions and the pH of the solution. (Atomic mass of Sr = 87.6)

Sol. Molar mass of $Sr(OH)_2 = 87.6 + 34 = 121.6\,g\,mol^{-1}$

Solubility of $Sr(OH)_2$ in moles

$$L^{-1} = \frac{19.23gL^{-1}}{121.6g\,mol^{-1}} = 0.1581M$$

Assuming complete dissociation,

$Sr(OH)_2 \to Sr^{2+} + 2\,OH^-$

$\therefore [Sr^{2+}] = 0.1581M. [OH^-] = 2\times0.1581 = 0.3162M$

$pOH = -\log 0.3162 = 0.5, \therefore pH = 14 - 0.5 = 13.5$

Example - 8

The pH of 0.1M solution of cyanic acid (HCNO) is 2.34. Calculate the ionization constant of the acid and its degree of ionization in the solution.

Sol. $HCNO \rightleftharpoons H^+ + CNO^-$

pH=2.34 mean $-\log[H^+] = 2.34$ or $\log[H^+] = -2.34 = \bar{3}.66$

or $[H^+] = \text{Anti}\log\bar{3}.66 = 4.57\times10^{-3}\,M$

$[CNO^-] = [H^+] = 4.57\times10^{-3}\,M$

$$K_a = \frac{(4.57\times10^{-3})(4.57\times10^{-3})}{0.1} = 2.09\times10^{-4}$$

$\alpha = \sqrt{K_a/C} = \sqrt{2.09\times10^{-4}/0.1} = 0.0457$

Example - 9

The ionic product of water at 310 K is 2.7×10^{-14}. What is the pH of neutral water at this temperature?

Sol. $[H^+] = \sqrt{K_w} = \sqrt{2.7\times10^{-14}} = 1.643\times10^{-7}M$

$pH = -\log[H^+] = -\log(1.643\times10^{-7})$

$= 7 - 0.2156 = 6.78$

Example - 10

One the basis of the equation pH =– log [H$^+$], the pH of 10^{-8} mol dm^{-3} solution of HCl should be 8. However, it is observed to be less than 7.0. Explain the reason.

Sol. pH of 10^{-8} M HCl solution is not 8 because this concentration is so low that H$^+$ ion produced from H_2O in the solution (viz. 10^{-7}M) cannot be neglected. Total [H$^+$] = 10^{-8} + 10^{-7} M. Solving and calculating pH, we get the value close to 7 but less than 7 as the solution is acidic.

Example - 11

pH of a solution of a strong acid is 5.0. What will be the pH of the solution obtained after diluting the given solution 100 times?

Sol. pH = 5 means [H$^+$]= 10^{-5} M. On diluting 100 times,

$$\left[H^+\right] = \frac{10^{-5}}{100} = 10^{-7}\,M$$

This should give pH =7 but it cannot be so because solution is acidic and pH should be less than 7. The reason is that [H$^+$] from H_2O cannot be neglected. Thus, total [H$^+$] = 10^{-7} M (from HCl) + 10^{-7} M (from H_2O) = 2 × 10^{-7} M

$$\therefore\ pH = -\log(2\times10^{-7}) = 7 - 0.3010 = 6.699.$$

Example - 12

pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its Ionisation constant.

Sol. pH of HOCl=2.85 i.e., –log [H$^+$] = – 2.85

or log [H$^+$] = – 2.85 = $\bar{3}.15$

or [H$^+$] = antilog $\bar{3}.15$ = 1.413 × 10^{-3} M

For weak monobasic acid $HA \rightleftharpoons H^+ + A^-$

$$K_a = \frac{\left[H^+\right]^2}{[HA]} = \frac{\left(1.413\times10^{-3}\right)^2}{0.08} = \mathbf{2.4957 \times 10^{-5}}.$$

Example - 13

Prove that the degree of dissociation of a weak monoprotic acid is given by

$$\alpha = \frac{1}{1+10^{(pK_a - pH)}}$$ **where K_a is the dissociation constant of the acid.**

Sol. Suppose we start with C mol L^{-1} of the weak monoprotic acid HA. Then

$$HA \rightleftharpoons H^+ + A^-$$

Initial molar conc. C

Molar conc $\quad C - C\alpha \quad C\alpha \quad C\alpha$

after dissociation= $C(1-\alpha)$

$$\text{Thus, } K_a = \frac{C\alpha.C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} \text{ or } C = \frac{K_a(1-\alpha)}{\alpha^2} \quad ..(i)$$

Also, $\left[H^+\right] = C\alpha$

Substituning the value of C from eqn. (i), we get

$$\left[H^+\right] = \frac{K_a(1-\alpha)}{\alpha^2} \times \alpha = \frac{K_a(1-\alpha)}{\alpha}$$

$$\therefore \quad -\log\left[H^+\right] = -[\log K_a + \log(1-\alpha) - \log\alpha]$$

$$\text{or } \ pH = pK_a - \log(1-\alpha) + \log\alpha$$

$$\text{or} \quad \log\frac{1-\alpha}{\alpha} = pK_a - pH \text{ or } \frac{1-\alpha}{\alpha} = 10^{pK_a - pH}$$

$$\text{or } \frac{1}{\alpha} - 1 = 10^{\,pK_a - pH}$$

$$\text{or } \ \frac{1}{\alpha} = 1 + 10^{pK_a - pH} \text{ or } \alpha = \frac{1}{1+10^{pK_a - pH}}$$

Example - 14

Arrange the given compounds in the decreasing order of basicity on the basis of Bronsted–Lowry concept: BaO, CO_2, SO_3, B_2O_3, Cl_2O_7.

Sol $BaO + H_2O \rightleftharpoons Ba(OH)_2$ (Basic)

$CO_2 + H_2O \rightleftharpoons H_2CO_3$ (weakly acidic)

$SO_3 + H_2O \rightleftharpoons H_2SO_4$ (Strongly acidic)

$B_2O_3 + 3H_2O \rightleftharpoons 2H_3BO_3$ (Very weaky acidic)

$Cl_2O_7 + H_2O \rightleftharpoons 2HClO_4$ (Very strongly acidic)

Hence, in the decreasing order of basicity, we gave $BaO > B_2O_3 > CO_2 > SO_3 > Cl_2O_7$.

Example - 15

What are the conjugate bases of the following? $CH_3OH, HN_3, [Al(H_2O)_6]^{3+}$.

Sol. $\underset{\text{methoxideion,}}{CH_3O^-}$ $\underset{\text{azideion}}{N_3^-}$ $[Al(H_2O)_5OH]^{2+}$ (H^+ ion has been removed from one H_2O molecule).

Example - 16

Glycine is an α–amino acid which exists in the form of Zwitter ion as $\overset{+}{N}H_3CH_2COO^-$. Write the formula of its conjugate base.

Sol. Conjugate acid =

$$\overset{+}{N}H_3CH_2COO^- + H^+ = \overset{+}{N}H_3CH_2COOH$$

Conjugate base =

$$\overset{+}{N}H_3CH_2COO^- - H^+ = NH_2CH_2COO^-$$

Example - 17

Write reaction for autoprotolysis of water. How is ionic product of water related to ionization constant of water? Derive the relationship.

Sol. Autoprotolysis of H_2O takes place as:

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

For ionization of H_2O, $H_2O \rightleftharpoons H^+ + OH^-$

$$K_i = \frac{[H^+][OH^-]}{[H_2O]} = \frac{K_2}{[H_2O]} = \frac{K_w}{55.55\,\text{mol}\,L^{-1}} \text{ or}$$

$$K_w = K_i \times 55.55.$$

Example - 18

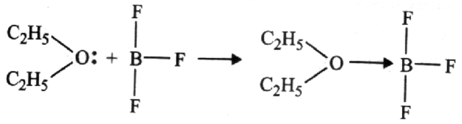
Why PO_4^{3-} ion is not amphiprotic?

Sol. An amphiprotic ion is one which can donate proton as well as accept proton. PO_4^{3-} ion can accept proton(s) but cannot donate any proton. Hence, PO_4^{3-} is not amphiprotic.

Example - 19

In the reaction between BF_3 and $C_2H_5OC_2H_5$ which one of them will act as an acid? Justify your anwer.

Sol. The reaction between BF_3 and $C_2H_5OC_2H_5$ is



As BF_3 accepts a pair of electrons, hence BF_3 is the Lewis acid.

Example - 20

Which is a stronger base in each of the following pairs and why?

(i) H_2O, Cl^- (ii) CH_3COO^-, OH^-

Sol (i) H_2O (ii) OH^-

Refer to Bronsted – Lowry concept for relative strengths.

Example - 21

Classify the following species as Lewis acids and Lewis bases

NH_3, BF_3, $SnCl_4$, C_5H_5N, CO, Ni^{2+}

Sol. Lewis acids: BF_3, $SnCl_4$, Ni^{2+}

Lewis bases: NH_3, C_5H_5N, CO.

Example - 22

Explain why pH of 0.1 molar solution of acetic acid will be higher than that of 0.1 molar solution of HCl?

Sol. Acetic acid is a weak electrolyte. It is not completely ionized and hence gives less H^+ ion concentration. HCl is a strong acid. It is completely ionized giving more H^+ ion concentration. As pH =–log $[H^+]$; less the $[H^+]$, greater will be the pH.

Example - 23

Calculate the approximate pH of a 0.100 M aqueous H_2S solution. K_1 and K_2 for H_2S are 1.00×10^{-7} and 1.30×10^{-13} respectively at 25°C,

Sol. $K_2 << K_1$. Hence H^+ ions are mainly from 1st dissociation, i.e. $H_2S \rightleftharpoons H^+ + HS^-$

$$K_1 = \frac{\left[H^+\right]\left[HS^-\right]}{[H_2S]} = \frac{\left[H^+\right]^2}{[H_2S]} \text{ or} \left[H^+\right] = \sqrt{K_1[H_2S]}$$

$$\therefore \quad [H^+] = \sqrt{10^{-7} \times 10^{-1}} = 10^{-4}$$

Hence, pH=4

Example - 24

Calculate the pH at equivalence point when a solution of 0.10 M acetic acid is titrated with a solution of 0.10 M NaOH solution, K_a for acetic acid = 1.9×10^{-5}

Sol. At the equivalence point, CH_3COONa is formed and its concentration = $\frac{0.1}{2}M = 0.05M$. It is a salt of weak acid and strong base. The formula for finding the pH of such a salt is

$$pH = -\frac{1}{2}[\log K_2 + \log K_a - \log c]$$

$$\therefore \ pH = -\frac{1}{2}[\log 10^{-14} + \log(1.9 \times 10^{-5}) - \log(5 \times 10^{-2})]$$

$$= -\frac{1}{2}[-14 + (-5 + 0.2788) - (-2 + 0.6990)]$$

$$= \frac{1}{2}(14 + 5 - 0.2788 - 2 + 0.6990)$$

$$= \frac{17.42}{2} = 8.71$$

Example - 25

A certain weak acid has $K_a = 1.0 \times 10^{-4}$. Calculate the equilibrium constant for its reaction with a strong base.

Sol. $\underset{\text{weak}}{HA} + \underset{\text{strong}}{BOH} \rightleftharpoons BA + H_2O$

or $HA + B^+ + OH^- \rightleftharpoons B^+ + A^- + H_2O$ or

$$HA + OH^- \rightleftharpoons A^- + H_2O$$

$$K = \frac{[A^-]}{[HA][OH^-]} \qquad \text{.......(i)}$$

Further, for the weak acid, $HA \rightleftharpoons H^+ + A^-$,

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad \text{......(ii)}$$

Also $K_w = [H^+][OH^-]$ .....(iii)

From eqns. (i), (ii) and (iii),

$$K = \frac{K_a}{K_w} = \frac{10^{-4}}{10^{-14}} = \mathbf{10^{10}}$$

Example - 26

The pH of 0.05 M aqueous solution of diethylamine is 12.0. Calculate its K_b

Sol. $(C_2H_5)_2NH + H_2O \rightleftharpoons (C_2H_5)_2NH_2^+ + OH^-$

As pH = 12, $\therefore [H^+] = 10^{-12}$ M or $[OH^-] = 10^{-2}$M,

$$[(C_2H_5)_2NH] = 0.05 - 0.01 = 0.04M$$

$$K_b = \frac{[(C_2H_5)_2NH_2^+][OH^-]}{[(C_2H_5)_2NH]} = \frac{10^2 \times 10^{-2}}{0.04} = 2.5 \times 10^{-3}$$

$$[(C_2H_5)_2NH_2^+] = [OH^-]$$

Example - 27

An aqueous solution contains 10% ammonia by mass and has a densityof 0.99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. K_a for $NH_4^+ = 5.0 \times 10^{-10}$ M

Sol. 10% ammonia by mass means 10g NH_3 are present in 100g of the solution.

$\therefore$ Molarity of the solution

$$= \frac{10}{17} \times \frac{1}{100/0.99} \times 1000 = 5.82\,M$$

$$NH_3 + H_2 \rightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

Initial conc.	$C \text{ mol } L^{-1}$		
After dissociation	$C - C\alpha$ $= C(1-\alpha)$	$C\alpha$	$C\alpha$

$$\therefore\ [OH^-] = C\,\alpha = C\sqrt{\frac{K_h}{C}} = \sqrt{K_h C}$$

$$= \sqrt{\frac{K_w}{K_a}\times C} = \sqrt{\frac{10^{-14}}{5.0\times10^{-10}}\times 5.82}\ \ \mathbf{= 1.079 \times 10^{-2}\ M}$$

$$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.079\times10^{-2}}$$

$= 0.9268 \times 10^{-12}$ M $\mathbf{= 9.268 \times 10^{-13}\ M}$

Example - 28

The ionization constant of NH_4^+ in water is 5.6×10^{-10} at 25ºC. The rate constant for reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25ºC is 3.4×10^{10} s litre mol^{-1} sec^{-1}. Calculate the rate constant for prton transfer from water of NH_3.

Sol. $NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+, K_a = 5.6\times10^{-10}$

$$NH_3 + H_2O \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_4^+ + OH^-, k_b = 3.4\times10^{10}$$

Aim. To find k_f

We know that for a conjugate acid–base pair $K_{acid}\times K_{base} = K_w$, i.e., $K_a \times K_b = K_w$

$$\therefore\ K_b = \frac{K_w}{K_a} = \frac{10^{-14}}{5.6\times10^{-10}}$$

$$\text{But } K_b = \frac{k_f}{k_b}\ \therefore k_f = K_b \times k_b$$

$$= \frac{10^{-14}}{5.6\times10^{-10}}\times 3.4\times10^{10} = 0.607\times10^{6} = 6.07\times10^{5}$$

Example - 29

What will be the resultant pH when 200 ml of an aqueous solution of HCl (pH=2.0) is mixed with 300 ml of an aqueous solution of NaOH (pH=12.0)?

Sol. pH = 2 means $[H^+] = 10^{-2}$M

pH = 12 means $[H^+] = 10^{-12}$ or $[OH^-] = 10^{-2}$ M

Thus, 200 ml of 10^{-2} M HCl are mixed with 300 ml of 10^{-2} M NaOH. After neutralisation NaOH left = 100 ml of 10^{-2} M

Total volume after mixing = 500 ml

$\therefore$ In the final solution, after mixing , $[OH^-]$=

$$\frac{10^{-2}}{5} = 2\times10^{-3}\,M \text{ or } [H^+] = \frac{10^{-14}}{2\times10^{-3}} = 5\times10^{-12}$$

$$\therefore\ pH = -\log[H^+] = -\log(5\times10^{-12}) = 12 - 0.69 = 11.31$$

Example - 30

Calculate the degree of dissociation of 0.5 M NH_3 at 25ºC in a solution of pH=12.

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

	NH_4OH	NH_4^+	OH^-
Initial conc.	C mol L^{-1}	0	0
After disso.	$C - C\alpha$	$C\alpha$	$C\alpha$

$$pH = 12 \text{ means } [H^+] = 10^{-12} \text{ or } [OH^-] = 10^{-2}$$

$$\therefore [OH^-] = C\alpha = 10^{-2} \text{ or } \alpha = \frac{10^{-2}}{C}$$

$$= \frac{10^{-2}}{0.5} = 2\times10^{-2} \text{ or } 2\%.$$

Example - 31

Calculate the ratio of pH of a solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre to that of a solution containing 1 mole of CH_3COONa + 1 mole of CH_3 COOH per litre.

Sol. **Case I.** Calculation of pH of solution containing 1 mole of CH_3COONa + 1 mole of HCl per litre

$$CH_3COONa + HCl \rightarrow CH_3COOH + NaCl$$

	CH_3COONa	HCl	CH_3COOH	NaCl
Initial moles	1 mole	1 mole	0	0
Moles after reaction	0	0	1	1

$$\text{i.e }\ [CH_3COOH] = 1\,mol\,L^{-1}$$

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

	CH_3COOH	CH_3COO^-	H^+
Initial conc.	C mol L^{-1}		
After dissociation	$C - C\alpha$	$C\alpha$	$C\alpha$

$$\therefore [H^+] = C\alpha.\ \text{But }\ \alpha = \sqrt{\frac{K_a}{C}}$$

$$\therefore\ [H^+]=C\sqrt{\frac{K_a}{C}}=\sqrt{K_aC}=\sqrt{K_a}=K_a^{1/2}\quad (\because C=1\,mol\,L^{-1})$$

$$\therefore\ -\log[H^+]=-\frac{1}{2}\log K_a,\ \text{i.e.}(pH)_1=-\frac{1}{2}\log K_a\ \ ...(i)$$

Case II. Calculation of pH of solution containing 1 mole of CH_3COONa + 1 mole of CH_3 COOH per litre

Applying Henderson equation,

$$(pH)_2=pK_a+\log\frac{[Salt]}{[Acid]}=pK_a=-\log K_a\ \ ...(ii)$$

$$[Salt]=[Acid]=1\,mol\,L^{-1}]$$

Example - 32

0.1 M CH_3 COOH (pH=3) is titrated with 0.05 M NaOH solution. Calculate the pH when (i) 1/4th of the acid has been neutralized. (ii)3/4th of acid has been neutralized.

Sol. Calculation of dissociation constant of the acid

As $pH=3,\ \therefore [H^+]=10^{-3}M,\ [CH_3COO^-]=[H^+]=10^{-3}M$

$$K_a=\frac{[CH_3COO^-][H^+]}{[CH_3COOH]}=\frac{10^{-3}\times10^{-3}}{0.1}=10^{-5}$$

(i) When 1/4th of the acid has been neutralized

$$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$$

Initial conc. 0.1 M

After 1/4th

neutralization $0.1\times\frac{3}{4}$ $\qquad 0.1\times\frac{1}{4}$

$=0.075M$ $\qquad =0.025M$

$$\therefore pH=pK_a+\log\frac{[Salt]}{[Acid]}=-\log10^{-5}+\log\frac{0.025}{0.075}$$

$$=5-0.4771=4.5229$$

(ii) When 3/4th of the acid has been neutralized

$$CH_3COOH+NaOH\rightarrow CH_3COONa+H_2O$$

Initial conc. 0.1M

After 3/4th $0.1\times\frac{1}{4}M$ $\qquad 0.1\times\frac{3}{4}M$

neutralization $=0.025$ M $\qquad =0.075$ M

$$\therefore pH=-\log10^{-5}+\log\frac{0.075}{0.025}=5+0.4771=\mathbf{5.4771.}$$

Example - 33

Calculate the amount of $(NH_4)_2SO_4$ in g which must be added to 500 mL of 0.2 M NH_3 to yield a solution of pH = 9.35. K_b for $NH_3=1.78\times10^{-5}$.

Sol. As it is a basic buffer, $pOH=pK_b+\log\frac{[Salt]}{[Base]}$

$$=-\log K_b+\log\frac{[NH_4^+]}{[NH_4OH]}$$

As $pH=9.35,\ \therefore pOH=14-9.35=4.65$

Millimoles of NH_4OH is solution $=0.2\times500=100$ Suppose millimoles of NH_4^+ to be added=x

$$\therefore\quad 4.65=-\log(1.78\times10^{-5})+\log\frac{x/500}{100/500}$$

$$=(5-0.2504)+\log\frac{x}{100}$$

or $\log\frac{x}{100}=-0.0996=\bar{1}.004\simeq0.1$

or $\log x=2.1$ or $x=125.9$

$\therefore$ Millimoles of $(NH_4)_2SO_4$ to be added $=\frac{125.9}{2}=62.95$

$(\because 1$ millimole of $(NH_4)_2\ SO_4\equiv 2$ millimoles of $NH_4^+)$

$\therefore$ Mass of $(NH_4)_2SO_4$ to be added = $(62.95\times10^{-3}$ moles) $(132\ g\,mol^{-1})=8.3094$ g.

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

Theory of Electrolytes, Acid-Base Strength Comparison

1. Which one of the following substance has the highest proton affinity

(a) H_2O (b) H_2S

(c) NH_3 (d) PH_3

2. Which of the following is not a Lewis acid

(a) BF_3 (b) $FeCl_3$

(c) SiF_4 (d) C_2H_4

3. The conjugate base of NH_2^- is

(a) NH_3 (b) NH^{2-}

(c) NH_4^+ (d) N_3^-

4. Which of the following is the weakest acid

(a) HF (b) HCl

(c) HBr (d) HI

5. Among the following, the weakest Lewis base is

(a) H^- (b) OH^-

(c) Cl^- (d) HCO_3^-

6. Cl^- is the conjugate base of

(a) $HClO_4$ (b) HCl

(c) HOCl (d) $HClO_3$

7. Which one is the weakest acid

(a) HNO_3 (b) $HClO_4$

(c) H_2SO_4 (d) HBr

8. Which one is lewis acid

(a) Cl^- (b) Ag^+

(c) C_2H_5OH (d) S^{2-}

9. The correct order of acid strength is

(a) $HClO < HClO_2 < HClO_3 < HClO_4$

(b) $HClO_4 < HClO < HClO_2 < HClO_3$

(c) $HClO_2 < HClO_3 < HClO_4 < HClO$

(d) $HClO_4 < HClO_3 < HClO_2 < HClO$

10. Which of the following is the weakest base

(a) NaOH (b) $Ca(OH)_2$

(c) NH_4OH (d) KOH

11. Conjugate base of NH_3 is

(a) $NH_4^{\oplus}$ (b) $NH_2^{\oplus}$

(c) $NH_2^{\ominus}$ (d) N_2

12. According to Bronsted principle, an aqueous solution of HNO_3 will contain

(a) NO_2^- (b) NO_3^-

(c) NO_2^+ (d) NO^+

13. Ammonium ion is

(a) Neither an acid nor base

(b) Both an acid and a base

(c) A conjugate acid (d) A conjugate base

14. Which shows weak ionisation in water

(a) H_2SO_4 (b) NaCl

(c) HNO_3 (d) NH_3

15. The conjugate acid of HPO_4^{2-} is

(a) $H_2PO_4^-$ (b) PO_4^{3-}

(c) H_3PO_4 (d) H_3PO_3

Weak Acids and Bases : Analysis

16. A monoprotic acid in 1.00 M solution is 0.01% ionised. The dissociation constant of this acid is

(a) 1×10^{-8} (b) 1×10^{-4}

(c) 1×10^{-6} (d) 10^{-5}

17. If α is the degree of ionization, C the concentration of a weak electrolyte and K_a the acid ionization constant, then the correct relationship between α, C and K_a is

(a) $\alpha^2 = \sqrt{\frac{K_a}{C}}$ (b) $\alpha^2 = \sqrt{\frac{C}{K_a}}$

(c) $\alpha = \sqrt{\frac{K_a}{C}}$ (d) $\alpha = \sqrt{\frac{C}{K_a}}$

18. For a weak acid HA, Ostwald's dilution law is represented by the equation

(a) $K_a = \frac{\alpha c}{1-\alpha^2}$ (b) $K_a = \frac{\alpha^2 c}{1-\alpha}$

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

19. In which of the following dissociation of NH_4OH will be minimum

(a) NaOH (b) H_2O

(c) NH_4Cl (d) NaCl

20. The following equilibrium exists inaqueous solution, $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ if dil HCl is added, without change in temperature, the

(a) Concentration of CH_3COO^- will increase

(b) Concentration of CH_3COO^- will decrease

(c) The equilibrium constant will increase

(d) The equilibrium constant will decrease

21. The degree of dissociation of 0.1 M HCN solution is 0.01%. Its ionisation constant would be

(a) 10^{-3} (b) 10^{-5}

(c) 10^{-7} (d) 10^{-9}

22. The hydrogen ion concentration in weak acid of dissociation constant K_a and concentration c is nearly equal to

(a) $\sqrt{K_a / c}$ (b) c/K_a

(c) $K_a c$ (d) $\sqrt{K_a c}$

23. Degree of dissociation of 0.1 N CH_3COOH is

(Dissociation constant = 1×10^{-5})

(a) 10^{-5} (b) 10^{-4}

(c) 10^{-3} (d) 10^{-2}

24. 0.2 molar solution of formic acid is ionized 3.2%. Its ionization constant is

(a) 9.6×10^{-3} (b) 2.1×10^{-4}

(c) 1.25×10^{-6} (d) 4.8×10^{-5}

25. The values of dissociation constants of some acids (at 25°C) are as follows. Indicate which is the strongest acid in water

(a) 1.4×10^{-2} (b) 1.6×10^{-4}

(c) 4.4×10^{-10} (d) 4.3×10^{-7}

26. Concentration CN^- in 0.1 M HCN is [$K_a = 4 \times 10^{-10}$]

(a) 2.5×10^{-6} M (b) 4.5×10^{-6} M

(c) 6.3×10^{-6} M (d) 9.2×10^{-6} M

27. Review the equilibrium and choose the correct statement $HClO_4 + H_2O \rightleftharpoons H_3O^+ + ClO_4^-$

(a) $HClO_4$ is the conjugate acid of H_2O

(b) H_3O^+ is the conjugate base of H_2O

(c) H_2O is the conjugate acid of H_3O^+

(d) ClO_4^- is the conjugate base of $HClO_4$

28. In the reaction $2H_2O \rightleftharpoons H_3O^+ + OH^-$, water is

(a) A weak base

(b) A weak acid

(c) Both a weak acid and a weak base

(d) Neither an acid nor a base

29. The unit of ionic product of water K_w are

(a) $Mol^{-1}L^{-1}$ (b) $Mol^{-2}L^{-2}$

(c) $Mol^{-2}L^{-1}$ (d) $Mol^{2}L^{-2}$

30. Ionic product of water increases, if

(a) Pressure is reduced (b) H^+ is added

(c) OH^- is added (d) Temperature increases

31. At 90ºC, pure water has $[H_3O^+] = 10^{-6}$ mole $litre^{-1}$. What is the value of K_w at 90º C ?

(a) 10^{-6} (b) 10^{-12}

(c) 10^{-14} (d) 10^{-8}

32. HCOOH and CH_3COOH solution have equal pH. If K_1/K_2 (ratio of acid dissociation constants) is 4, ratio of their molar concentration will be :

(a) 2 (b) 0.5

(c) 4 (d) 0.25

33. $2H_2O \rightleftharpoons H_3O^+ + OH^-$, $K_w = 1 \times 10^{-14}$ at 25ºC hence K_a is:

(a) 1×10^{-14} (b) 5.55×10^{-3}

(c) 18×10^{-17} (d) 1.00×10^{-7}

34. For a "c molar" concentrated solution of a weak electrolyte A_xB_y, the degree of dissociation is given as

(a) $\alpha = \sqrt{K_{eq} / c\,(x+y)}$

(b) $\alpha = \sqrt{K_{eq} c/(xy)}$

(c) $\alpha = \left(K_{eq} / c^{x+y-1} x^x y^y\right)^{1/(x+y)}$

(d) $\sqrt{K_{eq} / xyc}$

35. The pH of a 0.1 M aqueous solution of a weak acid (HA) is 3. What is its degree of dissociation ?

(a) 1% (b) 10%

(c) 50% (d) 25%

36. Autoprotolysis constant of NH_3 is

(a) $[NH_4^+][NH_3]$ (b) $[NH_2^-][NH_3]$

(c) $[NH_4^+][NH_2^-]$ (d) $[NH_4^+]/[NH_2^-]$

pH of Solutions

37. What is the pH value of N/1000 KOH solution

(a) 10^{-11} (b) 3

(c) 2 (d) 11

38. The pH of a 0.001 M NaOH will be

(a) 3 (b) 2

(c) 11 (d) 12

39. The pH of a 10^{-9} M solution of HCl in water is

(a) 8 (b) – 8

(c) Between 7 and 8 (d) Between 6 and 7

40. A is an aqueous acid; B is an aqueous base. They are diluted separately, then

(a) pH of A increases and pH of B decreases

(b) pH of A increases and pH of B decreases till pH in each case is 7

(c) pH of A and B increase

(d) pH of B and A decrease

41. Pure water is kept in a vessel and it remains exposed to atmospheric CO_2 which is absorbed, then its pH will be

(a) Greater than 7 (b) Less than 7

(c) 7

(d) Depends on ionic product of water

42. An acid solution of pH = 6 is diluted hundred times. The pH the solution becomes :

(a) 6.95 (b) 6

(c) 4 (d) 8

43. The number of H^+ ions present in 1 mL of a solution having pH = 13 is :

(a) 10^{13} (b) 6.023×10^{13}

(c) 6.023×10^{7} (d) 6.023×10^{10}

44. For a pure water,

(a) pH increases and pOH decreases with increase in temperature

(b) pH decreases and pOH increases with increase in temperature

(c) both pH and pOH increase with increase in temperature

(d) both pH and pOH decrease with increase in temperature

45. Equal volumes of two solutions of hydrochloric acid are mixed. One solution has a pH 1 while the other has a pH5. The pH of the resulting solution is :

(a) less than 1 (b) Between 1 and 2

(c) 3 (d) Between 4 and 5

46. The dissociation constants of monobasic acids A, B, C and D are 6×10^{-4}, 5×10^{-5}, 3.6×10^{-6} and 7×10^{-10} respectively. The pH values of their 0.1 molar aqueous solutions are in the order :

(a) $A < B < C < D$ (b) $A > B > C > D$

(c) $A = B = C = D$ (d) None of these

47. The pH of a solution is increased from 3 to 6; its H^+ ion concentration will be :

(a) reduced to half (b) doubled

(c) reduced by 1000 times (d) increased by 1000 times

48. Aspirin (acetyl salicyclic acid, molar mass = 180 g mol^{-1}) used as analgesic has pK_a value of 2. Two tablets of aspirin each weighing 90 mg are dissolved in 100 mL of water. The pH of the solution is

(a) 0.5 (b) 1.0

(c) 2.0 (d) 4.0

49. A patient is said to suffer from acidosis when the pH of his blood

(a) falls below 7.35

(b) rises above 7.35

(c) Shows sudden fall and rise

(d) has strong basic character

50. What is the pH of a 0.015 M $Ba(OH)_2$ solution ?

(a) 1.82 (b) 1.52

(c) 12.48 (d) 12.18

51. Equal volumes of two solutions of HCl are mixed. One solution has a pH = 1, while the other has a pH = 5. The pH of the resulting solution is

(a) < 1 (b) Between 1 and 2

(c) 3 (d) Between 4 and 5

52. At a certain temperature the value of pK_w is 13.4 and the measured pH of soln is 7. The solution is

(a) Acidic (b) Basic

(c) Neutral (d) Unpredictable

Buffer Solutions

53. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be ($K_a = 10^{-5}$)

(a) 1 : 10 (b) 10 : 1

(c) 100 : 1 (d) 1 : 100

54. In a mixture of a weak acid and its salt, the ratio of concentration of acid to salt is increased ten-fold. The pH of the solution

(a) Decreases by one (b) Increases by one-tenth

(c) Increases by one (d) Increases ten-fold

55. The dissociation constant of HCN is 5×10^{-10}. The pH of the solution prepared by mixing 1.5 mole of HCN and 0.15 moles of KCN in water and making up the total volume to 0.5 dm^3 is

(a) 7.302 (b) 9.302

(c) 8.302 (d) 10.302

56. The principal buffer present in human blood is

(a) $NaH_2PO_4 + Na_2HPO_4$

(b) $H_3PO_4 + NaH_2PO_4$

(c) $CH_3COOH + CH_3COONa$

(d) $H_2CO_3 + HCO_3^-$

57. 0.1 mole of CH_3NH_2 ($K_b = 5 \times 10^{-4}$) is mixed with 0.08 mole of HCl and the solution diluted to one litre. The H^+ ion concentration in the solution will be

(a) 1.6×10^{-11} (b) 8×10^{-11}

(c) 5×10^{-5} (d) 8×10^{-2}

58. The pK_a of weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is

(a) 7.0 (b) 4.5

(c) 2.5 (d) 9.5

59. How many moles of HCOONa must be added to 1L of 0.1 M HCOOH to prepare a buffer solution with a pH of 3.4 ?

(Given : K_a for HCOOH = 2×10^{-4})

(a) 0.01 (b) 0.05

(c) 0.1 (d) 0.2

60. What is the pH of a buffer solution which is 0.250 M in benzoic acid, C_6H_5COOH, and 0.150 M in sodium benzoate, C_6H_5COONa, if Ka for benzoic acid is 6.5×10^{-5} ?

(a) 3.40 (b) 3.97

(c) 4.19 (d) 4.41

61. Calculate the pH of a buffer prepared by mixing 0.10 mol of sodium formate and 0.05 mole of formic acid in 1.0 L of solution. [$HCO_2H : K_a = 1.8 \times 10^{-4}$]

(a) 1.8×10^{-4} (b) 3.44

(c) 4.05 (d) 5.31

62. 100 mL of a buffer solution contains 0.1 M each of weak acid HA and salt NaA. How many gram of NaOH should be added to the buffer so that its pH will be 6 ? (K_a of HA = 10^{-5}).

(a) 0.328 (b) 0458

(c) 4.19 (d) None

63. Two buffer solutions, A and B, each made with acetic acid and sodium acetate differ in their pH by one unit, A has salt : acid = x : y, B has salt : acid = y : x. If x > y, then the value of x : y is

(a) 10,000 (b) 3.17

(c) 6.61 (d) 2.10

64. Buffer solutions can be prepared from mixtures of

(a) HCl and NaCl (b) NaH_2PO_4 and Na_2HPO_4

(c) $CH_3COOH + NaCl$ (d) $NH_4OH + NH_3$

65. A certain buffer solution contains equal concentration of $X^{\ominus}$ and HX. The K_b for $X^{\ominus}$ is 10^{-10}. The pH of the buffer is

(a) 4 (b) 7

(c) 10 (d) 14

66. The pK_b of $CN^{\ominus}$ is 4.7. The pH of solution prepared by mixing 2.5 mol of KCN of 2.5 mol of HCN in water and making the total volume upto 500 mL is

(a) 10.3 (b) 9.3

(c) 8.3 (d) 4.7

67. The pH of a dilute solution of acetic acid was found to be 4.3. The addition of a small crystal of sodium acetate will cause pH to

(a) Become less than 4.3 (b) Become more than 4.3

(c) Remain equal to 4.3 (d) Unpredictable

68. To 1.0 L solution containing 0.1 mol each of NH_3 and NH_4Cl, 0.05 mol NaOH is added. The change in pH will be (pK_a for $CH_3COOH = 4.74$)

(a) 0.30 (b) –0.30

(c) 0.48 (d) –0.48

69. The pH of blood is maintained by the balance between H_2CO_3 and $NaHCO_3$. If the amount of CO_2 in the blood is increased, how will it effect the pH of blood ?

(a) pH will remain same (b) pH will be 7

(c) pH will increase (d) pH will decrease

70. Fixed volume of 0.1 M benzoic acid ($pK_a = 4.2$) solution is added into 0.2 M sodium benzoate solution and formed a 300 mL, resulting acidic buffer solution. If pH of the resulting solution is 3.9, then added volume of benzoic acid is

(a) 240 mL (b) 150 mL

(c) 100 mL (d) None

Polyprotic Acids and Bases

71. In a 0.010 M solution of oxalic acid, $H_2C_2O_4$, $K_{a1} = 5.9 \times 10^{-2}$, $K_{a2} = 6.4 \times 10^{-5}$, the species present in the lowest concentration is

(a) $H_2C_2O_4$ (b) H_3O^+

(c) $HC_2O_4^-$ (d) $C_2O_4^{2-}$

72. Calculate the carbonate ion concentration in a 0.10 M solution of the weak acid, carbonic acid are (H_2CO_3). The dissociation constants of carbonic acid are $K_{a1} = 4.5 \times 10^{-7}$ and $K_{a2} = 4.7 \times 10^{-11}$.

(a) 4.7×10^{-11} M (b) 1.0×10^{-7} M

(c) 4.5×10^{-7} M (d) 2.1×10^{-4} M

73. In a saturated solution of H_2S, DECREASING the pH of the solution will cause

(a) the S^{2-} concentration to decrease

(b) the H_2S concentration to decrease

(c) the S^{2-} concentration to increase

(d) no change in either the H_2S or S^{2-} concentration

74. Which one of the following statements is true with regard to a 0.10 M H_2SO_4 solution ?

(a) $[H_2SO_4] > [H^+]$ (b) $[H^+] = [SO_4^{2-}]$

(c) $[SO_4^{2-}] > [HSO_4^-]$ (d) $[H^+] > [HSO_4^-]$

75. What is the pH of 0.01 M glycine solution ? For glycine

$K_{a_1} = 4.5 \times 10^{-3}$ and $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K

(a) 3.0 (b) 10.0

(c) 6.1 (d) 7.2

Salt Hydrolysis

76. Aq. solution of sodium cyanide is

(a) Acidic (b) Amphoteric

(c) Basic (d) Netural

77. The solution of strong acid and weak base ($FeCl_3$) is

(a) Acidic (b) Basic

(c) Neutral (d) none of these

78. Which one of the following salts gives an acidic solution in water

(a) CH_3COONa (b) NH_4Cl

(c) NaCl (d) CH_3COONH_4

79. An aqueous solution of aluminium sulphate would show

(a) An acidic reaction

(b) A neutral reaction

(c) A basic reaction

(d) Both acidic and basic reaction

80. An aqueous solution of sodium carbonate is alkaline because sodium carbonate is a salt of

(a) Weak acid and weak base

(b) Strong acid and weak base

(c) Weak acid and strong base

(d) Strong acid and strong base

81. The aqueous solution of ammonium chloride is

(a) Neutral (b) Basic

(c) Acidic (d) Amphoteric

82. The aqueous solution of $FeCl_3$ is acidic due to

(a) Acidic impurities (b) Ionisation

(c) Hydrolysis (d) Dissociation

83. Which is the correct alternate for hydrolysis constant of NH_4CN

(a) $\sqrt{\dfrac{K_w}{K_a}}$ (b) $\dfrac{K_w}{K_a \times K_b}$

(c) $\sqrt{\dfrac{K_b}{c}}$ (d) $\dfrac{K_a}{K_b}$

84. The pH 0.1 M solution of the following salts increases in the order :

(a) $NaCl < NH_4Cl < NaCN < HCl$

(b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$

(d) $HCl < NaCl < NaCN < NH_4Cl$.

85. The pK_{a_1} and pK_{a_2} of an amino acid are 2.3 and 9.7 respectively. The isoelectric point of amino acid is :

(a) 12 (b) 7.4

(c) 6.0 (d) 3.7

86. HCN is a weak acid ($K_a = 6.2 \times 10^{-10}$). NH_4OH is a weak base ($K_b = 1.8 \times 10^{-5}$). A 1M solutionk of NH_4CN would be :

(a) strongly acidic (b) weakly acidic

(c) neutral (d) weakly basic

87. The equilibrium constant for this reaction is 3.6×10^{-7}.

$$OCl^-(aq.) + H_2O(l) \rightleftharpoons HOCl(aq.) + OH^-(aq.)$$

What is K_a for HOCl ?

(a) 2.8×10^{-8} (b) 3.6×10^{-7}

(c) 6×10^{-4} (d) 2.8×10^{-6}

88. Ka for hydrofluoric acid is 6.9×10^{-4}. What is the equilibrium constant K for the following reaction ?

$$F^-(aq.) + H_2O(l) \rightleftharpoons HF(aq.) + OH^-(aq.)$$

(a) 6.9×10^{-11} (b) 1.4×10^{-11}

(c) 2.6×10^{-9} (d) 8.3×10^{-6}

89. K_a for HF is 3.5×10^{-4}. Calculate K_b for the fluoride ion.

(a) 3.5×10^{-4} (b) 1.0×10^{-7}

(c) 2.9×10^{-11} (d) 1.0×10^{-14}

90. Which of the following salt is basic ?

(a) HOCl (b) NaOCl

(c) $NaHSO_4$ (d) NH_4NO_3

Solubility Equilibria

91. The solubility product of a salt having general formula MX_2, in water is : 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is

(a) 2.0×10^{-6} M (b) 1.0×10^{-4} M

(c) 1.6×10^{-4} M (d) 4.0×10^{-10} M

92. Let the solubility of an aqueous solution of $Mg(OH)_2$ be x then its k_{sp} is

(a) $4x^3$ (b) $108x^5$

(c) $27x^4$ (d) 9x

93. The solubility in water of a sparingly soluble salt AB_2 is 1.0×10^{-5} mol l^{-1}. Its solubility product number will be

(a) 4×10^{-15} (b) 4×10^{-10}

(c) 1×10^{-15} (d) 1×10^{-10}

94. The solubility of CaF_2 is a moles/litre. Then its solubility product is........

(a) s^2 (b) $4s^3$

(c) $3s^2$ (d) s^3

95. Which is the correct representation of the solubility product constant of Ag_2CrO_4

(a) $[Ag^+]^2[CrO_4^{-2}]$ (b) $[Ag^+][CrO_4^{-2}]$

(c) $[2Ag^+][CrO_4^{-2}]$ (d) $[2Ag^+]^2[CrO_4^{-2}]$

96. A precipitate of AgCl is formed when equal volumes of the following are mixed. [K_{sp} for AgCl = 10^{-10}]

(a) 10^{-4} M $AgNO_3$ and 10^{-7} M HCl

(b) 10^{-5} M $AgNO_3$ and 10^{-6} M HCl

(c) 10^{-5} M $AgNO_3$ and 10^{-4} M HCl

(d) 10^{-6} M $AgNO_3$ and 10^{-6} M HCl

97. The correct representation for solubility product of SnS_2 is

(a) $[Sn^{4+}][S^{2-}]^2$ (b) $[Sn^{2+}][S^{2-}]^2$

(c) $[Sn^{2+}][2S^{2-}]$ (d) $[Sn^{4+}][2S^{2-}]^2$

98. Solubility product of $BaCl_2$ is 4×10^{-9}. Its solubility in moles/litre would be

(a) 1×10^{-3} (b) 1×10^{-9}

(c) 4×10^{-27} (d) 1×10^{-27}

99. Solubility of AgCl will be minimum in

(a) 0.001 M $AgNO_3$ (b) Pure water

(c) 0.01 M $CaCl_2$ (d) 0.01 M NaCl

100. At 298 K, the solubility product of $PbCl_2$ is 1.0×10^{-6}. What will be the solubility of $PbCl_2$ in moles/litre

(a) 6.3×10^{-3} (b) 1.0×10^{-3}

(c) 3.0×10^{-3} (d) 4.6×10^{-14}

101. K_{sp} for $Ca(OH)_2$ is 5.5×10^{-6}. What is the maximum pH that can be attained in a sewage tank treated with slaked lime ?

(a) 9.35 (b) 10.35

(c) 11.35 (d) 12.35

102. For a sparingly soluble salt $A_p B_q$, the relationship of its solubility product (L_S) with its solubility (S) is :

(a) $L_S = S^{p+q} . p^p . q^q$ (b) $L_S = S^{p+q} . p^q . q^p$

(c) $L_S = S^{pq} . p^p . q^q$ (d) $L_S = S^{pq} (pq)^{p+q}$

103. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with :

(a) 10^{-4} M (Ag^+) and 10^{-4}M (Cl^-)

(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)

(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)

(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

104. The solubility product of different sparingly soluble salts are :

1. $XY = 4 \times 10^{-20}$ 2. $X_2Y = 3.2 \times 10^{-11}$

3. $XY_3 = 2.7 \times 10^{-31}$

The increasing order of solubility is :

(a) 1, 3, 2 (b) 2, 1, 3

(c) 1, 2, 3 (d) 3, 1, 2

105. Solubility of AgCN is maximum in :

(a) acidic buffer solution (b) basic buffer solution

(c) in pure water (d) equal in all solution

106. The solubility of CH_3COOAg in a buffer solution with pH = 4, whose $K_{sp} = 10^{-12}$ and $K_a = \frac{10^{-4}}{3}$ is

(a) 10^{-6} (b) 0.5×10^{-6}

(c) 5×10^{-6} (d) 2×10^{-6}

107. K_{sp} of $Mg(OH)_2$ is 4.0×10^{-6}. At what minimum pH, Mg^{2+} ions starts precipitating 0.01 MgCl

(a) 2 + log 2 (b) 2 – log 2

(c) 12 + log 2 (d) 12 – log 2

108. The pH of an aqueous solution of $Ba(OH)_2$ is 10. If the K_{sp} of $Ba(OH)_2$ is 1×10^{-9}, then the concentration of Ba^{2+} ions in the solution in mol L^{-1} is

(a) 1×10^{-2} (b) 1×10^{-4}

(c) 1×10^{-1} (d) 1×10^{-5}

109. $CaCO_3$ and $BaCO_3$ have solubility product values 1×10^{-8} and 5×10^{-9}, respectively. If water is shaken up with both solids till equilibrium is reached, the concentration of CO_3^{2-} ion is

(a) 1.5×10^{-8} (b) 1.225×10^{-4}

(c) 2.25×10^{-9} (d) None of these

Indicators and Titrations

110. What will be the pH of a solution formed by mixing 40 ml of 0.10 M HCl with 10 ml of 0.45 M NaOH

(a) 12 (b) 10

(c) 8 (d) 6

111. The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentrations of the conjugate acid (HIn) and base (In^-) forms of the indicator by the expression

(a) $\log\frac{[HIn]}{[In^-]} = pH - pK_{In}$

(b) $\log\frac{[In^-]}{[HIn]} = pH - pK_{In}$

(c) $\log\frac{[In^-]}{[HIn]} = pK_{In} - pH$

(d) $\log\frac{[HIn]}{[In^-]} = pK_{In} - pH$

112. The pH indicators are :

(a) salts of strong acids and strong bases

(b) salts of weak acids and weak bases

(c) either weak acids or weak bases

(d) either strong acids or strong bases

113. In which of the following acid-base titration, pH is greater than 8 at the equivalence point ?

(a) Acetic acid versus ammonia

(b) Acetic acid versus sodium hydroxide

(c) Hydrochloric acid versus ammonia

(d) Hydrochloric and versus sodium hydroxide

114. Why are strong acids generally used as standard solutions in acid-base titrations ?

(a) The pH at the equivalent point will always be 7

(b) They can be used to titrate both strong and weak bases

(c) Strong acids form more stable solutions than weak acids

(d) The salts of strong acid do not hydrolyze

115. The best indicator for detection of end point in titration of a weak acid and a strong base is :

(a) methyl orange (3 to 4)

(b) methyl red (5 to 6)

(c) bromothymol blue (6 to 7.5)

(d) phenolphthalein (8 to 9.6)

116. Which of the following mixture will have the pH close to 1 ?

(a) 100 ml of M/10 HCl + 100 ml of M/10 NaOH

(b) 55 ml of M/10 HCl + 45ml of M/10 NaOH

(c) 10 ml of M/10 HCl + 90 ml of M/10 NaOH

(d) 75 ml of M/5 HCl + 25 ml of M/5 NaOH

117. Consider the titratiokns listed below. In which is the pH at the equivalence point described incorrectly ?

	Acid	Base	pH at equiv.pt.
(a)	CH_3COOH	NaOH	> 7.00
(b)	HNO_3	$Ca(OH)_2$	$= 7.00$
(c)	HCl	NH_3	< 7.00
(d)	HF	NaOH	< 7.00

118. Which indicator is suitable for the titrations :

Titration	Indicator
(i) HCOOH/NaOH	(A) Bromothymol blue or phenolphthalein or methyl orange or thymolphthalein
(ii) HBr/KOH	(B) Methyl orange or methyl red or bromocresol green
(iii) $NH_4OH.HNO_3$	(C) Phenolphthalein or thymolphthalein

(a) (i) → A, (ii) → B, (iii) → C

(b) (i) → A, (ii) → C, (iii) → B

(c) (i) → B, (ii) → C, (iii) → A

(d) (i) → C, (ii) → A, (iii) → B

119. In which of the following acid-base titration, pH is greater than 8 at the equivalence point ?

(a) Aceitic acid vs ammonia

(b) Acetic acid vs sodium ammonia

(c) Hydrochloric acid vs ammonia

(d) Hydrochloric acid vs sodium hydroxide

120. 20 cm^3 of x M solution of HCl is exactly neutralised by 40 cm^3 of 0.05 M NaOH solution, the pH of HCl solution is

(a) 1.0 (b) 2

(c) 1.5 (d) 2.5

121. Phenolphthalein does not act as an indicator for the titration between

(a) HCl and NH_4OH (b) $Ca(OH)_2$ and HCl

(c) NaOH and H_2SO_4 (d) KOH and CH_3COOH

122. Methyl orange gives red colour in

(a) KOH solution (b) HCl solution

(c) Na_2CO_3 solution (d) NaCl solution

123. Which acid-base indicator should be used in an aqueous solution titration which is complete at about 0.001 M H^+(aq) ? The transition range in pH is given in parenthesis.

(a) Methyl violet (0.5 – 1.5)

(b) Methyl red (4.2 – 6.3)

(c) Methyl yellow (2.9 – 4.0)

(d) Phenol red (6.4 – 8.0)

124. A sample of 50.0 mL of 0.10 M NH_3 ($K_b = 1.8 \times 10^{-5}$) is titrated with 0.10 M HCl. Calculate the pH at the equivalence point.

(a) 6.98 (b) 2.87

(c) 7.78 (d) 5.28

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTIONS

1. The molar solubility (in mol L^{-1}) of a sparingly soluble salt MX_4 is 's'. The corresponding solubility product is K_{sp}. 's' is given in terms of K_{sp} by the relation **(2004)**

(a) $s = \left(\frac{K_{sp}}{128}\right)^{1/4}$ (b) $s = \left(\frac{K_{sp}}{256}\right)^{1/5}$

(c) $s = (256\,K_{sp})^{1/5}$ (d) $s = (128\,K_{sp})^{1/4}$

2. The conjugate base of $H_2PO_4^-$ **(2004)**

(a) PO_4^{3-} (b) HPO_4^{2-}

(c) H_3PO_4 (d) P_2O_5

3. The solubility product of a salt having general formula MX_2; in water is 4×10^{-12}. The concentration of M^{2+} ions in the aqueous solution of the salt is **(2005)**

(a) 4.0×10^{-10} M (b) 1.6×10^{-4} M

(c) 1.0×10^{-4} M (d) 2.0×10^{-6} M

4. What is the conjugate base of OH^- ? **(2005)**

(a) O^{2-} (b) O^-

(c) H_2O (d) O_2

5. The pKa of a weak acid (HA) is 4.5. The pOH of an aqueous buffered solution of HA in which 50% of the acid is ionized is **(2007)**

(a) 4.5 (b) 2.5

(c) 9.5 (d) 7.0

6. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is

$$AgIO_{3(s)} \rightleftharpoons Ag^+_{(aq.)} + IO^-_{3(aq.)}$$

If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution ? **(2007)**

(a) 28.3×10^{-2}g (b) 2.83×10^{-3}g

(c) 1.0×10^{-7}g (d) 1.0×10^{-4}g

7. The first and second dissociation constant of an acid H_2A are 1.0×10^{-5} and 5.0×10^{-10} respectively. The overall dissociation constant of the acid will be **(2007)**

(a) 5.0×10^{-5} (b) 5.0×10^{15}

(c) 5.0×10^{-15} (d) 0.2×10^{15}

8. Four species are listed below

(i) HCO_3^- (ii) H_3O^+

(iii) HSO_4^- (iv) HSO_3F

Which of the following is the correct sequence of their acid strength ? **(2008)**

(a) iv < ii < iii < i (b) ii < iii < i < iv

(c) i < iii < ii < iv (d) iii < i < iv < ii

9. The pK_a of a weak acid, HA, is 4.80. The pK_b of a weak base, BOH, is 4.78. The pH of an aqueous solution of the corresponding salt, BA, will be **(2008)**

(a) 8.58 (b) 4.79

(c) 7.01 (d) 9.22

10. Solid Ba $(NO_3)_2$ is gradually dissolved in a 1.0×10^{-4} M Na_2CO_3 solution. At what concentration of Ba^{+2} will a precipitate being to form ? (K_{sp} for $BaCO_3 = 5.1 \times 10^{-9}$); **(2009)**

(a) 4.1×10^{-5} M (b) 5.1×10^{-5} M

(c) 8.1×10^{-8} M (d) 8.1×10^{-7} M

11. At 25°C, the solubility product of $Mg(OH)_2$ is 1.0×10^{-11}. At which pH, will Mg^{2+} ions start precipitating in the form of $Mg(OH)_2$ from a solution of 0.001 M Mg^{2+} ions ? **(2010)**

(a) 9 (b) 10

(c) 11 (d) 8

12. Solubility product of silver bromie is 5.0×10^{-13}. The quantity of potassium bromide (molar mass taken as 120 g mol^{-1}) to be added to 1L of 0.05 M solution of silver nitrate to start the precipitation of AgBr is **(2010)**

(a) 1.2×10^{-10} g (b) 1.2×10^{-9} g

(c) 6.2×10^{-5} g (d) 5.0×10^{-8} g

13. In aqueous solution, the ionisation constants for carbonic acid are **(2010)**

$K_1 = 4.2 \times 10^{-7}$ and $K_2 = 4.8 \times 10^{-11}$

Select the correct statement for a saturated 0.034 M solution of the carbonic acid.

(a) The concentration of CO_3^{2-} is 0.034 M

(b) The concentration of CO_3^{2-} is greater than that of HCO_3^-

(c) The concentration of H^+ and HCO_3^- are approximately equal

(d) The concentration of H^+ is double that of CO_3^{2-}

14. Three reactions involving $H_2PO_4^-$ are given below : **(2010)**

I. $H_3PO_4 + H_2O \rightarrow H_3O^+ + H_2PO_4^-$

II. $H_2PO_4^- + H_2O \rightarrow HPO_4^{2-} + H_3O^+$

III. $H_2PO_4^- + OH^- \rightarrow H_3PO_4 + O^{2-}$

In which of the above does $H_2PO_4^-$ act as an acid ?

(a) II only (b) I and II

(c) III only (d) I only

15. The K_{sp} for $Cr(OH)_3$ is 1.6×10^{-30}. The molar solubility of this compound in water is **(2011)**

(a) $\sqrt[2]{1.6\times10^{-30}}$ (b) $\sqrt[4]{1.6\times10^{-30}}$

(c) $\sqrt[4]{1.6\times10^{-30}/27}$ (d) $1.6\times10^{-30}/27$

16. An acid HA ionises as

$$HA \rightleftharpoons H^+ + A^-$$

The pH of 1.0 M solution is 5. Its dissociation constant would be **(2011)**

(a) 1×10^{-10} (b) 5

(c) 5×10^{-8} (d) 1×10^{-5}

17. Among the following oxoacids, the correct decreasing order of acid strength is : **(2014)**

(a) $HClO_4 > HOCl > HClO_2 > HClO_3$

(b) $HClO_4 > HClO_3 > HClO_2 > HOCl$

(c) $HClO_2 > HClO_4 > HClO_3 > HOCl$

(d) $HOCl > HClO_2 > HClO_3 > HClO_4$

18. Which has the highest pH ? **(2015)**

(a) CH_3COONH_4 (b) Na_2CO_3

(c) NH_4Cl (d) $NaNO_3$

19. pK_a of a weak acid (HA) and pK_b of a weak base (BOH) are 3.2 and 3.4, respectively. The pH of their salt (AB) solution is : **(2017)**

(a) 6.9 (b) 7.0

(c) 1.0 (d) 7.2

20. Which of the following salts is the most basic in aqueous solution? **(2018)**

(a) $Pb(CH_3COO)_2$ (b) $Al(CN)_3$

(c) CH_3COOK (d) $FeCl_3$

21. An alkali is titrated against an acid with methyl orange as indicator, which of the following is a correct combination **(2018)**

Base	**Acid**	**End Point**
(a) Strong	Strong	Pink to colourless
(b) Weak	Strong	Colourless to pink
(c) Strong	Strong	Pinkish red to yellow
(d) Weak	Strong	Yellow to pinkish red

JEE MAINS ONLINE QUESTION

1. Assuming that the degree of hydrolysis is small, the pH of 0.1 M solution of sodium acetate ($K_a = 1.0 \times 10^{-5}$) will be: **Online 2014 SET (2)**

(a) 8.0 (b) 6.0

(c) 9.0 (d) 5.0

2. In some solutions, the concentration of H_3O^+ remains constant even when small amounts of strong acid or strong base are added to them. These solutions are known as: **Online 2014 SET (2)**

(a) Buffer solutions

(b) True solutions

(c) Ideal solutions

(d) Colloidal solutions

3. The conjugate base of hydrazoic acid is:

Online 2014 SET (3)

(a) N_2^- (b) N_3^-

(c) N^{-3} (d) HN_3^-

4. Zirconium phosphate $[Zr_3(PO_4)_4]$ dissociates into three zirconium cations of charge +4 and four phosphate anions of charge –3. If molar solubility of zirconium phosphate is denoted by S and its solubility product by K_{sp} then which of the following relationship between S and K_{sp} is correct ? **Online 2014 SET (4)**

(a) $S = \{K_{sp}/(6912)^{1/7}\}$ (b) $S = (K_{sp}/6912)^{1/7}$

(c) $S = \{K_{sp}/144\}^{1/7}$ (d) $S = \{K_{sp}/6912\}^7$

5. Addition of sodium hydroxide solution to a weak acid (HA) results in a buffer of pH 6. If ionisation constant of HA is $10^{"5}$, the ratio of salt to acid concentration in the buffer solution will be : **Online 2017 SET (1)**

(a) 4 : 5 (b) 1 : 10

(c) 10 : 1 (d) 5 : 4

6. 50 mL of 0.2 M ammonia solution is treated with 25 mL of 0.2 M HCl. If pK_b of ammonia solution is 4.75, the pH of the mixture will be : **Online 2017 SET (2)**

(a) 3.75 (b) 4.75

(c) 8.25 (d) 9.25

7. The minimum volume of water required to dissolve 0.1 g lead(II) chloride to get a saturated solution (K_{sp} of $PbCl_2 = 3.2 \times 10^{-8}$; atomic mass of Pb =207u) is : **Online 2018 SET (1)**

(a) 0.36 L (b) 17.98 L

(c) 0.18 L (d) 1.798 L

8. Which of the following is a Lewis acid ?

Online 2018 SET (1)

(a) PH_3 (b) $B(CH_3)_3$

(c) NaH (d) NF_3

9. Following four solutions are prepared by mixing different volumes of NaOH and HCl of different concentrations, pH of which one of them will be equal to 1 ? **(Online 2018 SET 2)**

(1) $100mL\frac{M}{10}HCl + 100mL\frac{M}{10}NaOH$

(2) $75mL\frac{M}{5}HCl + 25mL\frac{M}{5}NaOH$

(3) $60mL\frac{M}{10}HCl + 40mL\frac{M}{10}NaOH$

(4) $55mL\frac{M}{10}HCl + 45mL\frac{M}{10}NaOH$

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

1. All questions marked **"S"** are single choice questions
2. All questions marked **"M"** are multiple choice questions
3. All questions marked **"C"** are comprehension based questions
4. All questions marked **"A"** are assertion–reason type questions

   (A) If both assertion and reason are correct and reason is the correct explanation of assertion.

   (B) If both assertion and reason are true but reason is not the correct explanation of assertion.

   (C) If assertion is true but reason is false.

   (D) If reason is true but assertion is false.
5. All questions marked **"X"** are matrix–match type questions
6. All questions marked **"I"** are integer type questions

Theory of Electrolytes, Acid-Base Strength Comparison

1. (A) **Assertion :** $[Al(H_2O)_6]^{3+}$ is a stronger acid than $[Mg(H_2O)_6]^{2+}$.

Reason : Size of $[Al(H_2O)_6]^{3+}$ smaller than $[Mg(H_2O)_6]^{2+}$ and possesses more effective nuclear charge.

(a) A (b) B

(c) C (d) D

2. (M) Which among the following represent the conjugate acid/base pairs ?

(a) H_3O^+/H_2O (b) H_2SO_4/SO_4^{2-}

(c) HCO_3^-/CO_3^{2-}

(d) All are conjugate acid/base paires

3. (S) The equilibrium constant for this reaction is approximately 10^{-3}.

$$HPO_4^{2-}(aq.) + HCO_3^-(aq.) \rightleftharpoons H_2PO_4^-(aq.) + CO_3^{2-}(aq.)$$

Which is the strongest conjugate base in this reaction ?

(a) $HPO_4^{2-}(aq.)$ (b) $HCO_3^-(aq.)$

(c) $H_2PO_4^-(aq.)$ (d) $CO_3^{2-}(aq.)$

4. (S) In the following reaction :

$$HCO_3^- + H_2O \rightleftharpoons CO_3^{2-} + H_3O^+$$

Which two substances are Bronsted bases ?

(a) CO_3^{2-} and H_3O^+ (b) HCO_3^- and H_3O^+

(c) HCO_3^- and CO_3^{2-} (d) CO_3^{2-} and H_2O

5. (S) Arrange the following acids in increasing order of their acid strength :

I. $HClO_4$ II. H_2SO_4

III. H_3PO_4

(a) III < II < I (b) I < II < III

(c) II < III < I (d) III < I < II

6. (S) Consider the following reaction which proceeds predominantly from

$$HSO_4^- + NH_3 \rightleftharpoons NH_4^+ + SO_4^{2-}$$

From the information given it is clear that

(a) HSO_4^- is a stronger acid than NH_4^+.

(b) NH_3 is a weaker base than SO_4^{2-}

(c) HSO_4^- is a stronger base than NH_4^+

(d) NH_3 is a weaker base than NH_4^+

7. (A) **Assertion :** H_2SO_4 acts as a base in the presence of $HClO_4$.

Reason : Perchloric acid is stronger acid than H_2SO_4.

(a) A (b) B

(c) C (d) D

Weak Acids and Bases : Analysis

8. (S) A mixture of weak acid is 0.1 M in HCOOH ($Ka = 1.8 \times 10^{-4}$) and 0.1 M in HOCN ($Ka = 3.1 \times 10^{-4}$). Hence, $[H_3O^{\oplus}]$ is

(a) 7.0×10^{-3} M (b) 4.1×10^{-4} M

(c) 0.20 M (d) 4.1×10^{-3} M

9. (S) Like water, ammonia (NH_3) is an amphoteric substance that can be used as a solvent for acid base reactions. The phase label (am) means solvated by ammonia (ammoniated). Which statement is correct, extrapolating from your knowledge of acid base reactions in water ?

(a) Auto-ionization of ammonia is described by

$$2NH_3(l) \rightleftharpoons NH_4^+(am) + NH_2^-(am)$$

(b) The strongest acid that can exist in ammonia solution is H_3O^+ (am).

(c) The strongest base, which can exist in ammonia solution, is NH_4^+ (am).

(d) The addition of an acid to an ammonia solution will increase the concentration of NH_2^- (am).

10. (S) The concentration of NaOH solution is 10^{-8} M. Find out the (OH^-) concentration

(a) 10^{-8} (b) Greater than 10^{-6}

(c) 10^{-6} (d) Lies between 10^{-6} and 10^{-7}

11. (M) The percentage ionization of a weak base is given by

(a) $\left(\sqrt{\frac{K_a}{c}}\right)\times 100$ (b) $\left(\frac{1}{1+10^{pK_b - pOH}}\right)\times 100$

(c) $\left(\sqrt{\frac{K_b}{c}}\right)\times 100$

(d) $\left(\sqrt{\frac{K_w}{c\times K_a \text{ of conjugate acid}}}\right)\times 100$

Comprehension

The concentration of hydrogen ion is a measure of acidity or alkalinity of a solution.

For mono basic acids :

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

$$\alpha = \sqrt{\frac{K_a}{C}}$$

where, K_a = Dissociation constant of acid

C = molarity of acid

$$[H^+] = C\alpha, [H^+] = \frac{K_a}{\alpha},\ [H^+] = \sqrt{CK_a}$$

pH of a weak acid can be calculated using $[H^+]$ by any of above methods.

$[H^+]_{Total} = \sqrt{C_1K_{a_1} + C_2K_{a_2}}$ (When two weak acids are mixed)

$[H^+]$ of polyprotic acid (weak, H_3A) (has dissociation constants $K_{a_1} >> K_{a_2} >> K_{a_3}$); will be contributed by first dissociation at the most.

12. (C) What will be the value of $[H^+]$ of 10^{-6} M CH_3COOH ? ($K_a = 1.8\times 10^{-5}$)

(a) 4.24×10^{-6} M (b) 10^{-6} M

(c) 9.5×10^{-7} M (d) 10^{-8} M

13. (C) What will be sulphide ion concentration of a dilute solution that has been saturated with 0.1 M H_2S if the pH of the solution is 3 ?

$K_{a_1} = 1\times 10^{-7}$; $K_{a_2} = 1.3\times 10^{-13}$

(a) 1.25×10^{-11} (b) 1.3×10^{-13}

(c) 1.45×10^{-9} (d) 1.30×10^{-15}

14. (C) The pH of 0.01 M HCOOH ($K_a = 1.4\times 10^{-4}$) will be :

(a) 2.926 (b) 3.296

(c) 4.962 (d) 5.926

15. (I) Ionic product of water is 10^{-12}. pH of water is _____.

16. (M) Which of the following statements is/are correct about the ionic product of water ?

(a) K_a (equilibrium constant of water) < K_w (ionic product of water)

(b) $pK > pK_w$

(c) At 100°C, K_w of water becomes 10^{-12}

(d) Ionic product of water at 25°C is 10^{-14}

17. (A) **Assertion :** Water acts as levelling solvent for various acids.

Reason : Levelling effect of water is due to high dielectric constant and strong proton accepting tendency.

(a) A (b) B

(c) C (d) D

18. (A) **Assertion :** Addition of HCl(aq.) to HCOOH(aq.) decreases the ionization of HCOOH.

Reason : Common ion effect of H^+ ion, reduces the ionization of HCOOH.

(a) A (b) B

(c) C (d) D

19. (S) The charge balance equation of species in 0.1 M CH_3COOH solution is given by :

(a) $[H^+] = [OH^-]$

(b) $[H^+] = [CH_3COO^-]$

(c) $[H^+] = [OH^-] + [CH_3COO^-]$

(d) $2[H^+] = [OH^-] + [CH_3COO^-]$

20. (S) A solution of 2M formic acid (HCOOH) is 0.95% ionized. What is the K_a of formic acid ?

(a) 1.9×10^{-2} (b) 1.8×10^{-4}

(c) 9×10^{-5} (d) 4.5×10^{-5}

21. (S) What is the K_b of a weak base that produces one OH^- per molecule if a 0.05 M solution is 2.5% ionized ?

(a) 7.8×10^{-8} (b) 1.6×10^{-6}

(c) 3.2×10^{-5} (d) 1.2×10^{-3}

22. (M) A solution is prepared by mixing 100 mL 0.50 M hydrazoic acid (HN_3), whose $K_a = 3.6 \times 10^{-4}$, with 400 mL of 0.10M cyanic acid (HOCN), whose $K_a = 8 \times 10^{-4}$. Which of the following is (are) true regarding

(a) $[H^+] = 10^{-2}$ M (b) $[N_3^-] = 3.6 \times 10^{-3}$

(c) $[OCN^-] = 4.57 \times 10^{-3}$ (d) $[OH^-] = 7.14 \times 10^{-13}$

23. (M) At 25°C, pH of a 0.01 M solution of a monobasic acid (HA) is 4. The correct statement(s) regarding HA and its given solution is (are)

(a) HA is a weak acid

(b) The ionization constant (K_a) of acid is approximately 10^{-6} at 25ºC

(c) Increasing the temperature of solution would cause the pH to decrease

(d) Addition of 0.1 M HCl solution would lower pH by increasing degree of ionization.

pH of Solutions

24. (S) The pK_a of acetylsalicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2-3 and the pH in the small intestine is about 8. Aspirin will be :

(a) unionised in the small intestine and in the stomach

(b) completely ionized in the small intestine and in the stomach

(c) ionised in the stomach and almost unionised in the small intestine

(d) ionised in the small intestine and almost unionised in the stomach

25. (A) **Assertion :** pH of HCl solution is less than that of acetic acid of the same concentration.

Reason : In equimolar solutions, the number of titrable protons present in HCl in less than that present in acetic acid.

(a) A (b) B

(c) C (d) D

26. (A) **Assertion :** pH of water increases with an increase in temperature.

Reason : K_w of water increases with increase in temperature.

(a) A (b) B

(c) C (d) D

27. (A) **Assertion :** pH of 10^{-8} M HCl lies between 6 and 7.

Reason : For very dilute solutions of acids, H^+ ion contribution from water is also taken into consideration.

(a) A (b) B

(c) C (d) D

28. (S) In our body, carbon dioxide (CO_2) combines with water (H_2O) to form carbonic acid.

$$H_2O + CO_2 \longrightarrow H_2CO_3$$

Carbonic acid undergoes dissociation as,

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

During the physical and mental stress, the rate of respiration increses, which results in the decrease in concentration of CO_2 in the blood. What will be the effect on pH of human blood during the stress ?

(a) Decreases (b) Remains same

(c) Increases (d) Cannot be predicted

29. (S) **Assertion :** If Ka of HA is 10^{-3} and Ka of HB is 10^{-4} at 25ºC, pH of an aqueous solution of HB will be one unit greater than pH of equimolar solution of HA.

Reason : For weak acids, both concentration and ionization constant affects the pH.

(a) A (b) B

(c) C (d) D

30. (S) **Assertion :** Increasing the temperature of an aqueous acetic acid solution decreases pH.

Reason : Ionization of acetic acid is endothermic in nature.

(a) A (b) B

(c) C (d) D

31. (S) What is the pH of a solution at 25°C that is 0.010 M in HCl and 0.025 M in HNO_3 ?

(a) 1.49 (b) 1.60

(c) 1.82 (d) 3.60

32. (S) If 112 mL of HCl(g) at S.T.P. conditions become the solute in 500 mL of water solution, what will be the pH of this mixture ?

(a) 0.5 (b) 1.0

(c) 1.5 (d) 2.0

33. (S) Why is it necessary to take the acid-base properties of water into account when computing the hydronium ion concentration of very dilute solutions of strong acids ?

(a) The hydroxide ion produced from the dissociation of water reacts with most of the H^+ ion produced from the acid.

(b) The dissociation constant for water is larger in dilute rather than in concentrated solutions of acids.

(c) The amount of H^+ ion produced by the dissociation of water is significant compared to that produced by the acid.

(d) The conjugate base of the strong acid reacts with the hydroxide ion produced from the dissociation of water.

34. (S) When one drop of a concentrated HCl is added to 1 L of pure water at 25°C, the pH drops suddenly from 7 to 4. When the second drop of the same acid is added, the pH of the solution further drops to about

(a) 0 (b) 1.0

(c) 2.0 (d) 3.7

35. (S) The pH of 10^{-5} M HCl solution if 1 ml of it is diluted to 1000 ml is :

(a) 5 (b) 8

(c) 7.02 (d) 6.98

Buffer Solutions

36. (S) On diluting a buffer solution, its pH :

(a) increases (b) decreases

(c) remains same (d) can't say

37. (M) Choose the correct statement :

(a) pH of acidic buffer solution decreases if more salt is added

(b) pH of acidic buffer solution increases if more salt is added

(c) pH of basic buffer decreases if more salt is added

(d) pH of basic buffer increases if more salt is added

38. (M) Which of the following is (are) correct for buffer solution ?

(a) Acidic buffer will be effective within in the pH range $(pK_a \pm 1)$

(b) Basic buffer will be effective within the pH range $(pK_w - pK_b \pm 1)$

(c) $H_3PO_4 + NaH_2PO_4$ is not a buffer solution

(d) Buffer behaves most effectively when the [Salt]/[Acid] ratio equal to one

39. (A) **Assertion :** pH value of HCN solution decreases when NaCN is added to it

Reason : NaCN provides a common ion CN^- to HCN.

(a) A (b) B

(c) C (d) D

Comprehension

Hydrogen carbonate and phosphate buffers in the blood prevent excess hydrogen ions $[H^+]$ produced by metabolic activity, from decreasing the pH of the blood. Carbon dioxide released into the blood during respiration is regulated by this system and prevented from causing changes in plasma pH prior to its excretion from the lungs. Excessive change in blood chemistry which would change the plasma pH from its normal level 7.4. This excretes hydrogen ions and retains hydrogen carbonate ions and retains hydrogen ions if the pH rises. This may produce change in the pH of the urine from 4.5 to 8.5. A fall in pH also stimulates the kidney cells to produce the base ion ammonia (NH_4^+) which combines with acids brought to the kidney and is then excreted as ammonium salts.

40. (C) The normal pH of blood is

(a) 4.5 (b) 8.5

(c) 7.32 (d) 7.4

41. (C) Which of the following buffer present in the blood ?

(a) $HCO_3^- + H_2CO_3$ and $PO_4^{3-} + HPO_4^{2-}$

(b) $HCO_3^- + CO_3^{2-}$ and $HPO_4^{2-} + H_2PO_4^-$

(c) $HCO_3^- + H_2CO_3$ and $PO_4^{3-} + H_3PO_4$

(d) None of these

42. (C) Assuming that the buffer in blood is $CO_2 - HCO_3^-$. Calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH.

(K_1 of $H_2CO_3 = 4.2 \times 10^{-7}$)

(a) 15 (b) 16

(c) 14 (d) 11

43. (A) **Assertion :** An aqueous solution of ammonium acetate can act as a buffer.

Reason : Acetic acid is a weak acid and NH_4OH is a weak base.

(a) A (b) B

(c) C (d) D

44. (M) Which of the following will function as buffer ?

(a) NaCl + NaOH (b) Borax + Boric acid

(c) $NaH_2PO_4 + NaHPO_4$ (d) $NH_4Cl + NH_4OH$

45. (M) Which of the following mixtures is (are) buffer ?

(a) 10 mL 0.1 M NH_4Cl + 10 mL 0.08 M NaOH

(b) 20 mL 0.22 M CH_3COOH + 30 mL 0.15 M NaOH

(c) A 0.10 M $NaHCO_3$ solution

(d) 15 mL 0.12 M CH_3NH_2 + 10 mL 0.07 M HCl

46. (S) Calculate the $[NH_3]/[NH_4^+]$ ratio in an ammonia-ammonium chloride buffer with a pH of 9.00. ($K_b = 1.8 \times 10^{-5}$ for ammonia)

(a) 0.56 : 1.00 (b) 0.74 : 1.00

(c) 0.86 : 1.00 (d) 1.12 : 1.00

47. (S) How many milliliters of 0.250 M NH_4Cl would have to be added to 450 mL of 0.350 M KOH in order to produce a buffer solution with a pH of 9.10 ? ($K_b(NH_3) = 1.8 \times 10^{-5}$)

(a) 450 mL (b) 600 mL

(c) 750 mL (d) 350 mL

48. (S) A buffer solution of pH = 9.00 is made by dissolving ammonium chloride and ammonia in water. How many moles of ammonium chloride must be added to 1.0 L of 0.25 M ammonia to prepare this buffer ?

$NH_3(aq) + H_2O \rightleftharpoons NH_4^-(aq) + OH^-(aq);\ K_b = 1.8 \times 10^{-5}$

(a) 0.25 mol (b) 0.45 mol

(c) 0.65 mol (d) 2.2 mol

49. (S) Which of these aqueous solutions are buffers ?

1. A solution that is 0.1 M HNO_3 and 0.1 M HCl.
2. A solution that is 0.1 M NaH_2PO_4 and 0.1 M Na_2HPO_4.
3. A solution made by mixing 10 mL of 0.1 M HF and 5.0 mL of 0.1 M NaOH.
4. A solution made by mixing 10 mL of 0.1 M KOH and 20 mL of 0.1 M HCl.

(a) 1 and 2 (b) 2 and 3

(c) 3 and 4 (d) 1 and 4

50. (S) A solution was prepared by mixing 10.0 mL of 0.50 M NaOH with 10.0 mL of 1.00 M acetic acid, $K_a = 1.8 \times 10^{-5}$. Find the pH of solution.

(a) 2.45 (b) 1.67

(c) 2.37 (d) 4.74

51. (S) How many milliliters (mL) of a 0.0500 M NaOH (a strong base) solution should be added to 1.00 L of 0.100 M H_3PO_4, solution to produce a buffer of pH = 2.00 ? For H_3PO_4, $K_{a_1} = 6.67 \times 10^{-3}$

Given : $H_3PO_4 + OH^-$ (from NaOH) $\rightarrow H_2PO_4^- + H_2O$

(a) 200 (b) 400

(c) 600 (d) 800

52. (I) A buffer solution is formed by mixing 100 mL 0.01 M CH_3COOH with 200 mL 0.02 M CH_3COONa. If this buffer solution is made to 1.0 L by adding 700 mL of water, pH will change by a factor of

53. (S) What volume of 0.40 M NH_3 solution must be added to 1.0 L of 0.10 M NH_4Cl solution to give a buffer having pH of 10.00 ? For NH_3, $K_b = 1.8 \times 10^{-5}$

(a) 1.4 L (b) 1.1 L

(c) 0.97 L (d) 0.61 L

54. (S) For the overall reaction

$H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$, the value of K_a is 1×10^{-22}. The K_{sp} for ZnS is 1.2×10^{-23}. What would be the maximum concentration of $Zn^{+2}(aq)$ ion in a 0.01 M solution of H_2S that has its pH adjusted to 5 by mixing a strong acid with the H_2S ?

(a) 1.2×10^{-9} M (b) 2.4×10^{-6} M

(c) 3.8×10^{-4} M (d) 1.8×10^{-1} M

55. (S) For the overall reaction $H_2S(aq) \rightleftharpoons 2H^+(aq) + S^{2-}(aq)$, the value of K_A is 1×10^{-22}. The K_{sp} for FeS is 4×10^{-19}. What would be the maximum concentration of Fe^{+2} (aq) ion in a 0.1 M solution of H_2S that has has its pH adjusted to 2 by mixing a strong acid with the H_2S ?

(a) 4×10^{-38} M
(b) 6×10^{-10} M
(c) 6×10^{-6} M
(d) 4.0 M

Polyprotic Acids and Bases

56. (S) $H_3PO_4 + H_2O \rightleftharpoons H_3O^+ + H_2PO_4^-$; $pK_1 = 2.15$

$H_2PO_4^- + H_2O \rightleftharpoons H_3O^+ + HPO_4^{2-}$ $pK_2 = 7.20$

Hence pH of 0.01 M NaH_2PO_4 is :

(a) 9.35
(b) 4.675
(c) 2.675
(d) 7.350

57. (S) Calculate the molar concentrations of H_3O^+, HSO_4^-, and SO_4^{2-} in a 0.250 M solution of H_2SO_4. Assume K_{a_1} is very large ; $K_{a_2} = 1.20 \times 10^{-2}$.

	$[H_3O^+]$, M	$[HSO_4^-]$, M	$[SO_4^{2-}]$, M
(a)	0.250	0.250	0.000
(b)	0.250	0.250	0.0120
(c)	0.500	0.000	0.500
(d)	0.261	0.239	0.0110

58. (S) What is the equilibrium $[OH^-]$ in 0.1413 M H_2CO_3 ?

$H_2CO_3 + H_2O \rightleftharpoons H_3O^+ + HCO_3^-$ $(K_a = 4.30 \times 10^{-7})$

(a) 7.07×10^{-14} M
(b) 2.46×10^{-4} M
(c) 4.06×10^{-11} M
(d) 6.84×10^{-6} M

Comprehension

H_3PO_4 is a tribasic acid with pK_{a_1}, pK_{a_2} and pK_{a_3} 2.12, 7.21, and 12.32, respectively. It is used in fertiliser productions and its various salts are used in food, dtergent, toothpaste, and in metal treatment.

Small quantities of H_3PO_4 are used in imparting the sour or tart taste to soft drinkes, such as Coca Cola, and beers, in which H_3PO_4 in present 0.05% by weight (density = 1.0 g mL^{-1}).

10^{-3} M H_3PO_4 (pH = 7) is used in fertilisers as an aqueous soil digesting. Plants can absorb zinc in water soluble form only. Zinc phosphate is the source of zinc and PO_4^{3-} ions in the soil. K_{sp} of zinc phosphate $= 9.1 \times 10^{-33}$.

59. (C) $[PO_4^{3-}]$ ion in the soil with pH = 7, is

(a) 10^{-3} M
(b) 1.2×10^{-4} M
(c) 2.2×10^{-4} M
(d) 1.1×10^{-10} M

60. (C) $[Zn^{2+}]$ ion in the soil is

(a) 2.9×10^{-11} M
(b) 4.0×10^{-10} M
(c) 3.0×10^{-6} M
(d) 9.1×10^{-5} M

Salt Hydrolysis

61. (S) A 100 mL portion of water is added to each of the following two solutions.

(i) 100 mL of 0.02 M KCl (ii) 100 mL of 0.02 M HCl

Which of the following statements is correct ?

(a) There will be no change in pH of solution (i) and (ii)
(b) The pH of solution (i) will remain the same but pH of solution (ii) will increase
(c) The pH of solution (i) will remain same but of solution (ii) will decrease
(d) The pH of solution (ii) will remain same but of solution (i) will increase

62. (S) The correct order of increasing $[H_3O^+]$ in the following aqueous solution is :

(a) 0.01 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M $NaNO_3$
(b) 0.01 M NaCl < 0.01 M $NaNO_3$ < 0.01 M H_2S < 0.01 M H_2SO_4
(c) 0.01 M H_2S < 0.01 M $NaNO_3$ = 0.01 M NaCl < 0.01 M H_2SO_4
(d) 0.01 M H_2S < 0.01 M $NaNO_3$ < 0.01 M NaCl < 0.01 M H_2SO_4

63. (S) pH of water is 7. When a substance Y is dissolved in water, the pH becomes 11. The substances Y is a salt of :

(a) weak acid and weak base
(b) strong acid and strong base
(c) strong acid and weak base
(d) weak acid and strong base

64. (M) Degree of hydrolysis for a salt of strong acid and weak base is :

(a) independent of dilution

(b) increase with dilution

(c) increase with decrease in K_b of the bases

(d) decreases with decrease in temperature

65. (M) A 0.1 M sodium acetate solution was prepared. The $K_h = 5.6 \times 10^{-10}$

(a) The degree of hydrolysis is 7.48×10^{-5}

(b) The $[OH^-]$ concentration is 7.48×10^{-3} M

(c) The $[OH^-]$ concentration is 7.48×10^{-6} M

(d) The pH is approximately 8.88

66. (X) Match the following :

Column I	**Column II**
(A) Degree of hydrolysis for salts of strong acid and weak base	(P) the hydrolysis of anion which is irreversible.
(B) Hydrolysis constant	(Q) is not possible because of the reaction of strong base with strong acid.
(C) Na_2O in water is basic due to	(R) is affected when temperature is changed and concentration is changed.
(D) $Na^+ + H_2O \rightleftharpoons NaOH + H^+$	(S) is independent of volume of solution taken but depends upon temperature.

67. (A) **Assertion :** Aqueous solution of ammonium carbonate is basic.

Reason : Acidic or Basic nature of a salt solution of a salt of weak acid and weak base depends on K_a and K_b of the acid and base forming it.

(a) A (b) B

(c) C (d) D

68. (A) **Assertion :** H_3BO_3 is aprotic acid.

Reason : Borax is salt of H_3BO_3 and NaOH ; its aqueous solution is alkaline in nature.

(a) A (b) B

(c) C (d) D

69. (X) Match the Column-I with Column-II :

Column-I **(Salt)**	**Column-II** **(Nature of hydrolysis)**
(A) NH_4CN	(p) Only cation hydrolysis
(B) CH_3COONa	(q) Only anion hydrolysis
(C) $NaClO_4$	(r) Both cation and anion hydrolysis
(D) $Fe(NO_3)_2$	(s) No hydrolysis

70. (X) Match the Column-I with Column-II :

Column-I	**Column-II**
(A) NH_4Cl	(p) No hydrolysis
(B) NaCl	(q) $h = \sqrt{K_h / C}$
(C) CH_3COONa	(r) $h = \sqrt{\dfrac{K_w}{CK_b}}$
(D) CH_3COONH_4	(s) $h = \sqrt{K_h}$

where, C = Concentration of Salt ; K_h = hydrolysis constant K_w = Ionic product of water ; K_b = Dissociation constant of weak base

71. (A) **Assertion :** When aqueous, solution of CH_3COONH_4 is diluted, then its degree of hydrolysis increases.

Reason : Ammonium acetate is the salt of weak acid and weak base, its degree of hydrolysis does not depend on the concentration.

(a) A (b) B

(c) C (d) D

72. (M) Which among the following salts will give basic solution on hydrolysis ?

(a) NaH_2PO_4 (b) NH_4Cl

(c) NaCl (d) K_2CO_3

73. (S) Calcium lactate is a salt of weak acid i.e., lactic acid having general formula $Ca(Lac)_2$. Aqueous solution of salt has 0.3 M concentration. pOH of solution is 5.60. If 90% of the salt is dissociated then what will be the value of pK_a ?

(a) $2.8 - \log(0.54)$ (b) $2.8 + \log(0.54)$

(c) $2.8 + \log(0.27)$ (d) None of these

74. (S) If 0.1 mol of salt is added to 1L water, which of these salts is expected to produce the most acidic solution ?

(a) $NaC_2H_3O_2$ (b) NH_4NO_3

(c) $CuSO_4$ (d) $AlCl_3$

75. (S) Hydrolysis constants of two salts KA and KB of weak acids HA and HB are 10^{-8} and 10^{-6}. If the dissociation constant of third acid HC is 10^{-2}. The order of acidic strengths of three acids will be :

(a) HA > HB > HC (b) HB > HA > HC

(c) HC > HA > HB (d) HA = HB = HC

76. (M) The equilibrium constant (K_c) for the reaction of a weak acid HA with strong base NaOH is 10^9 at 25°C. Which of the following are correct deduction ?

(a) The ionization constant (K_a) at 25°C is 10^{-5} for HA.

(b) pH of a 0.01 M aqueous solution of HA at 25°C will be 3.5

(c) pH of a 0.10 M aqueous solution of NaA at 25°C will be 9.

(d) If K_b of a weak base BOH is 10^{-4} at 25°C, equilibrium constant for neutralization of HA with BOH at 25°C will be 10^{-5}

77. (I) If the equilibrium constant of the reaction of a weak acid HA with a strong base is 10^9, then pH of a 0.10 M NaA solution is

78. (A) **Assertion :** If HA and HB are two weak non-basic acids with $K_a(HA) < K_b(HB)$, then, the aqueous solution of NaA will have higher pH than pH of aqueous solution of NaB of same concentration.

Reason : Conjugate base of a weaker acid is stronger than the same of stronger acid.

(a) A (b) B

(c) C (d) D

79. (A) **Assertion :** Knowing K_{a_2} of CO_2 can determine pH of an aqueous solution of Na_2CO_3 of known concentration.

Reason : Only first hydrolysis of CO_3^{2-} ion is significant because for most of the dibasic acids, $K_{a_1} >> K_{a_2}$.

(a) A (b) B

(c) C (d) D

80. (S) A solution of 0.1 M NaZ has pH = 8.90. The K_a of HZ is

(a) 6.3×10^{-11} (b) 6.3×10^{-10}

(c) 1.6×10^{-5} (d) 1.6×10^{-6}

81. (S) If pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid in water at this temperature is

(a) 1.74×10^{-5} (b) 3.52×10^{-3}

(c) 6.75×10^{-4} (d) 5.38×10^{-2}

Solubility Equilibria

82. (S) The solubility of silver benzoate (C_6H_5COOAg) in H_2O and in a buffer solution of pH = 2, 3, and 4 are S_1, S_2, S_3 and S_4 respectively. The decreasing order of solubility is

(a) $S_1 > S_2 > S_3 > S_4$ (b) $S_4 > S_3 > S_2 > S_1$

(c) $S_2 > S_3 > S_4 > S_1$ (d) $S_3 > S_2 > S_4 > S_1$

83. (S) K_{sp} of Mg $(OH)_2$ is 1×10^{-12}. 0.01 M $MgCl_2$ will be precipitating at the limiting pH :

(a) 8 (b) 9

(c) 10 (d) 12

84. (S) The solubility products of MA, MB, MC and MD are 1.8×10^{-10}, 4×10^{-3}, 4×10^{-8} and 6×10^{-5} respectively. If a 0.01 M solution of MX is added dropwise to a mixture containing A^-, B^-, C^- and D^- ions then the one to be precipitated first will be :

(a) MA (b) MB

(c) MC (d) MD

85. (M) A solution containing a mixture of 0.05 M NaCl and 0.05 M NaI is taken. (K_{sp} of AgCl = 10^{-10} and K_{sp} of AgI = 4×10^{-16}). When $AgNO_3$ is added to such a solution:

(a) the concentration of Ag^+ required to precipitate Cl^- is 2×10^{-9} mol/L

(b) the concentration of Ag^+ required to precipitate I^- is 8×10^{-15} mol/L

(c) AgCl and AgI will be precipitate together

(d) first AgI will be precipitated

86. (M) Which of the following is (are) correct when 0.1 L of 0.0015 M $MgCl_2$ and 0.1L of 0.025 M NaF are mixed together ?
(K_{sp} of MgF_2 = 3.7×10^{-8})

(a) MgF_2 remains in solution

(b) MgF_2 precipitates out

(c) $MgCl_2$ precipitates out

(d) Cl^- ions remain in solution

Comprehension

Solubility of a salt is defined as the maximum amount of a salt which can be dissolved in a given amount of solvent at a particular temperature. Unit of solubility is mole per litre of solution. The solubility of a salt of weak acid with strong base (CH_3COOAg) in acidic buffer can be calculated as

$$CH_3COOAg \rightleftharpoons \underset{S-X}{CH_3COO^-(aq)} + \underset{S}{Ag^+(aq)}$$

S = Solubility of salt

$$\underset{(S-X)}{CH_3COO^-(aq)} + \underset{\text{(from acidic buffer)}}{H^+} \rightleftharpoons \underset{X}{CH_3COOH}$$

$$K_{sp} = [Ag^+][CH_3COO^-] = S(S-X)$$

Dissociation constant of weak acid

$$(K_a) = \frac{(S-X)[H^+]}{X}$$

87. (C) The solubility of LiOH in a solution with pH = 8 is ($K_{sp} = 1.8 \times 10^{-12}$)

(a) 1.8×10^{-18} (b) 1.8×10^{-6}

(c) 10^{-6} (d) 1.8×10^{-4}

88. (C) The solubility of AgCl is maximum in

(a) 0.1 M NaCl (b) 0.1 M HCl

(c) 55.5 M H_2O (d) None of these

89. (C) The solubility of $CaCO_3$ is 7 mg/L. Calculate the solubility product of $BaCO_3$ from this information and from the fact that when Na_2CO_3 is added slowly to a solution containing equimolar concentration of Ca^{2+} and Ba^{2+}, no precipitate is formed until 90% of Ba^{2+} has been precipitated as $BaCO_3$.

(a) 4.9×10^{-10} (b) 5.9×10^{-5}

(c) 6.9×10^{-10} (d) 8.3×10^{-5}

90. (X) Match the following :

Column I	**Column II**
(A) $[A^{+Y}]^X[B^{-X}]^Y > K_{sp}$	(P) Precipitation just starts
(B) $[A^{+Y}]^X[B^{-X}]^Y < K_{sp}$	(Q) Buffer capacity
(C) $[A^{+Y}]^X[B^{-X}]^Y = K_{sp}$	(R) The solid AXB_4 will precipitate out
(D) d(n)/dpH	(S) No precipitation

91. (I) How much AgBr could dissolve in 1.0 L of 0.4 M NH_3 ? Assume that $Ag(NH_3)_2^+$ is the only complex formed Given : The dissociation constant for

$$Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3;\ K_d = 6.0 \times 10^{-8} \text{ and}$$

$K_{sp}(AgBr) = 5.0 \times 10^{-13}$.

(As in 10^{-3} M)

92. (I) HN_3 (hydroazoic acid) is a weak acid dissociating as :

$$HN_3 \rightleftharpoons H^+ + N_3^-.$$

Find the concentration of Ag^+ ions, if excess of solid AgN_3 is added to a solution maintained at ph = 4. The ionisation constant K_a of HN_3 is 2.0×10^{-5}. The solubility of AgN_3 in pure water is found to be 5.4×10^{-3} M at 25°C.

Comprehension

The product of the concentrations of the ions of an electrolyte raised to power of their coefficients in the balanced chemical equation in the solution at any concentration. Its value is not constant and varies with change in concentration. Ionic product of the saturated solution is called solubility product K_{sp}.

(i) When $K_{ip} = K_{sp}$, the solution is just saturated and no precipitation takes place.

(ii) When $K_{ip} < K_{sp}$, the solution is unsaturated and precipitation will not take place.

(iii) When $K_{ip} > K_{sp}$, the solution is supersaturated and precipitation takes place.

93. (C) Which of the following is most soluble ?

(a) Bi_2S_3 ($K_{sp} = 1 \times 10^{-70}$) (b) MnS ($K_{sp} = 7 \times 10^{-16}$)

(c) CuS ($K_{sp} = 8 \times 10^{-37}$) (d) Ag_2S ($K_{sp} = 6 \times 10^{-51}$)

94. (C) The concentration of Ag^+ ions in a given saturated solution of AgCl at 25°C is 1.06×10^{-5} g ion per litre. The solubility product of AgCl is :

(a) 0.353×10^{-10} (b) 0.530×10^{-10}

(c) 1.12×10^{-10} (d) 2.12×10^{-10}

95. (C) If the solubility of $Li_3Na_3(AlF_6)_2$ is x mol L^{-1}, then its solubility product is equal to :

(a) $12x^3$ (b) $18x^3$

(c) x^8 (d) $2916x^8$

96. (I) $M(OH)_x$ has K_{sp} of 4×10^{-9} and its solubility of 10^{-3} M. The value of x is ______ .

97. (A) **Assertion :** On miximg 500 mL of 10^{-6} M Ca^{2+} ion and 500 mL of 10^{-6} M F^- ion, the precipitate of CaF_2 will be obtained $K_{sp}(CaF_2) = 10^{-18}$.

Reason : If K_{sp} is less than ionic product, precipitate will be obtained.

(a) A (b) B

(c) C (d) D

98. (S) Solubility of calcium phosphate (molecular mass, M) in water is W g per 100 mL at 25°C. Its solubility product at 25°C will be approximately :

(a) $10^9\left(\frac{W}{M}\right)^5$ (b) $10^7\left(\frac{W}{M}\right)^5$

(c) $10^5\left(\frac{W}{M}\right)^5$ (d) $10^3\left(\frac{W}{M}\right)^5$

Comprehension

The solubility product constant of AgCN is 2.5×10^{-16}. The acid dissociation constant of HCN is 6.2×10^{-10}. Now solid AgCN is dissolved in a buffer solution of pH 3.

Answer the following questions :

99. (C) The concentration ratio of HCN to CN^- in the solution is

(a) 6.25×10^{-7} (b) 1.6×10^6

(c) 1.6×10^9 (d) 6.2×10^{-10}

100. (C) The solubility of AgCN (mol-L^{-1}) in the above solution is

(a) 1.58×10^{-8} (b) 6.2×10^{-10}

(c) 2×10^{-5} (d) 4×10^{-7}

101. (C) The factor by which the solubility of AgCN is increased in the above solution as compared to its solubility in pure water is

(a) 10 (b) 100

(c) 1250 (d) 5000

102. (S) How many grams of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will dissolve in 1.0 L of 6.0 M NH_3 ($K_b = 1.8 \times 10^{-5}$). The Kformation for $Ag(NH_3)_2^+$ is 1.7×10^7.

(a) 0.0013 g (b) 43 g

(c) 1.3 g (d) 12 g

103. (S) What is the highest pH at which 0.050 M Mn^{2+} remains entirely in a solution that is saturated with H_2S, at a concentration of, $[H_2S] = 0.10$ M. Given for the reaction,

$$MnS(s) \rightleftharpoons Mn^{2+} + S^{2-}, K_{sp} = 3.6 \times 10^{-15}$$

For H_2S : $K_{a_1} = 9.2 \times 10^{-8}$, and $K_{a_2} = 1.2 \times 10^{-15}$

(a) 2.9 (b) 3.9

(c) 4.4 (d) 4.9

104. (S) For Ag_2CO_3, $K_{sp} = 6.2 \times 10^{-12}$, For AgCl, $K_{sp} = 2.8 \times 10^{-10}$. Solid Ag_2CO_3 and solid AgCl are added to a beaker containing 1.00 M Na_2CO_3(aq). Under these conditions the $[CO_3^{2-}] = 1.00$ M. Calculate the $[Cl^-]$ in solution when equilibrium is established.

(a) 1.1×10^{-4} (b) 1.26×10^{-6}

(c) 0.15 (d) 2.8×10^{-6}

105. (S) Given the following K_{sp} values : for $M(OH)_4$, $K_{sp}(M) = 4.0 \times 10^{-19}$; for $Z(OH)_2$, $K_{sp}(Z) = 1.0 \times 10^{-14}$. One mole of each of the above solids is placed in a beaker containing 1 (one) litre of pure water. These solids go into equilibrium with their ions. Calculate the pH required for the metal ion concentrations to be equal, $[M^{4+}] = [Z^{2+}]$.

(a) 12.6 (b) 9.6

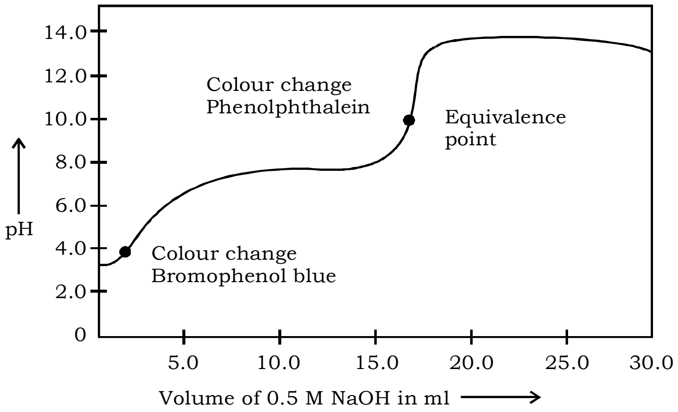
(c) 6.7 (d) 11.8

106. (I) Solubility product constant of a springly soluble salt MCl_2 is 4×10^{-12} at 25°C. Also, at 25°C, solubility of MCl_2 is an aqueous solution of $CaCl_2$ is 4×10^{8} times less compared to its solubility in pure water. Hence, concentration (molarity) of $CaCl_2$ solution is

107. (I) The solubility product constant of a metal carbonate MCO_3 is 2×10^{-12} at 25°C. A solution is 0.1 M in $M(NO_3)_2$ and it is saturated with 0.01 M CO_2. Also the ionization constant of CO_2 are $K_{a_1} = 4 \times 10^{-7}$ and $K_{a_2} = 5 \times 10^{-11}$ at 25°C. The minimum pH that must be maintained to start any precipitation is

Indicators and Titrations

108. (M) Titration curve for a weak acid with a strong base is



Which of the following s/are correct for the above curve ?

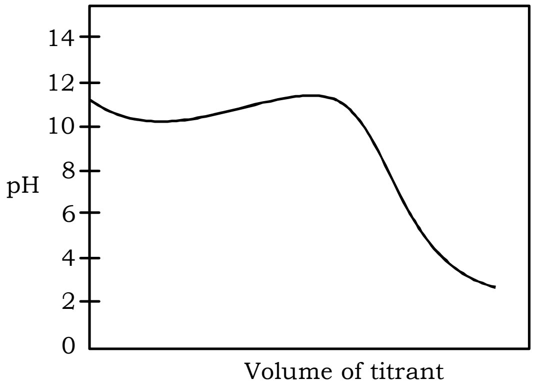
(a) At the half-neutralization point pH = pK_a

(b) The pH is greater than 7 at the equivalence point

(c) The colour change in basic medium

(d) The solution at the half neutralization is buffer solution

109. (M) The titration curve given below involves 1.0 M solutions of an acid and a base.



Which of the following is/are correct for the given curve ?

(a) The solution being titrated is a base and the titrant is an acid

(b) The pH at the equivalence point must be less than 7

(c) The titrated solution is strong acid

(d) The titrated solution is strong base

110. (A) **Assertion :** The pH of the solution at the mid point of the weak acid strong base titration becomes equal to the pK_a of the acid.

Reason : The molar concentrations of proton acceptor and proton donor become equal at mid point of a weak acid.

(a) A (b) B

(c) C (d) D

111. (I) The equivalence point in a titration of 40.0 mL of a solution of a weak monoprotic acid occurs when 35.0 mL of a 0.10 M NaOH solution has been added. The pH of the solution is 5.5 after the addition of 20.0 mL of NaOH solution. What is the dissociation constant of the acid ? (in 10^{-6})

112. (I) When a 40 mL of a 0.1 M weak base, BOH is titrated with 0.10 M HCl, the pH of the solution at the end point is 5.5. What will be the pH if 10 mL of 0.10 M NaOH is added to the resulting solution ?

113. (X) Match the Column-I with Column-II :

Column-I	**Column-II**
(A) has highest pH at end point when titrated against standard NaOH	(p) CH_3COOH $K_a = 1.8 \times 10^{-5}$
(B) has lowest pH at the end point when titrated against standard NaOH	(q) HCN $K_a = 5 \times 10^{-10}$
(C) release maximum heat when neutralized with NaOH	(r) HF $K_a = 5 \times 10^{-4}$
(D) release equal amount of heat when neutralized with strong acid or base	(s) NH_4OH $K_b = 1.8 \times 10^{-5}$

114. (X) Match the Column-I with Column-II :

Column-I **(Titration)**	**Column-II** **(Indicator used)**
(A) Strong acid versus strong base	(p) Methyl orange (3 – 4.4)
(B) Weak acid versus strong base	(q) Methyl red (4.3 – 6.3)
(C) Strong acid versus weak base	(r) Phenolphthalein (8 – 10)
(D) Weak acid versus weak base	(s) No suitable indicator

115. (X) Match the Column-I with Column-II :

Column-I (Indicator)	**Column-II (pH range)**
(A) Phenolphthalein	(p) 4.2 – 6.3
(B) Litmus	(q) 3.1 – 4.4
(C) Methyl red	(r) 8.3 – 10.0
(D) Methyl orange	(s) 5.0 – 8.0

116. (S) During the titration of weak diprotic acid H_2A against strong base NaOH, the pH of the solution half-way to the first equivalence point and that at first equivalence point are given respectively by :

(a) pK_{a_1} and pK_{a_2} (b) pK_{a_1} and $\frac{pK_{a_1}+pK_{a_2}}{2}$

(c) pK_a and $(pK_{a_1}+pK_{a_2})$

(d) $\sqrt{CK_{a_1}}$ and $\frac{pK_{a_1}+pK_{a_2}}{2}$

117. (S) 0.2 g sample of benzoic acid, C_6H_5COOH is titrated with 0.12 M Ba $(OH)_2$ solution. What volume of $Ba(OH)_2$ solution is required to reach the equivalence point ?

Molar mass of benzoic acid is 122 g mol^{-1}

(a) 6.82 mL (b) 13.6 mL

(c) 17.6 mL (d) 35.2 mL

Comprehension

Consider the titration of a diprotic acid (H_2A ; $K_{a_1} = 3.1 \times 10^{-6}$, $K_{a_2} = 4.8 \times 10^{-12}$) with a solution of NaOH. Specifically, you titrate 50.0 mL of 0.100 M H_2A with 0.100 M NaOH.

Answer the following question based on this titration experiment.

118. (C) Determine the pH after 20.0 mL of 0.100 M NaOH has been added.

(a) 3.25 (b) 5.33

(c) 5.50 (d) 6.18

119. (C) Determine the pH after a total of 50.0 mL of 0.100 M NaOH has been added.

(a) 5.50 (b) 7.00

(c) 8.41 (d) 9.24

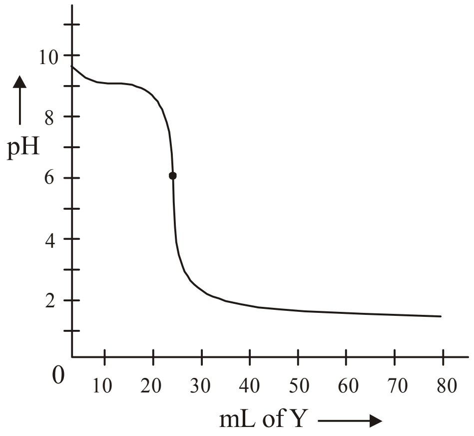
120. (C) Determine the pH after a total of 75.0 mL of 0.100 M NaOH has been added.

(a) 8.41 (b) 9.24

(c) 11.24 (d) 11.32

Comprehension

100 mL of a solution of X is titrated with a 0.1 M solution of Y giving the following titration curve :



Answer the following four questions based on the information provided.

121. (C) Y is a

(a) strong acid (b) strong base

(c) weak base (d) weak acid

122. (C) X is a

(a) strong acid (b) strong base

(c) weak base (d) weak acid

123. (C) The initial concentration of X is

(a) 0.10 M (b) 0.02 M

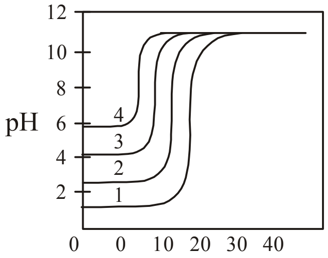
(c) 0.05 M (d) 0.01 M

124. (C) The approximate value of ionization constant (K_a/K_b) of X is

(a) 5×10^{-9} (b) 5×10^{-6}

(c) 2×10^{-4} (d) 3×10^{-5}

125. (S) Following figure represents simulated titration curves for solutions of four acids titrated with the same standard base solution. Based on these titration curves, we can accurately predict that



(a) Curve 4 represents the smallest concentration and the weakest acid.

(b) Curve 1 represents the largest concentration and the strongest acid.

(c) The dissociation constant for the acid represented by curve 3 is about 1×10^{-4} (i.e., $K_a = 1 \times 10^{-4}$).

(d) All the responses above are correct.

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

1. The pH of 10^{-8} M solution of HCl in water is **(1981)**

(a) 8 (b) –8

(c) between 7 and 8 (d) between 6 and 7

2. At 90ºC, pure water has $[H_3O^+]$ as 10^{-6} mol L^{-1}. What is the value of K_w at 90ºC ? **(1981)**

(a) 10^{-6} (b) 10^{-12}

(c) 10^{-14} (d) 10^{-8}

3. Of the given anions, the strongest base is **(1981)**

(a) ClO^- (b) ClO_2^-

(c) ClO_3^- (d) ClO_4^-

4. An acidic buffer solution can be prepared by mixing the solution of **(1981)**

(a) solution of acetate and acetic acid

(b) ammonium chloride and ammonium hydroxide

(c) sulphuric acid and sodium sulphate

(d) sodium chloride and sodium hydroxide

5. The precipitate of CaF_2 ($K_{sp} = 1.7 \times 10^{-10}$) is obtained, when equal volumes of the following are mixed **(1982)**

(a) 10^{-4} M Ca^{2+} + 10^{-4} M F^-

(b) 10^{-2} M Ca^{2+} + 10^{-3} M F^-

(c) 10^{-5} M Ca^{2+} + 10^{-3} M F^-

(d) 10^{-3} M Ca^{2+} + 10^{-5} M F^-

6. A certain buffer solution contains equal concentration of X^- and HX. The K_b for X^- is 10^{-10}. The pH of the buffer is **(1984)**

(a) 4 (b) 7

(c) 10 (d) 14

7. A certain weak acid has a dissociation constant of 1.0×10^{-4}. The equilibrium constant for its reaction with a strong base is **(1984)**

(a) 1.0×10^{-4} (b) 1.0×10^{-10}

(c) 1.0×10^{10} (d) 1.0×10^{-14}

8. An example of a reversible reaction is **(1985)**

(a) $Pb(NO_3)_2\,(aq) + 2NaI\,(aq) = PbI_2\,(s) + 2NaNO_3\,(aq)$

(b) $AgNO_3\,(aq) + HCl\,(aq) + AgCl\,(s) + HNO_3\,(aq)$

(c) $2Na\,(s) + 2H_2O(l) = 2\,NaOH\,(aq) + H_2(g)$

(d) $KNO_3\,(aq) + NaCl\,(aq) = KCl\,(aq) + NaNO_3\,(aq)$

9. The best indicator for detection of end point in titration of a weak acid and a strong base is **(1985)**

(a) methyl orange (3 to 4) (b) methyl red (5 to 6)

(c) bromothymol blue (6 to 7.5)

(d) phenophthalein (8 to 9.6)

10. The compound that is not a Lewis acid is **(1985)**

(a) BF_3 (b) $AlCl_3$

(c) $BeCl_2$ (d) $SnCl_4$

11. The conjugate acid of NH_2^- is **(1985)**

(a) NH_3 (b) NH_2OH

(c) NH_4^+ (d) N_2H_4

12. The pK_a of acetyl salicylic acid (aspirin) is 3.5. The pH of gastric juice in human stomach is about 2–3 and the pH in the small intestine is about 8. Aspirin will be **(1988)**

(a) unionised in the small intestine and in the stomach

(b) completely ionised in the small intestine in the small intestine

(c) ionised in the stomach and almost unionised in the small intestine

(d) ionised in the small intestine and almost unionised in the stomach

13. When equal volumes of the following solutions are mixed, precipitation of AgCl ($K_{sp} = 1.8 \times 10^{-10}$) will occur only with **(1988)**

(a) 10^{-4} M (Ag^+) and 10^{-4} M (Cl^-)

(b) 10^{-5} M (Ag^+) and 10^{-5} M (Cl^-)

(c) 10^{-6} M (Ag^+) and 10^{-6} M (Cl^-)

(d) 10^{-10} M (Ag^+) and 10^{-10} M (Cl^-)

14. Which of the following is the strongest acid ? **(1989)**

(a) $ClO_3(OH)$ (b) $ClO_2(OH)$

(c) $SO(OH)_2$ (d) $SO_2(OH)_2$

15. Amongst the following hydroxides, the one which has the lowest value of K_{sp} at ordinary temperature (about 25ºC) is **(1990)**

(a) $Mg(OH)_2$ (b) $Ca(OH)_2$

(c) $Ba(OH)_2$ (d) $Be(OH)_2$

16. Which of the following solutions will have pH close to 1.0 ? **(1992)**

(a) 100 Ml of (M/10) HCl + 100 mL of (M/10) NaOH

(b) 55 mL of (M/10) HCl + 45 mL of (M/10) NaOH

(c) 10 mL of (M/10) HCl + 90 mL of (M/10) NaOH

(d) 75 mL of (M/5) HCl + 25 mL of (M/5) NaOH

17. The solubility of A_2X_3 is y mol dm^{-3}. Its solubility product is **(1997)**

(a) $6y^4$ (b) $64y^4$

(c) $36y^5$ (d) $108y^5$

18. The pH of 0.1 M solution of the following salts increase in the order **(1999)**

(a) $NaCl < NH_4Cl < NaCN < HCl$

(b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$

(d) $HCl < NaCl < NaCN < NH_4Cl$

19. For a sparingly soluble salt A_pB_q, the relationship of its solubility product (L_s) with its solubility (S) is **(2001)**

(a) $L_s = S^{p+q} . p^p .q^q$ (b) $L_s = S^{p+q} . p^q.q^p$

(c) $L_s = S^{pq} . p^p.q^q$ (d) $L_s = S^{pq}. (p.q)^{(p+q)}$

20. Identify the correct order of solubility of Na_2S, CuS and ZnS in aqueous medium **(2002)**

(a) $CuS > ZnS > Na_2S$ (b) $ZnS > Na_2S > CuS$

(c) $Na_2S > CuS > ZnS$ (d) $Na_2S > ZnS > CuS$

21. A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are 10^{-15}, 10^{-23}, 10^{-20} and 10^{-54} respectively, which one will precipitate first ? **(2003)**

(a) FeS (b) MgS

(c) HgS (d) ZnS

22. HX is a weak acid ($K_a = 10^{-5}$). It forms a salt NaX (0.1 M) on reacting with caustic soda. The degree of hydrolysis of NaX is **(2004)**

(a) 0.01% (b) 0.0001%

(c) 0.1% (d) 0.5%

23. The pH of 0.1 M solution of the following salts increases in the order **(2004)**

(a) $NaCl < NH_4Cl < NaCN < HCl$

(b) $HCl < NH_4Cl < NaCl < NaCN$

(c) $NaCN < NH_4Cl < NaCl < HCl$

(d) $HCl < NaCl < NaCN < NH_4Cl$

24. A weak acid HX has the dissociation constant 1×10^{-5}M. It forms a salt NaX on reaction with alkali. The precentage hydrolysis of 0.1 M solution of NaX ? **(2004)**

(a) 0.0001% (b) 0.01%

(c) 0.1% (d) 0.15%

25. A 0.004 M solution of Na_2SO_4 is isotonic with 0.010 M solution of glucose at same temperature. The percentage dissociation of Na_2SO_4 is **(2004)**

(a) 25% (b) 50%

(c) 75% (d) 85%

26. CH_3NH_2 (0.1 mole, $K_b = 5 \times 10^{-4}$) is added to 0.08 moles of HCl and the solution is diluted to one litre, resulting hydrogen ion concentration is **(2005)**

(a) 1.6×10^{-11} (b) 8×10^{-11}

(c) 5×10^{-5} (d) 8×10^{-2}

27. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+ ;\ k_1 = 3.5 \times 10^{-3}$

$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+ ;$

$$k_2 = 1.7 \times 10^{-3}$$

then the formation constant of $[Ag(NH_3)_2]^+$ is **(2006)**

(a) 6.08 × 10–6 (b) 6.08 × 106

(c) 6.08 × 10–9 (d) None of these

28. The species present in solution when CO_2 is dissolved in water are **(2006)**

(a) $CO_2, H_2CO_3, HCO_3^-, CO_3^{2-}$

(b) H_2CO_3, CO_3^{2-}

(c) HCO_3^-, CO_3^{2-} (d) CO_2, H_2CO_3

29. $N_2 + 3H_3 \rightleftharpoons 2NH_3$

Which is correct statement if N_2 is added at equilibrium condition ? **(2006)**

(a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction

(b) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_3}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward directions to the same extent

(c) The catalyst will increase the rate of forward reaction by β

(d) Catalyst will not alter the rate of either of the reaction.

30. Solubility product constant (K_{sp}) of salts of types MX, MX_2 and M_3X at temperature 'T' are 4.0×10^{-8}, 3.2×10^{-14} and 2.7×10^{-15}, respectively. Solubilities (mol, dm^{-3}) of the salts at temperature 'T' are in the order **(2008)**

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$

(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

31. 2.5 mL of $\frac{2}{5}$M weak monoacidic base ($K_b = 1 \times 10^{-12}$ at 25°C) is titrated with $\frac{2}{15}$M HCl in water at 25°C. The concentration of H^+ at equivalence point is ($K_w = 1 \times 10^{-14}$ at 25°C) **(2008)**

(a) 3.7×10^{-13} M (b) 3.2×10^{-7} M

(c) 3.2×10^{-2} M (d) 2.7×10^{-2} M

Paragraph

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (−57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant. In a second experiment (Expt. 2), 100 mL of 2.0 M acetic ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

(Consider heat capacity of all solutions as 4.2J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

32. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is

(a) 1.0 (b) 10.0

(c) 24.5 (d) 51.4

33. The pH of the solution after Expt. 2 is

(a) 2.8 (b) 4.7

(c) 5.0 (d) 7.0

Objective Questions (One or more than one correct option)

34. Which of the following statement (s) is (are) correct ? **(1998)**

(a) The pH of 1.0×10^{-8} M solution of HCl is 8

(b) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}

(c) Autoprotolysis constant of water increases with temperature

(d) When a solution of a weak monoprotic acid is titrated against a strong base, at half-neutralisation point pH = $\left(\frac{1}{2}\right)pK_a$

35. A buffer solution can be prepared from a mixture of **(1999)**

(a) sodium acetate and acetic acid in water

(b) sodium acetate and HCl in water

(c) ammonia and ammonium chloride in water

(d) ammonia and sodium hydroxide in water

Fill in the Blanks

36. The conjugate base of HSO_4^- in aqueous solution is .... **(1982)**

37. An element which can exist as a positive ion in acidic solution and also as a negative ion in basic solution is said to be .... **(1984)**

38. Silver chloride is sparingly soluble in water because its lattice energy is greater than .... energy. **(1987)**

39. In the reaction $I^- + I_2 \longrightarrow I_3^-$, the Lewis acid is .... **(1997)**

40. $(CH3OH_2)^+$ is .... acidic than ($CH_3NH_3^+$). **(1997)**

True/False

41. Aluminium chloride ($AlCl_3$) is a Lewis acid because it can donate electrons. **(1982)**

42. Solubility of sodium hydroxide increases with increase in temperature. **(1985)**

43. The following species are in increasing order of their acidic property : ZnO, Na_2O_2, P_2O_5, MgO **(1985)**

Subjective Questions

44. How many moles of sodium propionate should be added to 1 L of an aqueous solution containing 0.020 moles of propionic acid to obtain a buffer solution of pH 4.75 ? What will be pH if 0.010 moles of HCl are dissolved in the above buffer solution ? Compare the last pH value with the pH of 0.010 M HCl solution. Dissociation constant of propionic acid, K_a at 25ºC is 1.34×10^{-5}. **(1981)**

45. 20 mL of 0.2 M sodium hydroxide is added to 50 mL of 0.2 M acetic acid solution to give 70 mL of the solution. What is the pH of this solution ? Calculate the additional volume of 0.2 M NaOH required to make the pH of the solution 4.74. (Ionisation constant of $CH_3COOH = 1.8 \times 10^{-5}$). **(1982)**

46. Give reason for the statement that "the pH of an aqueous solution of sodium acetate is more than seven". **(1982)**

47. The dissociation constant of a weak acid HA is 4.9×10^{-8}.

After making the necessary approximations, calculate :

(i) pH

(ii) OH^- concentration in a decimolar solution of the acid. Water has a pH of 7. **(1983)**

48. A solution contains a mixture of Ag^+ (0.10 M) and Hg^{2+} (0.10 M) which are to be separated by selective precipitation. Calculate the maximum concentration of iodide ion an which one of them gets precipitated almost completely. What percentage of that metal ion is precipitated ? **(1984)**

Ksp : $AgI = 8.5 \times 10^{-17}$, $HgI_2 = 2.5 \times 10^{-26}$

49. The concentration of hydrogen ions in a 0.20 M solution of formic acid is 6.4×10^{-3} mol/L. To this solution, sodium formate is added so as to adjust the concentration of sodium formate to one mole per litre. What will be the pH of this solution ? The dissociation constant of formic acid is solution ? The dissociation constant of formic acid is 2.4×10^{-4} and the degree of dissociation of sodium formate is 0.75. **(1985)**

50. The solubility of $Mg(OH)_2$ in pure water is 9.57×10^{-3} g/litre. Calculate its solubility (in g/litre) in 0.02 M $Mg(NO_3)_2$ solution. **(1986)**

51. What is the pH of the solution when 0.2 mole of hydrochloric acid is added to one litre of a solution containing

(i) 1 M each of acetic acid and acetate ion ?

(ii) 0.1 M each of acetic acid and acetate ion ?

Assume the total volume is one litre. K_a for acetic acid $= 1.8 \times 10^{-5}$. **(1987)**

52. Freshly precipitated aluminium and magnesium hydroxides are stirred vigorously in a buffer solution containing 0.25 mol/L of NH_4Cl and 0.05 M of ammonium hydroxide calculate the concentration of alminimum and magnesium ions in solution

$$K_b[NH_4OH] = 1.8 \times 10^{-5}$$

$$K_{sp}[Mg(OH)_2] = 8.9 \times 10^{-12}$$

$$K_{sp}[Al(OH)_3] = 6 \times 10^{-32}$$

(1989)

53. What is the pH of 1.0 M solution of acetic acid ? To what volume must one litre of this solution be diluted so that the pH of the resulting solution will be twice the original value ?

Given : $K_a = 1.8 \times 10^{-5}$. **(1990)**

54. The solubility product of $Ag_2C_2O_4$ at 25°C is 1.29×10^{-11} $mol^3 L^{-3}$. A solution of $K_2C_2O_4$ containing 0.1520 mole in 500 mL water is shaken at 25°C with excess of Ag_2CO_3 till the following equilibrium is reached

$$Ag_2CO_3 + K_2C_2O_4 \rightleftharpoons Ag_2C_2O_4 + K_2CO_3$$

At equilibrium, the solution contains 0.0358 mole of K_2CO_3. Assuming the degree of dissociation of $K_2C_2O_4$ and K_2CO_3 to be equal, calculate the solubility product of Ag_2CO_3. **(1991)**

55. A 40 mL solution of a weak base, BOH is titrated with 0.1N HCl solution. The pH of the solution is found to be 10.04 and 9.14 after the addition of 5.0 mL and 20.0 mL of the acid respectively. Find out the dissociation constant of the base. **(1991)**

56. The solubility product (K_{sp}) of $Ca(OH)_2$ at 25°C is 4.42×10^{-5}. A 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in milligrams is precipitated ? **(1992)**

57. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which in 2 M in H_2CO_3, in order to maintain a pH of 7.4 ? (K_a for H_2CO_3 in blood is 7.8×10^{-7}) **(1993)**

58. An aqueous solution of a metal bromide MBr_2 (0.05 M) is saturated with H_2S. What is the minimum pH at which MS will precipitate ?

K_{sp} for MS = 6.0×10^{-21}, conc. of saturated H_2S = 0.1 M and $K_1 = 10^{-7}$ and $K_2 = 1.3 \times 10^{-13}$, for H_2S. **(1993)**

59. For the reaction,

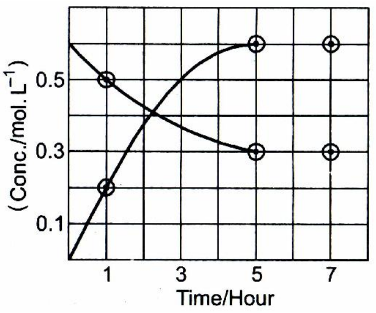
$$[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$$

The equilibrium constant, at 25°C, is 4.0×10^{-19}. Calculate the silver ion concentration in a solution which was originally 0.10 M in KCN and 0.03 M in $AgNO_3$. **(1994)**

60. The progress of reaction,

$$A \rightleftharpoons nB$$

with time, is represented in fig. given below. Determine



(i) the value of n

(ii) the equilibrium constant, K and

(iii) the initial rate of conversion of A. **(1994)**

61. Calculate the pH of an aqueous solution of 1.0 M ammonium formate assuming complete dissciation

(pK_a of formic acid = 3.8 and pK_b of ammonia = 4.8)

(1995)

62. What is the pH of a 0.50 M aqueous NaCN solution ?

(pK_b of CN^- = 4.70) **(1996)**

63. The ionisation constant of NH_4^+ in water is 5.6×10^{-10} at 25°C. The rate constant for the reaction of NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L/mol/s. Calculate the rate constant per proton transfer from wate to NH_3.

(1996)

64. A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- ions per litre. Calculate the solubility product of AgCl. **(1997)**

[Ksp (Ag_2CO_3) = 8.2×10^{-12}]

65. An acid type indicator, HIn differs in colour from its conjugate base (In^-). The human eye is sensitive to colour differences only when the ratio $[In^-]/[HIn]$ is greater than 10 or smaller than 0.1. What should be the minimum change in the pH of the solution to observe a complete colour change ? ($K_a = 1.0 \times 10^{-5}$) **(1997)**

66. The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6}M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.

(1999)

67. The average concentration of SO_2 in the atmosphere over a city on a certain day is 10 ppm, when the average temperature is 298 K. Given that the solubility of SO_2 in water at 298 K is 1.36653 mol/L and pK_a of H_2SO_3 is 1.92, estimate the pH of rain on that day. **(2000)**

68. 500 mL of 0.2 M aqueous solution of acetic acid is mixed with 500 mL of 0.2 M HCl at 25°C.

(i) Calculate the degree of dissociation of acetic acid in the resulting solution and pH of the solution.

(ii) If 6 g of NaOH is added to the above solution, determine the final pH. [Assume there is no change in volume on mixing : K_a of acetic acid is 1.75×10^{-5} mol L^{-1}.]

(2002)

69. (a) In the following equilibrium

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

when 5 moles of each are taken, the temperature is kept at 298 K the total pressure was found to be 20 bar. Given that

$$\Delta G_f^o\,(N_2O_4) = 100\text{kJ}$$

$$\Delta G_f^o\,(NO_2) = 50\text{kJ}$$

(i) Fina ΔG of the reaction

(ii) The direction of the reaction in which the equilibrium shifts

(b) A graph is plotted for a real gas which follows van der Waals' equation with pV_m taken on Y-axis and p on X-axis. Find the intercept of the line where V_m is molar volume. **(2004)**

70. 0.1 M of HA is titrated with 0.1 M NaOH, calculate the pH at end point, Given, K_a (HA) = 5×10^{-6} and $\alpha << 1$. **(2004)**

71. The dissociation constant of a substituted benzoic acid at 25°C is 1.0×10^{-4}. The pH of 0.01 M solution of its sodium salt is **(2009)**

Answer Key

Exercise-1 (Basic Objective Questions)

1. (c) **2.** (d) **3.** (b) **4.** (a) **5.** (c) **6.** (b) **7.** (a) **8.** (b) **9.** (a) **10.** (c)
11. (c) **12.** (b) **13.** (c) **14.** (d) **15.** (a) **16.** (a) **17.** (c) **18.** (b) **19.** (a,c) **20.** (b)
21. (d) **22.** (d) **23.** (d) **24.** (b) **25.** (a) **26.** (c) **27.** (d) **28.** (c) **29.** (d) **30.** (d)
31. (b) **32.** (d) **33.** (c) **34.** (c) **35.** (a) **36.** (c) **37.** (d) **38.** (c) **39.** (d) **40.** (a)
41. (b) **42.** (a) **43.** (c) **44.** (d) **45.** (b) **46.** (a) **47.** (c) **48.** (c) **49.** (a) **50.** (c)
51. (b) **52.** (b) **53.** (b) **54.** (a) **55.** (c) **56.** (d) **57.** (b) **58.** (d) **59.** (b) **60.** (b)
61. (c) **62.** (a) **63.** (b) **64.** (b) **65.** (a) **66.** (b) **67.** (b) **68.** (c) **69.** (d) **70.** (a)
71. (d) **72.** (a) **73.** (a) **74.** (d) **75.** (c) **76.** (c) **77.** (a) **78.** (b) **79.** (a) **80.** (c)
81. (c) **82.** (c) **83.** (b) **84.** (b) **85.** (c) **86.** (d) **87.** (a) **88.** (b) **89.** (c) **90.** (b)
91. (b) **92.** (a) **93.** (a) **94.** (b) **95.** (a) **96.** (c) **97.** (a) **98.** (a) **99.** (c) **100.** (a)
101. (d) **102.** (a) **103.** (a) **104.** (a) **105.** (a) **106.** (d) **107.** (c) **108.** (c) **109.** (b) **110.** (a)
111. (b) **112.** (c) **113.** (b) **114.** (c) **115.** (d) **116.** (d) **117.** (d) **118.** (d) **119.** (b) **120.** (a)
121. (a) **122.** (b) **123.** (c) **124.** (d)

Exercise-2 (Previous Year JEE Mains Questions)

1. (b) **2.** (b) **3.** (c) **4.** (a) **5.** (c) **6.** (b) **7.** (c) **8.** (c) **9.** (c) **10.** (b)
11. (b) **12.** (b) **13.** (c) **14.** (a) **15.** (c) **16.** (a) **17.** (b) **18.** (b) **19.** (a) **20.** (c)
21. (d)

JEE Mains Online

1. (c) **2.** (a) **3.** (b) **4.** (b) **5.** (c) **6.** (d) **7.** (c) **8.** (b) **9.** (b)

Exercise-3 (Advanced Objective Questions)

1. (a) **2.** (a,c) **3.** (d) **4.** (d) **5.** (a) **6.** (a) **7.** (a) **8.** (a) **9.** (a) **10.** (d)
11. (b,c,d) **12.** (a) **13.** (d) **14.** (a) **15.** (0006) **16.** (a,b,c,d) **17.** (a) **18.** (a) **19.** (c) **20.** (b)
21. (c) **22.** (a,b) **23.** (a,b,c) **24.** (d) **25.** (c) **26.** (d) **27.** (a) **28.** (c) **29.** (d) **30.** (a)
31. (a) **32.** (d) **33.** (c) **34.** (d) **35.** (d) **36.** (c) **37.** (b,c) **38.** (a,b,d) **39.** (d) **40.** (d)
41. (a) **42.** (d) **43.** (b) **44.** (b,d) **45.** (a,c,d) **46.** (a) **47.** (b) **48.** (b) **49.** (a) **50.** (d)

51. (d) **52.** (0000) **53.** (a) **54.** (a) **55.** (d) **56.** (b) **57.** (d) **58.** (c) **59.** (c) **60.** (a)

61. (b) **62.** (b) **63.** (d) **64.** (b,c,d) **65.** (a,c,d) **66.** $A \to R, B \to S, C \to P, D \to Q$ **67.** (a) **68.** (b)

69. (A-r), (B-r), (C-s), (D-p) **70.** (A-q,r), (B-p), (C-q), (D-s) **71.** (d) **72.** (a,d) **73.** (a) **74.** (b)

75. (c) **76.** (a,b,c,d) **77.** (0009) **78.** (a) **79.** (a) **80.** **(c)** **81.** **(c)** **82.** (c) **83.** (b) **84.** (a)

85. (a,b,d) **86.** (b,d) **87.** (b) **88.** (c) **89.** (a) **90.** $A \to R, B \to S, C \to P, D \to Q$ **91.** (0001) **92.** (0000)

93. (b) **94.** (c) **95.** (d) **96.** (0002) **97.** (d) **98.** (b) **99.** (b) **100.** (c) **101.** (c) **102.** (b)

103. (d) **104.** (a) **105.** (d) **106.** (0002) **107.** (0004) **108.** (a,b,c,d) **109.** (a,b,c) **110.** (a) **111.** (0004)

112. (0009) **113.** (A–q), (B–r), (C–r), (D–p,s) **114.** (A–p,q,r), (B–r), (C–p,q), (D–s) **115.** (A–r), (B–s), (C–p), (D–q)

116. (b) **117.**(a) **118.** (b) **119.** (d) **120.** (d) **121.** (a) **122.** (c) **123.** (b) **124.** (c) **125.** (d)

Exercise-4 (Previous Year JEE Advanced Questions)

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1. (d) **2.** (b) **3.** (a) **4.** (a) **5.** (b) **6.** (a) **7.** (c) **8.** (d) **9.** (d) **10.** (c)

11. (a) **12.** (d) **13.** (a) **14.** (a) **15.** (d) **16.** (d) **17.** (d) **18.** (b) **19.** (a) **20.** (d)

21. (c) **22.** (a) **23.** (b) **24.** (b) **25.** (c) **26.** (b) **27.** (a) **28.** (a) **29.** (b) **30.** (d)

31. (d) **32.** (a) **33.** (b) **34.** (bc) **35.** (abc) **36.** SO_2^- **37.** amphoteric **38.** hydration

39. I_2 **40.** more **41.** (F) **42.** (F) **43.** (F)

47. **(i)** 4.15, **(ii)** 1.43×10^{-10}m **48.** 5×10^{-13}M, 99.83 **49.** 4.20 **50.** 8.7×10^{-4} g/lit **51.** 4.5686 ; 1

52. 1.28×10^{-15}m, 0.68 M **53.** 2.3724 ; 2.78×10^{4} lit. **54.** 9.675×10^{-11} **55.** $K_b = 1.8 \times 10^{-5}$

56. 747.4 mg **57.** 80mL **58.** 1 **59.** 7.50×10^{-18} M Ag^+ **60.** **(i)** n = 2, **(ii)** 1.2 **61.** 6.50

62. 11.5 **63.** 6.12×10^{5} **64.** 2×10^{-8} **66.** 1.2×10^{-3} M **67.** 4.86

68. **(i)** 1.75×10^{-4} **(ii)** 4.75 **69.** (a) (i) O, (ii) Forward direction **70.** (9) **71.** (8)