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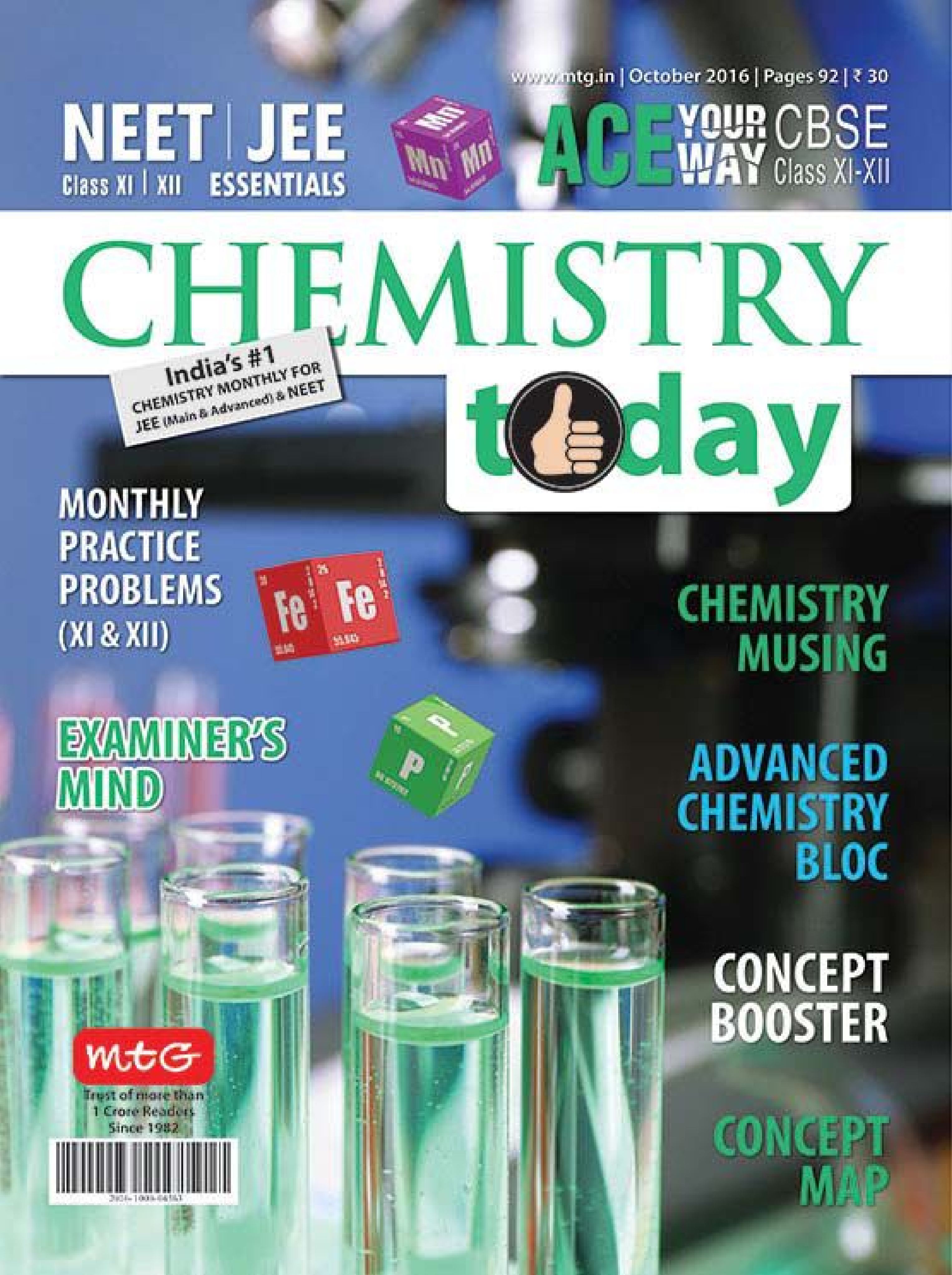

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Unit 4

Equilibrium | Redox Reactions

EQUILIBRIUM

- Equilibrium is the state attained by a system in which the system has no tendency for a change without external stimulation and hence, no net change occurs.

EQUILIBRIA INVOLVING PHYSICAL PROCESSES

- **Physical equilibrium :** Equilibrium attained between different physical forms of a chemical entity.

Type	Name	Equilibrium	Constant value at equilibrium
Solid-Liquid	Fusion	$H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$	Melting point at constant pressure
Liquid-Gas	Vaporisation	$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$	Vapour pressure of H_2O at constant temperature
Solid-Gas	Sublimation	$NH_4Cl_{(s)} \rightleftharpoons NH_4Cl_{(g)}$	Vapour pressure of NH_4Cl at constant temperature
Solid in Liquids	Dissolution	$Sugar_{(s)} \rightleftharpoons$ Sugar (in solution)	Solubility at constant temperature
Gases in Liquids	Dissolution	$CO_{2(g)} \rightleftharpoons CO_2$ (in solution)	Ratio of concentration of $CO_{2(aq)}$ and $CO_{2(g)}$ at constant temperature

EQUILIBRIA INVOLVING CHEMICAL PROCESSES

- **Chemical equilibrium :** Equilibrium attained between opposing chemical reactions.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

$$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$

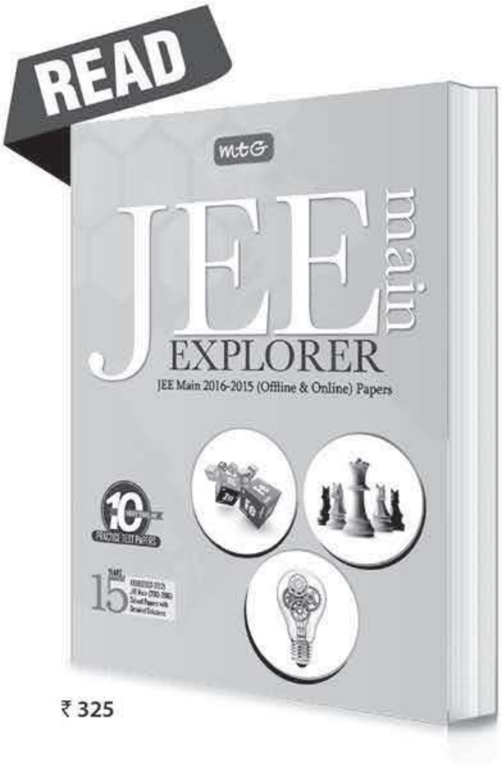
$$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$

- **Law of chemical equilibrium :**

$$aA_{(g \text{ or } aq)} + bB_{(g \text{ or } aq)} \underset{R_b}{\overset{R_f}{\rightleftharpoons}} cC_{(g \text{ or } aq)} + dD_{(g \text{ or } aq)}$$

$$R_f = R_b$$

$$K_{eq} = \frac{[C]^c \times [D]^d}{[A]^a \times [B]^b}$$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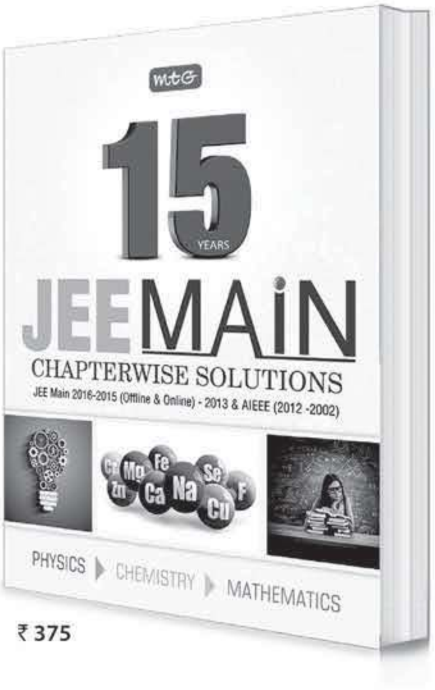
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- $K_{eq} << 1$; Position lies to the left, Reactants are favoured
- $K_{eq} >> 1$; Position lies to the right, Products are favoured
- **Unit :** Equilibrium constant (K_{eq}) is a dimensionless quantity.
- Relation between K_p and K_c, $K_p = K_c(RT)^{\Delta n_g}$

At 12.18 K temperature, $K_p = K_c$ for all reactions independent of the value of Δn.

When $RT > 1$, $K_p > K_c$ if Δn is +ve
$K_p = K_c$ if $\Delta n = 0$
$K_p < K_c$ if Δn is –ve

When $RT < 1$, $K_p < K_c$ if Δn is + ve
$K_p = K_c$ if $\Delta n = 0$
$K_p > K_c$ if Δn is –ve

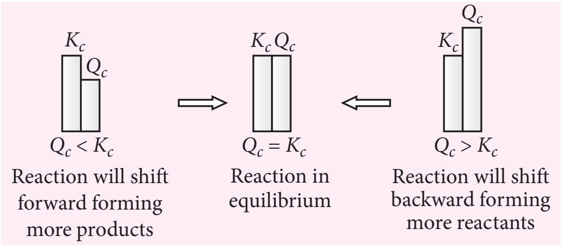
General Characteristics of *K*

- At particular temperature, equilibrium constant has a definite value.
- Independent of initial concentration of reacting species and presence of catalyst.
- Dependent on stoichiometry of reactants and products at equilibrium.
- If reaction is reversed, equilibrium constant is inversed *i.e.*, $K' = 1/K$.
- If equation for a reaction is divided by a factor of '*n*', the new equilibrium constant becomes n^{th} root of the previous equilibrium constant. *i.e.*, $K' = \sqrt[n]{K}$
- If equation for a reaction is multiplied by a factor '*n*' then the new equilibrium constant (K') becomes equal to K^n. *i.e.*, $K' = K^n$
- If equation is written in a number of steps, then its equilibrium constant will be multiple of equilibrium constants of each step, *i.e.*, $K = K_1 \times K_2 \times K_3 \times \ldots K_n$

Effect of temperature on equilibrium constant :

- For endothermic reactions, the equilibrium constant increases (k_f increases more than k_b) with rise in temperature and decreases with decrease in temperature.
- For exothermic reactions, equilibrium constant decreases (k_b increases more than k_f) with rise in temperature and increases with fall in temperature.

For the reaction, $aA + bB \rightleftharpoons xX + yY$ the expression $\frac{[X]^x[Y]^y}{[A]^a[B]^b}$ is called *reaction quotient* Q_c, at any stage other than the equilibrium.



Le-Chatelier's principle : If a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed.

Effect on Chemical Equilibria

Type of Effect or Change	**Direction of Equilibrium**
Addition of one or more reactants	Forward direction
Addition of one or more products	Backward direction
Increase in pressure	Where the number of gaseous moles are less
Decrease in pressure	Where the number of gaseous moles are more
Addition of catalyst	No effect
Addition of inert gas at constant volume	No effect
Addition of inert gas at constant pressure	Where the number of gaseous moles are more

Equilibrium constant and free energy change :

$\Delta G = \Delta G° + RT \ln Q_c$
At equilibrium, $\Delta G = 0$, $Q_c = K_c$
$\Delta G° = -2.303RT \log K_c$ (van't Hoff isotherm)
When $K_c = 1$, $\Delta G° = 0$ (Reaction is in equilibrium.)
When $K_c > 1$, $\Delta G° = -ve$
(Forward reaction is favoured.)
When $K_c < 1$, $\Delta G° = +ve$
(Backward reaction is favoured.)

IONIC EQUILIBRIUM

A substance whose aqueous solution or melt conducts electricity is called *electrolyte* while a substance whose aqueous solution or melt does not conduct electricity is called *non-electrolyte*.

Degree of dissociation (α) **:**

- For strong electrolytes, $\alpha = 1$.
- For weak electrolytes, $\alpha < 1$.

Ostwald's dilution law : For the reaction,

	$AB \rightleftharpoons$	A^+	B^-
Initially :	C	0	0
At equilibrium :	$C(1-\alpha)$	$C\alpha$	$C\alpha$

So, dissociation constant may be given as :

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \qquad \text{... (i)}$$

For very weak electrolytes,

$\alpha <<< 1,\ (1-\alpha) \approx 1$

$\therefore\ K = C\alpha^2$

$$\alpha = \sqrt{\frac{K}{C}} \qquad \text{... (ii)}$$

Concentration of any ion $= C\alpha = \sqrt{CK}$

Various concepts of acids and bases :

Concepts

Arrhenius concept	**Bronsted-Lowry concept**	**Lewis concept**
Acid : Produces H^+ ions in aq. solution *e.g.*, HCl, H_2SO_4	**Acid :** Protogenic substances or proton donors *e.g.*, CH_3COOH, HCl	**Acid :** Electrophiles or electron pair acceptors *e.g.*, BF_3, $AlCl_3$
Base : Produces OH^- ions in aq. solution *e.g.*, NaOH, KOH, NH_4OH	**Base :** Protophilic or proton acceptors. *e.g.*, NH_3	**Base :** Nucleophiles or electron pair donors *e.g.*, $\ddot{N}H_3$, $H_2\ddot{O}:$, F^-

Conjugate acid-base pair : A pair of acid and base, which differs by a proton is known as conjugate acid-base pair.

$$\begin{tikzcd}
\text{Acid} \arrow[rrrr, bend left, "-H^+"] & + & \text{Base} \arrow[rrrr, bend right, "+H^+"'] & \rightleftharpoons & \text{Conjugate Base} & + & \text{Conjugate Acid}
\end{tikzcd}$$

Self - ionisation of water :

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

At 25°, $[H_3O^+] = [OH^-] = 1 \times 10^{-7}$

K_w is a constant at 25 °C :

$K_w = [H_3O^+][OH^-]$

$K_w = (1 \times 10^{-7})(1 \times 10^{-7}) = 1 \times 10^{-14}$

- **Effect of temperature on K_w :** With increase in temperature, dissociation of water increases therefore, value of K_w increases with increase in temperature.

pH, pOH, pK_w, pK_b, pK_a terms :

$$\begin{tikzcd}
{[H^+]} \arrow[rr, leftrightarrow, "K_w = {[H^+]} \times {[OH^-]} = 1 \times 10^{-14}"] \arrow[d, bend right, "pH = -\log{[H^+]}"'] & & {[OH^-]} \arrow[d, bend right, "pOH = -\log{[OH^-]}"'] \\
pH \arrow[u, bend right, "{[H^+]} = 10^{-pH}"'] \arrow[rr, leftrightarrow, "pH + pOH = 14"'] & & pOH \arrow[u, bend right, "{[OH^-]} = 10^{-pOH}"']
\end{tikzcd}$$

$$\begin{tikzcd}
K_a \arrow[rr, leftrightarrow, "K_a = 10^{pK_a}", "pK_a = -\log{[K_a]}"'] \arrow[d, leftrightarrow, "\begin{array}{l} K_a \times K_b = K_w \\ K_a \times K_b = 1 \times 10^{-14} \end{array}"] & & pK_a \arrow[d, leftrightarrow, "\begin{array}{l} pK_a + pK_b = pK_w \\ pK_a + pK_b = 14 \end{array}"'] \\
K_b \arrow[rr, leftrightarrow, "K_b = 10^{pK_b}", "pK_b = -\log{[K_b]}"'] & & pK_b
\end{tikzcd}$$

$$\begin{tikzcd}
\text{STRONG ACID} \arrow[d, shift left, "\begin{array}{l} K_a \text{ decrease} \\ pK_a \text{ increase} \end{array}"] & & \text{STRONG BASE} \arrow[d, shift left, "\begin{array}{l} K_b \text{ decrease} \\ pK_b \text{ increase} \end{array}"] \\
\text{WEAK ACID} \arrow[u, shift left, "\begin{array}{r} K_a \text{ increase} \\ pK_a \text{ decrease} \end{array}"] & & \text{WEAK BASE} \arrow[u, shift left, "\begin{array}{r} K_b \text{ increase} \\ pK_b \text{ decrease} \end{array}"]
\end{tikzcd}$$

$pH = -\log_{10}[H^+]$
$pOH = -\log_{10}[OH^-]$
$pH + pOH = 14$
$pH + pOH = pK_w$

$pK_a = -\log_{10}K_a$
$pK_b = -\log_{10}K_b$
$pK_a + pK_b = pK_w$
$pK_a + pK_b = 14$

$K_w = [H^+][OH^-]$
$K_a \times K_b = K_w$
$K_a \times K_b = 1 \times 10^{-14}$

Salt hydrolysis :

- Salt hydrolysis is the phenomenon of interaction of cations and anions of a salt with water molecules to produce acidic / alkaline solution.
- Salts of strong acids and strong bases do not undergo hydrolysis and the resulting solution is *neutral*.

Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K_h)	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline pH > 7	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a + \log C]$
Strong acid and Weak base	Cationic	Acidic pH < 7	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$\text{pH} = \frac{1}{2}[\text{p}K_w - \text{p}K_b - \log C]$
Weak acid and Weak base	Anionic and cationic both	Neutral, pH = 7 (If $K_a = K_b$)	$K_h = \frac{K_w}{K_aK_b}$	$h = \sqrt{K_h}$	$\text{pH} = \frac{1}{2}[\text{p}K_w + \text{p}K_a - \text{p}K_b]$

Solubility product : It is defined as the product of the molar concentrations of ions of an electrolyte in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.

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

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

Types of Salt

Binary electrolyte 1 : 1 (AB)	Ternary electrolyte 1 : 2 (AB_2)	Ternary electrolyte 2 : 1 (A_2B)	Quaternary electrolyte 1 : 3 (AB_3)	3 : 2 (A_3B_2)
e.g., AgCl, $BaSO_4$, etc.	*e.g.*, $PbCl_2$, $Ca(OH)_2$, etc.	*e.g.*, Ag_2CrO_4, Ag_2CO_3, etc.	*e.g.*, $Fe(OH)_3$, $Al(OH)_3$, etc.	*e.g.*, $Ca_3(PO_4)_2$, $Ba_3(PO_4)_2$, etc.
$s = \sqrt{K_{sp}}$ or $K_{sp} = s^2$	$s = \sqrt[3]{K_{sp}/4}$ or $K_{sp} = 4s^3$	$s = \sqrt[3]{K_{sp}/4}$ or $K_{sp} = 4s^3$	$s = \sqrt[4]{K_{sp}/27}$ or $K_{sp} = 27s^4$	$s = \sqrt[5]{K_{sp}/108}$ or $K_{sp} = 108s^5$

Common - ion effect : The shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

The presence of a common ion suppresses the ionisation of a weak acid or a weak base.

Consider mixture of CH_3COONa (strong electrolyte) and CH_3COOH (weak acid).

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

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

CH_3COO^- (common ion) ion suppresses the ionisation of CH_3COOH (weak acid).

Buffer solution : A solution which resists the change in its pH value when small amount of an acid or a base is added to it or when the solution is diluted. It has a definite pH value at specific temperature.

Types of buffer solutions :

- **Simple buffer solution :** Salt of weak acid and weak base. *i.e.*, CH_3COONH_4
- **Acidic buffer solution :**
  - A mixture of weak acid and its salt with a strong base, *i.e.*, $CH_3COOH + CH_3COONa$
  - pH is less than 7.
  - $\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$
- **Basic buffer solution :**
  - A mixture of weak base and its salt with a strong acid, *i.e.*, $NH_4OH + NH_4Cl$
  - pH is greater than 7.
  - $\text{pOH} = \text{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$

Buffer capacity : It is the number of moles of an acid or a base added to change pH of one litre of a buffer solution by one unit.

Hence, buffer capacity

$$= \frac{\text{Number of moles of acid or base added per litre of buffer}}{\text{Change in pH}} = \frac{dn}{d(\text{pH})}$$

REDOX REACTIONS

- Chemical reactions which involves the transfer of electrons from one chemical substance to another are called *Redox* or *oxidation-reduction reactions*.

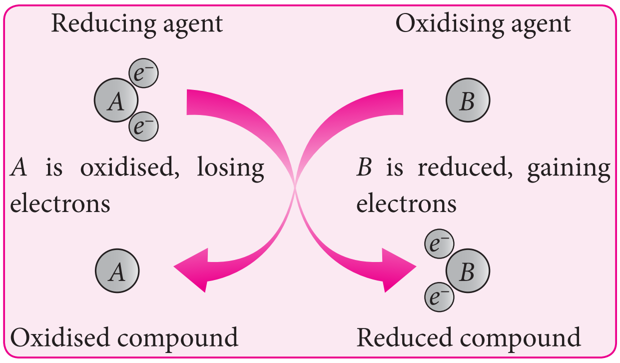
Redox

Oxidation

- Addition of Oxygen
- Removal of Hydrogen
- Addition of an electronegative element or group
- Removal of an electropositive element or group
- Increase in valency of an electropositive element
- Loss of electrons by an atom or ion

Reduction

- Removal of Oxygen
- Addition of Hydrogen
- Removal of an electronegative element or group
- Addition of an electropositive element or group
- Decrease in valency of electropositive element
- Gain of one or more electrons by an atom or ion



Valency	Oxidation number
1. It is the combining capacity of the element. No plus or minus sign is attached to it.	Oxidation number is the charge (real or imaginary) present on the atom of the element when it is in combination. It may have plus or minus sign.
2. Valency of an element is usually fixed.	Oxidation number of an element may have different values. It depends on the nature of the compound in which it is present.
3. Valency is always a whole number.	Oxidation number of the element may be a whole number or fractional.
4. Valency of the element is never zero except of noble gases.	Oxidation number of the element may be zero.

Types of redox reactions :

Redox Reactions

Displacement reaction :

$AB + C \longrightarrow AC + B$

Combination reaction :

$A + B \xrightarrow{\Delta} AB$

Disproportionation reaction :

$Cl_2 + 2NaOH \longrightarrow NaCl + NaClO + H_2O$

Decomposition reaction :

$AB \longrightarrow A + B$

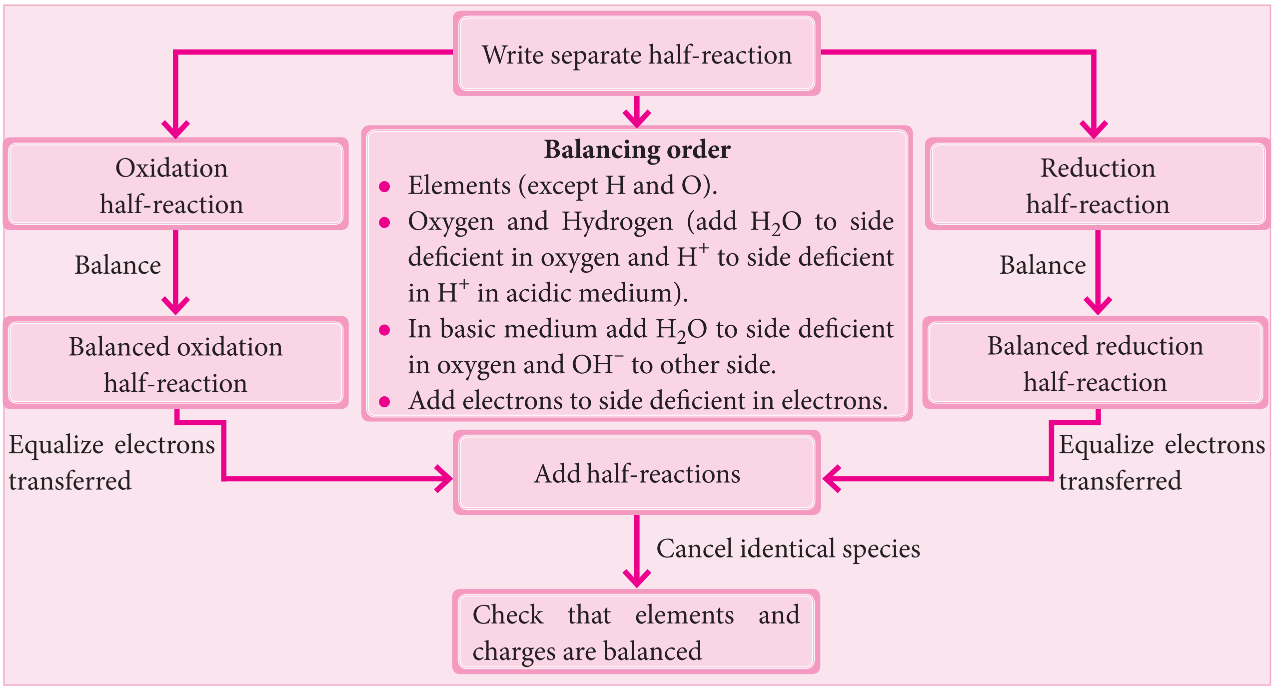
INFOSHOTS

Redox reactions are important to cell living chemistry !

The NIST technique measures changes in a living cell's internal redox (reduction-oxidation) potential, that expresses the favorability of reactions in which molecules or atoms either gain or lose electrons. Redox reactions are important to living cell chemistry. Redox reactions regulate many genes and the proteins they produce. An accurate measure of redox potential can provide insight into how well these genes are working, and in turn, whether or not the activities they control - such as differentiation and growth - are functioning normally. To assess this, scientists customarily measure the levels of both the reduced (electrons added) and oxidized (electrons lost) forms of glutathione, a peptide the cell uses as an antioxidant. Glutathione in cells is found predominately in the reduced state, known as GSH, but some gets converted to the oxidized form, known as GSSG. A high amount of GSSG indicates a cell has suffered oxidative stress, a process believed to contribute to cell ageing, breakdown, malfunction and eventual death.

BALANCING OF REDOX REACTIONS

Ion-electron / half-equation method :



Balancing order

- Elements (except H and O).
- Oxygen and Hydrogen (add H_2O to side deficient in oxygen and H^+ to side deficient in H^+ in acidic medium).
- In basic medium add H_2O to side deficient in oxygen and OH^- to other side.
- Add electrons to side deficient in electrons.

Oxidation number method :

Step 1. To find the atoms whose oxidation numbers change

$$Mg + HNO_3 \longrightarrow Mg(NO_3)_2 + N_2O + H_2O$$

O.N. increase by 2

$$\overset{0}{Mg} + \overset{+1}{H}\overset{+5}{N}\overset{-2}{O_3} \longrightarrow \overset{+2}{Mg}(\overset{+5}{N}\overset{-2}{O_3})_2 + \overset{+1}{N_2}\overset{-2}{O} + \overset{+1}{H_2}\overset{-2}{O}$$

O.N. decrease by 4 per N atom

Step 2. To find out total increase and decrease in O.N.

$$\underbrace{\overset{0}{Mg} \longrightarrow \overset{+2}{Mg}}_{\text{Total increase = 2}}\ ,\quad \underbrace{2H\overset{+5}{N}O_3 \longrightarrow \overset{+1}{N_2}O}_{\text{Total decrease = 8}}$$

Step 3. To balance total increase and decrease in O.N.

$$4Mg + 2HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O + H_2O$$

Step 4. To balance all atoms other than H and O (N atom on RHS = 10). Hence, replace $2HNO_3$ by $10HNO_3$

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O + H_2O$$

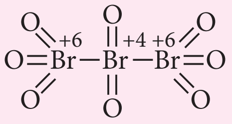
Step 5. To balance first O-atom (LHS = 30, RHS = 26. Add $4H_2O$ on RHS)

$$4Mg + 10HNO_3 \longrightarrow 4Mg(NO_3)_2 + N_2O + 5H_2O$$

Now H atom on LHS = 10, RHS = 10, Hence, the equation is balanced.

PARADOX OF FRACTIONAL OXIDATION NUMBER

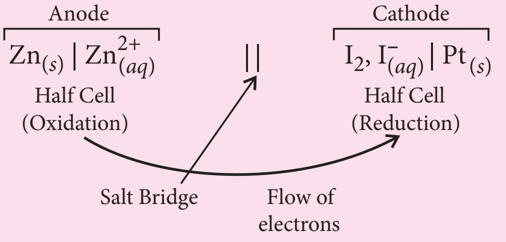
Compounds in which the oxidation number of a particular element in the compound is in fraction. Examples are :

Atom	Compound	Structure	O.N.
C	C_3O_2	$\overset{-2}{O}=\overset{+2}{C}=\overset{0}{C}=\overset{+2}{C}=\overset{-2}{O}$	4/3
Br	Br_3O_8		16/3

ELECTROCHEMICAL CELLS

Zn/I_2, I^-cell

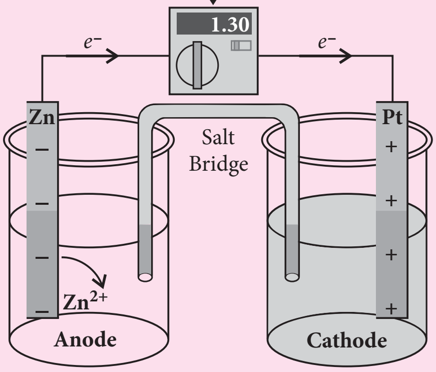
Cell representation



$$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel I_2, I^-_{(aq)} \mid Pt_{(s)}$$

- $E^\circ_{cell} = E^\circ_{(cathode)} - E^\circ_{(anode)}$
- +ve / high electrode potential is cathode (+)
- –ve / low electrode potential is anode (–)
- Electrons flow from anode (–) to cathode (+)

Cell diagram



Zn half cell (–ve)
Oxidation

I_2 half cell (+ve)
Reduction

Find E°_{cell} (use reduction potential)

At cathode : $Zn^{2+} + 2e^- \rightarrow Zn$; $E^\circ = -0.76$ V
At anode : $I_2 + 2e^- \rightarrow 2I^-$; $E^\circ = +0.54$ V

$Zn + I_2 \longrightarrow Zn^{2+} + 2I^-$; $E^\circ = ?$

$$\begin{aligned} Zn &\rightarrow Zn^{2+} + 2e^- ; \; E^\circ = +0.76 \\ I_2 + 2e^- &\rightarrow 2I^- ; \; E^\circ = +0.54 \\ \hline Zn + I_2 &\rightarrow Zn^{2+} + 2I^- \; E^\circ = +1.30 \text{ V} \end{aligned}$$

ELECTROCHEMICAL SERIES

Electrochemical Series

↓

Standard Reduction Potential – H_2 as std

Increasing strength of oxidising agent ↓

Oxidised std.		Reduced pot.	E°/V
$Li^+ + e^-$	→	Li	–3.04
$K^+ + e^-$	→	K	–2.93
$Ca^{2+} + 2e^-$	→	Ca	–2.87
$Na^+ + e^-$	→	Na	–2.71
$Mg^{2+} + 2e^-$	→	Mg	–2.37
$Al^{3+} + 3e^-$	→	Al	–1.66
$Mn^{2+} + 2e^-$	→	Mn	–1.19
$H_2O + e^-$	→	$H_2 + OH^-$	–0.83
$Zn^{2+} + 2e^-$	→	Zn	–0.76
$Fe^{2+} + 2e^-$	→	Fe	–0.45
$Ni^{2+} + 2e^-$	→	Ni	–0.26
$Sn^{2+} + 2e^-$	→	Sn	–0.14
$Pb^{2+} + 2e^-$	→	Pb	–0.13
$H^+ + e^-$	→	$1/2H_2$	0.00
$Cu^{2+} + e^-$	→	Cu^+	+0.15
$SO_4 + 4H^+ + 2e^-$	→	$H_2SO_4 + H_2O$	+0.17
$Cu^{2+} + 2e^-$	→	Cu	+0.34
$1/2O_2 + H_2O + 2e^-$	→	$2OH^-$	+0.40
$Cu^+ + e^-$	→	Cu	+0.52
$1/2I_2 + e^-$	→	I^-	+0.54
$Fe^{3+} + e^-$	→	Fe^{2+}	+0.77
$Ag^+ + e^-$	→	Ag	+0.80
$1/2Br_2 + e^-$	→	Br^-	+1.07
$1/2O_2 + 2H^+ + 2e^-$	→	H_2O	+1.23
$Cr_2O_7 + 14H^+ + 6e^-$	→	$2Cr^{2+} + 7H_2O$	+1.33
$1/2Cl_2 + e^-$	→	Cl^-	+1.36
$MnO_4^- + 8H^+ + 5e^-$	→	$Mn^{2+} + 4H_2O$	+1.51
$1/2F_2 + e^-$	→	F^-	+2.87

Increasing strength of reducing agent ↑

SPEED PRACTICE

1. The number of electrons required to balance the following equation,
$NO_3^- + 4H^+ + e^- \longrightarrow 2H_2O + NO$ is
(a) 5 (b) 4 (c) 3 (d) 2

2. The equilibrium constant at 298 K for a reaction, $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be
(a) 0.182 (b) 0.818 (c) 1.818 (d) 1.182
(JEE Main 2016)

3. Find the disproportionation reaction among the following.
(a) $Te_{(s)} + NO_{3(aq)}^- \longrightarrow TeO_{2(s)} + NO_{(g)}$
(b) $H_2O_{2(aq)} + Fe_{(aq)}^{2+} \longrightarrow Fe_{(aq)}^{3+} + H_2O_{(l)}$
(c) $Mn_{(s)} + NO_{3(aq)}^- \longrightarrow Mn_{(aq)}^{2+} + NO_{2(g)}$
(d) $Mn_{(aq)}^{3+} \longrightarrow MnO_{2(s)} + Mn_{(aq)}^{2+}$

4. Consider the following equilibrium in a closed container, $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$.
At a fixed temperature, the volume of the reaction mixture is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_p) and degree of dissociation (α)?
(a) Neither K_p nor α changes.
(b) Both K_p and α change.
(c) K_p changes but α does not.
(d) K_p does not change but α changes

5. For the reaction,
$3Br_2 + 6OH^- \longrightarrow 5Br^- + BrO_3^- + 3H_2O$
equivalent weight of Br_2 (if molecular weight is 'M') is
(a) $\frac{M}{2}$ (b) $\frac{M}{10}$
(c) $\left(\frac{M}{2} + \frac{M}{10}\right)$ (d) $\left(\frac{M}{6}\right)$

6. The standard Gibbs energy change at 300 K for the reaction, $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, $[B] = 2$ and $[C] = \frac{1}{2}$.
The reaction proceeds in the [R = 8.314 J/K/mol]
(a) forward direction because $Q_c < K_c$
(b) reverse direction because $Q_c < K_c$
(c) forward direction because $Q_c > K_c$
(d) reverse direction because $Q_c > K_c$.
(JEE Main 2015)

7. Which of the following is the strongest reducing agent in aqueous medium?
(a) Mg (b) Na (c) Li (d) Ca

8. At 627°C and one atmospheric pressure, SO_3 is partially dissociated into SO_2 and O_2 as

$$SO_{3(g)} \rightleftharpoons SO_{2(g)} + \frac{1}{2}O_{2(g)}$$

The density of the equilibrium mixture is found to be 0.925 g L^{-1}. The degree of dissociation of SO_3 under these conditions is
(a) 8.5% (b) 17% (c) 34% (d) 68%

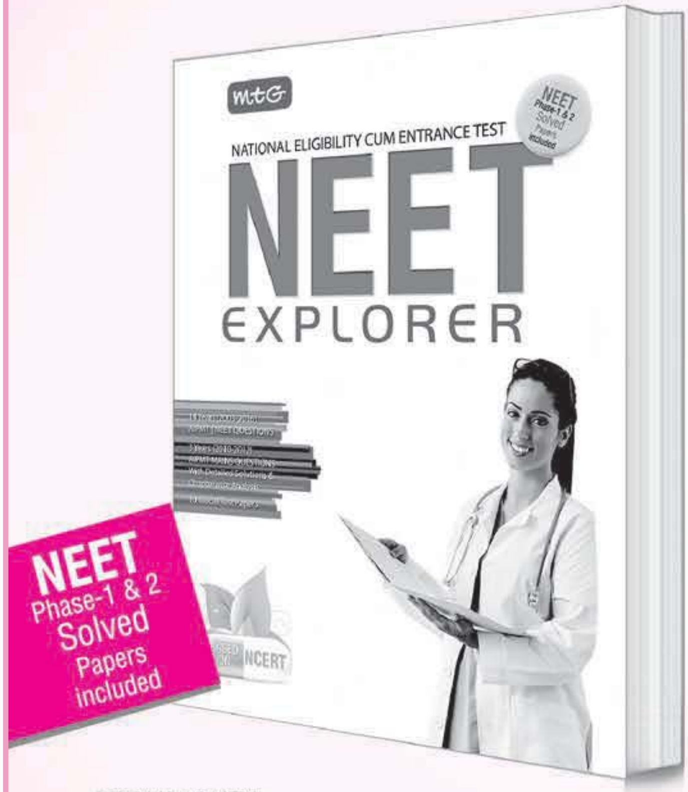
9. In an experiment, 20 g of vanadium (V) oxide (molar mass = 182) was reduced by excess of zinc dust in acidic solution to vanadium (II) ions. The required number of moles of iodine to re-oxidise vanadium (II) to VO^{2+} is
(a) 0.22 (b) 0.11 (c) 0.30 (d) 0.23

10. A solid XY kept in an evacuated sealed container undergoes decomposition to form a mixture of gases X and Y at temperature T. The equilibrium pressure is 10 bar in this vessel. K_p for this reaction is
(a) 25 (b) 100 (c) 10 (d) 5
(JEE Main 2016)

11. Which combination appears odd w.r.t. oxidation number per atom of the underlined species?
(a) $H_2\underline{S}O_5$, $H_2\underline{S}_2O_8$, $K_2\underline{Cr}_2O_7$
(b) $\underline{Cr}O_5$, $\underline{Cr}O_4^{2-}$, $\underline{S}O_4^{2-}$
(c) Both (a) and (b) (d) None of these

12. For a sparingly soluble salt A_pB_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) $L_s = S^{pq}.(pq)^{p+q}$

13. Which of the following pairs has the largest difference in the oxidation numbers of the underlined elements?
(a) $\underline{N}O_2$ and $\underline{N}_2O_4$ (b) $\underline{P}_2O_5$ and $\underline{P}_4O_{10}$
(c) $\underline{N}_2O$ and $\underline{N}O$ (d) $\underline{S}O_2$ and $\underline{S}O_3$


MTG
NATIONAL ELIGIBILITY CUM ENTRANCE TEST
NEET
EXPLORER
NEET Phase-1 & 2 Solved Papers included
NEET
Phase-1 & 2
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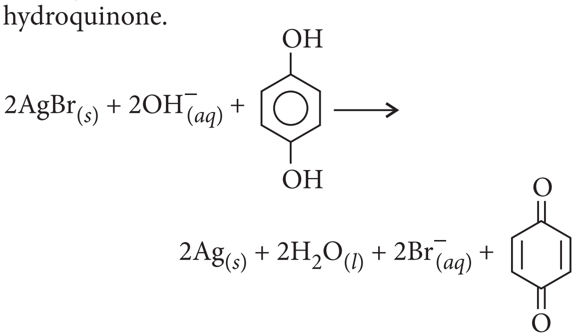
NCERT

14. The pK_b of CN^- 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

15. Photographic paper is developed with alkaline hydroquinone.



Select the correct statement.
(a) Hydroquinone is the oxidant.
(b) Ag^+ is the oxidant.
(c) Br^- is the oxidant.
(d) Ag^+ is the reductant.

16. Calculate the change in pH if 0.02 mol CH_3COONa is added to 1.0 L of 0.01 M HCl.
(K_a of $CH_3COOH = 1.8 \times 10^{-5}$)
(a) 3.00 (b) 5.23 (c) 2.74 (d) 10.23

17. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M $ZnSO_4$?
(a) The copper metal will dissolve with evolution of oxygen gas.
(b) The copper metal will dissolve with evolution of hydrogen gas.
(c) No reaction will occur.
(d) The copper metal will dissolve and zinc metal will be deposited. **(JEE Main 2016)**

18. How much of 0.3 M NH_4OH should be mixed with 30 mL of 0.2 M solution of NH_4Cl to give buffer solution of pH 8.65? ($pK_b = 4.75$)
(a) 5 mL (b) 10 mL (c) 2 mL (d) 18 mL

19. Formula weight divided by the change in oxidation number gives
(a) equivalent weight of an oxidant
(b) equivalent weight of the reductant
(c) the number of electrons gained in the reaction
(d) the equivalent weight of the oxidant or reductant.

20. Degree of hydrolysis of a mixture of aniline and acetic acid if each of them being 0.01 M is (Given : K_a of acetic acid $= 1.8 \times 10^{-5}$ and K_b of aniline $= 4.5 \times 10^{-10}$) .
(a) 0.78 (b) 0.57 (c) 0.62 (d) 0.52

21. Hydrogen peroxide in its reaction with KIO_4 and NH_2OH respectively, is acting as a
(a) reducing agent, oxidising agent
(b) reducing agent, reducing agent
(c) oxidising agent, oxidising agent
(d) oxidising agent, reducing agent. **(JEE Advanced 2014)**

22. The salt of which one of the following four weak acids will be the most hydrolysed?
(a) $HA : K_a = 1 \times 10^{-8}$ (b) $HB : K_a = 2 \times 10^{-6}$
(c) $HC : K_a = 3 \times 10^{-8}$ (d) $HD : K_a = 4 \times 10^{-10}$

23. (I) $H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$
(II) $H_2O_2 + Ag_2O \longrightarrow 2Ag + H_2O + O_2$

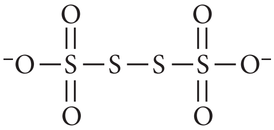
Role of hydrogen peroxide in the above reactions is respectively
(a) oxidizing in (I) and reducing in (II)
(b) reducing in (I) and oxidizing in (II)
(c) reducing in (I) and (II) both
(d) oxidizing in (I) and (II) both. **(AIPMT 2014)**

24. $Ag^+ + NH_3 \rightleftharpoons [Ag(NH_3)]^+$; $k_1 = 6.8 \times 10^{-3}$
$[Ag(NH_3)]^+ + NH_3 \rightleftharpoons [Ag(NH_3)_2]^+$; $k_2 = 1.6 \times 10^{-3}$
then the formation constant of $[Ag(NH_3)_2]^+$ is
(a) 1.08×10^{-7} (b) 1.08×10^{-5}
(c) 1.08×10^{-9} (d) none of these.

25. Which of the following statements are correct concerning redox properties?
(i) A metal M for which $E°$ for the half reaction $M^{n+} + ne^- \rightleftharpoons M$ is very negative will be a good reducing agent.
(ii) The oxidising power of halogens decreases from chlorine to iodine.
(iii) The reducing power of hydrogen halides increases from hydrogen chloride to hydrogen iodide.
(a) (i), (ii), (iii) (b) (i) and (ii)
(c) (i) only (d) (ii) and (iii) only

26. The pH of an acid buffer can be raised by 2 units by
(a) increasing the concentration of both weak acid and salt by two moles
(b) increasing the concentration of both the acid and salt by 10 times.
(c) diluting the solution by 10 times
(d) increasing the concentration of the salt by 10 times and decreasing concentration of the acid by 10 times.

27. The oxidation states of S atoms in $S_4O_6^{2-}$ from left to right respectively are



$$^{-}O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-S-S-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O^{-}$$

(a) +6, 0, 0, +6 (b) +3, +1, +1, +3
(c) +5, 0, 0, + 5 (d) +4, +1, +1, +4

28. According to Bronsted Lowry concept, the relative strengths of the bases CH_3COO^-, OH^- and Cl^- are in the order
(a) $OH^- > CH_3COO^- > Cl^-$
(b) $Cl^- > OH^- > CH_3COO^-$
(c) $CH_3COO^- > OH^- > Cl^-$
(d) $OH^- > Cl^- > CH_3COO^-$

29. Match the entries of column I with appropriate entries of column II and choose the correct option from the codes given below.

	Column I		Column II
P.	$2H_2O \xrightarrow{\Delta} 2H_2 + O_2$	1.	Disproportionation reaction
Q.	$CuSO_4 + Zn \longrightarrow Cu + ZnSO_4$	2.	Non-metal displacement reaction
R.	$Cl_2 + 6OH^- \xrightarrow{\Delta} 5Cl^- + ClO_3^- + 3H_2O$	3.	Decomposition reaction
S.	$Zn + 2HCl \longrightarrow ZnCl_2 + H_2$	4.	Metal displacement reaction

	P	Q	R	S
(a)	2	1	4	3
(b)	3	4	1	2
(c)	4	1	2	3
(d)	1	2	3	4

30. If for the given reactions, the equilibrium constants (K) are : $A_2 + B_2 \longrightarrow C,\ \frac{K}{m} = 4$,
$C + 2B_2 \longrightarrow 2D_2 = 16$ then match the reactions given in column I with the equilibrium constant values given in column II.
Choose the correct option from the codes given below.

	Column I		Column II
P.	$\frac{1}{2}A_2 + \frac{3}{2}B_2 \longrightarrow D_2$	1.	$\frac{1}{4}$
Q.	$2D_2 \longrightarrow A_2 + 3B_2$	2.	64
R.	$A_2 + 3B_2 \longrightarrow 2D_2$	3.	$\frac{1}{64}$
S.	$D_2 \longrightarrow B_2 + \frac{1}{2}C$	4.	8

	P	Q	R	S
(a)	1	2	3	4
(b)	1	3	2	4
(c)	4	2	3	1
(d)	4	3	2	1

SOLUTIONS

1. (c) : $NO_3^- + 4H^+ \longrightarrow 2H_2O + NO$
In this equation, all the atoms are balanced. To balance charge add $3e^-$ to L.H.S. .
$NO_3^- + 4H^+ + 3e^- \longrightarrow 2H_2O + NO$

2. (c) : $A + B \rightleftharpoons C + D$
Initial conc. : 1 1 1 1
At equilibrium. : $1 - x$ $1 - x$ $1 + x$ $1 + x$

$$\text{Now, } K_c = \frac{[C][D]}{[A][B]} \quad i.e.,\ 100 = \frac{(1+x)^2}{(1-x)^2}$$

$$\Rightarrow \quad 10 = \frac{1+x}{1-x}$$

$10 - 10x = 1 + x \Rightarrow 9 = 11x \Rightarrow x = 0.818$
So, concentration of D at equilibrium = 1 + 0.818
= 1.818 M

3. (d)

4. (d): K_p is constant at constant temperature. As volume is halved, pressure will be doubled. Hence, equilibrium will shift in the backward direction *i.e.*, degree of dissociation decreases.

5. (c) : Here, Br_2 disproportionates (simultaneous oxidation and reduction), so its equivalent weight is the sum of equivalent weights of the half reactions.
$2e^- + Br_2 \longrightarrow 2Br^-\ (x = 2)$ (reduction)
$Br_2 \longrightarrow 2BrO_3^- + 10e^-\ (x = 10)$ (oxidation)

$$\therefore \quad \text{Eq. wt.} = \frac{M}{2} + \frac{M}{10}$$

6. (d): $2A \rightleftharpoons B + C$
Given : $T = 300$ K, $\Delta G° = 2494.2$ J,
$R = 8.314\ JK^{-1}\ mol^{-1}$
$\Delta G° = -2.303\ RT \log K_c$
$2494.2 = -2.303 \times 8.314 \times 300 \times \log K_c$
$\log K_c = \text{antilog}\ (-0.4342)$
$K_c = 0.3679$

$$Q_c = \frac{[B][C]}{[A]^2} = \frac{2 \times \frac{1}{2}}{\left(\frac{1}{2}\right)^2} = 4$$

Here, $Q_c > K_c$ thus, the reaction will proceed in the reverse direction.

7. (c)

8. (c) : $d = \dfrac{PM}{RT}$

or $M = \dfrac{dRT}{P} = \dfrac{0.925 \times 0.0821 \times 900}{1} = 68.35$

i.e., Molecular mass of mixture (M_{mix}) = 68.35
Normal molecular mass of $SO_3(M)$ = 80

	SO_3	$\rightleftharpoons$ SO_2	+ $\frac{1}{2}O_2$
Initial moles :	1	0	0
Moles at eqm. :	$1 - \alpha$	α	$\frac{\alpha}{2}$

Total no. of moles at eqm. $= 1 + \dfrac{\alpha}{2}$

If volume of one mole of vapour = V

Volume of $\left(1 + \dfrac{\alpha}{2}\right)$ mole of vapour

$$= \left(1 + \frac{\alpha}{2}\right)V$$

$d \propto \dfrac{1}{V}$ and molecular mass = 2 × V.D.

$$\therefore \quad \text{Mol. mass} \propto \frac{1}{V}$$

$$\therefore \quad \frac{\text{Observed mol. mass}}{\text{Normal mol. mass}} = \frac{1}{1 + \frac{\alpha}{2}}$$

$$\text{or} \quad \frac{68.35}{80} = \frac{1}{1 + \frac{\alpha}{2}} \quad \text{or} \quad 1 + \frac{\alpha}{2} = \frac{80}{68.35}$$

or $\alpha = 0.34$ or 34%

9. (a) : $V_2O_5 \longrightarrow V^{2+} \longrightarrow VO^{2+}$

$$\underset{\substack{20\text{ g}\\0.11\text{ mol}}}{V_2O_5} \longrightarrow \underset{0.22\text{ mol}}{2V^{2+}}$$

$$\underset{+2}{V^{2+}} + \underset{0}{I_2} \longrightarrow \underset{+4}{VO^{2+}} + \underset{-2}{2I^-}$$

Thus, $\underset{0.11\text{ mol}}{V_2O_5} \equiv 2V^{2+} = 2VO^{2+} \equiv \underset{0.22\text{ mol}}{2I_2}$

10. (a) : $XY_{(s)} \rightleftharpoons X_{(g)} + Y_{(g)}$; $K_p = (p_X)(p_Y)$

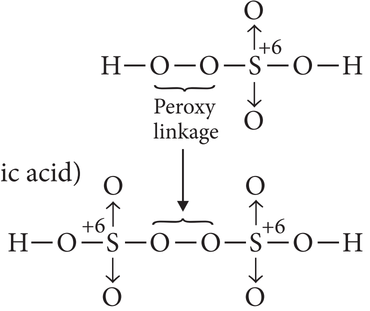
$p_X = x_X \times P_{\text{Total}} = \dfrac{1}{2} \times 10 = 5$ bar

Similarly, $p_Y = \dfrac{1}{2} \times 10 = 5$ bar

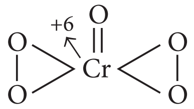
Now, $K_p = 5 \times 5 = 25$

11. (d): H_2SO_5 (peroxy sulphuric acid)

$H_2S_2O_8$
(peroxy disulphuric acid)



All of the above sulphur have O.N. = 6
Peroxy linkage (—O—O—) has –1 O.N. for oxygen, CrO_5 has two peroxy linkage, thus O.N. of Cr = +6



$K_2Cr_2O_7$ and CrO_4^{2-} both has +6 oxidation number for Cr. In SO_4^{2-} sulphur also has +6 oxidation number.

12. (a) : $A_pB_{q(s)} \rightleftharpoons \underset{pS}{pA^{+q}} + \underset{qS}{qB^{-p}}$

$L_s = (p.S)^p . (q.S)^q$
$= p^p \times S^p \times q^q \times S^q$ or $p^p \times q^q \times S^{(p+q)}$

13. (d): $NO_2(x = 4)$, $N_2O_4(x = 4)$

14. (b): It forms basic buffer.

$$\text{pOH} = \text{p}K_b + \log\left(\frac{2.5/500}{2.5/500}\right) = 4.7$$

pH = 14 –4.7 = 9.3

15. (b): Ag^+ is being reduced hence, it is oxidant.
Hydroquinone is oxidised hence, it is reductant.

16. (c) : pH of 0.01 M HCl solution,

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

$$[H^+] = \frac{0.01}{1\text{ L}} = 10^{-2}\text{ M} \quad \therefore \quad \text{pH} = 2.0$$

CH_3COONa contains CH_3COO^- ions which react with H_3O^+ ion from HCl. Assume complete reaction of H_3O^+ with CH_3COO^- ion.

	CH_3COO^- +	H_3O^+ $\longrightarrow$	CH_3COOH +	H_2O
Initial conc.	0.02 M	0.01 M	—	—
Final conc.	0.01 M (excess)	0	0.01 M	0.01 M

$$CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$$

$$K_a = \frac{[CH_3COO^-][H_3O^+]}{[CH_3COOH]} = \frac{[0.01][H_3O^+]}{0.01}$$

$$= 1.8 \times 10^{-5}$$

$\therefore \quad [H_3O^+] = 1.8 \times 10^{-5}$, so pH = 4.74
Change in pH (ΔpH) = 4.74 – 2.00 = 2.74

17. (c) : No reaction will occur. As reduction potential of Zn^{2+} ions to Zn atom is lower than that for Cu^{2+} ions. Hence, Cu metal cannot displace Zn^{2+} ions in $ZnSO_4$ solution.

18. (a) : It is a basic buffer.
pH = 8.65, pOH = 14 – 8.65 = 5.35

$$pOH = pK_b + \log\frac{[NH_4^+]}{[NH_4OH]}$$

$$5.35 = 4.75 + \log\frac{[NH_4^+]}{[NH_4OH]}$$

$$\frac{[NH_4^+]}{[NH_4OH]} = \text{antilog}\,(5.35 - 4.75)$$

$$= \text{antilog}\,(0.6) \approx 4.0$$

$$\therefore \quad \frac{[NH_4^+]}{[NH_4OH]} = \frac{30 \times 0.2}{0.3 \times V} \approx 4.0$$

$$\therefore \quad V = 5 \text{ mL}$$

19. (d)

20. (d): $C_6H_5NH_2 + CH_3COOH \rightleftharpoons$
$C_6H_5NHCOCH_3 + H_2O$
(Acetanilide)

Now, when we mix equal concentrations of aniline and acetic acid, they will neutralise each other to form acetanilide (salt). The salt is of weak base and weak acid, so hydrolysis takes place. The degree of hydrolysis of the salt of weak acid and weak base is given by

$$h = \frac{\sqrt{K_h}}{1 + \sqrt{K_h}}$$

$$\text{Here, } K_h = \frac{K_w}{K_a K_b} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 4.5 \times 10^{-10}} = 1.23$$

$$\Rightarrow \quad h = \frac{\sqrt{1.23}}{1 + \sqrt{1.23}} = \frac{1.109}{1 + 1.109} = \frac{1.109}{2.109} = 0.52$$

21. (a) :

(Decrease in O.N.)

$$\overset{+7}{KIO_4} + H_2O_2 \longrightarrow \overset{+5}{KIO_3} + H_2O + O_2$$

(Reducing agent)

$$\overset{-1}{NH_2OH} + 3H_2O_2 \longrightarrow \overset{+5}{HNO_3} + 4H_2O$$

(Oxidising agent)

Increase in O.N.

22. (d): $K_h = \frac{K_w}{K_a}$, so the smallest value of K_a will produce the largest value of K_h and hence, causes the most hydrolysis.

23. (c) :

Increase in oxidation state
(reducing agent)

$$\overset{-1}{H_2O_2} + O_3 \longrightarrow H_2O + 2\overset{0}{O_2}$$

Increase in oxidation state (reducing agent)

$$\overset{-1}{H_2O_2} + \overset{+1}{Ag_2O} \longrightarrow 2\overset{0}{Ag} + H_2O + \overset{0}{O_2}$$

H_2O_2 acts as reducing agent in all those reactions in which O_2 is evolved.

24. (b): As the reaction takes place in two steps:
$k = k_1 \times k_2 = 6.8 \times 10^{-3} \times 1.6 \times 10^{-3} = 10.8 \times 10^{-6}$
$= 1.08 \times 10^{-5}$

25. (a)

26. (d): $pH_1 = pK_a + \log\left(\frac{\text{Salt}}{\text{Acid}}\right)$

$$pH_1 = pK_a + \log\left(\frac{x_1}{y_1}\right),\ pH_2 = pK_a + \log\left(\frac{x_2}{y_2}\right)$$

$$pH_2 - pH_1 = \log\frac{x_2}{y_2} - \log\frac{x_1}{y_1}$$

$$2 = \log\left(\frac{x_2 / y_2}{x_1 / y_1}\right)$$

$$\therefore \quad \frac{x_2 / y_2}{x_1 / y_1} = 10^2 = 100$$

This is only possible, if the concentration of salt is increased by 10 times and the concentration of acid is decreased by 10 times.

27. (c)

28. (a) : Acidic strength order : HCl > CH_3COOH > H_2O
Conjugate base strength:
$Cl^- < CH_3COO^- < OH^-$

29. (b)

30. (d): Adding given equations, we get
$A_2 + 3B_2 \longrightarrow 2D_2$, $K = 4 \times 16 = 64$
(P) Dividing by 2, $\frac{1}{2}A_2 + \frac{3}{2}B_2 \longrightarrow D_2$,
$K = \sqrt{64} = 8$
(Q) Reversing, $2D_2 \longrightarrow A_2 + 3B_2$, $K = 1/64$
(R) $A_2 + 3B_2 \longrightarrow 2D_2$, $K = 64$
(S) Reversing and dividing by 2, $C + 2B_2 \longrightarrow 2D_2$,
$K = 16$

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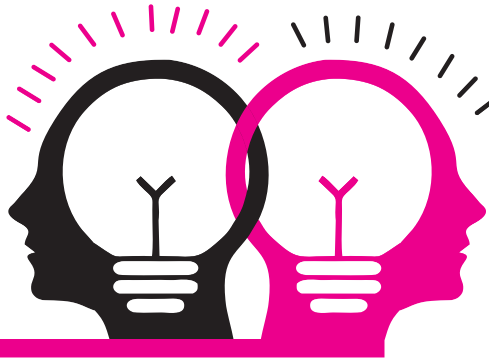
EXAMiNER'S MiND CLASS XI



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true 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 both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

STATES OF MATTER

SECTION - I

Only One Option Correct Type

1. The compressibility factor for definite amount of van der Waals' gas at 0°C and 100 atm is found to be 0.5. Assuming the volume of gas molecules negligible, the van der Waals' constant *a* for a gas is
(a) 1.256 $L^2\ mol^{-2}$ atm (b) 0.256 $L^2\ mol^{-2}$ atm
(c) 2.256 $L^2\ mol^{-2}$ atm (d) 0.0256 $L^2\ mol^{-2}$ atm

2. NH_3 gas is liquefied more easily than N_2 as
(a) van der Waals constants *a* and *b* of NH_3 > *a* and *b* of N_2
(b) van der Waals constants *a* and *b* of NH_3 < *a* and *b* of N_2
(c) $a(NH_3) > a(N_2)$ but $b(NH_3) < b(N_2)$
(d) $a(NH_3) < a(N_2)$ but $b(NH_3) > b(N_2)$.

3. At what temperature will hydrogen molecules have the same *K.E.* as nitrogen molecules at 280 K?
(a) 280 K (b) 40 K (c) 400 K (d) 50 K

4. A vessel has nitrogen gas and water vapours at a total pressure of 1 atm. The partial pressure of water vapours is 0.3 atm. The contents of this vessel are transferred to another vessel having one third of the capacity of original volume, completely at the same temperature, the total pressure of the system in the new vessel is
(a) 3.0 atm (b) 1 atm (c) 3.33 atm (d) 2.4 atm

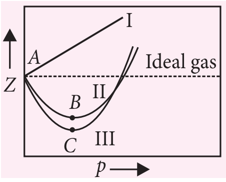
5. Four gases H_2, CH_4, O_2 and CO_2 are kept at same temperature, order of their most probable speeds (u_{mp}) is
(a) $u_{mp(H_2)} < u_{mp(O_2)} < u_{mp(CH_4)} < u_{mp(CO_2)}$
(b) $u_{mp(CO_2)} < u_{mp(O_2)} < u_{mp(CH_4)} < u_{mp\ (H_2)}$
(c) $u_{mp(O_2)} < u_{mp(H_2)} < u_{mp(CH_4)} < u_{mp\ (CO_2)}$
(d) $u_{mp(CO_2)} < u_{mp(CH_4)} < u_{mp(O_2)} < u_{mp\ (H_2)}$

6. A mixture of $NH_{3(g)}$ and $N_2H_{4(g)}$ is placed in a sealed container at 300 K. The total pressure is 0.5 atm. The container is heated to 1200 K, at this time both substances decompose completely according to the following equations :

$$2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$$
$$N_2H_{4(g)} \rightarrow N_{2(g)} + 2H_{2(g)}$$

After decomposition is complete, the total pressure at 1200 K is found to be 4.5 atm. The amount (in mole percent) of $N_2H_{4(g)}$ in the original mixture is
(a) 10 (b) 20 (c) 25 (d) 50

7. Consider isotherms I, II and III :



Select the correct statements.

(a) For light gases (like H_2), isotherm I is obtained.

(b) When force of attraction is negligible, isotherms II and III are followed after point *B* or *C*.

(c) When co-volume is neglected, isotherms II and III are followed *A* to *B* or *A* to *C*.

(d) All of these.

8. Molar volume of CO_2 is maximum at

(a) STP (b) 400 K and 1 atm

(c) 273 K and 2 atm (d) 546 K and 2 atm

9. Atmospheric pressure is 76 cm Hg and pressure of the gas is 77 cm Hg. Hence, height '*h*' of the mercury column in open arm is

(a) 1 cm (b) $\frac{1}{13.6\times 980}$ cm

(c) 153 cm (d) $1 \times 1.36 \times 980$ cm

10. Which of the assumptions of the kinetic-molecular theory best explains the observation that a balloon collapses when exposed to liquid nitrogen (which is much colder than a cold winter day)?

(a) Gas molecules move at random with no attractive forces between them.

(b) The velocity of gas molecules is proportional to their Kelvin temperature.

(c) The amount of space occupied by a gas is much greater than the space occupied by the actual gas molecules.

(d) Collisions with the walls of the container or with other molecules are elastic.

SECTION - II

More than One Options Correct Type

11. A gas described by van der Waals equation

(a) behaves similar to an ideal gas in the limit of large molar volumes

(b) behaves similar to an ideal gas in the limit of large pressures

(c) is characterised by van der Waals coefficients that are dependent on identity of the gas but are independent of the temperature

(d) has the pressure that is lower than the pressure exerted by the same behaving ideally.

12. If a gas is expanded at constant temperature,

(a) the pressure decreases

(b) the kinetic energy of the molecules remains the same

(c) the kinetic energy of the molecules decreases

(d) the number of molecules of the gas increases.

13. According to kinetic theory of gases, for a diatomic molecule which among the following statements are incorrect?

(a) The pressure exerted by the gas is proportional to the mean speed of the molecule.

(b) The pressure exerted by the gas is proportional to the root mean square speed of the molecule.

(c) The root mean square speed of the molecule is inversely proportional to the temperature.

(d) The mean translational kinetic energy of the molecule is proportional to the absolute temperature.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

On the basis of postulates of kinetic theory of gases, it is possible to derive the mathematical expression, commonly called as kinetic gas equation.

$$PV = \frac{1}{3} mn' u_{\text{rms}}^2$$

here P = Pressure of the gas, V = Volume of the gas, m = Mass of the molecule of the gas, n = Number of the molecules present.

This has been derived by considering that a certain mass of gas enclosed in a cubical vessel of side '*l*' centimetre having '*n*' molecules and mass of each molecule being *m*. The speed can be resolved into three components, *i.e.*, u_x, u_y and u_z parallel to the container as shown $u_{\text{rms}}^2 = u_x^2 + u_y^2 + u_z^2$.

14. The pressure exerted by the gas is directly proportional to

(a) most probable speed (b) average speed

(c) root mean square speed

(d) all of these.

15. The rate of diffusion of gas is proportional to the speed of gas molecules. Hence, rate of diffusion of the gas is

(a) directly proportional to $\sqrt{\frac{P}{M_0}}$ at constant temperature.

(b) directly proportional to $\frac{P}{\sqrt{M_0}}$ at constant temperature.

(c) directly proportional to $\frac{P}{M_0}$ at constant temperature.

(d) directly proportional to $\frac{M_0}{P}$ at constant temperature.

Paragraph for Questions 16 and 17

Like gases, liquids also possess certain characteristic properties, the most common being vapour pressure, surface tension and viscosity. Lower the vapour pressure of a liquid, higher is its boiling point. The liquid rises in a capillary tube due to force of surface tension. Liquids are distinguished from each other on the basis of their viscosity, *i.e.*, tendency to flow. All these properties of a liquid not only depend upon the nature of the liquid but also on temperature.

16. The vapour pressure of 1 L of a liquid at 25°C is p mm. The vapour pressure of 2 L of the liquid at the same temperature will be

(a) $2p$ mm (b) $p/2$ mm

(c) p mm (d) $4p$ mm

17. The effect of increase of temperature on surface tension and viscosity is

(a) surface tension increases, viscosity decreases

(b) surface tension decreases, viscosity increases

(c) both decreases (d) both increases.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
A.	Between phosphine molecules	p.	London forces.
B.	Between neo-pentane molecules	q.	Dipole-induced dipole interactions.
C.	Between CH_4 and HCl molecules	r.	Dipole-dipole interactions.
D.	Between NH_3 molecules	s.	Hydrogen bonding.

(a) A-p, B-r, C-s, D-q (b) A-r, B-p, C-q, D-s

(c) A-q, B-r, C-p, D-s (d) A-s, B-p, C-q, D-r

19. Match the List I with List II and select the correct answer using the codes given below the lists :

	List I		List II
A.	X = 100 mL of H_2 at 1 bar, 25°C Y = 200 mL of O_2 at 1 bar, 25°C	p.	1 : 1·225
B.	X = 100 mL of O_2 at 1 bar, 25°C Y = 200 mL of O_3 at 2 bar, 25°C	q.	1 : 0·7
C.	X = 100 mL of SO_2 at 1 bar, 25°C Y = 100 mL of O_2 at 1 bar, 25°C	r.	1 : 1·36
D.	X = HCl gas to travel 100 cm length in a tube Y = NH_3 gas to travel 200 cm length using the same tube (P, V, T = same in both cases)	s.	1 : 8

(a) A-s, B-p, C-q, D-r (b) A-s, B-q, C-p, D-r

(c) A-q, B-s, C-r, D-p (d) A-p, B-r, C-q, D-s

SECTION - V

Assertion Reason Type

20. **Assertion :** The pressure of a fixed amount of an ideal gas is proportional to its temperature.

Reason : The frequency of collisions and their impact both increases in proportion to the square root of temperature.

21. **Assertion :** A lighter gas diffuses more rapidly than a heavier gas.

Reason : At a given temperature, the rate of diffusion of a gas is inversely proportional to the square root of its density.

22. **Assertion :** A gas can be easily liquefied at any temperature below its critical temperature.

Reason : Liquification of a gas takes place when the average kinetic energy of the molecules is low.

SECTION - VI

Integer Value Correct Type

23. The volume occupied by 8.8 g of CO_2 at 31.1°C and 1 bar pressure (in L) is

24. At identical temperature and pressure the rate of diffusion of hydrogen gas is $3\sqrt{3}$ times that of a hydrocarbon having molecular formula C_nH_{2n-2}. The value of n is

25. 2 g of a gas X are introduced into an evacuated flask kept at 25°C. The pressure is found to be 1 atm. If 3 g of another gas Y are added to the same flask, the total pressure becomes 1.5 atm. Assuming that ideal behaviour, the molecular mass ratio of M_x and M_y is

SECTION - I

Only One Option Correct Type

1. The stability of the following alkali metal chlorides follows the order
(a) LiCl > KCl > NaCl > CsCl
(b) CsCl > KCl > NaCl > LiCl
(c) NaCl > KCl > LiCl > CsCl
(d) KCl > CsCl > NaCl > LiCl

2. The solubility of sulphates of alkaline earth metals in water shows the order
(a) Be > Ca > Mg > Ba > Sr
(b) Mg > Be > Ba > Ca > Sr
(c) Be > Mg > Ca > Sr > Ba
(d) Mg > Ca > Ba > Be > Sr

3. Chemical '*A*' is used for water softening to remove temporary hardness. '*A*' reacts with sodium carbonate to generate caustic soda. When CO_2 is bubbled through '*A*', it turns cloudy. What is the chemical formula of '*A*'?
(a) $CaCO_3$ (b) CaO
(c) $Ca(OH)_2$ (d) $Ca(HCO_3)_2$

4. The dilute solution of alkaline earth metals in liquid ammonia shows
(a) a bright blue colour due to formation of metal cluster.
(b) a bright blue colour due to solvated electrons.
(c) a bronze colour due to solvated electrons.
(d) a bronze colour due to formation of metal cluster.

5. Lithium shows similarities with magnesium in its chemical behaviour because
(a) similar size, greater elecronegativity and lower polarising power
(b) similar size, same electronegativity and lower polarising power
(c) similar size, same electronegativity and similar high polarising power
(d) none of the above.

6. Select the incorrect statement.
(a) Li_2CO_3 is only sparingly soluble in water and no $LiHCO_3$ has been isolated.
(b) K_2CO_3 cannot be made by a method similar to the ammonia-soda process.
(c) Li_2CO_3 and $MgCO_3$ both are thermally stable.
(d) $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$ is a mineral called trona.

7. The stability of K_2O, K_2O_2 and KO_2 is in order $K_2O < K_2O_2 < KO_2$. This increasing stability as the size of metal ion increases is due to the stabilisation of
(a) larger cation by smaller anions
(b) larger cation by larger anions
(c) smaller cations by smaller anions
(d) smaller cations by larger anions.

8. The charge/size ratio of a cation determines its polarising power. Which one of the following sequences represents the increasing order of the polarising power of cationic species; K^+, Ca^{2+}, Mg^{2+}, Be^{2+}?
(a) $Mg^{2+} < Be^{2+} < K^+ < Ca^{2+}$
(b) $Be^{2+} < K^+ < Ca^{2+} < Mg^{2+}$
(c) $K^+ < Ca^{2+} < Mg^{2+} < Be^{2+}$
(d) $Ca^{2+} < Mg^{2+} < Be^{2+} < K^+$

9. A solid compound '*X*' on heating gives CO_2 gas and a residue. The residue mixed with water forms '*Y*'. On passing an excess of CO_2 through '*Y*' in water, a clear solution '*Z*' is obtained. On boiling '*Z*' compound '*X*' is formed. The compound '*X*' is
(a) $CaCO_3$ (b) Na_2CO_3
(c) K_2CO_3 (d) $Ca(HCO_3)_2$

10. Correct order of stability of group II A metal carbonates is
(a) $MgCO_3 > CaCO_3 > SrCO_3 > BaCO_3$
(b) $BaCO_3 > SrCO_3 > CaCO_3 > MgCO_3$
(c) $SrCO_3 > BaCO_3 > CaCO_3 > MgCO_3$
(d) $CaCO_3 > MgCO_3 > BaCO_3 > SrCO_3$

SECTION - II

More than One Options Correct Type

11. Which of the following do not represent the correct order?
(a) Thermal stability : $MgCO_3 < CaCO_3 < BaCO_3$
(b) Reactivity with O_2 : Be < Mg < Ca
(c) Solubility in water : $MgSO_4 < CaSO_4 < SrSO_4$
(d) Enthalpy of formation : CaO < SrO < BeO

12. Which of the following statements are correct?
(a) Sodium is most abundant among alkali metals.
(b) Among group I elements, radium is the only radioactive element.
(c) Lattice energy of NaI is more than that of NaBr.
(d) The mobility of Li^+ in water is less than Na^+.

13. Which of the following statements are correct?

(a) Beryllium is not readily attacked by acids because of the presence of an oxide film on the surface of the metal.

(b) Beryllium sulphate is readily soluble in water as the greater hydration enthalpy of Be^{2+} overcomes the lattice enthalpy factor.

(c) Beryllium exhibits coordination number more than four.

(d) Beryllium oxide is purely acidic in nature.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

$\underset{\text{(Element)}}{\text{‘}A\text{’}}$ burns in nitrogen and forms $\underset{\text{(Ionic Compound)}}{\text{‘}B\text{’}}$

$$\underset{\text{(Ionic Compound)}}{\text{‘}B\text{’}} + H_2O \longrightarrow \text{‘}C\text{’} + \text{‘}D\text{’}$$

$$\text{‘}C\text{’}_{(aq)} + CO_2 \longrightarrow \text{milkiness appears}$$

14. The element '*A*' is

(a) alkali metal (b) beryllium

(c) magnesium (d) barium.

15. The milkiness that appears is due to

(a) $Ca(OH)_2$ (b) $Ca(HCO_3)_2$

(c) $Ba(HCO_3)_2$ (d) $BaCO_3$

Paragraph for Questions 16 and 17

Hydration energy $\Delta H_{hydr.}$(kJ mol^{-1})		Lattice energy ΔU(kJ mol^{-1})	
Li^+	−499	LiCl	−840
Na^+	−390	NaCl	−776
K^+	−305	KCl	−703
Cl^+	−382		

16. Heat of hydration (numerical value) of LiCl, NaCl and KCl in the increasing order is

(a) LiCl < KCl < NaCl (b) LiCl < NaCl < KCl

(c) LiCl = KCl < NaCl (d) KCl < NaCl < LiCl

17. Maximum heat is absorbed in the dissolution of one mole of

(a) LiCl (b) NaCl (c) KCl (d) equally.

SECTION - IV

Matching List Type

18. Match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	BeO	1.	Amphoteric
Q.	Al_2O_3	2.	Diagonal relationship
R.	MgO	3.	Lime water
S.	CaO	4.	Baryta water
T.	BaO	5.	Water insoluble
		6.	Maximum soluble in water
		7.	Estimation by EDTA

	P	Q	R	S	T
(a)	5,2,1	2,7,5	7,5,3	5,2	6,5,2
(b)	3,2,1	6,5,4	1,2,3	7,1,3	2,1,5
(c)	1,2,5	1,2,5	2,7	3,7	4,6
(d)	3,4,1	5,4,3	3,4	7,2	5,1,3

19. Match the List I with List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Li_3N	1.	Paramagnetic
Q.	LiCl	2.	Ether soluble
R.	KO_2	3.	Humidity control
S.	Rb_2O_3	4.	Automobiles air bags
		5.	Coloured compounds

	P	Q	R	S
(a)	4,2	3,5	2	2,5
(b)	4,5	2,3	1,5	1,5
(c)	2,3	2,4	2,3	1,3
(d)	1,5	5	1,4	3,5

SECTION - V

Assertion Reason Type

20. Assertion : K, Rb and Cs (all belonging to group 1) form superoxides.

Reason : The ionic radii of K, Rb and Cs show the following trend $Cs^+ < Rb^+ < K^+$.

21. Assertion : Of the various chlorides of alkaline earth metals $BeCl_2$ is covalent in nature, where as $MgCl_2$ and $CaCl_2$ are ionic compounds.

Reason : Be is the first member of group 2.

22. Assertion : Alkali metals can form ionic hydrides which contain the hydride ion H^-.

Reason : Alkali metals are highly electropositive.

SECTION - VI

Integer Value Correct Type

23. When $NaNO_3$ is heated, change in oxidation number of N is

24. The number of unpaired electron(s) in potassium superoxide is

25. One mole of lithium nitride is decomposed by H_2O and resultant solution is neutralised by HCl. Number of moles of HCl required is

SOLUTIONS

STATES OF MATTER

1. (a) : $Z = \frac{PV}{nRT} = 0.5$

Now, $\left[P + \frac{n^2a}{V^2}\right][V - nb] = nRT$

$\left[P + \frac{n^2a}{V^2}\right][V] = nRT$ (b is negligible)

$PV^2 - nRTV + n^2a = 0$

$\therefore V = \frac{nRT \pm \sqrt{n^2R^2T^2 - 4n^2a \times P}}{2P}$

Since, V is constant at given P and T, thus discriminant is 0.

$\therefore n^2R^2T^2 = 4n^2aP$ or $a = \frac{R^2T^2}{4P} = \frac{(0.0821)^2 \times (273)^2}{4 \times 100}$

$= 1.256\ L^2\ mol^{-2}\ atm$

2. (c) : Gases which can be liquefied easily have high value of *a* and low value of *b*.

3. (a) : $K.E. = \frac{3}{2}RT$

$K.E. \propto T$

4. (d) **5. (b)**

6. (c) : For decomposition of NH_3, (T = 1200 K)

$$2NH_{3(g)} \rightarrow N_{2(g)} + 3H_{2(g)}$$

At $t = 0$: p_{NH_3} 0 0

After decomposition : 0 $(p_{NH_3}/2)$ $(3/2)p_{NH_3}$

For decomposition of N_2H_4, (T = 1200 K)

$$N_2H_{4(g)} \longrightarrow N_{2(g)} + 2H_{2(g)}$$

at $t = 0$: $p_{N_2H_4}$ 0 0

After decomposition : 0 $p_{N_2H_4}$ $2p_{N_2H_4}$

Initially at 300 K, $p_{NH_3} + p_{N_2H_4} = 0.5$ atm

or initially at 1200 K,

$p_{NH_3} + p_{N_2H_4} = 4 \times 0.5 = 2.0$ atm $\left(\because \frac{p_1}{T_1} = \frac{p_2}{T_2}\right)$ ...(i)

or P_{total} after decomposition

$= \frac{p_{NH_3}}{2} + \frac{3}{2}p_{NH_3} + p_{N_2H_4} + 2p_{N_2H_4}$

$= \frac{4}{2}p_{NH_3} + 3p_{N_2H_4} = 4.5$ atm

or

$= 2p_{NH_3} + 3p_{N_2H_4} = 4.5$ atm ...(ii)

Solving eqs. (i) and (ii),

$p_{N_2H_4} = 0.5$ atm and $p_{NH_3} = 1.5$ atm

$x_{NH_3} = \frac{1.5}{2} = 0.75$ and $x_{N_2H_4} = \frac{0.5}{2} = 0.25$

$\therefore$ Mole% of $N_2H_4 = 0.25 \times 100 = 25\%$

7. (d)

8. (b) : $PV = RT$

$V = \frac{RT}{P}$, $V \propto \frac{T}{P}$

Greater the value of (T/P) greater the molar volume.

9. (a) : $P_{gas} = P_{atm} + hdg$

$\therefore$ $hdg = P_{gas} - P_{atm}$

$\therefore$ $= 77 - 76 = 1$ cm Hg $= 1 \times d \times g$

$\therefore$ $h = 1$ cm

10. (b)

11. (a, c) : van der Waals equation is given as

$\left(P + \frac{n^2a}{V^2}\right)(V - nb) = nRT$

The term $\left(P + \frac{n^2a}{V^2}\right)$ represents the pressure exerted by real gases. Whereas P is the pressure exerted by ideal gases.

$P + \frac{a}{V_m^2} \approx P$ and $V_m - b = V_m$

and van der Waals coefficients a and b are independent of temperature.

12. (a, b) : When a gas is expanded at constant temperature, then the kinetic energy of the molecules remains the same, but the pressure decreases because $P \propto \frac{1}{V}$

13. (a, b, c) **14. (c)** **15. (b)**

16. (c) : Vapour pressure of a liquid depends only on temperature and not on the amount of the liquid.

17. (c) : Surface tension and viscosity both decrease with increase of temperature.

18. (b) **19. (a)**

20. (b): The pressure of a fixed amount of an ideal gas is proportional to its temperature.

$v_{rms} \propto \sqrt{T}$

Collision frequency is directly proportional to v_{rms}. On increasing the collision frequency, the pressure increases.

21. (a) **22. (a)** **23. (5)**

24. (4): $\frac{r_{H_2}}{r_{HC}} = \sqrt{\frac{M_{HC}}{M_{H_2}}}$

$3\sqrt{3} = \sqrt{\frac{M_{HC}}{2}}$ or $M_{HC} = \left(3\sqrt{3}\right)^2 \times 2 = 54$

$\therefore$ C_nH_{2n-2}, $12 \times n + (2n - 2) = 54$

or $n = 4$

25. (3): Daltons' law, $p = p'_x + p'_y$

$1.5 = 1.0 + p'_y$ or $p'_y = 0.5$ atm

For gas X, $p'_X \times V = \frac{2}{M_X}RT$

For gas Y, $p'_Y \times V = \frac{3}{M_Y}RT$

$\frac{p'_X}{p'_Y} = \frac{2}{3}\frac{M_Y}{M_X}$ or $\frac{M_Y}{M_X} = \frac{3}{2} \times \frac{p'_X}{p'_Y} = \frac{3 \times 1.0}{2 \times 0.5} = 3$

s-BLOCK ELEMENTS

1. (d): More negative is heat of formation, greater is stability; $\Delta H_f = -97.7, -98.6, -103.5, -104.2$ kcal for LiCl, NaCl, CsCl and KCl respectively.

2. (c) **3. (c)** **4. (b)** **5. (c)**

6. (c) : Li_2CO_3 and $MgCO_3$ are decomposed by heating,

$Li_2CO_3 \longrightarrow Li_2O + CO_2$

$MgCO_3 \longrightarrow MgO + CO_2$

7. (b) **8. (c)**

9. (a) : $\underset{(X)}{CaCO_3} \xrightarrow{\Delta} CO_2 + CaO$

$CaO + H_2O \xrightarrow{\Delta} \underset{(Y)}{Ca(OH_2)}$

$Ca(OH)_2 + \underset{(excess)}{2CO_2} \xrightarrow{\Delta} \underset{(Z)}{Ca(HCO_3)_2}$

$\underset{(Z)}{Ca(HCO_3)_2} \xrightarrow{\Delta} \underset{(X)}{CaCO_3} + CO_2 + H_2O$

10. (b): On moving down the group, the size of cation increases and therefore, tendency to stabilize large CO_3^{2-}ion increases. Hence, stability increases.

11. (c, d) **12. (a, d)**

13. (a, b)

14. (d): Element '*A*' is Barium (Ba)

$3'A' + N_2 \longrightarrow \underset{'B'}{A_3N_2}$

$\underset{'B'}{A_3N_2} + 6H_2O \longrightarrow \underset{'C'}{3A(OH)_2} + \underset{'D'}{2NH_3}$

$\underset{'C'}{A(OH)_2} + CO_2 \longrightarrow \underset{\text{Milkiness}}{ACO_3} + H_2O$

Thus, element '*A*' could be either Ca or Ba. However, it is not magnesium because $Mg(OH)_2$ has a very low solubility. Hence, the element '*A*' is Ba.

15. (d): Since '*C*' is $Ba(OH)_2$.

$Ba(OH)_{2(aq)} + CO_2 \longrightarrow \underset{\text{(Milkiness)}}{BaCO_3} + H_2O$

16. (d) **17. (c)** **18 (c)**

19 (b) **20. (c)**

21. (b): The ionic nature of $MgCl_2$ and $CaCl_2$ is due to the large difference in electronegativity values of Mg and Ca to that of chlorine.

22. (a) **23. (2)**

24. (1) **25. (4)**

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CLASS XI **Series 4**

ACE YOUR WAY CBSE

Equilibrium
Redox Reactions

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

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1. Determine K_c for the reaction :

$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$

(Given : $K_p = 3.4\ \text{bar}^{-1}$ at 1000°C)

2. Arrange the following molecules in the decreasing order of oxidation state of nitrogen :

NO_2, NH_3, HN_3, NO_2^-, N_2H_4.

3. A tank is full of water. Water is coming in as well as going out at the same rate. What will happen to the level of water in a tank? What is the name given to such state?

4. Name an inorganic compound which undergoes intramolecular redox reaction. Give equation.

5. The compound $YBa_2Cu_3O_7$, which shows superconductivity, has copper in x oxidation state. Assuming that the rare earth element yttrium is in its usual +3 oxidation state. Predict the value of x.

6. Urine has a pH of 6.0. If a patient eliminates 1300 mL of urine per day, how many gram equivalents of the acid he eliminates per day?

7. The value of K_w is 9.55×10^{-14} at a certain temperature. Calculate the pH of water at this temperature.

8. When concentrated sulphuric acid is added to an inorganic mixture containing chloride, we get colourless pungent smelling gas HCl, but if the mixture contains bromide then we get red vapours of bromine. Why?

OR

Consider the elements : Cs, Ne, I and F

(a) Identify the element that exhibits only negative oxidation state.

(b) Identify the element that exhibits only positive oxidation state.

(c) Identify the element that exhibits both positive and negative oxidation states.

(d) Identify the element which exhibits neither the negative nor does the positive oxidation state.

9. Give reasons for the following :

(i) Magnesium is not precipitated from a solution of its salt by NH_4OH in the presence of NH_4Cl.

(ii) Ammonium chloride is acidic in liquid ammonia solvent.

10. Out of aluminium and silver vessel, which one will be more suitable to store 1 M HCl solution and why?

(Given : $E^\circ_{Al^{3+}|Al} = -1.66$ V, $E^\circ_{Ag^+|Ag} = +0.80$ V.)

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

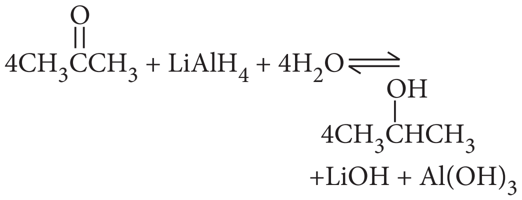
12. Arrange the following in increasing order of pH.

$KNO_{3(aq)}$, $CH_3COONa_{(aq)}$, $NH_4Cl_{(aq)}$, $C_6H_5COONH_{4(aq)}$

Also give reason.

13. Which of the following is a redox reaction? Also, identify the species that undergo oxidation and reduction.

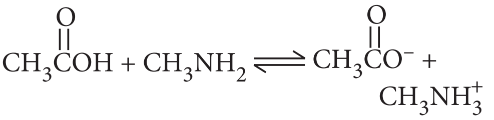
(i)



$$4CH_3\overset{\overset{O}{||}}{C}CH_3 + LiAlH_4 + 4H_2O \rightleftharpoons 4CH_3\overset{\overset{OH}{|}}{C}HCH_3 + LiOH + Al(OH)_3$$

(ii) $CH_3CH_2OH \xrightarrow{H_2SO_4} H_2C{=}CH_2 + H_2O$

(iii)



$$CH_3\overset{\overset{O}{||}}{C}OH + CH_3NH_2 \rightleftharpoons CH_3\overset{\overset{O}{||}}{C}O^- + CH_3NH_3^+$$

14. **(i)** Nitric acid acts only as an oxidising agent while nitrous acid acts both as an oxidising as well as reducing agent. Explain.

(ii) Does the oxidation number of an element in any molecule or any polyatomic ion represent the actual charge on it?

15. What happens to the following processes, if these are subjected to a change as mentioned in the brackets?

(i) Ice $\xrightleftharpoons{\text{Melting point}}$ Water (Pressure is increased)

(ii) Dissolution of NaOH in water (Temperature is increased)

(iii) $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$ $\Delta H = +180.7$ kJ (Pressure is increased and temperature is decreased.)

OR

(i) From the given data of equilibrium constants of the following reactions :

$CuO_{(s)} + H_{2(g)} \rightleftharpoons Cu_{(s)} + H_2O_{(g)}$; $K = 67$

$CuO_{(s)} + CO_{(g)} \rightleftharpoons Cu_{(s)} + CO_{2(g)}$; $K = 490$

Calculate the equilibrium constant of the reaction,

$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

(ii) pK_a values of acids A, B, C, D are 1.5, 3.5, 2.0 and 5.0. Which of them is strongest acid?

16. Balance the following equations by the oxidation number method.

(i) $Fe^{2+} + H^+ + Cr_2O_7^{2-} \rightarrow Cr^{3+} + Fe^{3+} + H_2O$

(ii) $I_2 + S_2O_3^{2-} \rightarrow I^- + S_4O_6^{2-}$

(iii) $MnO_2 + C_2O_4^{2-} \rightarrow Mn^{2+} + CO_2$

17. **(i)** The Mn^{3+} ion is unstable in solution and undergoes disproportionation to give Mn^{2+}, MnO_2 and H^+ ion. Write a balanced ionic equation for the reaction.

(ii) Fluorine reacts with ice and results in the following change :

$H_2O_{(s)} + F_{2(g)} \rightarrow HF_{(g)} + HOF_{(g)}$

Justify that this reaction is a redox reaction.

18. At 298 K, a 0.1 M solution of acetic acid is 1.34% ionised. What is the ionisation constant K_a of acetic acid?

19. Balance the following equations in basic medium by ion-electron method and identify the oxidising agent and the reducing agent.

(i) $P_{4(s)} + OH^-_{(aq)} \rightarrow PH_{3(g)} + H_2PO^-_{2(aq)}$

(ii) $N_2H_{4(l)} + ClO^-_{3(aq)} \rightarrow NO_{(g)} + Cl^-_{(aq)}$

(iii) $Cl_2O_{7(g)} + H_2O_{2(aq)} \rightarrow ClO^-_{2(aq)} + O_{2(g)} + H^+_{(aq)}$

20. The equilibrium constant K_p of the reaction, $2SO_2 + O_2 \rightleftharpoons 2SO_3$ is 900 atm^{-1} at 800 K. A mixture containing SO_3 and O_2 having initial pressure of 1 atm and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K at equilibrium.

21. Depict the galvanic cell in which the following reaction takes place :

$Zn_{(s)} + 2Ag^+_{(aq)} \rightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$

Further show

(i) which of the electrode is negatively charged?

(ii) the carriers of current in the cell and

(iii) individual reaction at each electrode.

22. **(i)** The solubility product of $Al(OH)_3$ is 2.7×10^{-11}. Calculate its solubility in gL^{-1} and also find out pH of this solution. (Atomic mass of Al = 27u).

(ii) Arrange the following bases in decreasing order of their basic strength.

OH^-, RO^-, CH_3COO^-, Cl^-

23. Sanjay wanted to perform an experiment using UV light but Rakesh warned him that he should not see the UV light with naked eyes and suggested him to wear photochromic glasses while doing these experiments. After reading the above passage, answer the following questions :

(i) What are the values expressed by Rakesh?
(ii) What are photochromic glasses?
(iii) How do photochromic glasses protect us from UV radiations?
(iv) How darken lenses becomes colourless in normal light?

24. (i) Calculate
(a) the hydrolysis constant
(b) the degree of hydrolysis and
(c) the pH of 0.1 M sodium acetate solution.

(Given : The dissociation constant of CH_3COOH at room temperature is 1.8×10^{-5}.)

(ii) Show that the degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of the salt.

OR

Calculate the pH of a buffer which is 0.1 M in acetic acid and 0.15 M in sodium acetate. Calculate the change in pH of the buffer if, to 1 L of the buffer (i) 1 cc of 1 M NaOH is added. (ii) 1 cc of 1 M HCl is added. (Assume that the change in volume is negligible). (iii) What will be the buffer index of the above buffer?

(Given : The ionisation constant of acetic acid is 1.75×10^{-5}.)

25. (i) Chlorine is used to purify drinking water. Excess of chlorine is harmful. The excess of chlorine is removed by treating with sulphur dioxide. Write a balanced equation for this redox change taking place in water.

(ii) Predict the oxidation number of the underlined elements in each of the following cases and rationalise your results.
(a) $K\underline{I}_3$ (b) $H_2\underline{S}_4O_6$ (c) $\underline{Fe}_3O_4$

OR

(i) Predict whether the reaction between the following is feasible or not by using the given standard electrode potentials.

$(E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77\text{ V}, E^\circ_{Br_2/Br^-} = 1.09\text{ V}, E^\circ_{Cu^{2+}/Cu} = 0.34\text{ V})$

(a) $Fe^{3+}_{(aq)}$ and $Cu_{(s)}$ (b) $Br_{2(aq)}$ and $Fe^{2+}_{(aq)}$

(ii) What will be observed after an hour when Zn rod is immersed in $CuSO_4$ solution? Write the overall redox reaction.

26. (i) 0.15 mole of pyridinium chloride has been added to 500 cm^3 of 0.2 M pyridine solution. Calculate pH and hydroxyl ion concentration in the resulting solution assuming no change in the volume (K_b for pyridine $= 1.5 \times 10^{-9}$).

(ii) Describe the effect of (a) addition of H_2 (b) addition of CH_3OH (c) removal of CO (d) removal of CH_3OH, on the equilibrium of the reaction : $2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$

OR

(i) K_p for the reaction $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ at 400°C is 1.64×10^{-4} atm^{-2}. Find K_c. Also calculate ΔG° using K_p and K_c values.

(ii) Under what conditions, $K_c = K_p$ for a gaseous reactions?

SOLUTIONS

1. $K_p = K_c(RT)^{\Delta n}$ or $K_c = K_p\,(RT)^{-\Delta n}$

$\Delta n = 2 - (2 + 1) = -1$

$\therefore\ K_c = 3.4 \times (0.083 \times 1273)^1 = 359.24$

2. Oxidation states of N are :

$NO_2 : +4, NH_3 : -3, HN_3 : -\frac{1}{3}, NO_2^- : +3, N_2H_4 : -2$

Decreasing order of oxidation state :

$NO_2 > NO_2^- > HN_3 > N_2H_4 > NH_3$

3. It will remain same because rate of inflow is equal to rate of outflow. The state is called state of 'equilibrium'.

4. Decomposition of ammonium dichromate may be regarded as an intramolecular redox reaction.

$$(\overset{-3}{N}H_4)_2\overset{+6}{Cr}_2O_7 \xrightarrow{\text{Heat}} \overset{0}{N}_2 + \overset{+3}{Cr}_2O_3 + 4H_2O$$

5. $(+3) + 2 \times (+2) + 3x + 7 \times (-2) = 0$

or $3 + 4 + 3x - 14 = 0$ or $3x = 7$ $\therefore$ $x = \frac{7}{3}$

6. $\because$ pH = 6.0

$\therefore\ [H_3O^+] = 10^{-6}$ M

i.e., $[\text{Acid}] = 10^{-6}\text{ M} = 10^{-6}$ N

Thus, 1000 mL of the urine contain acid $= 10^{-6}$ g eq.

$\therefore$ 1300 mL of the urine will contain acid $= 1.3 \times 10^{-6}$ g eq.

7. $K_w = 9.55 \times 10^{-14}$

For water $[H_3O^+] = [OH^-]$ and

$K_w = [H_3O^+]\,[OH^-] = 9.55 \times 10^{-14}$

or $[H_3O^+]\,[H_3O^+] = 9.55 \times 10^{-14}$

$[H_3O^+] = \sqrt{9.55 \times 10^{-14}} = 3.09 \times 10^{-7}$ M

$pH = -\log(3.09 \times 10^{-7})$

$= -(\log 3.09 + \log 10^{-7})$

$= -(0.489 - 7) = 6.51$

8. When conc. H_2SO_4 is added to an inorganic mixture containing chloride, a pungent smelling gas HCl is produced because a stronger acid displaces a weaker acid from its salt.

$2NaCl + 2H_2SO_4 \rightarrow 2NaHSO_4 + 2HCl$

$2HCl + H_2SO_4 \nrightarrow Cl_2 + SO_2 + 2H_2O$

Since, HCl is a weak reducing agent, it cannot reduce H_2SO_4 to SO_2 and therefore, HCl is not oxidised to chlorine.

However, if the mixture contains bromide ion, the initially produced HBr is a stronger reducing agent. Therefore, it reduces H_2SO_4 to SO_2 and itself gets oxidised to produce red vapour of Br_2.

$2NaBr + 2H_2SO_4 \rightarrow 2NaHSO_4 + 2HBr$

$2HBr + H_2SO_4 \rightarrow Br_2 + SO_2 + 2H_2O$

OR

(a) F exhibits only negative oxidation state because it is the most electronegative element.

(b) Cs exhibits only positive oxidation state because it is the most electropositive element.

(c) I exhibits both positive and negative oxidation states. Iodine exhibits –1, 0, +1, +3, +5 and +7 oxidation states (+3, +5 and +7 oxidation states are exhibited by I due to the presence of vacant *d*-orbitals).

(d) Ne is an inert gas, so it neither exhibits negative nor positive oxidation states.

9. (i) The solubility product of $Mg(OH)_2$ is high. Presence of NH_4Cl suppresses the dissociation of NH_4OH due to common ion effect thus giving low concentration of $[OH^-]$. The ionic product, therefore, cannot exceed the solubility product.

(ii) In solution of NH_4Cl in liquid NH_3, the following reaction takes place :

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

Thus, NH_4Cl gives proton. Hence, it is acidic.

10. Since, reduction potential of silver is more than that of hydrogen $(E^\circ_{H^+|H_2,\,Pt} = 0)$, silver vessel will be suitable to store 1 M HCl. On the other hand, $E^\circ_{Al^{3+}|Al}$ is less than that of hydrogen $(E^\circ_{H^+|H_2,\,Pt})$ so that hydrogen will be liberated if stored in aluminium vessel.

11. Given, pH = 4.18 = –log $[H^+]$

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

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

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

or $\quad 4.45 \times 10^{-7} = \dfrac{[6.61\times10^{-5}][HCO_3^-]}{[0.01]}$

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

Again for dissociation of HCO_3^-,

$[HCO_3^-] \rightleftharpoons H^+ + CO_3^{2-}$

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

or $\quad 4.69 \times 10^{-11} = \dfrac{[6.61\times10^{-5}][CO_3^{2-}]}{[6.73\times10^{-5}]}$

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

12. (i) KNO_3 is a salt of strong acid HNO_3 and strong base KOH, hence, its aqueous solution is neutral ; pH = 7

(ii) CH_3COONa is a salt of weak acid CH_3COOH and strong base NaOH, hence, its aqueous solution is basic ; pH > 7.

(iii) NH_4Cl is a salt of strong acid HCl and weak base NH_4OH, hence, its aqueous solution is acidic ; pH < 7.

(iv) $C_6H_5COONH_4$ is a salt of weak acid, C_6H_5COOH and weak base, NH_4OH. But NH_4OH is slightly stronger than C_6H_5COOH. Hence, pH is slightly > 7.

Therefore, increasing order of pH of the given salts is,

$NH_4Cl < KNO_3 < C_6H_5COONH_4 < CH_3COONa$

13. (i) In this redox reaction, H in $LiAlH_4$ gets oxidised because of the addition of oxygen atom that leads to the formation of OH^-. Propanone (CH_3COCH_3) gets reduced because of addition of hydrogen atom to 2-propanol $(CH_3CH(OH)CH_3)$.

(ii) This is not a redox reaction as neither hydrogen or oxygen or e^- is removed or added.

(iii) This is not a redox reaction as neither hydrogen or oxygen or e^- is removed or added.

14. (i) Oxidation number of N in HNO_3 and HNO_2 is +5 and +3 respectively. Since, oxidation number of N in HNO_3 is maximum, therefore, it can only decrease and thus act as an oxidising agent. Whereas, the oxidation number of N in HNO_2 can either increase by losing electrons or decrease by accepting electrons. Thus, HNO_2 can act both as an oxidising as well as reducing agent.

(ii) No, the oxidation number of an element in any species is an apparent charge on the atom which it appears to have acquired when all other atoms in the species are removed as ions.

15. (i) Equilibrium will shift in the forward direction, *i.e.*, more of ice will melt.

(ii) Solubility will decrease because it is an exothermic process.

(iii) Pressure has no effect. Decrease of temperature will shift the equilibrium in the backward direction.

OR

(i) $CuO_{(s)} + H_{2(g)} \rightleftharpoons Cu_{(s)} + H_2O_{(g)}; K_1 = 67$

Now reversing the second reaction,

$Cu_{(s)} + CO_{2(g)} \rightleftharpoons CuO_{(s)} + CO_{(g)};\ K_2 = \frac{1}{490}$

Adding the above two reactions, the net reaction is

$CO_{2(g)} + H_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

for which $K = K_1.K_2 = 67 \times \frac{1}{490} = 0.137$

(ii) $pK_a = -\log K_a$, *i.e.*, lower the value of pK_a stronger will be the acid. Therefore, acid A with $pK_a = 1.5$ is strongest acid.

16. (i) $Fe^{2+} + H^+ + \overset{+6}{Cr_2}O_7^{2-} \longrightarrow Cr^{3+} + Fe^{3+} + H_2O$

Total increase in O.N. = 1

Total decrease in O.N. = 3 × 2 = 6

Balance the increase and decrease in O.N.

$6Fe^{2+} + H^+ + \overset{+6}{Cr_2}O_7^{2-} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + H_2O$

Balancing H and O atoms by adding H^+ and H_2O molecules.

$6Fe^{2+} + 14H^+ + Cr_2O_7^{2-} \rightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$

(ii) $\overset{0}{I_2} + \overset{+2}{S_2}O_3^{2-} \longrightarrow I^- + \overset{+2.5}{S_4}O_6^{2-}$

Total increase in O.N. = 0.5 × 4 = 2

Total decrease in O.N. = 1 × 2 = 2

To equalise O.N. multiply $S_2O_3^{2-}$ and I^- by 2.

$I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$

(iii) $\overset{+4}{Mn}O_2 + \overset{+3}{C_2}O_4^{2-} \longrightarrow Mn^{2+} + \overset{+4}{C}O_2$

Total increase in O.N. = 1 × 2 = 2

Total decrease in O.N. = 2

To equalise O.N. multiply CO_2 by 2.

$MnO_2 + C_2O_4^{2-} \longrightarrow Mn^{2+} + 2CO_2$

Balance H and O by adding $2H_2O$ on right side and $4H^+$ on left side of equation.

$MnO_2 + C_2O_4^{2-} + 4H^+ \rightarrow Mn^{2+} + 2CO_2 + 2H_2O$

17. (i) The skeletal equation is :

$Mn^{3+}_{(aq)} \rightarrow Mn^{2+}_{(aq)} + MnO_{2(s)} + H^+_{(aq)}$

Oxidation half equation : $Mn^{3+}_{(aq)} \rightarrow \overset{+4}{Mn}O_{2(s)}$

or, $Mn^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow MnO_{2(s)} + 4H^+_{(aq)} + e^-$ ...(i)

Reduction half equation : $Mn^{3+}_{(aq)} \rightarrow Mn^{2+}_{(aq)}$

or, $Mn^{3+}_{(aq)} + e^- \rightarrow Mn^{2+}_{(aq)}$ ...(ii)

Adding Eq. (i) and Eq. (ii), the balanced equation for the disproportionation reaction is

$2Mn^{3+}_{(aq)} + 2H_2O_{(l)} \rightarrow MnO_{2(s)} + Mn^{2+}_{(aq)} + 4H^+_{(aq)}$

(ii) $\overset{+1}{H_2}\overset{-2}{O} + \overset{0}{F_2} \longrightarrow \overset{+1}{H}\overset{-1}{F} + \overset{+1}{H}\overset{-2}{O}\overset{+1}{F}$

Since, fluorine can undergo oxidation as well as reduction hence, it is an example of redox reaction.

18. Degree of ionisation, α = 1.34% = 0.0134

Concentration at equilibrium,

$CH_3COOH_{(aq)} + H_2O \rightleftharpoons CH_3COO^-_{(aq)} + H_3O^+$

Since, the initial concentration is 0.1 M, the number of moles of acetic acid ionised = 0.1 × 0.0134
= 0.00134 mol

Number of moles of acetic acid unionised
= 0.1 – 0.00134 = 0.09866 mol

According to the reaction, 1 mol of acetic acid gives 1 mol of CH_3COO^- and 1 mol of H_3O^+ ions. Therefore, 0.00134 mol of CH_3COOH will give 0.00134 mol of CH_3COO^- and 0.00134 mol of H_3O^+ ions. Thus, the concentrations at equilibrium are :

$$\underset{0.09866\text{ mol}}{CH_3COOH_{(aq)}} + H_2O \rightleftharpoons \underset{0.00134\text{ mol}}{CH_3COO^-_{(aq)}} + \underset{0.00134\text{ mol}}{H_3O^+}$$

$$K_a = \frac{[CH_3COO^-_{(aq)}][H_3O^+_{(aq)}]}{[CH_3COOH_{(aq)}]}$$

$$= \frac{(0.00134)\times(0.00134)}{0.09866} = 1.82 \times 10^{-5}$$

19. (i) $P_{4(s)} + OH^-_{(aq)} \rightarrow PH_{3(g)} + H_2PO^-_{2(aq)}$

The two half reactions are :

Oxidation half reaction :

$P_{4(s)} + 8OH^-_{(aq)} \rightarrow 4H_2PO^-_{2(aq)} + 4e^-$ ... (i)

Reduction half reaction :

$P_{4(s)} + 12H_2O_{(l)} + 12e^- \rightarrow 4PH_{3(g)} + 12OH^-_{(aq)}$ ... (ii)

Multiply eq. (i) by 3 and add it to eq. (ii), we get

$4P_{4(s)} + 24OH^-_{(aq)} + 12H_2O_{(l)} \rightarrow 4PH_{3(g)} + 12H_2PO^-_{2(aq)} + 12OH^-_{(aq)}$

or, $P_{4(s)} + 3OH^-_{(aq)} + 3H_2O_{(l)} \rightarrow PH_{3(g)} + 3H_2PO^-_{2(aq)}$

Reductant - phosphorus ; oxidant-phosphorus

(ii) $N_2H_{4(l)} + ClO^-_{3(aq)} \rightarrow NO_{(g)} + Cl^-_{(aq)}$

The two half reactions are :

Oxidation half-reaction :

$[N_2H_4 + 8OH^- \rightarrow 2NO + 8e^- + 6H_2O] \times 6$

Reduction half-reaction :

$[ClO_3^- + 6e^- + 3H_2O \rightarrow Cl^- + 6OH^-] \times 8$

Net reaction is

$6N_2H_4 + 8ClO_3^- \rightarrow 12NO + 8Cl^- + 12H_2O$

$3N_2H_4 + 4ClO_3^- \rightarrow 6NO + 4Cl^- + 6H_2O$

Reductant : N_2H_4 ; Oxidant : ClO_3^-

(iii) $Cl_2O_{7(g)} + H_2O_{2(aq)} \rightarrow ClO^-_{2(aq)} + O_{2(g)} + H^+_{(aq)}$

The two half reactions are :

Oxidation half-reaction :

$[H_2O_2 + 2OH^- \rightarrow O_2 + 2e^- + 2H_2O] \times 4$

Reduction half-reaction :

$Cl_2O_7 + 8e^- + 3H_2O \rightarrow 2ClO_2^- + 6OH^-$

Net reaction is

$Cl_2O_7 + 4H_2O_2 + 2OH^- \rightarrow 2ClO_2^- + 5H_2O + 4O_2$

Reductant : H_2O_2 ; Oxidant : Cl_2O_7

20. Considering the reverse reaction,

$$\begin{array}{llll} & 2SO_3 \rightleftharpoons & 2SO_2 + & O_2,\ K_p = \frac{1}{900}\text{ atm} \\ \text{Initial pressure} & 1\text{ atm} & 0 & 2\text{ atm} \\ \text{Pressure at eqm.} & 1-x & x & 2+\frac{x}{2} \end{array}$$

$$K_p = \frac{p^2_{SO_2} \times p_{O_2}}{p^2_{SO_3}} = \frac{x^2 \times \left(2+\frac{x}{2}\right)}{(1-x)^2} = \frac{1}{900}$$

As K_p for this reaction is very small, $x << 1$.

Taking $2 + \frac{x}{2} \approx 2$ and $(1 - x) \approx 1$,

$$x^2(2) = \frac{1}{900} \quad \text{or} \quad x^2 = \frac{1}{1800} \quad \text{or} \quad x = 0.0236$$

Hence, at equilibrium,

$p_{SO_3} = 1 - x = 1 - 0.0236$ atm $= 0.9764$ atm,

$p_{SO_2} = x = 0.0236$ atm

$p_{O_2} = 2 + \frac{x}{2} = 2 + \frac{0.0236}{2} = 2.0118$ atm

21. The given redox reaction is

$$Zn_{(s)} + 2Ag^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2Ag_{(s)}$$

Since, Zn gets oxidized to Zn^{2+} ions, and Ag^+ gets reduced to Ag metal, therefore, oxidation occurs at zinc electrode and reduction occurs at the silver electrode.

Thus, galvanic cell corresponding to the above redox reaction may be depicted as :

$Zn \mid Zn^{2+}_{(aq)} \parallel Ag^+_{(aq)} \mid Ag$

(i) Since oxidation occurs at the zinc electrode, therefore, electrons accumulate on the zinc electrode and hence, zinc electrode is negatively charged.

(ii) The ions carry current. The electrons flow from Zn to Ag electrode while the current flows from Ag to Zn electrode.

(iii) The reactions occurring at the two electrodes are :

At anode : $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

At cathode : $Ag^+_{(aq)} + e^- \rightarrow Ag_{(s)}$

22. (i) Suppose the solubility is S mol L^{-1}. Then

$$\begin{array}{lll} Al(OH)_3 \rightleftharpoons & Al^{3+} + & 3OH^- \\ & S & 3S \end{array}$$

$K_{sp} = S \times (3S)^3 = 27S^4$

$\therefore$ $27S^4 = 2.7 \times 10^{-11}$ or $S^4 = 10^{-12}$

or $S = 10^{-3}$ mol L^{-1}

Molar mass of $Al(OH)_3 = 27 + 3(16 + 1) = 78$

$\therefore$ Solubility of $Al(OH)_3$ in g $L^{-1} = 10^{-3} \times 78$

$= 7.8 \times 10^{-2}$ g L^{-1}

$[OH^-] = 3S = 3 \times 10^{-3}$ mol L^{-1}

$\therefore$ $pOH = -\log(3 \times 10^{-3}) = 3 - 0.4771 = 2.5229$

$pH = 14 - 2.5229 = 11.4771$.

(ii) Conjugate acids of given bases are :

H_2O, ROH, CH_3COOH, HCl

Their acidic strength is in the order :

$HCl > CH_3COOH > H_2O > ROH$

Hence, their conjugate bases have strength in the order :

$Cl^- < CH_3COO^- < OH^- < RO^-$

or $RO^- > OH^- > CH_3COO^- > Cl^-$

23. (i) The value expressed by Rakesh is about the eyecare. Since, the UV radiations are very energetic, they may either impair the vision temporarily or may even damage the retina of the eyes causing severe damage beyond cure.

(ii) Photochromic lenses darken when exposed to bright UV light and become colourless in normal and dim light.

(iii) Silver chloride is susceptible to oxidation and reduction by light. First, UV light displaces an electron from chloride ion.

$Cl^- \xrightarrow{\text{Oxidation}} Cl + e^-$

The electron thus ejected reduces silver ion to silver atom,

$Ag^+ + e^- \rightarrow Ag$

The clusters of Ag atoms thus produced block the transmission of light, causing the lenses to darken.

(iv) The darkening process is reversed by CuCl. When the bright light is gone, or the light becomes normal, the Cl atoms produced in Eq. (i) oxidise Cu^+ to Cu^{2+} ions.

$Cl + Cu^+ \rightarrow Cl^- + Cu^{2+}$

The Cu^{2+} ions thus produced oxidise Ag atoms to Ag^+ ions.

$Cu^{2+} + Ag \rightarrow Cu^+ + Ag^+$

The net effect of these oxidation-reduction reactions is that original AgCl and CuCl are formed and the lenses become colourless once again.

24. (i) For sodium acetate, the hydrolysis reaction is
$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$

(a) The hydrolysis constant, $K_h = \dfrac{K_w}{K_a}$

$K_w = 1.0 \times 10^{-14}$, $K_a = 1.8 \times 10^{-5}$

$\therefore \quad K_h = \dfrac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56 \times 10^{-10}$

(b) The degree of hydrolysis is, $h = \sqrt{\dfrac{K_w}{K_a.C}}$

$= \sqrt{\dfrac{1.0\times10^{-14}}{1.8\times10^{-5}\times0.1}} = 7.42 \times 10^{-5}$

(c) $\text{pH} = \dfrac{1}{2}\text{p}K_w + \dfrac{1}{2}\text{p}K_a + \dfrac{1}{2}\log C$

$\text{p}K_w = -\log(1 \times 10^{-14}) = 14$

$\text{p}K_a = -\log(1.8 \times 10^{-5}) = 4.745$

$\log c = \log(0.1) = -1$

$\therefore \quad \text{pH} = \dfrac{1}{2}(14) + \dfrac{1}{2}(4.745) - \dfrac{1}{2}\times1$

$\text{pH} = 7 + 2.372 - 0.5 = 8.87$

(ii) Degree of hydrolysis for weak acid and weak base can be calculated as :

$$\begin{array}{lcccc} & B^+ & + \; A^- + H_2O \rightleftharpoons & BOH & + \; HA \\ \text{Initial conc.} & c & c & 0 & 0 \\ \text{Conc. at eqm. :} & c(1-h) & c(1-h) & ch & ch \end{array}$$

$$\therefore \quad K_h = \frac{[BOH][HA]}{[B^+][A^-]} = \frac{ch.ch}{c(1-h).c(1-h)} = \frac{h^2}{(1-h)^2}$$

Here, the relationship between K_h and h does not involve c. Thus, the degree of hydrolysis of such a salt is independent of the concentration of the solution.

If h is very small in comparison to 1, we can take $1 - h = 1$ so that equation becomes

$K_h = h^2 \quad \text{or} \quad h = \sqrt{K_h} = \sqrt{\dfrac{K_w}{K_a.K_b}}$

OR

$\text{pH} = \text{p}K_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]} = -\log(1.75 \times 10^{-5}) + \log\dfrac{0.15}{0.10}$

$= (5 - 0.2430) + 0.1761 = 4.757 + 0.1761 = 4.933.$

(i) 1 cc of 1 M NaOH contains NaOH = 10^{-3} mol. This will convert 10^{-3} mol of acetic acid into the salt so that salt formed = 10^{-3} mol.

Now, [Acid] = 0.10 – 0.001 = 0.099 M
[Salt] = 0.15 + 0.001 = 0.151 M

$\text{pH} = 4.757 + \log\dfrac{0.151}{0.099} = 4.757 + 0.183 = 4.940$

$\therefore$ Increase in pH = 4.940 – 4.933 = 0.007 which is negligible.

(ii) 1 cc of 1 M HCl contains HCl = 10^{-3} mol. This will convert 10^{-3} mol CH_3COONa into CH_3COOH.

$\therefore$ Now, [Acid] = 0.10 + 0.001 = 0.101 M
[Salt] = 0.15 – 0.001 = 0.149 M

$\therefore \quad \text{pH} = 4.757 + \log\dfrac{0.149}{0.101} = 4.757 + 0.169 = 4.926$

$\therefore$ Decrease in pH = 4.933 – 4.926 = 0.007 which is again negligible.

(iii) Buffer Index = $\dfrac{dn}{d\text{pH}}$

No. of moles of HCl or NaOH added = 0.001 mol
Change in pH = 0.007

Hence, buffer index = $\dfrac{0.001}{0.007} = \dfrac{1}{7} = 0.143$

25. (i) The skeletal equation is :
$Cl_{2(g)} + SO_{2(g)} + H_2O_{(l)} \longrightarrow Cl^-_{(aq)} + SO^{2-}_{4\,(aq)}$

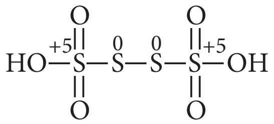
Reduction half equation :
$Cl_{2(g)} + 2e^- \longrightarrow 2Cl^-_{(aq)}$ ...(i)

Oxidation half equation :
$SO_{2(g)} + 2H_2O_{(l)} \longrightarrow SO^{2-}_{4\,(aq)} + 4H^+_{(aq)} + 2e^-$ ...(ii)

Adding Eq. (i) and Eq. (ii), the balanced redox reaction is :
$Cl_{2(g)} + SO_{2(g)} + 2H_2O_{(l)} \longrightarrow 2Cl^-_{(aq)} + SO^{2-}_{4\,(aq)} + 4H^+_{(aq)}$

(ii) (a) In KI_3, since the oxidation number of K is +1, therefore, the average oxidation number of iodine = –1/3. In the structure, $K^+[I\text{—}I \leftarrow I]^-$, a coordinate bond is formed between I_2 molecule and I^- ion. The oxidation number of two iodine atoms forming the I_2 molecule is zero while that of iodine ion forming the coordinate bond is –1. Thus, the O.N. of three iodine atoms in KI_3 are 0, 0 and –1 respectively.

(b) The structure of $H_2S_4O_6$ is shown below :



The O.N. of each of the S atoms linked with each other in the middle is zero while that of each of the remaining two S-atoms is +5.

(c) $\overset{x}{Fe_3}\,\overset{-2}{O_4}$

Let O.N. of Fe = x, then $3x + 4(-2) = 0$
or $x = + 8/3$ (average)

By stoichiometry Fe_3O_4 is $\overset{+2}{Fe}\,\overset{-2}{O}\cdot\overset{+3}{Fe_2}\,\overset{-2}{O_3}$.
Thus, Fe has O.N. +2 and +3.

OR

(i) (a) There are two probabilities for reaction between Cu and Fe^{3+}. The reaction between $Fe^{3+}_{(aq)}$ and $Cu_{(s)}$ occurs according to the following equation :

$$Cu_{(s)} + 2Fe^{3+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Fe^{2+}_{(aq)}$$

The two half reactions are,

Oxidation :

$$Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} + 2e^-; \quad E^\circ_{oxi} = -\ 0.34\ V$$

Reduction :

$$[Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}] \times 2\ ; \ E^\circ_{red} = +\ 0.77\ V$$

Overall reaction :

$$Cu_{(s)} + 2Fe^{3+}_{(aq)} \longrightarrow Cu^{2+}_{(aq)} + 2Fe^{2+}_{(aq)};\ E^\circ = +\,0.43\ V$$

Since, the EMF for the above reaction is positive, therefore, the above reaction is feasible.

(b) The reaction between $Br_{2(aq)}$ and $Fe^{2+}_{(aq)}$ occurs according to the following equation :

$$Br_{2(aq)} + 2Fe^{2+}_{(aq)} \longrightarrow 2Br^-_{(aq)} + 2Fe^{3+}_{(aq)}$$

The two half reactions are

Oxidation :

$$[Fe^{2+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + e^-] \times 2\ ; \quad E^\circ_{oxi} = -\ 0.77\ V$$

Reduction :

$$Br_{2(aq)} + 2e^- \longrightarrow 2Br^-_{(aq)}; \quad E^\circ_{red} = +\ 1.09\ V$$

Overall reaction :

$$2Fe^{2+}_{(aq)} + Br_{2(aq)} \longrightarrow 2Fe^{3+}_{(aq)} + 2Br^-_{(aq)}\ ; \quad E^\circ = +\ 0.32\ V$$

Since the EMF for the above reaction is positive, therefore, the above reaction is feasible.

(ii) Since zinc loses electrons to give Zn^{2+}. Oxidation half reaction is :

$$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2e^-$$

Cu^{2+} gain these electrons to give Cu.

Reduction half reaction is :

$$Cu^{2+}_{(aq)} + 2e^- \longrightarrow Cu_{(s)}$$

On combining the above two reactions, the net reaction is :

$$Zn_{(s)} + \underset{\text{Blue}}{Cu^{2+}_{(aq)}} \longrightarrow \underset{\substack{\text{Colourless}\\ \text{solution}}}{Zn^{2+}_{(aq)}} + \underset{\substack{\text{Deposited on}\\ \text{zinc strip}}}{Cu_{(s)}}$$

The blue colour will get discharged and reddish brown copper metal will get deposited.

26. (i) Pyridine is a weak base. Thus, pyridine + pyridine chloride solution is a basic buffer. Hence,

$$pOH = pK_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

$$pK_b = -\log K_b = -\log(1.5 \times 10^{-9}) = 9 - 0.1761 = 8.8239$$

[Pyridine] = 0. 2 M (Given), [Pyridinium chloride]

$$= \frac{0.15}{500} \times 1000 = 0.30\ M$$

$$\therefore \quad pOH = 8.82 + \log\frac{0.30}{0.20} = 8.82 + 0.1761 = 8.896$$

i.e., $-\log[OH^-] = 8.896$ or $\log[OH^-] = -8.896$

$$= [OH^-] = 1.271 \times 10^{-9}$$

$[OH^-]$ from $H_2O = 10^{-7}$ M cannot be neglected.

Hence, total $[OH^-] = 1.27 \times 10^{-9} + 10^{-7}$

$= 10^{-9}(1.27 + 100) = 101.27 \times 10^{-9}\ M = 1.0127 \times 10^{-7}\ M$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.0127 \times 10^{-7}} = 9.875 \times 10^{-8}\ M$$

$$pH = -\log[H^+] = -\log(9.875 \times 10^{-8}) = 8 - 0.9945 = 7.0055$$

(ii) On the basis of Le Chatelier's principle in each case,

(a) Equilibrium will shift in the forward direction.

(b) Equilibrium will shift in the backward direction.

(c) Equilibrium will shift in the backward direction.

(d) Equilibrium will shift in the forward direction.

OR

(i) $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$

$\Delta n = 2 - 4 = -2$; ($T = 400 + 273$ K $= 673$ K)

$K_p = K_c\,(RT)^{\Delta n}$

$$1.64 \times 10^{-4}\ \text{atm}^{-2} = K_c\,(0.0821\ \text{L atm K}^{-1}\ \text{mol}^{-1} \times 673\ \text{K})^{-2}$$

$$\text{or} \quad K_c = \frac{1.64 \times 10^{-4}\ \text{atm}^{-2}}{(0.0821 \times 673\ \text{L atm}^{-1}\text{mol}^{-1})^2} = 0.5372\ \text{mol}^2\text{L}^{-2}$$

Now, $\Delta G^\circ = -2.303\ RT \log K$

If $K = K_p$,

$$\Delta G^\circ = -2.303 \times (8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\ (673\ \text{K}) \times \log(1.64 \times 10^{-4})$$

$$= -2.303 \times 8.314 \times 673 \times (-3.7852)\ \text{J mol}^{-1} = +48.78\ \text{kJ mol}^{-1}$$

If $K = K_c$,

$$\Delta G^\circ = -2.303 \times (8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\ (673\ \text{K}) \times \log(0.5372)$$

$$= -2.303 \times 8.314 \times 673 \times (-0.27)\ \text{J mol}^{-1} = +\ 3479\ \text{J mol}^{-1}$$

(ii) From the relation $K_p = K_c\,(RT)^{\Delta n}$,

(a) If $\Delta n = 0$, $K_p = K_c$

(b) If $\Delta n = +$ve (*i.e.*, $n_p > n_r$), $K_p > K_c$

(c) If $\Delta n = -$ve(*i.e.*, $n_p < n_r$), $K_p < K_c$.

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MPP-4 MONTHLY Practice Problems

Class XI

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Self check table given at the end will help you to check your readiness.

Thermodynamics and Equilibrium

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. K_c for $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ is 0.04 at 250°C. The number of moles of PCl_5 that must be added to a 3-litre flask to obtain a Cl_2 concentration of 0.15 M is

(a) 12 (b) 1.2 (c) 2.1 (d) 21

2. Which one of the following equations does not correctly represent the first law of thermodynamics for the given process?

(a) Isothermal process : $q = -w$

(b) Cyclic process : $q = -w$

(c) Isochoric process : $\Delta E = q$

(d) Adiabatic process : $\Delta E = -w$

3. Equimolar solution of aniline and acetic acid are mixed to form anilinium acetate. The pH of the solution is (At 18°C aniline and acetic acid have dissociation constants 5×10^{-10} and 1.8×10^{-5} respectively).

(a) 5.5 (b) 4 (c) 4.7 (d) 4.5

4. For a particular reversible reaction at temperature T, ΔH and ΔS were found to be both +ve. If T_e is the temperature at equilibrium, the reaction would be spontaneous when

(a) $T_e > T$ (b) $T > T_e$

(c) T_e is 5 times T (d) $T = T_e$

5. How many litres of water must be added to 1 litre of aqueous solution of HCl with a pH of 1 to create an aqueous solution with pH of 2?

(a) 2.0 L (b) 9.0 L (c) 0.1 L (d) 0.9 L

6. One mole of a liquid (1 bar, 100 mL) is taken in an adiabatic container and the pressure increases steadily to 100 bar. Then at constant pressure of 100 bar, volume decreases by 1 mL. Enthalpy change during the process will be

(a) 980 J (b) 990 J (c) 970 J (d) 950 J

7. For the reaction $AB_{(g)} \rightleftharpoons A_{(g)} + B_{(g)}$, AB is 33% dissociated at a total pressure of P. Therefore, P is related to K_p by one of the following option

(a) $P = K_p$ (b) $P = 3K_p$ (c) $P = 4K_p$ (d) $P = 8K_p$

8. The bond dissociation energies for Cl_2, I_2 and ICl are 242.3, 151 and 211.3 kJ/mol respectively. The enthalpy of sublimation of iodine is 62.8 kJ/mol. What is the standard enthalpy of formation of $ICl_{(g)}$?

(a) –211.3 kJ/mol (b) –14.6 kJ/mol

(c) 16.8 kJ/mol (d) 33.5 kJ/mol

9. 2.0 g of diborane (B_2H_6) reacts with water to produce 100 mL solution. If K_a for H_3BO_3 is 7.3×10^{-10}, the pH of solution is

(a) 4.5 (b) 3.5 (c) 4 (d) 3

10. Standard heat of formation of CH_4, CO_2 and $H_2O_{(g)}$ are –76.2, –394.8 and –241.6 kJ mol^{-1} respectively. The amount of heat evolved (in kJ mol^{-1}) by burning 1 m^3 of CH_4 measured under normal conditions is

(a) 35.7×10^3 (b) 37.5×10^3

(c) 8.73×10^3 (d) 3.75×10^3

11. Solubility product constants (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

(a) $MX > MX_2 > M_3X$ (b) $M_3X > MX_2 > MX$
(c) $MX_2 > M_3X > MX$ (d) $MX > M_3X > MX_2$

12. The standard enthalpy of formation ($\Delta_f H°$) at 298 K for methane ($CH_{4(g)}$) is –74.8 kJ mol^{-1}. The additional information required to determine the average energy for C – H bond formation would be

(a) the dissociation energy of H_2 and enthalpy of sublimation of carbon
(b) latent heat of vaporisation of methane
(c) the first four ionisation energy of carbon and electron gain enthalpy of hydrogen
(d) the dissociation energy of H_2 molecule.

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true 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 both assertion and reason are false.

13. Assertion : Heat of solution (ΔH) for hydrated salts and salts which do not form hydrates is +ve while it is – ve for anhydrous salts.

Reason : Anhydrous salts first undergo hydration in which heat is evolved.

14. Assertion : The equilibrium mixture

$$[Co(H_2O)_6]^{2+}_{(aq)} + 4Cl^-_{(aq)} \rightleftharpoons [CoCl_4]^{2-}_{(aq)} + 6H_2O_{(l)}$$

turns pink from deep blue on cooling in a freezing mixture.

Reason : The reaction is endothermic. On cooling, equilibrium shifts in the backward direction.

15. Assertion : Adding inert gas to dissociation equilibrium of N_2O_4 at constant pressure and temperature increases the dissociation.

Reason : Molar concentration of the reactants and products decreases.

JEE MAIN / JEE ADVANCED / PETs

Only One Option Correct Type

16. $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$

B.E.(H—H) = r_1 ; B.E. (O=O) = r_2 ; B.E. (O—H) = r_3

Latent heat of vaporisation of water liquid into water vapour = r_4, then $\Delta_f H$ (heat of formation of liquid water) is

(a) $r_1 + \frac{r_2}{2} - r_3 + r_4$ (b) $2r_3 - r_1 + \frac{r_2}{2} - r_4$
(c) $r_1 + \frac{r_2}{2} - 2r_3 - r_4$ (d) $r_1 + \frac{r_2}{2} - 2r_3 + r_4$

17. If $\Delta G = \Delta H - T\,\Delta S$ and $\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_P$, then variation of EMF of cell E with temperature T will be

(a) $\frac{\Delta H}{nF}$ (b) $\frac{\Delta G}{nF}$ (c) $\frac{\Delta S}{nF}$ (d) $-\frac{\Delta S}{nF}$

18. In the dissociation of PCl_5 as

$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$

if the degree of dissociation is α at equilibrium pressure P, then the equilibrium constant for the reaction is

(a) $K_p = \frac{\alpha^2}{1+\alpha^2 P}$ (b) $K_p = \frac{\alpha^2 P^2}{1-\alpha^2}$
(c) $K_p = \frac{P^2}{1-\alpha^2}$ (d) $K_p = \frac{\alpha^2 P}{1-\alpha^2}$

19. For the reversible reaction,

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

at 500°C, the value of K_p is 1.44×10^{-5} when the partial pressure is measured in atmosphere. The corresponding value of K_c with concentration in mol L^{-1} is

(a) $\frac{1.44\times10^{-5}}{(0.082\times500)^{-2}}$ (b) $\frac{1.44\times10^{-5}}{(8.314\times773)^{-2}}$
(c) $\frac{1.44\times10^{-5}}{(0.082\times773)^{2}}$ (d) $\frac{1.44\times10^{-5}}{(0.082\times773)^{-2}}$

More than One Options Correct Type

20. Equal volumes of the following solutions are mixed. The pH of the resulting solution will be, the average pH values of the two solutions in
[Given : K_a (HCN) = 10^{-10}, $K_a(CH_3COOH)$
$= K_b(NH_3)_{aq}$]

(a) HCl (pH = 2) and NaOH (pH = 12)
(b) HCl (pH = 2) and NaOH (pH = 4)
(c) HCN (pH = 2) and NaOH (pH = 12)
(d) CH_3COOH (pH = 5) and $(NH_3)_{aq}$ (pH = 9).

21. Select the correct statements for the equilibrium under standard conditions.

$$H_2O_{(s)} \rightleftharpoons H_2O_{(l)},\ \Delta S_1^\circ$$
$$H_2O_{(l)} \rightleftharpoons H_2O_{(g)},\ \Delta S_2^\circ$$
$$H_2O_{(s)} \rightleftharpoons H_2O_{(g)},\ \Delta S_3^\circ$$

(a) $\Delta S_1^\circ > \Delta S_2^\circ$ (b) $\Delta S_2^\circ >>> \Delta S_1^\circ$
(c) $\Delta S_3^\circ > \Delta S_2^\circ$ (d) $\Delta S_3^\circ > \Delta S_1^\circ$

22. A solution is prepared by dissolving 1.5 g of a monoacidic base into 1.5 kg of water at 300 K, which showed a depression in freezing point by 0.165°C. When 0.496 g of the same base is titrated, after dissolution, requires 40 mL of semimolar H_2SO_4 solution. If K_f of water is 1.86 K kg mol^{-1}, then select the correct statements out of the following (assuming molarity = molality) :

(a) The pH of the solution of weak base is 12.9.
(b) The ionisation constant of the base is 8×10^{-3}.
(c) The osmotic pressure of the aqueous solution of base is 21.67 atm.
(d) The base is 10% ionized in aqueous solution.

23. The standard enthalpies of formation of $CO_{2(g)}$ and $HCOOH_{(l)}$ are –393.7 kJ mol^{-1} and –409.2 kJ mol^{-1} respectively. Which of the following statements are correct?

(a) The enthalpy change for the reaction,
$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}$ is –393.7 kJ mol^{-1}
(b) The enthalpy change for the reaction,
$CO_{2(g)} + H_{2(g)} \longrightarrow HCOOH_{(l)}$ is –15.5 kJ mol^{-1}
(c) The enthalpy change for the reaction,
$H_2O + CO \longrightarrow HCOOH$, is –409.2 kJ mol^{-1}
(d) The enthalpy change for the reaction,
$H_{2(g)} + CO_{2(g)} \longrightarrow H_2O_{(l)} + CO_{(g)}$, is –409.2 kJ mol^{-1}

Integer Answer Type

24. For the reaction $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$, at 700 K, the value of K_p is 1.80×10^{-3} kPa. The value of K_c in moles L^{-1} for this reaction at the same temperature will be 3.09×10^{-x} where x is

25. For the reaction $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$, $\Delta H°$ and $\Delta S°$ are 80 kJ mol^{-1} and 120 J mol^{-1} respectively at 400 K. The value of equilibrium constant is 6.63×10^{-x}. The value of x is

26. Ionization constant of formic acid is 2×10^{-4} at 298 K. The H_3O^+ ion concentration in 0.01 M solution of formic acid will be 1.4×10^{-x} mol L^{-1} where x is

Comprehension Type

A sample of ideal gas undergoes isothermal expansion in a reversible manner from volume V_1 to volume V_2. The initial pressure is P_1 and the final pressure is P_2. The same sample is then allowed to undergo reversible expansion under adiabatic conditions from volume V_1 to V_2. The initial pressure being same but final pressure is P_2.

27. The work of expansion in adiabatic process (w_{adi}) is related to work of expansion in isothermal process (w_{iso}) as

(a) $w_{adi} = w_{iso}$
(b) $w_{adi} < w_{iso}$
(c) $w_{adi} = 2w_{iso}$
(d) $w_{adi} > w_{iso}$

28. Which of the following is correct?

(a) $P_1V_1 = P_2V_2$
(b) $P_1/P_2 = V_1/V_2$
(c) $P_1/P_2 = P_1/P_3$
(d) $P_1 = P_2$

Matrix Match Type

29. Match the entries listed in column I with appropriate entries listed in column II.

Column I	Column II
(A) HCO_3^-	(P) Bronsted acid
(B) NH_3	(Q) Bronsted base
(C) $AlCl_3$	(R) Lewis acid
(D) F^- ion	(S) Lewis base

	A	B	C	D
(a)	P, Q	R	P, Q, S	Q, S
(b)	P, Q	P, Q, S	R	Q, S
(c)	P, Q, S	P, Q	R	Q, S
(d)	Q, S	R	P, Q	P, Q, S

30. Match the entries listed in column I with appropriate entries listed in column II.

Column I	Column II
(A) $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$	(P) $\Delta S = 0$
(B) $2KI_{(aq)} + HgI_{2(aq)} \rightarrow K_2[HgI_4]_{(aq)}$	(Q) $\Delta S < 0$
(C) $PCl_{3(g)} + Cl_{2(g)} \rightarrow PCl_{5(g)}$	(R) $\Delta H > 0$
(D) $NH_{3(g)} + HCl_{(g)} \rightarrow NH_4Cl_{(g)}$	(S) $\Delta H < 0$

	A	B	C	D
(a)	P, Q	Q	Q, R	Q, S
(b)	P, Q	Q, R	Q	Q, S
(c)	Q, S	Q	Q, R	P, Q
(d)	P, Q	Q, S	Q, R	Q

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SELF CHECK

No. of questions attempted ……

No. of questions correct ……

Marks scored in percentage ……

Check your score! If your score is

> 90%	**EXCELLENT WORK !**	You are well prepared to take the challenge of final exam.
90-75%	**GOOD WORK !**	You can score good in the final exam.
74-60%	**SATISFACTORY !**	You need to score more next time.
< 60%	**NOT SATISFACTORY!**	Revise thoroughly and strengthen your concepts.

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ESSENTIALS

Class XII

Maximize your chance of success, and high rank in NEET, JEE (Main and Advanced) by reading this column. This specially designed column is updated year after year by a panel of highly qualified teaching experts well-tuned to the requirements of these Entrance Tests.

Unit 4

d - and *f*-BLOCK ELEMENTS COORDINATION COMPOUNDS

d - and *f*-BLOCK ELEMENTS

TRANSITION ELEMENTS

- Elements in which the last electron enters any one of the five *d*-orbitals of their respective penultimate shell are known as *transition elements.*
- General electronic configuration : $(n-1)d^{1-10}ns^{0-2}$
- The presence of unpaired and empty *d*-orbitals favours *covalent bonding.*

GENERAL CHARACTERISTICS

TRANSITION METAL

Physical Properties

- High electrical thermal conductivity.
- High mpt. and bpt. due to strong metallic bonding.
- Malleable
- Ductile
- Ferromagnetic

Chemical Properties

- **Complex formation :** Due to high nuclear charge, small size and availability of empty *d*-orbitals.
- **Form coloured compounds :** Due to *d*-*d* transition and charge transfer.
- **Variable oxidation state :** Due to involvement of *ns* and $(n-1)d$ electrons.
- **Catalytic behaviour :** Due to variable oxidation states and ability to form complexes.
- **Alloy formation :** Due to similar atomic sizes.
- **Magnetic behaviour :** Paramagnetic due to presence of unpaired electrons.

	Ionisation Energy	Atomic size	Electronegativity	Density
Atomic Properties	Increases slowly due to ineffective shielding of nuclear charge by *d* electrons which tend to attract the outer electron cloud with greater force.	Decreases slowly in the series upto the middle due to ineffective shielding of *d*-electrons and increased nuclear charge but at the end of the series there is a slight increase in atomic radii due to increased electron-electron repulsion between added electrons.	Increases slowly	Increases along a series because atomic size decreases whereas atomic mass increases.

SOME IMPORTANT COMPOUNDS

Compounds	Preparation	Properties	Uses
Potassium dichromate ($K_2Cr_2O_7$)	From sodium dichromate (obtained from chromite ore) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	Orange red, crystalline solid, oxidising agent having melting point 398°C. **Oxidising agent in acidic medium :** $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$ **Oxidises :** I^- to I_2, H_2S to S, Sn^{2+} to Sn^{4+} Fe^{2+} to Fe^{3+}	In dyeing, photography and leather industry.
Potassium permanganate ($KMnO_4$)	From potassium manganate (obtained from pyrolusite) $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$	Deep purple, crystalline solid, oxidising agent, having melting point 240° C. **Oxidising agent in acidic medium :** $MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$ **Oxidises :** I^- to I_2, Fe^{2+} to Fe^{3+}, $C_2O_4^{2-}$ to CO_2, S^{2-} to S, SO_3^{2-} to SO_4^{2-}, NO_2^- to NO_3^- **Oxidising agent in alkaline or neutral medium :** $MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^-$ **Oxidises :** I^- to IO_3^-, $S_2O_3^-$ to SO_4^-, Mn^{2+} to MnO_2	As a disinfectant, germicide, and Baeyer's reagent (alkaline $KMnO_4$).

INNER TRANSITION ELEMENTS

- **Lanthanoids :** The elements with atomic numbers 58 to 71 *i.e.*, cerium to lutetium (which come immediately after lanthanum, *Z* = 57) are called *lanthanoids*.
- **Actinoids :** The elements with atomic number 90 to 103 *i.e.*, thorium to lawrencium (which come immediately after actinium, *Z* = 89) are called *actinoids*.
- They are called *f*-block elements because last electron enters into *f*-orbital.
- General electronic configuration : $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$

INFO SHOTS

Therapeutic and Diagnostic Applications of Lanthanides !

The biological properties of the lanthanoides, primarily based on their similarity to calcium, have been the basis for research into potential therapeutic applications of lanthanoides. Up to date, cerium nitrate has been used as a topical cream with silver sulfadiazene for the treatment of burn wounds. A lanthanoide texaphyrin complex (Motexafin gadolinium) has been evaluated through phase III clinical trials for the treatment of brain metastases in non-small cell lung cancer. Lanthanum carbonate (Fosrenol) as a phosphate binder has been approved for the treatment of hyperphosphatemia in renal dialysis patients in both the USA and Europe.

GENERAL CHARACTERISTICS

INNER TRANSITION ELEMENTS

LANTHANOIDS

- They show mainly +3 oxidation state. +2 and +4 oxidation states also exist. They have greater shielding effect as compared to actinoids. Most of their ions are coloured. They are paramagnetic and their magnetic properties can be easily explained. Less tendency to form complexes. Except promethium, these are non-radioactive substances. These are less basic.
- The regular decrease in the size of lanthanoid atoms and ions from La/La^{3+} to Lu/Lu^{3+} is known as *lanthanoid contraction*. It is due to greater effect of the increased nuclear charge than that of the screening effect, which is attributed to the imperfect shielding of one electron by another in the same sub-shell.

ACTINOIDS

- In addition to +3 oxidation state, actinoid also show higher oxidation states like +4, +5, +6 and +7. They have poor shielding effect. Most of the actinoid ions are also coloured. They are also paramagnetic, but their magnetic properties cannot be easily explained. More tendency to form complexes. These are all radioactive. These are more basic.
- There is a regular decrease in ionic radii with increase in atomic number form Th to Lr. This is called *actinoid contraction* analogous to the lanthanoid contraction. It is caused due to imperfect shielding of one 5*f* electron by another in the same shell. This results in increase in the effective nuclear charge which causes contraction in size of the electron cloud.

CONSEQUENCES OF LANTHANOID CONTRACTION

- Separation of lanthanoids is difficult because of small difference in their size. Therefore, lanthanoids are mainly separated by ion exchange method.
- Basic strength of hydroxides decrease from Ce to Lu Thus, $La(OH)_3$ is most basic whereas $Lu(OH)_3$ is least basic.
- Radii of elements in same group from 4th to 12th groups in 4*d* and 5*d* series are very close and these elements in each group are called *chemical twins*. *e.g.*, Zr and Hf, Nb and Ta, etc.
- The properties of complex formation increase from La to Lu because of decrease in size and increase in "charge : size" ratio.
- There is a very slight increase in electronegativity from La to Lu.

COORDINATION COMPOUNDS

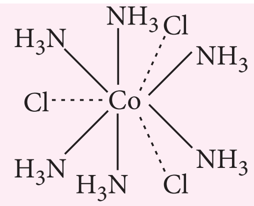
- Coordination compounds are those in which a central metal atom or ion is attached with a fixed number of groups or molecules (Ligands) through coordinate bonds.

Double Salt	Co-ordination Compound
1. These exist only in solid state and dissociate into constituent species in their solution.	1. They retain their identity in solid as well as in solution state.
2. They lose their identity in dissolved state.	2. They do not lose their identity in dissolved state.
3. Their properties are essentially the same as those of their constituent species.	3. Their properties are different from those of their constituents. For example, $K_4[Fe(CN)_6]$ does not show the test of Fe^{2+} and CN^- ions.
4. In double salts' the metal atom/ion exhibit normal valency.	4. In co-ordination compounds, the number of negative ions or molecules surrounding the central metal atom is different from its normal valency.

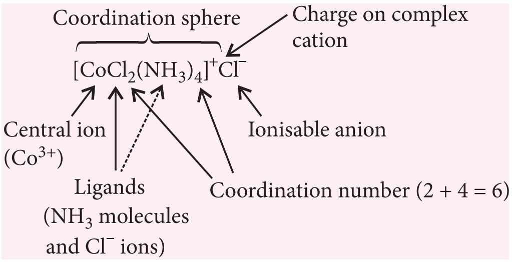
WERNER'S COORDINATION THEORY

- It explains the nature of bonding in complexes. Metals show two different kinds of valencies.
  - **Primary valency :** Non directional and ionisable. It is equal to the oxidation state of the central metal ion.
  - **Secondary valency :** Directional and non-ionisable. It is equal to the coordination number of the metal. It is commonly satisfied by neutral and negatively charged or some times by positively charged ligands.
- The ionisation of the coordination compound is written as :

$$[Co(NH_3)_6]Cl_3 \rightleftharpoons [Co(NH_3)_6]^{3+} + 3Cl^-$$


$[Co(NH_3)_6]Cl_3$

Representation of $CoCl_3{\cdot}6NH_3$ complex according to Werner's theory



When a polydentate ligand coordinates to a metal ion through more than one electron pairs of donor site simultaneously, is called **chelation**. The resulting complex has ring like structure and such ligand is called chelating ligand.
Chelating ligands form more stable complexes than similar ordinary complexes, in which the ligands act as monodentate.

Ambidentate Ligand : A unidentate ligand which can coordinate through two different atoms. *e.g.*, NO_2^-, SCN^-, etc.

Ligands

Mono or unidentate ligands : Ligands with one donor site. *e.g.*, F^-, Cl^-, Br^-, H_2O, CN^-, NO_2^-, OH^-, CO, etc.

Bidentate ligands : Ligands which have two donor atoms at two positions.
e.g., Ethylenediammine, oxalate, glycine, etc.

Polydentate ligands : The ligands having several donor atoms are called polydentate ligands. *e.g.*, Diethylenetriammine having 3 donor atoms is tridentate, EDTA with 6 donor atoms is hexadentate.

IUPAC NOMENCLATURE

Naming and writing formulas of coordination compounds -

- The cation comes first, then the anion(s)
  - diammine silver(I) chloride $[Ag(NH_3)_2]Cl$
  - potassium hexacyanoferrate(III) $K_3[Fe(CN)_6]$
- Complex ion is enclosed in brackets
  - Ligands are named first in alphabetical order followed by metal atom.
    - **Anionic ligands :** End in - *o e.g.*, Cl^- : Chlorido
    - **Neutral ligands :** Retain their names with a few exceptions *e.g.*, NH_3 : Ammine
    - **Cationic ligands :** End in *-ium*, *e.g.*, NO_2^+ : Nitronium
    - **Ambidentate ligands :** Named by using different names of ligands or by placing the symbol of donor atom. *e.g.*, $—SCN^-$ (Thiocyanato-S or Thiocyanato), $—ONO^-$ (Nitrito-O or Nitrito), $—NO_2^-$ (Nitrito-N or Nitro), $—NCS^-$ (Thiocyanato-N or Isothiocyanato).
  - Metal is written first in the formula
  - Naming is started with a small letter and complex part is written as one word.
  - Metal oxidation state in roman numerals in parentheses after the metal ion.
  - A space only between cation and anion.
  - When coordination sphere is anionic, name of central metal ends in *–ate*. For *e.g.*,
    - tetraamminecopper(II) sulphate $[Cu(NH_3)_4]SO_4$
    - hexaamminecobalt(III) chloride $[Co(NH_3)_6]Cl_3$

- Prefixes denote the number of each ligand type. Special prefixes and parentheses are used if the ligand already contains a prefix.

2	di	bis
3	tri	tris
4	tetra	tetrakis
5	penta	pentakis
6	hexa	hexakis
7	hepta	heptakis
8	octa	octakis
9	nona	nonakis
10	deca	decakis

Some examples -

Sodium *bis*(thiosulphato) argentate (I) : $Na_3[Ag(S_2O_3)_2]$

tris(ethylene diamine) cobalt (III) ion : $[Co(en)_3]^{3+}$

ISOMERISM

ISOMERISM

Structural isomerism

It is displayed by compounds that have different ligands within their coordination sphere.

Ionisation isomerism : Isomers that give different ions in solution. *e.g.*, $[Co(NH_3)_5Br]Cl$; $[Co(NH_3)_5Cl]Br$.

Hydrate isomerism : Isomers having different number of H_2O as a ligand and as water of hydration. *e.g.*, $[Cr(H_2O)_6]Cl_3$; $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$, $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$.

Coordination isomerism : The ligands are interchanged in both the cationic and anionic ions. *e.g.*, $[Co(NH_3)_6][Cr(CN)_6]$; $[Cr(NH_3)_6][Co(CN)_6]$

Linkage isomerism : This type of isomerism exists when ambidentate ligand is coordinated with its different donor atoms. *e.g.*, $[Co(NH_3)_5ONO]Cl_2$; $[Co(NH_3)_5NO_2]Cl_2$.

Stereoisomerism

Shown by compounds having same structural formula but differ only in the spatial arrangement of ligands around the central atom.

Geometrical isomerism

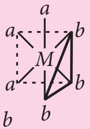
Arises due to different possible geometric arrangement of ligands.

Optical isomerism

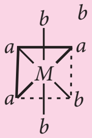
Shown by molecule which do not have plane of symmetry.

In octahedral complex $[Ma_3b_3]$

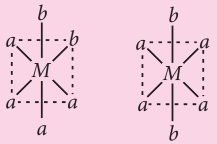
Facial (*fac*) : 3 donor atoms of same ligands occupy adjacent positions at the corners.



Meridional (*mer*) : When the positions are around the meridian .

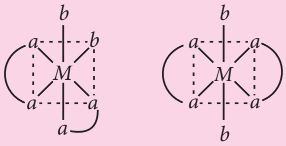


In octahedral complex $[Ma_4b_2]$



cis trans

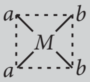
In octahedral complex $[M(aa)_2b_2]$ or $[M(aa)_2bc]$



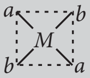
cis trans

In square planar complex $[Ma_2b_2]$

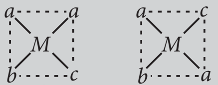
***cis* :** 2 same ligands are arranged adjacent to each other.



***trans* :** 2 same ligands are arranged opposite to each other.



In square planar complex $[Ma_2bc]$



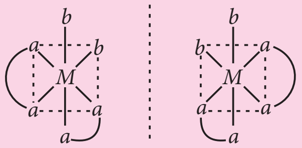
cis trans

In square planar complex$[Mabcd]$

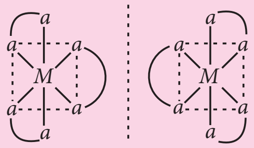
These isomers are obtained by selecting 1 ligand, (a) and then placing the remaining 3 ligands (b, c and d), one by one, trans to ligand (a). These type of complex shows three isomers – two *cis* and one *trans*.

Geometrical isomerism is not possible in tetrahedral complexes.

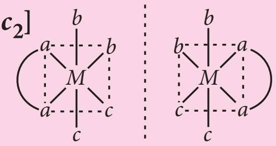
Optical isomerism in $[M(aa)_2b_2]$ and $[M(aa)_2bc]$



$[M(aa)_3]$



$[M(aa)b_2c_2]$



Optical isomerism in tetrahedral complex of type $M(AB)_2$ where AB is unsymmetrical bidentate ligand.

Square planar complexes do not show optical isomerism because of plane of symmetry.

BONDING IN COORDINATION COMPOUNDS

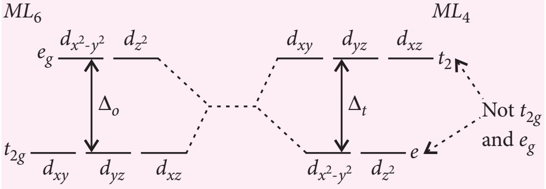
- **Valence Bond Theory :** According to this theory, the metal atom/ion makes available empty orbitals equal to its coordination number.
  - The orbitals may be inner orbitals (Low spin) *i.e.*, $(n-1)d$, ns and np or outer orbitals (High spin) *i.e.*, nd, ns and np depending upon the strength of ligand.
  - The vacant orbitals undergo hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral and square planar.
  - These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

C. No.	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[Ag(NH_3)_2]^+$, $[Ag(CN)_2]^-$
3	sp^2	Trigonal planar	$[HgI_3]^-$
4	sp^3	Tetrahedral	$Ni(CO)_4$, $[NiX_4]^{2-}$, $[ZnCl_4]^{2-}$, $[CuX_4]^{2-}$ where $X = Cl^-, Br^-, I^-$
	dsp^2	Square planar	$[Ni(CN)_4]^{2-}$, $[Cu(NH_3)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$[Fe(CO)_5]$, $[CuCl_5]^{3-}$
	sp^3d	Square pyramidal	$[SbF_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[Cr(NH_3)_6]^{3+}$, $[Fe(CN)_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

- **Magnetic properties :**
  - Low spin complexes are generally diamagnetic and high spin complexes are paramagnetic.
  - Paramagnetism ∝ No. of unpaired electrons
  - Magnetic moment $= \sqrt{n(n+2)}$ B.M. where n = number of unpaired electrons.

- **Crystal Field Theory :** This theory is based on the assumption that the metal ion and the ligands act as a point charges and the interaction between them is purely electrostatic, *i.e.*, metal-ligand bonds are 100% ionic.

Octahedral *vs.* Tetrahedral



$\Delta_o = -0.4 \times n(t_{2g}) + 0.6 \times n(e_g)$ $\quad$ $\Delta_t = 0.4 \times n(t_2) - 0.6 \times n(e)$

- $\Delta_o > P$ (low spin complex)
- $\Delta_o < P$ (high spin complex)
- $\Delta_t = \frac{4}{9}\Delta_o$
- **Spectrochemical series :** Arrangement of ligands in the order of increasing field strength. $I^- < Br^- < S^{2-} < SCN^- < NO_3^- < F^- < OH^- < ox^{2-}$ and $< O^{2-} < H_2O < NCS^- < py \simeq NH_3 < en < dipy <$ $O - phen < NO_2^- < CN^- < CO$.

STABILITY OF COORDINATION COMPOUNDS

Stability depends on

- **Charge on the central metal ion (oxidation state) :** Greater the charge on central metal ion, more is the stability.
- **Basic nature of ligand :** More the basic strength of ligand, more is the stability of complex.
- **Presence of chelate rings :** Formation of chelate ring increases the stability of complex.
- **Size of the metal ion :** Smaller the size of metal ion, more is the stability.
- **Electronegativity and polarising power of the central metal ion :** More is the electronegativity and polarising power of the metal ion, more stable is the complex.

CONCEPT
MAP

ISOMERISM

The concept of isomerism illustrates the fundamental importance of molecular structure and shape in organic chemistry and the isomers play a vital role in biological processes.

Class XI

Class XII

NAME REACTIONS

Apart from the convenience of being able to identify a given transformation by a simple name and assign credit to specific individual(s) the designation of a name reaction implies a high standard of utility, generality or uniqueness.

CONCEPT
MAP

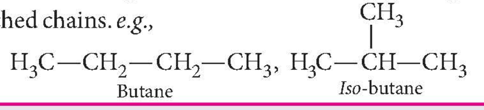
Isomerism

Structural Isomerism

Same molecular formula and different bond pattern *i.e.*, different arrangement of atoms or groups of atoms within the molecules.

Chain Isomerism

Due to different arrangements of carbon atoms leading to linear and branched chains. *e.g.*,



$H_3C-CH_2-CH_2-CH_3$, $H_3C-\overset{CH_3}{\overset{|}{CH}}-CH_3$

Butane, *Iso*-butane

Position Isomerism

Due to different positions of side chains, substituents, functional groups, double bonds, triple bonds, etc. on the parent chain. *e.g.*,

$H_2C{=}CH-CH_2-CH_3$, $H_3C-CH{=}CH-CH_3$

But-1-ene, But-2-ene

Functional Isomerism

Due to presence of different functional groups. *e.g.*,

H_3C-CH_2-OH, $H_3C-O-CH_3$

Ethyl alcohol, Dimethyl ether

Metamerism

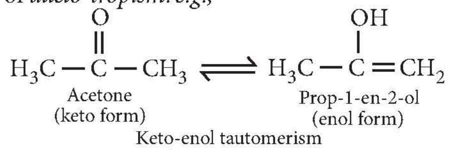
Arises when different alkyl groups are attached to the same functional group. *e.g.*,

$H_3C-CH_2-O-CH_2-CH_3$ $H_3C-O-CH_2-CH_2-CH_3$

Diethyl ether or Ethoxyethane, Methyl propyl ether or 1-Methoxypropane

Tautomerism

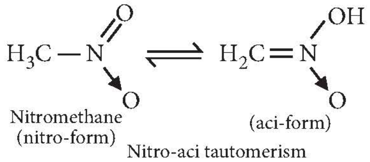
Tautomers have different functional groups and exist in dynamic equilibrium with each other due to a rapid interconversion from one form to another and the phenomenon is known as tautomerism. It is also called as *desmotropism* or *kryptotropism* or *prototropy* or *allelo-tropism*. *e.g.*,



$H_3C-\overset{O}{\overset{||}{C}}-CH_3 \rightleftharpoons H_3C-\overset{OH}{\overset{|}{C}}{=}CH_2$

Acetone (keto form), Prop-1-en-2-ol (enol form)

Keto-enol tautomerism

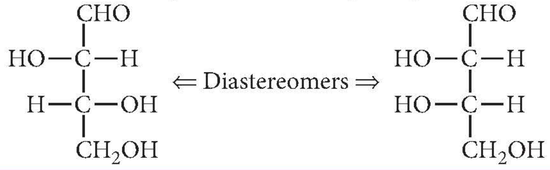


Nitromethane (nitro-form), (aci-form)

Nitro-aci tautomerism

Diastereoisomers

- Chiral molecules having different arrangement of groups or atoms at one or more (but not all) of the equivalent stereocentres.
- They are not mirror images and are non-superimposable.



Stereoisomerism

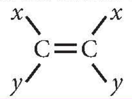
Same molecular formula and bond pattern but different arrangement of atoms or groups of atoms in space.

Geometrical Isomerism

Same structural formula but differ in the spatial arrangement of atoms or groups of atoms about double bond (C═C, C═N or N═N).

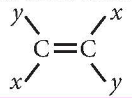
Cis

Similar groups on the same side of the double bond



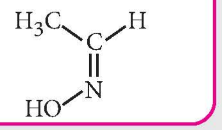
Trans

Similar groups on the different sides of the double bond



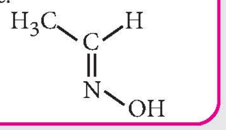
Syn

Two substituents (usually alkyl and hydroxyl) on the same side of the plane.



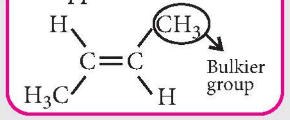
Anti

Two substituents (usually alkyl and hydroxyl) on the opposite side of the plane.



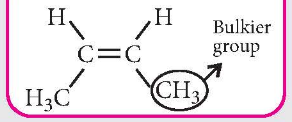
E

E is assigned to an isomer in which high priority atoms or groups are on the opposite sides.



Z

Z is assigned to an isomer in which high priority atoms or groups are on the same side.

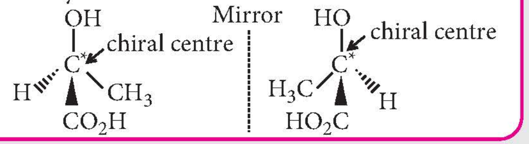


Optical Isomerism

Same molecular formula but differing only in the behaviour towards polarised light are called optical isomers and the phenomenon is called optical isomerism.

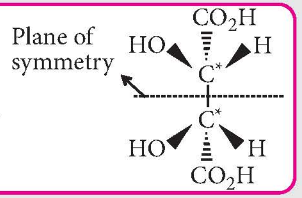
Enantiomers

- Chiral molecules with one or more stereocentres.
- Non-superimposable mirror images.
- No symmetry elements.



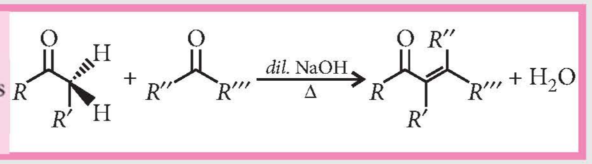
Meso Compounds

- Molecules with multiple stereocentres.
- Internal plane of symmetry thus, optically inactive.



Aldol Condensation

Aldehydes/Ketones (atleast one α-H) $\xrightarrow[\Delta]{\text{Alkali}(dil.)}$ α, β-unsaturated aldehydes or ketones



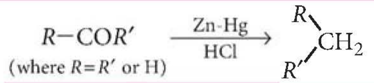
Cannizzaro Reaction

Aldehydes (no α-H) $\xrightarrow{conc.\ \text{NaOH}}$ Carboxylic acid salt (Oxidised form) + Alcohol (Reduced form)

$2RCHO \xrightarrow[\Delta]{conc.\ \text{NaOH/KOH}} RCH_2OH + RCOO^-Na^+$

Clemmensen Reduction

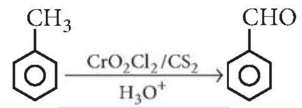
Aldehydes/Ketones $\xrightarrow[\text{HCl}]{\text{Zn-Hg}}$ Hydrocarbon(Alkanes)



$R-COR'$ (where $R = R'$ or H)

Etard Reaction

Aromatic/Heterocyclic bound Methyl Group $\xrightarrow{[O]}$ Aromatic/Heterocyclic Aldehyde



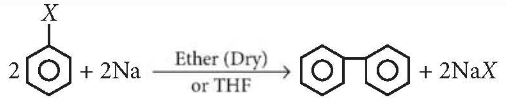
Finkelstein Reaction

Alkyl Chlorides/Bromides $\xrightarrow[\text{Acetone(dry)}]{\text{NaI}}$ Alkyl Iodides

$R-X$ (where X = Cl, Br) $\xrightarrow[\text{Acetone (dry)}]{\text{NaI}} R-I + NaX$

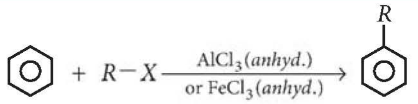
Fittig Reaction

Aryl Halides $\xrightarrow[\text{or THF}]{\text{Na/Dry Ether}}$ Biaryls



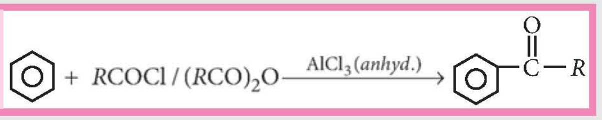
Friedel-Craft Alkylation

Aromatic Compound + $R-X$ $\xrightarrow[\text{or FeCl}_3(anhyd.)]{\text{AlCl}_3(anhyd.)}$ Alkyl benzene



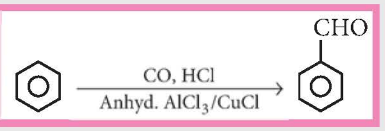
Friedel-Craft Acylation

Aromatic Compound + $RCOCl/(RCO)_2O$ $\xrightarrow{\text{AlCl}_3(anhyd.)}$ Acyl benzene



Gattermann-Koch Reaction

Benzene or its Derivatives $\xrightarrow[\text{AlCl}_3/\text{CuCl}\ (anhyd.)]{\text{CO, HCl}}$ Benzaldehyde or Substituted Benzaldehyde



Gabriel Phthalimide Reaction

Alkyl Halide $\xrightarrow[\text{2. NH}_2\text{NH}_2\text{, acid or base}]{\text{1. Phthalimide/base } (e.g., \text{ KOH})}$ Primary Amine

$R-X \xrightarrow[\text{2. NH}_2\text{NH}_2\text{, acid or base}]{\text{1. Phthalimide/base } (e.g., \text{ KOH})} RNH_2$

Gattermann Reaction

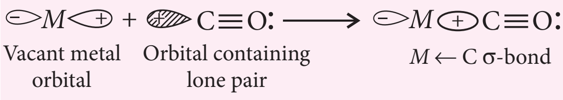
Benzenediazonium Chloride $\xrightarrow[\text{(where } X = \text{Cl, Br)}]{\text{Cu/HX}}$ Aryl Halide

$ArN_2^+Cl^- \xrightarrow[\text{(where } X = \text{Cl, Br)}]{\text{Cu/HX, }\Delta} ArX + N_2$

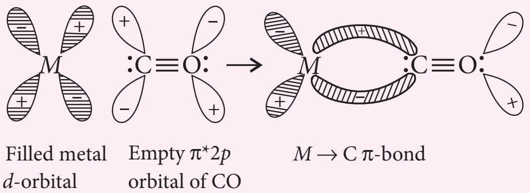
☺ To be continued in next issue....

BONDING IN METAL CARBONYLS

- There is an overlap of filled $\pi 2p$ orbital of CO with suitable empty orbital of metal resulting in the formation of sigma bond.



- Then there is a π-overlap involving filled metal *d*-orbital and empty antibonding π^*2p orbital of same CO. This results in formation of $M \rightarrow C$ π-bond. This is also called *back bonding*.



ORGANOMETALLIC COMPOUNDS

Compounds having one or more metal carbon bonds.

- **Types of organometallic compounds :**
  Based on nature of metal - carbon bond, they are classified into :
  - **σ-bonded organometallic compounds :** *e.g.*; $R-Mg-X$, $(C_2H_5)_2Zn$, etc.
  - **π-bonded organometallic compounds (π complexes) :** *e.g.*; Zeise's salt, $K[PtCl_3(\eta^2\text{-}C_2H_4)]$; ferrocene, $[Fe(\eta^5\text{-}C_5H_5)_2]$, etc.
  - **σ- and π- bonded organometallic compounds (Metal carbonyls) :** *e.g.*, $[Fe(CO)_5]$, $[Ni(CO)_4]$.

APPLICATIONS OF COORDINATION COMPOUNDS

- Complex *cis*-$[PtCl_2(NH_3)_2]$ known as *cis*-platin is used in cancer treatment.
- Coordination compounds are also used in electroplating, photography, dyes, etc.
- Hardness of water can be estimated by complex formation using EDTA.
- Coordination compounds are used as catalyst, *e.g.*, Wilkinson's catalyst, $(Ph_3P)_3RhCl$ Ziegler-Natta catalyst, $[TiCl_4 + (C_2H_5)_3Al]$
- EDTA is often used for treatment of lead poisoning.
- Coordination compounds are of great importance in biological system, *e.g.*, chlorophyll, haemoglobin, myoglobin, etc. are coordinate compounds of Mg, Fe and Co respectively.

INFOSHOTS

A Balancing Act : Stability versus Reactivity of Mn(O) Complexes !

A large class of heme and non-heme metalloenzymes utilize O_2 or its derivatives (*e.g.*, H_2O_2) to generate high-valent metal-oxo intermediates for performing challenging and selective oxidations. Due to their reactive nature, these intermediates are often short-lived and very difficult to characterize. Synthetic chemists have sought to prepare analogous metal-oxo complexes with ligands that impart enough stability to allow for their characterization and an examination of their inherent reactivity. The challenge in designing these molecules is to achieve a balance between their stability, which should allow for their in situ characterization or isolation, and their reactivity, in which they can still participate in interesting chemical transformations. This account focuses on our recent efforts to generate and stabilize high-valent manganese-oxo porphyrinoid complexes and tune their reactivity in the oxidation of organic substrates.

SPEED PRACTICE

1. Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^-, CN^- and H_2O, respectively, are

(a) octahedral, tetrahedral and square planar
(b) tetrahedral, square planar and octahedral
(c) square planar, tetrahedral and octahedral
(d) octahedral, square planar and octahedral.

2. The correct order of magnetic moments (spin only values in B.M.) among is

(a) $[MnCl_4]^{2-} > [CoCl_4]^{2-} > [Fe(CN)_6]^{4-}$
(b) $[MnCl_4]^{2-} > [Fe(CN)_6]^{4-} > [CoCl_4]^{2-}$
(c) $[Fe(CN)_6]^{4-} > [MnCl_4]^{2-} > [CoCl_4]^{2-}$
(d) $[Fe(CN)_6]^{4-} > [CoCl_4]^{2-} > [MnCl_4]^{2-}$.
(Atomic no.: Mn = 25, Fe = 26, Co = 27)

3. Among $[Ni(CO)_4]$, $[NiCl_4]^{2-}$, $[Co(NH_3)_4Cl_2]Cl$, $Na_3[CoF_6]$, Na_2O_2 and CsO_2, the total number of paramagnetic compounds is

(a) 2 (b) 3 (c) 4 (d) 5

(JEE Advanced 2016)

4. Select the incorrect statement.

(a) Ionisation energies of 5*d* elements are greater than those of 3*d* and 4*d* elements.
(b) Cu(I) is diamagnetic while Cu(II) is paramagnetic.
(c) $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless.
(d) Transition elements cannot form complexes.

5. Which of the following will exhibit optical isomerism?

(a) $[Cr(en)(H_2O)_4]^{3+}$ (b) $[Cr(en)_3]^{3+}$
(c) *trans*-$[Cr(en)_2Cl_2]^+$ (d) $[Cr(NH_3)_6]^{3+}$

6. Which one of the following species is stable in aqueous solution?

(a) Cr^{2+} (b) MnO_4^{2-} (c) MnO_3^{3-} (d) Cu^+

(JEE Main 2016)

7. In $Fe(CO)_5$, the Fe – C bond possesses

(a) π-character only (b) both σ and π characters
(c) ionic character (d) σ-character only.

8. The correct order of ionic radii of Y^{3+}, La^{3+}, Eu^{3+} and Lu^{3+} is
(Atomic number of Y = 39, La = 57, Eu = 63, Lu = 71)

(a) $Lu^{3+} < Eu^{3+} < La^{3+} < Y^{3+}$
(b) $La^{3+} < Eu^{3+} < Lu^{3+} < Y^{3+}$
(c) $Y^{3+} < La^{3+} < Eu^{3+} < Lu^{3+}$
(d) $Y^{3+} < Lu^{3+} < Eu^{3+} < La^{3+}$

9. When concentrated HCl is added to an aqueous solution of $CoCl_2$, its colour changes from reddish pink to deep blue. Which complex ion gives blue colour in this reaction?

(a) $[CoCl_6]^{4-}$ (b) $[CoCl_6]^{3-}$
(c) $[CoCl_4]^{2-}$ (d) $[Co(H_2O)_6]^{2+}$

(JEE Main 2015)

10. Among the following statements which one is correct?

(a) Cr^{2+} is a reducing agent.
(b) Mn^{2+} is a reducing agent.
(c) Both Cr^{2+} and Mn^{2+} exhibit d^4 electronic configuration.
(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration.

11. Consider the following complex $[Co(NH_3)_5CO_3]ClO_4$. The coordination number, oxidation number, number of *d*-electrons and number of unpaired *d*-electrons on the metal are respectively

(a) 6, 3, 6, 0 (b) 7, 2, 7, 1
(c) 7, 1, 6, 4 (d) 6, 2, 7, 3

12. Assuming complete ionisation, same moles of which of the following compounds will require the least amount of acidified $KMnO_4$ for complete oxidation?

(a) $FeSO_3$ (b) FeC_2O_4
(c) $Fe(NO_2)_2$ (d) $FeSO_4$

(AIPMT 2015)

13. In the complexes $[Fe(H_2O)_6]^{3+}$, $[Fe(CN)_6]^{3-}$, $[Fe(C_2O_4)_3]^{3-}$ and $[FeCl_6]^{3-}$, more stability is shown by

(a) $[Fe(H_2O)_6]^{3+}$ (b) $[Fe(CN)_6]^{3-}$
(c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[FeCl_6]^{3-}$

14. Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionization enthalpy?

(a) Vanadium ($Z = 23$)
(b) Chromium ($Z = 24$)
(c) Iron ($Z = 26$)
(d) Manganese ($Z = 25$)

15. Identify the correct trend given below :
(Atomic no. : Ti = 22, Cr = 24 and Mo = 42)
(a) Δ_o of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$
(b) Δ_o of $[Cr(H_2O)_6]^{2+} > [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$
(c) Δ_o of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{3+} > [Ti(H_2O)_6]^{2+}$
(d) Δ_o of $[Cr(H_2O)_6]^{2+} < [Mo(H_2O)_6]^{2+}$ and Δ_o of $[Ti(H_2O)_6]^{3+} < [Ti(H_2O)_6]^{2+}$
(JEE Main 2016)

16. The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because
(a) the 5*f* orbitals extend farther from the nucleus than the 4*f* orbitals.
(b) the 5*f* orbitals are more buried than the 4*f* orbitals.
(c) there is a similarity between 4*f* and 5*f* orbitals in their angular part of the wave function.
(d) the actinoids are more reactive than the lanthanoids.

17. Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 Å.)
(a) $[Fe(CO)_4]^{2-}$ (b) $[Mn(CO)_6]^+$
(c) $[Ni(CO)_4]$ (d) $[Co(CO)_4]^-$
(NEET 2016)

18. *P*, *Q* and *R* are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex *P* does not react with concentrated H_2SO_4, whereas complexes *Q* and *R* lose 6.75% and 13.5% of their original mass, respectively, on treatment with concentrated H_2SO_4. Identify *P*, *Q* and *R*.

	P	*Q*	*R*
(a)	$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_5Cl]\cdot(H_2O)Cl_2$	$[Cr(H_2O)_4Cl_2]\cdot(H_2O)_2Cl$
(b)	$[Cr(H_2O)_5Cl]\cdot(H_2O)Cl_2$	$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_4Cl_2]\cdot(H_2O)_2Cl$
(c)	$[Cr(H_2O)_4Cl_2]\cdot(H_2O)_2Cl$	$[Cr(H_2O)_5Cl]\cdot(H_2O)Cl_2$	$[Cr(H_2O)_6]Cl_3$
(d)	$[Cr(H_2O)_6]Cl_3$	$[Cr(H_2O)_4Cl_2]\cdot(H_2O)_2Cl$	$[Cr(H_2O)_5Cl]\cdot(H_2O)Cl_2$

19. Which one of the following complexes will consume more equivalents of aqueous solution of $AgNO_3$?
(a) $Na_2[CrCl_5(H_2O)]$ (b) $Na_3[CrCl_6]$
(c) $[Cr(H_2O)_5Cl]Cl_2$ (d) $[Cr(H_2O)_6]Cl_3$

20. The complex ion which has no *d* electrons in the central metal atom is
(a) $[MnO_4]^-$ (b) $[Co(NH_3)_6]^{3+}$
(c) $[Fe(CN)_6]^{3-}$ (d) $[Cr(H_2O)_6]^{3+}$

21. Cerium ($Z = 58$) is an important member of the lanthanides. Which of the following statements about cerium is incorrect?
(a) The common oxidation states of cerium are +3 and +4.
(b) Cerium (IV) acts as an oxidising agent.
(c) The +4 oxidation state of cerium is not known in solutions.
(d) The +3 oxidation state of cerium is more stable than the +4 oxidation state.

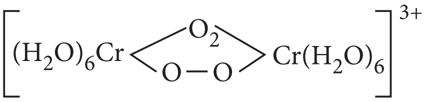
22. Which of the following complexes is diamagnetic?
(a) $[Mn(H_2O)_6]^{2+}$ (b) $[Cu(H_2O)_6]^{3+}$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(H_2O)_6]^{2+}$

23. If *M* is an element of actinoids series, the degree of complex formation decreases in the order
(a) $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^+$
(b) $MO_2^+ > MO_2^{2+} > M^{3+} > M^{4+}$
(c) $M^{4+} > MO_2^{2+} > \mathrm{M}^{3+} > MO_2^+$
(d) $MO_2^{2+} > MO_2^+ > M^{4+} > M^{3+}$

24. Which of the following has largest number of isomers? (*R* = alkyl group, *en* = ethylenediamine)
(a) $[Ru(NH_3)_4Cl_2]^+$ (b) $[Co(NH_3)_5Cl]^{2+}$
(c) $[Ir(PR_3)_2H(CO)]^{2+}$ (d) $[CoCl_2(en)_2]^+$

25. Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect?
(a) Ferrous oxide is more basic in nature than the ferric oxide.
(b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
(c) Ferrous compounds are less volatile than the corresponding ferric compounds.
(d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.

26. Oxidation number of Cr in the following complex is



(a) 3 (b) 6 (c) 4 (d) 5

27. MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state. It is due to

(a) oxygen gives colour to it.
(b) charge transfer when oxygen gives its electron to Mn making it Mn (+VI) hence, coloured.
(c) charge transfer when Mn gives its electron to oxygen.
(d) none of the above is correct.

28. Which one of the following complex species does not obey the EAN rule?

(a) $[Cu(CN)_4]^{3-}$ (b) $[Cr(NH_3)_6]^{3+}$
(c) $[Fe(CN)_6]^{4-}$ (d) $[Ni(CO)_4]$

29. A change in oxidation number is observed when

(a) aqueous solution of CrO_4^{2-} is acidified.
(b) SO_2 gas is passed into $Cr_2O_7^{2-}/H^+$.
(c) $Cr_2O_7^{2-}$ solution is made alkaline.
(d) CrO_2Cl_2 is dissolved in NaOH.

30. Black coloured solid (*A*) $\xrightarrow[\Delta]{KNO_3 + KOH}$ green colour solution (*B*) $\xrightarrow{CO_2} \underset{\text{pink}}{(C)} + (A)$

Pink compound (*C*) is decolourised by Fe^{2+}. The compound *A*, *B* and *C* are

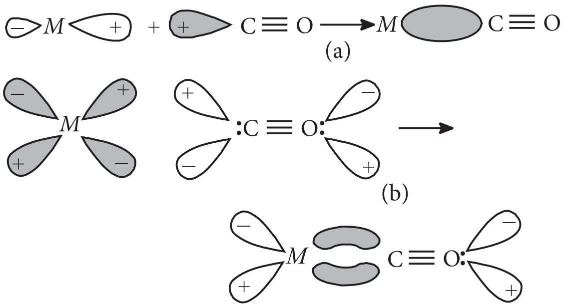
(a) MnO_2, K_2MnO_4, $KMnO_4$
(b) MnO_2, $KMnO_4$, K_2MnO_4
(c) $KMnO_4$, MnO_2, K_2MnO_4
(d) K_2MnO_4, MnO_2, $KMnO_4$

SOLUTIONS

1. (b) 2. (a) 3. (b) 4. (d) 5. (b)

6. (b): $Cr^{2+}(d^4)$ is unstable and oxidised to Cr^{3+} (d^3 *i.e.*, t_{2g}^3) which is more stable.
Cu^+ is unstable and is oxidised to Cu^{2+} which has more negative enthalpy of hydration.
Similarly, $Mn^{3+}(d^4)$ in MnO_3^{3-} is unstable and is reduced to $Mn^{2+}(d^5)$.
MnO_4^{2-} ion is far more likely to exist in a very high pH solution and is stable for a few hours in alkalies.

7. (b): In a metal carbonyl, the metal carbon bond possesses both the σ- and π-character. A σ-bond between metal and carbon atom is formed when a vacant hybrid bond of the metal atom overlaps with an orbital of C atom of carbon monoxide containing a lone pair of electrons.
Formation of π-bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π* orbital of C atom of CO. This overlap is also called back donation of electrons by metal atom to carbon.



(a) The formation of the metal ← carbon σ-bond using an unshared pair of the C atom. (b) The formation of the metal → carbon π-bond.

8. (d)

9. (c): $\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}} + 4Cl^- \longrightarrow \underset{\text{Blue}}{[CoCl_4]^{2-}} + 6H_2O$

10. (a): Cr^{2+} is a reducing agent, it gets oxidised to Cr^{3+} ($3d^3$ or t_{2g}^3, stable half-filled configuration).

11. (a): In $[Co(NH_3)_5CO_3]ClO_4$, C.N. of Co = 6 ;
O.N. = $x + 5x\,(0) + 1x\,(-2) + 1x\,(-1) = 0 \;\therefore\; x = +3$
Electronic configuration of Co^{3+} : $[Ar]3d^64s^0$;
Number of *d*-electrons = 6
All *d*-electrons are paired due to strong ligand hence, no unpaired electrons.

12. (d)

13. (c): $[Fe(C_2O_4)_3]^{3-}$. The iron is present in the highest oxidation state Fe^{3+} and $C_2O_4^{2-}$ is a chelating ligand. Chelates are always more stable complexes.

14. (d)

15. (c): Δ_o increases from 3*d*-series to 4*d*-series. Thus, $[Cr(H_2O)_6]^{2+}$ has lower Δ_o value than that of $[Mo(H_2O)_6]^{2+}$. Also, for a metal ion having lesser number of *d*-electrons, Δ_o value increases. Thus, $[Ti(H_2O)_6]^{3+}$ has greater Δ_o value than that of $[Ti(H_2O)_6]^{2+}$.

16. (a): More the distance between nucleus and outer orbitals, lesser will be force of attraction on them. Distance between nucleus and 5*f* orbitals is more as compared to distance between 4*f* orbital and nucleus. So actinoids exhibit more number of oxidation states in general than the lanthanoids.

17. (a): The greater the negative charge on the carbonyl complex, the more easy it would be for the metal to permit its electrons to participate in the back bonding, the higher would be the *M*—C bond order and simultaneously there would be larger reduction in the C—O bond order. Thus, $[Fe(CO)_4]^{2-}$ has the lowest C—O bond order means the longest bond length.

18. (a) : Since there is no action of concentrated H_2SO_4 on compound *P* so it can be assumed that all molecules of water in *P* are coordinated with Cr^{3+} ion. Its structure would be $[Cr(H_2O)_6]Cl_3$.

Compound *Q* loses 6.75% of its original mass on being treated with concentrated H_2SO_4. The loss in mass is due to removal of water molecules that are not directly coordinate to Cr^{3+} ion.

$\therefore$ Mass of water lost from Q per mole

$$= \frac{6.75}{100} \times 266.5\text{ g} = 17.98\text{ g} \quad [\text{Molar mass} = 266.5]$$

This loss of mass corresponds to loss of 1 molecule of water. Therefore the structure of complex *Q* is $[Cr(H_2O)_5Cl]\ (H_2O)Cl_2$.

In compound *R* the mass lost is 13.5%, when *R* is treated with concentrated H_2SO_4. The loss in mass is 2 times (2 × 6.75 = 13.5) the loss in mass in case of *Q*. This loss corresponds to 2 molecules of water. So, the structure of *R* is $[Cr(H_2O)_4Cl_2](H_2O)_2Cl$.

19. (d) : Chloride ions outside the coordination sphere are ionisable only. Hence, $[Cr(H_2O)_6]Cl_3$ will give $3Cl^-$ ions in aqueous solution which consume more equivalents of $AgNO_3$.

20. (a) : In MnO_4^- , the O.S. of Mn is +7 *i.e.* Mn^{7+}

$$\text{Mn}: \overset{3d}{\boxed{\uparrow\,|\,\uparrow\,|\,\uparrow\,|\,\uparrow\,|\,\uparrow}}\ \overset{4s}{\boxed{\uparrow\downarrow}}\ \overset{4p}{\boxed{\,|\,\,|\,}}$$

$$Mn^{7+}: \overset{3d}{\boxed{\,|\,\,|\,\,|\,\,|\,}}\ \overset{4s}{\boxed{}}\ \overset{4p}{\boxed{\,|\,\,|\,}}\ \ i.e.\ 3d^0 4s^0$$

In other species, we have

$$\left.\begin{array}{l}\text{Co in }[Co(NH_3)_6]^{3+}\text{ is }Co^{3+}\ i.e.\ 3d^6\\ \text{Fe in }[Fe(CN)_6]^{3-}\text{ is }Fe^{3+}\ i.e.\ 3d^5\\ \text{Cr in }[Cr(H_2O)_6]^{3+}\text{ is }Cr^{3+}\ i.e.\ 3d^3.\end{array}\right]\begin{array}{c}\text{All of these}\\ \text{have certain number}\\ \text{of } d\text{-electrons}\end{array}$$

21. (c)

22. (c) :

Mn^{2+}	Cu^{3+}	Co^{3+}	Co^{2+}
$[Ar]3d^5$	$[Ar]3d^8$	$[Ar]3d^6$	$[Ar]3d^7$
No pairing of e^-	No pairing of e^-	Pairing of e^-	No pairing of e^-
Paramagnetic	Paramagnetic	Diamagnetic	Paramagnetic

23. (c) : The higher the charge on the metal ion, smaller is the ionic size and more is the complex forming ability. Thus, the degree of complex formation decreases in the order

$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$

The higher tendency of complex formation of MO_2^{2+} as compared to M^{3+} is due to high concentration of charge on metal atom *M* in MO_2^{2+}.

24. (d) : Among the given complexes, $[CoCl_2(en)_2]^+$ is a $[M(AA)_2B_2]$ type complex, thus, it is possible for it to exhibit geometrical as well as optical isomerism, which is not possible in case of other given complexes. Thus, it exhibits largest number of isomers.

25. (d) : Greater the covalent nature, more easily they are hydrolysed. Thus, $FeCl_3$ is more easily hydrolysed than $FeCl_2$. Thus, statement (d) is incorrect.

26. (a)

27. (b) : The colour arise by charge transfer. In MnO_4^-, an electron is momentarily transferred from oxygen to the metal and thus oxygen changes from O^{2-} to O^- and Mn from (+7) to (+6).

28. (b)

29. (b) :

(a) $2\overset{+6}{Cr}O_4^{2-} + 2H^+ \longrightarrow \overset{+6}{Cr_2}O_7^{2-} + H_2O$

(No change in oxidation state of Cr)

(b) $\overset{+6}{Cr_2}O_7^{2-} + 2H^+ + 3SO_2 \longrightarrow$

$2Cr^{3+} + H_2O + 3SO_4^{2-}$

(Oxidation state of Cr changes from +6 to +3 in this reaction.)

(c) $\overset{+6}{Cr_2}O_7^{2-} + 2OH^- \longrightarrow 2\overset{+6}{Cr}O_4^{2-} + H_2O$

(No change in oxidation state of Cr)

(d) $\overset{+6}{Cr}O_2Cl_2 + 2NaOH \longrightarrow Na_2\overset{+6}{Cr}O_4 + 2HCl$

(No change in oxidation state of Cr)

30. (a) : Black colour compound is $MnO_2(A)$.

$$\underset{(A)}{2MnO_2} + 4KOH + O_2(KNO_3) \xrightarrow{\Delta} \underset{\text{green colour }(B)}{2K_2MnO_4} + 2H_2O$$

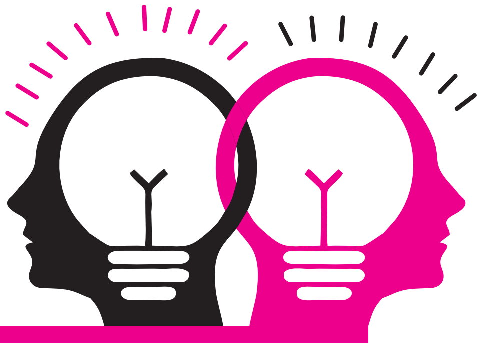
$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$$

$$3MnO_4^{2-} + 4H^+ \longrightarrow \underset{(A)}{MnO_2} + \underset{(C)}{2MnO_4^-} + 2H_2O$$

(disproportionation reaction)

◆ ◆

EXAMiNER'S MiND CLASS XII



The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII.
This year JEE (Main & Advanced)/NEET/AIIMS have drawn their papers heavily from NCERT books.

Section - I	Q. 1 to 10 Only One Option Correct Type MCQs.
Section - II	Q. 11 to 13 More than One Options Correct Type MCQs.
Section - III	Q. 14 to 17 Paragraph Type MCQs having Only One Option Correct.
Section - IV	Q. 18 & 19 Matching List Type MCQs having Only One Option Correct.
Section - V	Q. 20 to 22 Assertion Reason Type MCQs having Only One Option Correct. Mark the correct choice as : (a) If both assertion and reason are true 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 both assertion and reason are false.
Section - VI	Q. 23 to 25 Integer Value Correct Type Questions having Single Digit Integer Answer, ranging from 0 to 9 (both inclusive).

ELECTROCHEMISTRY

SECTION - I

Only One Option Correct Type

1. The pH of 0.5 L of 1.0 M NaCl solution after electrolysis for 965 s using 5.0 A current, is
(a) 1.0 (b) 12.7 (c) 13.0 (d) 1.30

2. The resistance of a 0.10 M weak acid HA in a conductivity cell is 2.0×10^3 ohm. The cell constant of the cell is 0.78 cm^{-1} and Λ_∞ of the acid is 390 S cm^2 mol^{-1}.
Consider the following statements
1. pH of the acid solution = 3
2. pK_a of the acid = 5
3. Degree of dissociation of the acid = 0.01

Which of the statements given above are correct?
(a) 1 and 2 only (b) 1 and 3 only
(c) 2 and 3 only (d) 1, 2 and 3

3. When a rod of metal A is dipped in an aqueous solution of metal B (concentration of B^{2+} = 1 M) at 25°C, the electrode potentials are $A^{2+}/A = -0.76$ V, $B^{2+}/B = +0.34$ V.
Which of the following statements are correct?
(a) A will gradually dissolve.
(b) B will deposit on A.
(c) No reaction will occur.
(d) Water will decompose into H_2 and O_2.

4. An electric current is passed through two electrolytic cells connected in series, one containing $AgNO_{3(aq)}$ and other $H_2SO_{4(aq)}$. What volume of O_2 would be liberated at 25°C and 750 mm in Hg from H_2SO_4 if 1 mole of Ag^+ are deposited from $AgNO_3$ solution?
(a) 6.20 L (b) 7.20 L (c) 8.00 L (d) 10.00 L

5. The standard reduction potential for Cu^{2+}/Cu is +0.34 V. What is the reduction potential at pH = 14 for the above couple.
(Given : K_{sp} of $Cu(OH)_2 = 1.0 \times 10^{-19}$).
(a) –0.2205 (b) –0.335
(c) –0.2705 (d) 0.535

6. Consider the following reactions :
$Cd^{2+}_{(aq)} + e^- \longrightarrow Cd_{(s)}$, $E° = -0.40$ V
$Ag^+_{(aq)} + e^- \longrightarrow Ag_{(s)}$, $E° = 0.80$ V
Which of the following statements is not correct for the galvanic cell involving the above reactions?

(a) E_{cell} increases when Cd^{2+} solution is diluted.
(b) E_{cell} decreases when Ag^+ solution is diluted.
(c) Twice as many electrons pass through the cadmium electrode as through silver electrode.
(d) Molar concentration of the cation in the cathodic compartment changes faster than that of the cation in anodic compartment.

7. The electrical work done during the reaction at 298 K :
$2Hg_{(l)} + Cl_{2(g)} \longrightarrow Hg_2Cl_{2(s)}$, is
(Given : $E^\circ_{Cl_2/Cl^-} = 1.36\text{ V} \cdot E^\circ_{Hg_2Cl_2/Hg,\ Cl^-} = 0.27\text{ V} : P_{Cl_2} = 1\text{ atm}$)
(a) 210.37 kJ mol^{-1} (b) 105.185 kJ mol^{-1}
(c) 420.74 kJ mol^{-1} (d) 110.37 kJ mol^{-1}

8. 0.04 N solution of a weak acid has specific conductance 4.23×10^{-4} mho cm^{-1} and degree of dissociation is 0.0612. The equivalent conductance (ohm^{-1} cm^2 $equiv^{-1}$) of weak acid at infinite dilution is
(a) 1.72 (b) 17.29 (c) 142.27 (d) 172.79

9. A hydrogen electrode placed in a buffer solution of CH_3COONa and acetic acid in the ratio's $x : y$ and $y : x$ has electrode potential values E_1 and E_2 volt respectively at 25°C. The pK_a values of acetic acid is (E_1 and E_2 are oxidation potential) :
(a) $\dfrac{E_1 + E_2}{0.118}$ (b) $\dfrac{E_2 - E_1}{0.118}$
(c) $-\dfrac{E_1 + E_2}{0.118}$ (d) $\dfrac{E_1 - E_2}{0.118}$

10. On electrolysis of $HCOONa_{(aq)}$, which gas is obtained both at anode and cathode?
(a) H_2 (b) O_2
(c) CO_2 (d) Impossible

SECTION - II

More than One Options Correct Type

11. Which of the following changes will cause the free energy of the cell reaction to decrease?
$Zn_{(s)} \mid ZnSO_{4(aq)}\ (x_1M) \parallel HCl_{(aq)}\ (x_2M) \mid H_{2(g)}$, Pt
(a) Increase in the volume of HCl solution from 100 mL to 200 mL.
(b) Increase in pressure of hydrogen from 1 atm to 2 atm.
(c) Increase in molarity x_2 from 0.1 to 1 M.
(d) Decrease in molarity x_1 from 1 M to 0.1 M.

12. If 90 g of water is electrolysed completely with 50% current efficiency then,
(a) 10 Faraday of electricity will be consumed
(b) 20 Faraday of electricity will be consumed
(c) 168 L (STP) of gases will be produced
(d) 84 L (STP) of gases will be produced.

13. The formation of rust on the surface of iron occurs through the reaction,
(a) $Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$ at anode
(b) $O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$ at cathode
(c) $4Fe^{2+}_{(aq)} + O_{2(g)} + 4H_2O_{(l)} \longrightarrow 2Fe_2O_{3(s)} + 8H^+$
(d) $Fe_2O_{3(s)} + xH_2O_{(l)} \longrightarrow Fe_2O_3.xH_2O$

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

Tollen's reagent is used for the detection of aldehyde. When a solution of $AgNO_3$ is added to glucose with NH_4OH, then gluconic acid is formed.

$Ag^+ + e^- \longrightarrow Ag\ ; E^\circ_{cell} = 0.8\text{ V}$
$C_6H_{12}O_6 + H_2O \longrightarrow \text{Gluconic acid}\ (C_6H_{12}O_7) + 2H^+ + 2e^-$
$E^\circ_{oxd} = -0.05\text{ V}$
$Ag(NH_3)_2^+ + e^- \longrightarrow Ag_{(s)} + 2NH_3\ ; E^\circ_{cell} = 0.337\text{ V}$

$$\left[\text{Use } 2.303 \times \frac{RT}{F} = 0.0591 \text{ and } \frac{F}{RT} = 38.92 \text{ at 298 K}\right]$$

14. $2Ag^+ + C_6H_{12}O_6 + H_2O \longrightarrow 2Ag_{(s)} + C_6H_{12}O_7 + 2H^+$
The value of ln K of given reaction is
(a) 66.13 (b) 58.38 (c) 28.30 (d) 46.29

15. When ammonia is added to the solution, pH is raised to 11. Then which half-cell reaction is affected by pH and how much?
(a) E_{oxd} increases over E°_{oxd} by 0.65 V
(b) E_{red} increases over E°_{red} by 0.65 V
(c) E_{oxd} decreases from E°_{oxd} by 0.65 V
(d) E_{red} decreases from E°_{red} by 0.65 V

Paragraph for Questions 16 and 17

The electrochemical cell shown below is a concentration cell.
$M \mid M^{2+}$ (saturated solution of a sparingly soluble salt, MX_2) $\parallel M^{2+}$ (0.001 mol dm^{-3}) $\mid M$
The emf of the cell depends on the difference in concentration of M^{2+} ions at the two electrodes.
The emf of the cell at 298 K is 0.059 V.

16. The solubility product (K_{sp} in mol^3 dm^{-9}) of MX_2 at 298 K based on the information available for the given concentration cell is
(use $2.303 \times R \times 298 / F = 0.059$ V)

(a) 1×10^{-15} (b) 4×10^{-15}
(c) 1×10^{-12} (d) 4×10^{-12}

17. The value of ΔG (kJ mol^{-1}) for the given cell is (Given, 1 F = 96500 C mol^{-1})
(a) −5.7 (b) 5.7 (c) 11.4 (d) −11.4

SECTION - IV

Matching List Type

18. Match the electrode of List I with its general name in List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Hg_2Cl_2	1.	Used in salt-bridge
Q.	Quinhydrone	2.	Measurement of cell constant
R.	Lead acetate	3.	Redox electrode
S.	NH_4NO_3	4.	Calomel electrode
T.	0.1 N KCl	5.	Used in platinising solution

	P	Q	R	S	T
(a)	4	5	3	2	1
(b)	1	3	2	4	5
(c)	5	2	4	1	3
(d)	4	3	5	1	2

19. Match the cells/cell reactions in List I with their values in List II and select the correct answer using the code given below the lists :

	List I		List II
P.	Oxidation potential of hydrogen electrode set up in a solution with pH = 2	1.	.018 V
Q.	Oxidation potential of hydrogen electrode set up in 0.5 M HCl solution	2.	0.059 V
R.	EMF of concentration cell with hydrogen electrodes set up in 0.1 M and 0.01 M HCl solutions	3.	0.035 V
S.	EMF of concentration cell with hydrogen electrodes set up in 0.1 M and 0.4 M HCl solutions	4.	0.118 V

	P	Q	R	S
(a)	2	1	3	4
(b)	4	1	2	3
(c)	1	2	4	3
(d)	4	2	1	3

SECTION - V

Assertion Reason Type

20. **Assertion :** KCl/NaCl/NH_4Cl etc. cannot be used in the salt bridge of a cell containing silver.
Reason : A salt bridge contains concentrated solution of an inert electrolyte like KCl, KNO_3, NH_4NO_3 etc or solidified solution of such an electrolyte in agar-agar and gelatine.

21. **Assertion :** Auric chloride ($AuCl_3$) solution cannot be stored in a vessel made of copper, iron, nickel, chromium, zinc or tin.
Reason : Gold is a very precious metal.

22. **Assertion :** For a cell reaction
$Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$,
voltmeter gives zero reading at the equilibrium.
Reason : At the equilibrium, there is no change in the concentration of Cu^{2+} and Zn^{2+} ions.

SECTION - VI

Integer Value Correct Type

23. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made to 100 mL. A silver electrode was dipped in the solution and EMF of the cell set up
$Pt_{(s)}, H_{2(g)} | H^+(1\ M) || Ag^+{}_{(aq)} | Ag_{(s)}$
was 0.62 V. The percentage of Ag in the alloy is
[E°_{cell} = 0.80 V, 2.303 RT/F = 0.06 at 25°C]

24. ΔG for the reaction,

$$\frac{4}{3}Al + O_2 \longrightarrow \frac{2}{3}Al_2O_3 \text{ is } -772 \text{ kJ mol}^{-1} \text{ of } O_2.$$

The minimum EMF in volts required to carry out an electrolysis of Al_2O_3 is

25. The conductivity of 0.001 M acetic acid solution is 5.0×10^{-5} S cm^{-1}. If Λ° for acetic acid is taken as 400 S cm^2 mol^{-1}, its dissociation constant will be 1.78×10^{-x} where x is

……

MPP-4 CLASS XI ANSWER KEY

1.	(c)	**2.**	(d)	**3.**	(c)	**4.**	(b)	**5.**	(b)
6.	(b)	**7.**	(d)	**8.**	(c)	**9.**	(a)	**10.**	(a)
11.	(d)	**12.**	(a)	**13.**	(a)	**14.**	(a)	**15.**	(a)
16.	(c)	**17.**	(c)	**18.**	(d)	**19.**	(d)	**20.**	(a,d)
21.	(b,c,d)	**22.**	(a,b,c,d)			**23.**	(a,b)	**24.**	(7)
25.	(5)	**26.**	(3)	**27.**	(b)	**28.**	(a)	**29.**	(b)
30.	(a)								

d – and *f* – BLOCK ELEMENTS

SECTION - I

Only One Option Correct Type

1. Find out the correct statement out of the following :
(a) The stability of either of $HgCl_2$ and $SnCl_2$ is not affected when present simultaneously in aqueous solution.
(b) Both $Cu(OH)_2$ and $Fe(OH)_2$ are soluble in aqueous NH_3.
(c) Copper (I) salts are not known in aqueous solution.
(d) White precipitate of $Zn(OH)_2$ is obtained on adding excess of NaOH to aqueous $ZnSO_4$.

2. For Ni and Pt different *IP* in J mol^{-1} are given below :

	$(IP)_1 + (IP)_2$	$(IP)_3 + (IP)_4$
Ni	2.49	8.80
Pt	2.60	6.70

Which of the following statements regarding the above observation is correct?
(a) Nickel (II) compounds tend to be thermodynamically more stable than platinum (II).
(b) Platinum (IV) compounds tend to be more stable than nickel (IV).
(c) Both (a) and (b) are correct.
(d) None of the above is correct.

3. Which of the following arrangements does not represent the correct order of the property stated against it?
(a) $V^{2+} < Cr^{2+} < Mn^{2+} < Fe^{2+}$: Paramagnetic behaviour
(b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+}$: Ionic size
(c) $Co^{3+} < Fe^{3+} < Cr^{3+} < Sc^{3+}$: Stability in aqueous solution
(d) SC < Ti < Cr < Mn : Number of oxidation states

4. Which of the following statements is not correct?
(a) $La(OH)_3$ is less basic than $Lu(OH)_3$.
(b) In lanthanide series ionic radius of Ln^{3+} ion decreases.
(c) La is actually an element of transition series rather lanthanide.
(d) Atomic radius of Zr and Hf are same because of lanthanide contraction.

5. Second ionisation energies of chromium and copper are larger than those of their neighbouring elements (V, Mn, Ni, Zn). It is due to the fact that
(a) second electron in each case is removed from 4*s* orbital.
(b) second electron is removed from stable half-filled 3*d* sub-orbit in case of chromium and from stable completely filled 3*d* sub-orbit in case of copper.
(c) electrode potential of these elements (Cr and Cu) are higher than those of their neighbouring elements.
(d) their atomic radii are different due to screening effect.

6. Effective atomic number (EAN) of Fe in brown ring complex $[Fe(H_2O)_5NO]^{2+}$ is
(a) 36 (b) 37 (c) 38 (d) 39

7. In which of the following ions, the colour is not due to *d*-*d* transition?
(a) $[Ti(H_2O)_6]^{3+}$ (b) $[Cu(NH_3)_4]^{2+}$
(c) $[CoF_6]^{3-}$ (d) CrO_4^{2-}

8. Mercury is the only metal which is liquid at 0°C. This is due to its
(a) very high ionisation enthalpy, weak metallic bond, fully filled *d*-orbital that prevents *d*-*d* overlapping of orbitals
(b) low ionisation enthalpy
(c) high atomic weight
(d) high vapour pressure.

9. Ionic character of halides of metals (3*d*-transition series) decreases in the order
(a) $M—\mathrm{I} > M—\mathrm{Br} > M—\mathrm{Cl} > M—\mathrm{F}$
(b) $M—\mathrm{Cl} > M—\mathrm{Br} > M—\mathrm{I} > M—\mathrm{F}$
(c) $M—\mathrm{Br} > M—\mathrm{Cl} > M—\mathrm{F} > M—\mathrm{I}$
(d) $M—\mathrm{F} > M—\mathrm{Cl} > M—\mathrm{Br} > M—\mathrm{I}$

10. The "spin only" magnetic moment [in unit of Bohr magneton (μ_B)] of Ni^{2+} in aqueous solution would be (At. No. Ni = 28)
(1) 0 (b) 1.73 (c) 2.83 (d) 4.90

SECTION - II

More than One Options Correct Type

11. Select the correct statements.
(a) When $FeCl_3$ solution is added to $K_4[Fe(CN)_6]$ solution, in addition to $Fe^{III}[Fe^{II}(CN)_6]^-$, $Fe^{II}[Fe^{III}(CN)_6]^-$ is also formed due to side redox reaction.

(b) When $FeCl_2$ solution is added to $K_3[Fe(CN)_6]$ solution, in addition to $Fe^{II}[Fe^{II}(CN)_6]^-$, $Fe^{III}[Fe^{II}(CN)_6]^-$ is also formed due to side redox reaction.
(c) $Fe^{III}[Fe^{II}(CN)_6]^-$ is paramagnetic while $Fe^{II}[Fe^{II}(CN)_6]^-$ is diamagnetic.
(d) $Fe^{III}[Fe^{II}(CN)_6]^-$ is diamagnetic while $Fe^{II}[Fe^{III}(CN)_6]^-$ is paramagnetic.

12. Potassium manganate (K_2MnO_4) is formed when
(a) chlorine is passed through aqueous solution of $KMnO_4$
(b) manganese dioxide is fused with potassium hydroxide in air
(c) formaldehyde reacts with potassium permanganate in the presence of strong alkali
(d) potassium permanganate reacts with H_2SO_4.

13. Which of the following statements are wrong?
(a) Ti^{4+} and Ag^+ are repelled by magnetic field.
(b) Mn^{2+} shows maximum magnetic character among the first transition series.
(c) Fe^{2+} is more stable than Mn^{2+} towards oxidation to +3 state.
(d) Cr in $Cr_2O_7^{2-}$ ion involves sp^3d^3 hybridisation.

SECTION - III

Paragraph Type

Paragraph for Questions 14 and 15

"Green solution of potassium manganate (VI), turns purple and a brown solid is precipitated when CO_2 is bubbled into the solution".

14. Purple colour is due to formation of
(a) manganese(IV) dioxide
(b) potassium permanganate(VII)
(c) manganese(II) ion
(d) none of the above.

15. Above change is observed when CO_2 is passed into aqueous solution of the given ion. Function of CO_2 is
(a) it makes the solution acidic due to formation of H_2CO_3
(b) it makes the solution basic due to formation of CO_3^{2-}
(c) it is simply the medium of the reaction
(d) none of the above is correct.

Paragraph for Questions 16 and 17

The *f*-block elements are those in which the differentiating electron enters the (n −2)*f* orbital. There are two series of *f*-block elements corresponding to filling of 4*f* and 5*f*-orbitals called lanthanides and actinides respectively. They show different oxidation states depending upon stability of f^0, f^7 and f^{14} configurations, though the principal oxidation states is +3. There is a regular decrease in size of lanthanides ions with increase in atomic number and it is known as lanthanide contraction. As a result of this, the basic character of oxides and hydroxides decreases from first element (La) to last element (Lu). All the actinides are radioactive and therefore, it is difficult to study their chemical nature.

16. The atomic numbers of three lanthanide elements *X*, *Y* and *Z* are 65,68 and 70 respectively. The basic character of their hydroxides will decrease as
(a) $X > Y > Z$ (b) $X > Z > Y$
(c) $Z > Y > X$ (d) $Z > Y > X$

17. Ce (Z = 58) and Yb (Z = 70) exhibit stable +4 and +2 oxidation states respectively. This is because
(a) Ce^{4+} and Yb^{2+} acquire f^7 configurations
(b) Ce^{4+} and Yb^{2+} acquire f^0 configurations
(c) Ce^{4+} and Yb^{2+} acquire f^0 and f^{14} configurations
(d) Ce^{4+} and Yb^{2+} acquire f^7 and f^{14} configurations.

SECTION - IV

Matching List Type

18. Match the entries of List I with appropriate entries of List II and select the correct answer using the code given below the lists :

	List I		List II
1.	MnO_4^{2-}	(p)	*d-d* transition
2.	$Ti^{3+}_{(aq)}$ ion	(q)	Charge transfer transition
3.	MnO_4^-	(r)	Green
4.	$Cr^{3+}_{(aq)}$ ion	(s)	Purple

	1	2	3	4
(a)	p, s	q, s	q, r	p, r
(b)	q, r	p, s	q, s	p, r
(c)	p, q	s, r	p, r	r, q
(d)	q, p	r, p	s, p	s, r

19. Match the entries of List I with appropriate entries of List II and select the correct answer using the code given below the lists :

	List I		List II
1.	Cr	(p)	$5d^{10}\,6s^1$
2.	Au	(q)	$3d^5\,4s^1$
3.	Pd	(r)	$4f^75d^16s^2$
4.	Gd	(s)	$4d^{10}5s^0$

	1	2	3	4
(a)	q	p	s	r
(b)	p	s	q	r
(c)	s	q	r	p
(d)	r	s	p	q

SECTION - V

Assertion Reason Type

20. **Assertion :** $E°$ value of $Mn^{3+} \mid Mn^{2+}$ is more positive than for $Cr^{3+} \mid Cr^{2+}$.

Reason : Cr^{3+} is more stable than Cr^{2+} but Mn^{3+} is less stable than Mn^{2+}.

21. **Assertion :** Copper metal gets covered with a green layer of basic copper carbonate.

Reason : Copper metal is unaffected when exposed to atmospheric CO_2 and moisture.

22. **Assertion :** CrO_3 reacts with HCl to form chromyl chloride gas.

Reason : Chromyl chloride (CrO_2Cl_2) has tetrahedral structure.

SECTION - VI

Integer Value Correct Type

23. How many of the following are paramagnetic as well as coloured species?
O_2, NO_2, Cu^{2+}, Hg_2^{2+}, Fe^{2+}, Fe^{3+}, $[Fe(CN)_6]^{4-}$, $[Fe(CN)_6]^{3-}$, $[Ni(H_2O)_6]^{2+}$, $[Ni(CN)_4]^{2-}$

24. 2.674 g of $CoCl_3 \cdot 6NH_3$ (molar mass = 267.4 g mol^{-1}) in aqueous solution gave 4.305 g of white precipitate of AgCl (molar mass = 143.5 g mol^{-1}) on reaction with excess of $AgNO_3$ solution. Thus, Cl atoms in outer sphere of the complex is

25. What is the sum of oxidation number of iron in Prussian blue?

SOLUTIONS

ELECTROCHEMISTRY

1. **(c) :** $$NaCl_{(aq)} + H_2O_{(l)} \xrightarrow{\text{Electrolysis}} \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} + NaOH_{(aq)}$$

Amount of NaCl present in 0.5 L of 1.0 M NaCl = 0.5 mole

Quantity of electricity passed = 965 × 5 coulombs = 4825 coulombs

1 mole of NaCl is decomposed by 96500 coulombs

$\therefore$ 4825 coulombs will decompose NaCl

$$= \frac{4825}{96500} \text{ mole} = 0.05 \text{ mole}$$

NaOH formed in the solution will also be 0.05 mole

Volume of solution = 0.5 L

$\therefore$ Molarity of NaOH in the solution $= \frac{0.05}{0.5}$

$$= 0.1 \text{ M} = 10^{-1} \text{ M}$$

$\therefore$ pOH = 1 or pH = 14 – 1 = 13

2. **(d)**

3. **(a) :** $A + B^{2+} \longrightarrow A^{2+} + B$ has a positive EMF.

4. **(a) :** Eq. of O_2 = Eq. of Ag

($\because$ 1 mole Ag = 1 Eq. Ag)

$w_{O_2} = 8\,g$

$T = 298$ K, $P = \frac{750}{760}$ atm.

Now, $PV = \frac{w}{M}RT$

$$V_{O_2} = \frac{8}{32} \times \frac{0.0821 \times 298 \times 760}{750} = 6.20 \text{ litre}$$

5. **(a) :** For $Cu(OH)_2$, $K_{sp} = [Cu^{2+}]\,[OH^-]^2$

$\because$ $[H^+] = 10^{-14}$; thus $[OH^-] = 10^0 = 1$

Therefore, $$[Cu^{2+}] = \frac{K_{sp}}{[OH^-]^2} = \frac{1.0 \times 10^{-19}}{1} = 1.0 \times 10^{-19}$$

Now, E_{RP} for the couple of Cu^{2+}/Cu is

$$E_{RP} = E°_{RP} + \frac{0.059}{2}\log_{10}[Cu^{2+}]$$

$$= 0.34 + \frac{0.059}{2}\log_{10}[1 \times 10^{-19}] = -0.2205 \text{ V}$$

6. **(c) :** Net cell reaction :

$$Cd_{(s)} + 2Ag^+_{(aq)} \longrightarrow Cd^{2+}_{(aq)} + 2Ag_{(s)}$$

$$E_{cell} = E°_{cell} - \frac{0.059}{2}\log\frac{[Cd^{2+}]}{[Ag^+]^2}$$

7. **(a)**

8. **(d):** Equivalent conductance of 0.04 N weak acid

$$= \frac{1000 \times 4.23 \times 10^{-4}}{0.04}$$

$$= 10.575\ \Omega^{-1}\ cm^2\ equiv^{-1}$$

Also, α(degree of ionisation) $= \dfrac{\Lambda_{eq}}{\Lambda_{\infty}}$

$$0.0612 = \frac{10.575}{\Lambda_{\infty}}$$

$$\Lambda_{\infty} = 172.79\ \Omega^{-1}\ \text{cm}^2\ \text{equiv}^{-1}$$

9. (a): $E_1 = E^\circ - \dfrac{0.059}{1}\log[\text{H}^+]_1$

$\therefore\ E_2 = E^\circ - \dfrac{0.059}{1}\log[\text{H}^+]_2$

On adding (also $E^\circ_{\text{H}} = 0$)

$$E_1 + E_2 = -\frac{0.059}{1}[\log[\text{H}^+]_1 + \log[\text{H}^+]_2]$$

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

$$[\text{H}^+] = \frac{K_a[CH_3COOH]}{[CH_3COO^-]}$$

$$\therefore\ [\text{H}^+]_1 = K_a \times \frac{y}{x} \quad \therefore\ [\text{H}^+]_2 = K_a \times \frac{x}{y}$$

$$\therefore\ E_1 + E_2 = -\frac{0.059}{1}\left[\log\frac{K_a \cdot y}{x} + \log\frac{K_a \cdot x}{y}\right]$$

$= -0.059\ [2 \log K_a]$

$$\log K_a = \frac{E_1 + E_2}{2 \times (-0.059)} = -\frac{E_1 + E_2}{0.118}$$

or $\quad pK_a = \dfrac{E_1 + E_2}{0.118}$

10. (a) **11. (c, d)**

12. (b, c) : $2H_2O \rightleftharpoons 2H^+_{(aq)} + 2OH^-_{(aq)}$

Cathode : $2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

Anode : $2OH^-_{(aq)} \longrightarrow H_2O_{(l)} + \frac{1}{2}O_{2(g)} + 2e^-$

1 mole of H_2O electrolysed ≡ 2 mol of electrons ≡ 2 F (efficiency = 100%)

1 mole of H_2O electrolysed ≡ 4 mol of electrons ≡ 4 F (efficiency = 50%)

Hence, 5 mole of H_2O ≡ 5 × 4 = 20 F

Volume of gases (STP) = 5 × (22.4 + 11.2) = 168.0 L

13. (a, b, c, d) **14. (b)**

15. (b): On adding NH_3, H^+ ion concentration decreases. Hence, the second cell reaction will be affected for which,

$$E_{\text{Red}} = E^\circ_{\text{Red}} - \frac{0.0591}{n}\log[\text{H}^+]^2$$

$$= E^\circ_{\text{Red}} - \frac{0.0591}{2}\log[\text{H}^+]^2$$

$= E^\circ_{\text{Red}} - 0.0591 \log[\text{H}^+]$

$= E^\circ_{\text{Red}} + 0.0591\ \text{pH}$ $\quad\{-\log[\text{H}^+] = \text{pH}\}$

$= E^\circ_{\text{Red}} + 0.0591 \times 11$

$= E^\circ_{\text{Red}} + 0.65$ V

16. (b): The given concentration cell is

$M \mid M^{2+}$ (saturated $= C_1$) $\parallel M^{2+}$ (0.001 M $= C_2$) $\mid M$

EMF of concentration cell is :

$$E_{\text{cell}} = \frac{2.303\,RT}{nF}\log\frac{C_2}{C_1} = \frac{0.059}{n}\log\frac{C_2}{C_1}$$

$$\therefore\ 0.059 = \frac{0.059}{2}\log\frac{0.001}{C_1}$$

or $\quad 1 = \dfrac{1}{2}\log\dfrac{10^{-3}}{C_1}$ $\quad$ or $\quad \log 10^{-3} - \log C_1 = 2$

or $\quad -3 - \log C_1 = 2$ or $\log C_1 = -5$ or $C_1 = 10^{-5}$ M

For the salt MX_2,

$$\underset{S}{MX_2} \rightleftharpoons \underset{S}{M^{2+}} + \underset{2S}{2X^-}$$

$K_{sp} = (S)\,(2S)^2 = 4S^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$

17. (d) **18. (d)**

19. (b): (P) $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

$$E_{H^+/\frac{1}{2}H_2} = E^\circ - \frac{0.059}{1}\log\frac{1}{[\text{H}^+]}$$

$= 0 - 0.059$ pH $= -0.059 \times 2 = -0.118$ V

$\therefore$ Consider potential = 0.118 V

(Q) $E_{H^+/\frac{1}{2}H_2} = -\dfrac{0.059}{1}\log\dfrac{1}{0.5}$

$= -0.059 \log 2 = -0.018$ V

$\therefore$ Ox. potential = 0.018 V

(R) $E_{\text{cell}} = \dfrac{0.059}{1}\log\dfrac{C_2}{C_1}$

$= 0.059 \log\dfrac{0.1}{0.01} = 0.059$ V

(S) $E_{\text{cell}} = \dfrac{0.059}{1}\log\dfrac{0.4}{0.1}$

$= 0.0591 \log 4 = 0.035$ V

20. (b): KCl/NaCl/NH_4Cl etc. cannot be used as salt bridge in a cell containing silver as one of the electrodes because they react to form a precipitate of AgCl.

21. (b): Gold has higher reduction potential than the given metals. Hence, $AuCl_3$ will react with these metals.

22. (a) : $Zn_{(s)} + Cu^{2+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + Cu_{(s)}$
As the time passes, the concentration of Zn^{2+} keeps on increasing while the concentration of Cu^{2+} keeps on decreasing. At the same time voltage of the cell keeps on decreasing. When there is no change in concentration of Cu^{2+} and Zn^{2+} ions, voltmeter gives zero reading and this state is known as equilibrium.

23. (1) **24. (2)** **25. (5)**

d – and *f* – BLOCK ELEMENTS

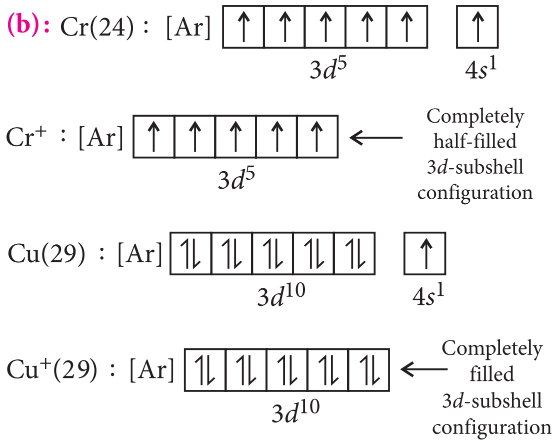
1. (c) : Cu^+ ion in aqueous solution disproportionates to $Cu_{(s)}$ and $Cu^{2+}_{(aq)}$.

2. (c) : Thermodynamic stability of the compounds of transition elements can be evaluated in terms of the magnitude of ionisation enthalpies of the metals – smaller the ionisation enthalpy of the metal, stable is its compound.

3. (a)

4. (a) : As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+}, the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $La(OH)_3$ is more basic whereas $Lu(OH)_3$ is least basic.

5. (b):



Both are stable configuration and removal of next electron requires very high energy. Thus, second IE is very high.

6. (b): $NO \longrightarrow NO^+ + e^-$
$Fe^{2+} + e^- \longrightarrow Fe^+(25\ e^-)$
(EAN = 25 + 12 = 37)

7. (d): In CrO_4^{2-}, Cr is in +6 oxidation and has d^0 configuration. The colour is due to charge transfer and not due to *d*-*d* transition.

8. (a) : Hg is liquid at 0°C which is due to its very high ionisation enthalpy and weak metallic bond as it has zero unpaired electron.

9. (d): F being highly electronegative and smaller in size forms F^- ion which is not polarised by the metal cation and thus forms an ionic bond.

10. (c) : Hence, the spin only magnetic moment

$$= \sqrt{n(n+2)} = \sqrt{2(2+2)} = \sqrt{8} = 2.83 \text{ B.M.}$$

11. (a, b, d) **12. (b, c)** **13. (c, d)** **14. (b)**

15. (b): $3K_2MnO_4 + 2CO_2 \longrightarrow$
$2KMnO_4 + MnO_2\downarrow + 2K_2CO_3$

16. (a) : The basic character of hydroxides of lanthanoids decreases with increase in atomic number. Hence, correct order is $X > Y > Z$.

17. (c) : Ce^{4+} becomes $[Xe]4f^0$ and Yb^{2+} becomes $[Xe]4f^{14}$

18. (b): MnO_4^{2-} ion is green and shows charge transfer transition, aq. Ti^{3+} ion shows *d*-*d* transitions and is purple in colour, MnO_4^- ions shows charge transfer transition and is purple in colour while aq. Cr^{3+} ion shows *d*-*d* transition and is green in colour.

19. (a) : Outer electronic configuration of Cr atom is $3d^5\ 4s^1$, Au is $5d^{10}\ 6s^1$, Pd is $4d^{10}\ 5s^0$ and Gd is $4f^7\ 5d^1\ 6s^2$.

20. (a) **21. (c)**

22. (b): $CrO_3 + 2HCl \xrightarrow{\Delta} CrO_2Cl_2 + H_2O$.

23. (7) **24. (3)** **25. (5)**

CLASS XII **Series 5**

ACE YOUR WAY CBSE

Haloalkanes and Haloarenes
Alcohols, Phenols and Ethers

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

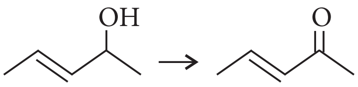
(i) All questions are compulsory.
(ii) Q. no. 1 to 5 are very short answer questions and carry 1 mark each.
(iii) Q. no. 6 to 10 are short answer questions and carry 2 marks each.
(iv) Q. no. 11 to 22 are also short answer questions and carry 3 marks each.
(v) Q. no. 23 is a value based question and carries 4 marks.
(vi) Q. no. 24 to 26 are long answer questions and carry 5 marks each.
(vii) Use log tables if necessary, use of calculators is not allowed.

Previous Years Analysis

	2016		2015		2014	
	Delhi	AI	Delhi	AI	Delhi	AI
VSA	1	2	2	2	1	1
SA-I	1	–	–	–	2	2
SA-II	2	2	2	2	–	1
VBQ	–	–	–	–	–	–
LA	–	–	–	–	–	–

1. Allyl chloride is more reactive than *n*-propyl chloride towards nucleophilic substitution reaction. Explain why?

2. Name a reagent used for the following conversion :



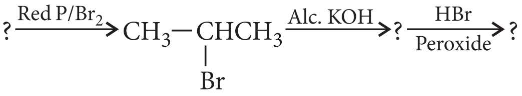
3. Which of the two $CH_3CH{=}CHCH_2Br$ or $CH_3CH(Br)CH{=}CH_2$ is achiral and chiral?

4. Although phenol is an acid, yet it does not react with sodium bicarbonate solution. Why?

5. Write the structure of 1-phenylpropan-2-ol.

6. Draw the structures of major monohalo products in each of the following reactions :

(i) $CH_3CH_2COO^-Ag^+ \xrightarrow{Br_2} ? \xrightarrow{Alc.\ KOH} ?$

(ii) 

$$? \xrightarrow{Red\ P/Br_2} CH_3-\underset{\displaystyle Br}{\underset{|}{C}}HCH_3 \xrightarrow{Alc.\ KOH} ? \xrightarrow[Peroxide]{HBr} ?$$

7. (i) Distinguish between 1-phenylethanol and 2-phenylethanol.

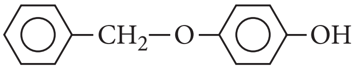
(ii) Arrange the following compounds in the decreasing order of their boiling points :
(a) Pentan-1-ol ; (b) 2-Methylbutan-2-ol ;
(c) 3-Methylbutan-2-ol

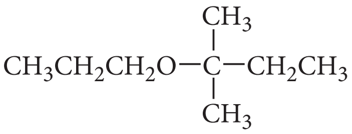
8. The *p*-isomer of dichlorobenzene has higher melting point than *o*- and *m*-isomer. Why?

OR

What are enantiomers? Draw the structures of the possible enantiomers of 3-methylpent-1-ene.

9. Give the major products that are formed by heating each of the following ethers with HI.

(i) 

(ii) 

$$CH_3CH_2CH_2O-\underset{\displaystyle CH_3}{\underset{|}{\overset{\displaystyle CH_3}{\overset{|}{C}}}}-CH_2CH_3$$

10. For the following reaction :

$$n\text{-BuBr} + \text{KCN} \xrightarrow{\text{EtOH-H}_2\text{O}} ?$$

(i) Write the resonating structures of KCN.
(ii) Which product will be formed preferentially in the presence of polar solvent?

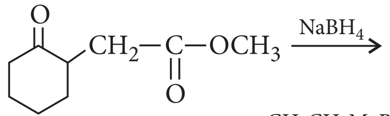
11. Compound *A* with molecular formula C_4H_9Br is treated with aq. KOH solution. The rate of this reaction depends upon the concentration of the compound *A* only. When another optically active isomer *B* of this compound was treated with aq. KOH solution, the rate of reaction was found to be dependent on concentration of compound and KOH both.
(i) Write down the structural formula of both compounds *A* and *B*.
(ii) Out of these two compounds, which one will be converted to the product with inverted configuration.

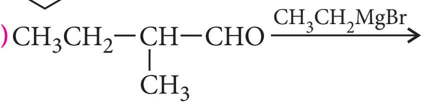
12. (i) How will you convert phenol to benzoic acid?
(ii) An organic compound *A* having molecular formula C_6H_6O gives a characteristic colour with aqueous $FeCl_3$ solution. *A* on treatment with CO_2 and NaOH at 400 K under pressure gives *B*, which on acidification gives a compound *C*. The compound *C* reacts with acetyl chloride to give *D* which is a popular pain killer. Deduce the structure of *A*, *B*, *C* and *D*.

13. (i) Give reasons :
(a) Racemic mixture is optically inactive.
(b) The presence of nitro group ($-NO_2$) at *o*/*p* positions increases the reactivity of haloarenes towards nucleophilic substitution reactions.
(ii) Explain the following :
Alkyl halides, though polar, are immiscible with water.

14. Write the structures of the products of the following reactions :

(i) $CH_3-CH=CH_2 \xrightarrow{H_2O/H^+}$

(ii) 

(iii) 

$$CH_3CH_2-\underset{\substack{|\\ CH_3}}{CH}-CHO \xrightarrow{CH_3CH_2MgBr}$$

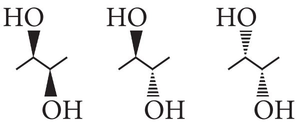
OR

Out of *ortho*-nitrophenol and *ortho*-methoxyphenol which one is more acidic and why? Write the resonating structures.

15. Why is iodination of benzene difficult?

16. An organic compound (*A*) reacts with PCl_5 to produce another compound (*B*). (*B*) reacts with magnesium metal in presence of ether to produce a Grignard reagent (*C*). (*C*) reacts with ethanal and the product is hydrolysed to produce propan-2-ol. Identify (*A*), (*B*) and (*C*) and explain the reactions.

17. Consider the following structures :

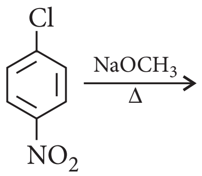


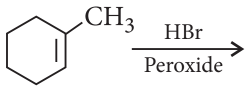
I II III

Which of these structures is/are :
(i) chiral **(ii)** achiral **(iii)** meso compound
(iv) enantiomers and **(v)** diastereomers?

18. (i) Explain the fact that in aryl alkyl ethers the alkoxy group activates the benzene ring towards electrophilic substitution and it directs the incoming substituents to *ortho* and *para* position in benzene ring. Write the equations involved.
(ii) Give the name of the alkyl halide and sodium alkoxide used to synthesise *tert*-butyl ethyl ether. Write the equation involved.

19. (i) What are the major products of the following reactions?

(a) 

(b) 

(ii) Write the IUPAC name of *o*-$BrC_6H_4CH(CH_3)CH_2CH_3$

20. (i) 3,3-Dimethylbutan-2-ol loses a molecule of water in the presence of concentrated sulphuric acid to give tetramethylethylene as the major product. Suggest a suitable mechanism.
(ii) Why do phenols not give protonation reactions readily in comparison to alcohols?

21. How will you carry out the following conversions :
(a) Benzyl alcohol to phenylethanenitrile
(b) But-1-ene to but-2-ene
(c) Isopropyl chloride to *n*-propyl chloride.

22. How is 1-propoxy propane synthesised from propan-1-ol? Explain any two reactions with mechanism.

23. Carbon tetrachloride (CCl_4) is widely used as a cleaning fluid in industry, as a degreasing agent and a spot remover at home and as a fire extinguisher. An NGO is demanding complete ban on the use of CCl_4.
Now answer the following questions :
(i) Write the structure and IUPAC name of carbon tetrachloride.
(ii) Why is the NGO demanding for ban on the use of this chemical? Give two reasons.

(iii) What value is associated with this demand of NGO?

24. (i) A compound *X* containing C, H and O is unreactive towards sodium. It does not react with bromine and Schiff's reagent. On refluxing with an excess of HI, *X* yields only one organic product *Y*. *Y* on hydrolysis yields a new compound *Z* which can be converted into *Y* by reaction with red phosphorus and iodine. The compound *Z* on oxidation with potassium permanganate gives a carboxylic acid. The equivalent weight of acid is 60. What are the compounds *X*, *Y* and *Z*? Write chemical equations leading to the conversion of *X* to *Y*.

(ii) Explain why is $O{=}C{=}O$ non-polar and $R{-}O{-}R$ is polar in nature ?

OR

Is acid-catalysed dehydration of secondary and tertiary alcohols a suitable method for the preparation of ethers? If not, explain why. Write mechanism of the reaction involved.

25. (i) How will you distinguish between the following (give one chemical test) :

(a) Chlorobenzene and chlorocyclohexane

(b) 3-Bromopropene and 1-bromopropane?

(ii) Propose mechanism of the reaction taking place when (–)-2-bromooctane reacts with sodium hydroxide to form (+)-octane-2-ol.

OR

(i) An aromatic compound $A(C_7H_8O)$ on reaction with bromine water gives a white ppt. of compound $B(C_7H_5OBr_3)$. Compound *A* is soluble in NaOH. Compound *C* which is isomer of *A* also gives the same reaction and give a white ppt. of compound $D(C_7H_5OBr_3)$ when reacts with bromine water. Compound *C* is insoluble in NaOH. Identify the compound *A* to *D*.

(ii) Arrange each set of compounds in order of increasing boiling points.

(a) Bromomethane, bromoform,
chloromethane, dibromomethane

(b) 1-chloropropane, *iso*-propylchloride,
1-chlorobutane.

26. (i) Show how will you synthesise :

(a) 1-phenylethanol from a suitable alkene

(b) cyclohexylmethanol using an alkyl halide by S_N2 reactions

(c) pentan-1-ol using a suitable alkyl halide?

(ii) Name the reagents and write the chemical equations for the preparation of the following compounds by Williamson's synthesis :

(a) Ethoxybenzene

(b) 2-Methyl-2-methoxypropane

OR

(i) Give chemical tests to distinguish between the following pairs of compounds :

(a) Pentan-2-ol and Pentan-3-ol

(b) Ethanol and Phenol

(ii) Write the equation involved in kolbe's reaction.

(iii) Name the different reagents needed to perform the following reactions :

(a) Phenol to Benzene

(b) Dehydration of propan-2-ol to propene

(c) Friedel-Crafts alkylation of anisole

(d) Dehydrogenation of ethanol to ethanal

SOLUTIONS

1. Allyl chloride is more reactive than *n*-propyl chloride towards nucleophilic substitution reaction. Due to the greater stabilisation of allylic carbocation intermediate formed by resonance.

$$H_2C{=}CH{-}H_2\overset{+}{C} \longleftrightarrow H_2\overset{+}{C}{-}CH{=}CH_2$$

2. Corey's reagent or pyridinium chlorochromate ($PCC, CrO_3.C_5H_5N.HCl$ or $C_5H_5NH^+CrO_3Cl^-$). It oxidises $>$CHOH to $>$C=O without carrying out oxidation of double bond.

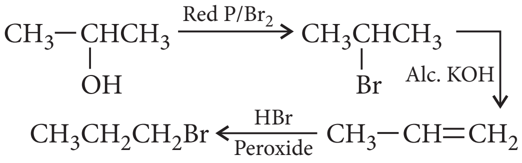
3. $CH_3CH{=}CHCH_2Br$ is achiral because it does not contain chiral carbon atom whereas $CH_3\overset{*}{C}H(Br)CH{=}CH_2$ is chiral because it contains chiral carbon atom.

4. As phenol is weaker acid than the carbonic acid and therefore, does not liberate CO_2 from sodium bicarbonate.

5. $C_6H_5{-}\overset{1}{C}H_2{-}\overset{2}{C}H(OH){-}\overset{3}{C}H_3$

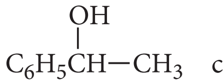
6. (i) $CH_3CH_2COO^-Ag^+ \xrightarrow{Br_2} CH_3CH_2Br \xrightarrow{Alc.\ KOH} H_2C{=}CH_2$

(ii)



$$\underset{\underset{OH}{|}}{CH_3{-}CHCH_3} \xrightarrow{Red\ P/Br_2} \underset{\underset{Br}{|}}{CH_3CHCH_3} \xrightarrow{Alc.\ KOH} CH_3{-}CH{=}CH_2 \xrightarrow[Peroxide]{HBr} CH_3CH_2CH_2Br$$

7. (i) 1-Phenylethanol,



$$C_6H_5\overset{\overset{OH}{|}}{C}H{-}CH_3$$

contains $-CH(OH)CH_3$ group and therefore, it will give iodoform test.

$$C_6H_5CH(OH)CH_3 \xrightarrow{I_2,\ NaOH} \underset{\text{Yellow ppt.}}{CHI_3} \uparrow$$

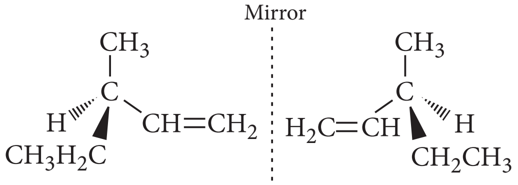
On the other hand, 2-phenylethanol, $C_6H_5CH_2CH_2OH$ does not contain $-CH(OH)CH_3$ group and therefore, it will not give iodoform test.

(ii) (a) > (c) > (b). This is because with branching the shape becomes spherical and therefore, van der Waals' forces decrease. As a result, boiling point decreases.

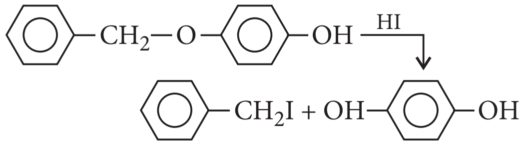
8. The melting point of *para*-isomer is quite higher than that of *ortho* or *meta*-isomers. This is due to the fact that *p*-isomer has symmetrical structure and therefore, its molecules can easily pack closely in crystal lattice. As a result intermolecular forces of attraction are stronger and therefore, greater energy is required to break its lattice and it melts at higher temperature.

OR

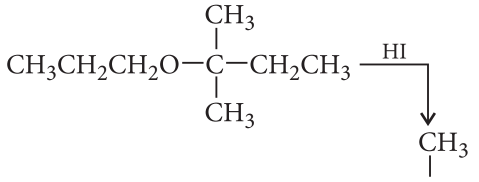
Stereoisomers which are non superimposable mirror images of each other are called enantiomers. The enantiomers of 3-methylpent-1-ene are :



9. (i)



(ii)



$$CH_3CH_2CH_2O-\underset{CH_3}{\overset{CH_3}{C}}-CH_2CH_3 \xrightarrow{HI} CH_3CH_2CH_2OH + CH_3CH_2-\underset{CH_3}{\overset{CH_3}{C}}-I$$

10. (i) Resonating structures of KCN are :

$$K^+[:\overset{-}{C}\equiv N:] \longleftrightarrow [:C=\ddot{N}:]K^+$$

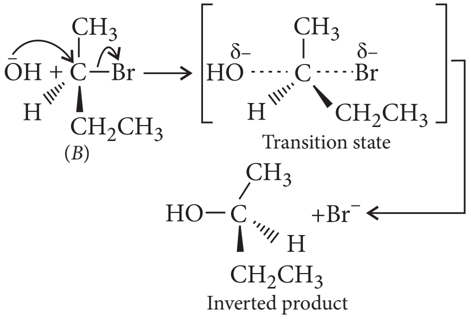
(ii) Cyanide ion is an ambident nucleophile. It can attack through C-atom or through N-atom. Thus, two possible products are cyanides and isocyanides, respectively. In the presence of the polar solvent, KCN readily ionises to furnish ions K^+ and CN^-. As C—C bond is more stable than C—N bond, so cyanide is predominantly formed.

$$KCN + \underset{n\text{-butyl bromide}}{CH_3-CH_2-CH_2-CH_2-Br} \longrightarrow \underset{n\text{-butyl cyanide}}{CH_3-CH_2-CH_2-CH_2C\equiv N} + KBr$$

11. (i) As the rate of reaction depends upon the concentration of compound *A* (C_4H_9Br) only therefore, the reaction is proceeded by S_N1 mechanism and the given compound will be tertiary alkyl halide, *i.e.*, 2-bromo-2-methylpropane and the structure (*A*) is $(CH_3)_3CBr$.

Optically active isomer of *A* is 2-bromobutane and its structural formula (*B*) is $CH_3CH_2\overset{*}{C}H(Br)CH_3$.

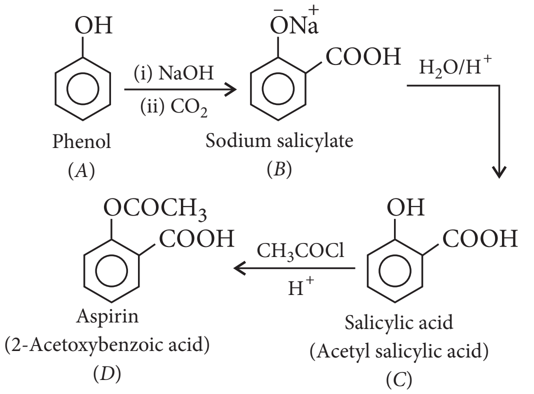
(ii) The rate of reaction of compound *B* depends both upon the concentration of compound *B* and KOH. Hence, the reaction follow S_N2 mechanism. In S_N2 reaction, nucleophile attack from, the backside, therefore the product of hydrolysis will have opposite configuration.



12. (i)

$$\underset{\text{Phenol}}{C_6H_5OH} \xrightarrow[\Delta]{\text{Zn dust}} \underset{\text{Benzene}}{C_6H_6} \xrightarrow{CH_3Cl/AlCl_3} \underset{\text{Toluene}}{C_6H_5CH_3} \xrightarrow[{[O]}]{KMnO_4/H_2SO_4} \underset{\text{Benzoic acid}}{C_6H_5COOH}$$

(ii)

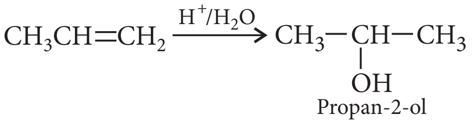


13. (i) (a) Racemic mixture contains equal amount of *d* and *l* forms, hence rotation due to one enantiomer is cancelled by another.

(b) The presence of nitro group at *o*-and *p*-positions withdraws electrons from the benzene ring and thus, facilitates the attack of the nucleophile on haloarenes. The carbanion thus formed is further stabilised by resonance.

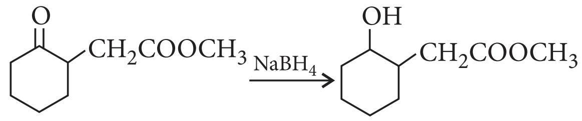
(ii) Alkyl halides are polar but are insoluble in water because energy required to break the intermolecular H–bond among water molecules is much higher than energy released by water halide interaction.

14. (i)



$$CH_3CH=CH_2 \xrightarrow{H^+/H_2O} \underset{\text{Propan-2-ol}}{CH_3-\underset{OH}{CH}-CH_3}$$

(ii)

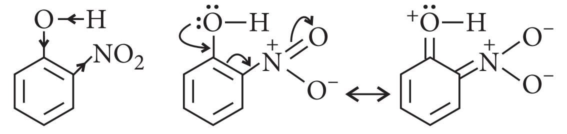


(iii) $CH_3CH_2CH(CH_3)CHO \xrightarrow[2.\ H_2O]{1.\ CH_3CH_2MgBr} CH_3CH_2CH(CH_3)CH(OH)CH_2CH_3$

4-Methylhexan-3-ol

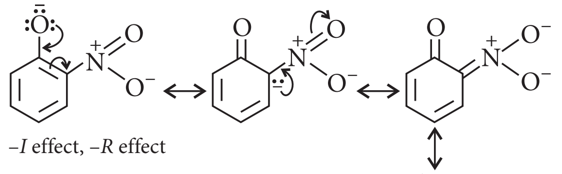
OR

o-Nitrophenol is more acidic than *o*-methoxyphenol, due to strong –*R* and –*I* effect of the —NO_2 group, electron density in the O—H bond decreases and hence, the loss of a proton becomes easy.



–*I* effect, –*R* effect

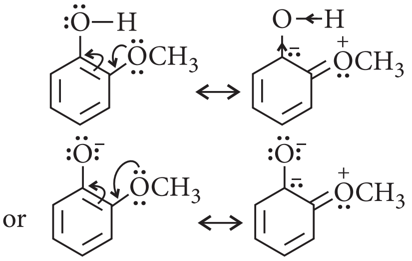
Now, after the loss of a proton, the *o*-nitrophenoxide ion left behind is stabilised by resonance and thus making *o*-nitrophenol, a stronger acid.



–*I* effect, –*R* effect

and so on

In contrast, due to +*R* effect, –OCH_3 group increases the electron density in the O—H bond. Thereby making the loss of proton difficult.



Now, the *o*-methoxyphenoxide ion left after the loss of a proton is not stabilised by resonance. The two negative charges repel each other, thereby destabilising the *o*-methoxyphenoxide ion. Therefore, *o*-nitrophenol is more acidic than *o*-methoxyphenol.

15. The reasons are :

(i) I_2 is least reactive element of all the halogens because C—I bond formed is much weaker than C—Cl and C—Br bonds.

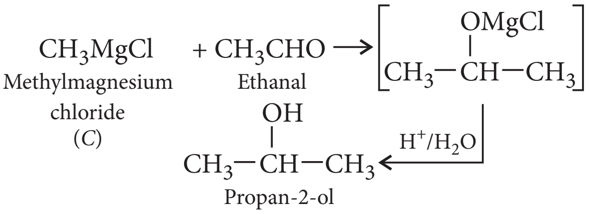
(ii) The reaction is reversible because HI produced during the reaction, being a reducing agent reduces iodobenzene, thus formed back to benzene.

$$C_6H_6 + I_2 \rightleftharpoons C_6H_5I + HI$$

Therefore, to push the reaction in the forward direction, iodination is usually carried out in presence of an oxidising agent such as nitric acid or iodic acid (HIO_3) which oxidises HI to I_2. Iodination can also be carried out in presence of mercuric oxide which eliminates HI as insoluble mercuric iodide.

$$2HI + 2HNO_3 \longrightarrow 2NO_2 + 2H_2O + I_2$$
$$5HI + HIO_3 \longrightarrow 3I_2 + 3H_2O$$
$$HgO + 2HI \longrightarrow HgI_2 + H_2O$$

16. (i) Since propan-2-ol is obtained by the action of a Grignard reagent (*C*) on ethanal followed by hydrolysis, therefore, Grignard reagent (*C*) must be CH_3MgCl.



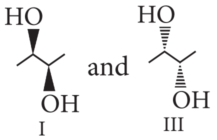
(ii) Since CH_3MgCl is obtained by the action of Mg metal on compound (*B*), therefore, compound (*B*) must be methyl chloride, CH_3Cl.

$$\underset{\substack{\text{Methyl chloride}\\(B)}}{CH_3Cl} + Mg \xrightarrow{\text{Ether}} \underset{\substack{\text{Methylmagnesium chloride}\\(C)}}{CH_3MgCl}$$

(iii) Since CH_3Cl is formed by the action of PCl_5 on compound (*A*), therefore, compound (*A*) must be methanol, CH_3OH.

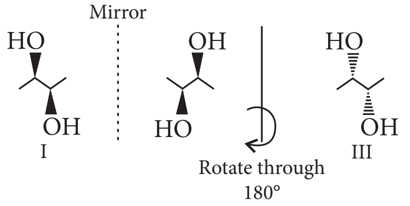
$$\underset{\substack{\text{Methanol}\\(A)}}{CH_3OH} + PCl_5 \longrightarrow \underset{\substack{\text{Methyl chloride}\\(B)}}{CH_3Cl} + POCl_3 + HCl$$

17. Structures I and III do not have a plane or a centre of symmetry and hence are chiral.

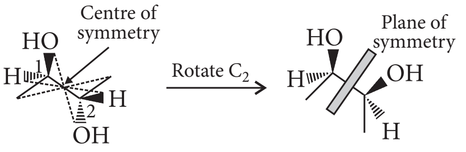


I III

Actually I and III are enantiomers as shown below :



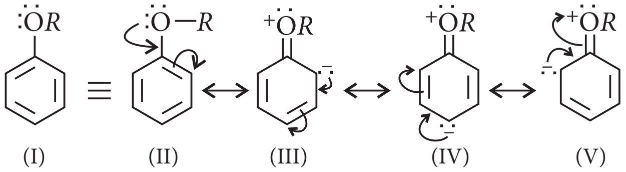
Structure (II) has a centre of symmetry and hence is achiral. It also has a plane of symmetry as shown below. Therefore, structure (II) represents a *meso*-compound.



II

Finally, structures (I and II) and (II and III) are not mirror images and hence are diastereomers.

18. (i) The alkoxy group increases the electron density on the benzene ring and therefore, activates the aromatic ring towards electrophilic substitution reaction as given below :

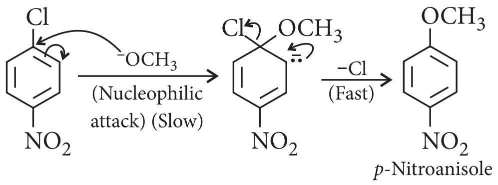


As it is clear from the structures III, IV and V that electron density is higher at *ortho* and *para* positions and therefore, direct the incoming substituents to *o*- and *p*-position in the benzene ring.

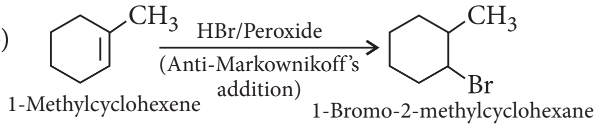
(ii) Ethyl bromide and sodium *tert*-butoxide.

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} + \underset{\text{Sod } tert\text{-butoxide}}{Na^+\bar{O}C(CH_3)_3} \xrightarrow{\Delta} \underset{tert\text{-Butyl ethyl ether}}{CH_3CH_2OC(CH_3)_3} + NaBr$$

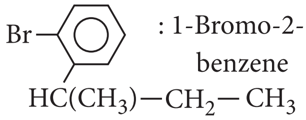
19. (i) (a)



(b)

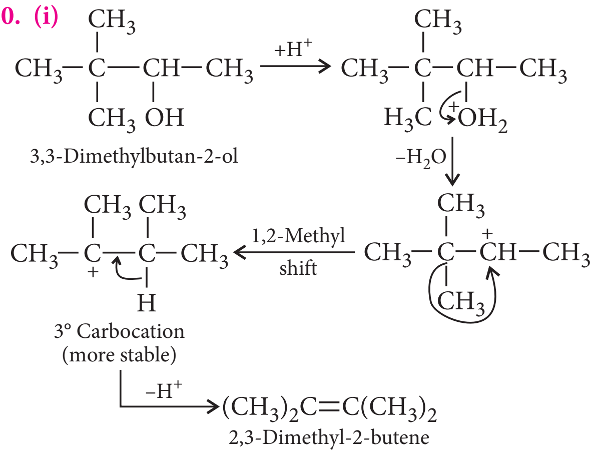


(ii)

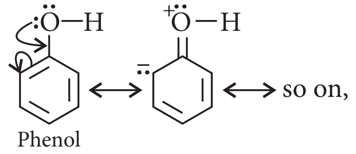


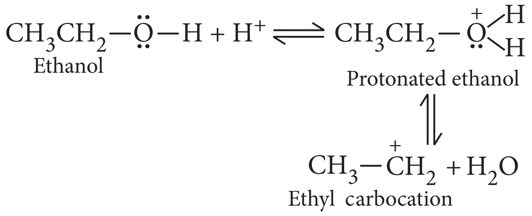
: 1-Bromo-2-(1-methylpropyl) benzene

20. (i)

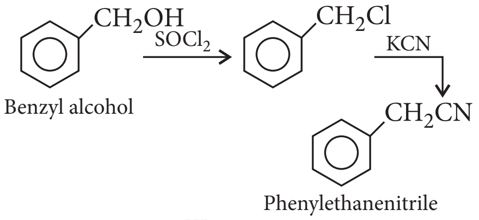


(ii) In phenols, the lone pairs of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily available for protonation whereas, in case of alcohols, the lone pairs of electrons on the oxygen atom are localised due to absence of resonance and hence are easily available for protonation.

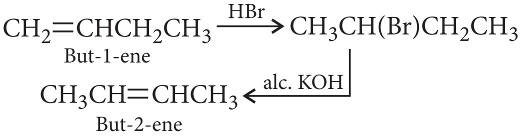




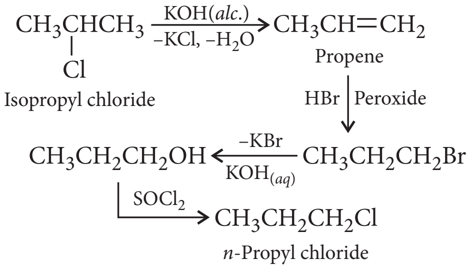
21. (a)



(b)



(c)



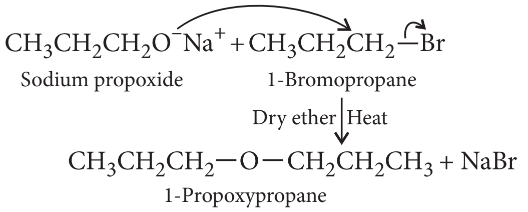
22. Two methods can be employed for this preparation :

(i) Williamson's synthesis :

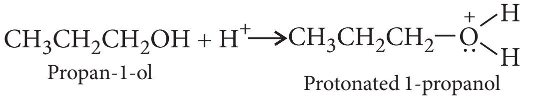
(a) $\underset{\text{Propan-1-ol}}{3CH_3CH_2CH_2OH} + PBr_3 \longrightarrow \underset{\text{1-Bromopropane}}{3CH_3CH_2CH_2Br} + H_3PO_3$

(b) $\underset{\text{Propan-1-ol}}{2CH_3CH_2CH_2OH} + 2Na \longrightarrow$

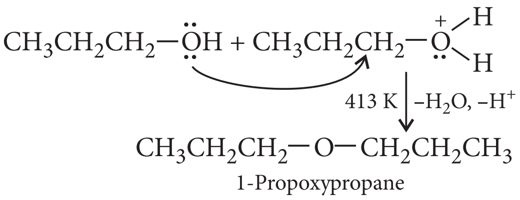
$\underset{\text{Sodium propoxide}}{2CH_3CH_2CH_2O^-Na^+} + H_2$



(ii) By dehydration of 1-propanol with conc. H_2SO_4 at 413 K



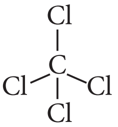
$$\underset{\text{Propan-1-ol}}{CH_3CH_2CH_2OH} + H^+ \longrightarrow \underset{\text{Protonated 1-propanol}}{CH_3CH_2CH_2-\overset{+}{\ddot{O}}\begin{smallmatrix}H\\H\end{smallmatrix}}$$



$$CH_3CH_2CH_2-\ddot{O}H + CH_3CH_2CH_2-\overset{+}{O}H_2 \xrightarrow[413\ K]{-H_2O,\ -H^+} CH_3CH_2CH_2-O-CH_2CH_2CH_3$$

1-Propoxypropane

23. (i) Structure :



Hybridisation : sp^3

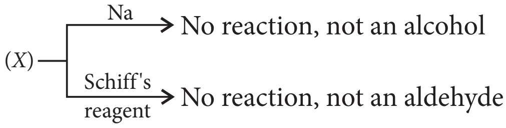
Structure : Tetrahedral

IUPAC name : Tetrachloromethane

(ii) There are evidences that exposure to carbon tetrachloride causes cancer and many other fatal diseases in humans. Carbon tetrachloride released in air rises to the atmosphere and depletes ozone layer. This depletion increases human exposure to ultraviolet rays leading to skin cancer and disruption of immune system.

(iii) Judicious use of chemicals to save atmosphere and human health.

24. (i) Compound X must be a symmetrical ether.



$$(X) \xrightarrow{Na} \text{No reaction, not an alcohol}$$

$$(X) \xrightarrow{\text{Schiff's reagent}} \text{No reaction, not an aldehyde}$$

$$\underset{(X)}{R-O-R} \xrightarrow{HI} \underset{(Y)}{2R-I}$$

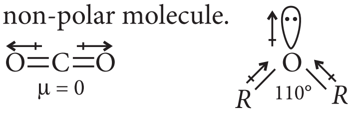
$$\begin{tikzcd} \underset{(Y)}{R-I} \arrow[r, "H_2O"] & \underset{(Z)}{R-OH} \arrow[r, "{[O]}"] \arrow[d, "I_2/P"] & \underset{\text{Eq. wt.} = 60}{\text{Acid}} \\ & \underset{(Y)}{R-I} & \end{tikzcd}$$

∴ Acid is CH_3COOH and $Z = CH_3CH_2OH$

$X = C_2H_5-O-C_2H_5$; $Y = CH_3-CH_2-I$

$$\underset{(X)}{CH_3CH_2-O-CH_2CH_3} \xrightarrow{HI} \underset{(Y)}{2CH_3CH_2I}$$

(ii) CO_2 is a linear molecule. The dipole moment of two C=O bonds are equal and opposite and they cancel each other. Hence the dipole moment of CO_2 is zero and it is a non-polar molecule.

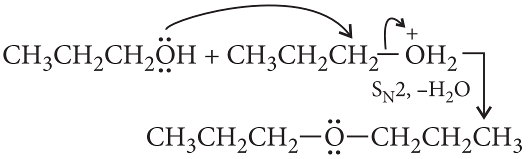


$\mu = 1.18\ D\ (R = C_2H_5)$

While for ethers, two dipoles are pointing in the same direction. These two dipoles do not cancel the effect of each other. Therefore, there is a finite resultant dipoles. Hence $R-O-R$ is a polar molecule.

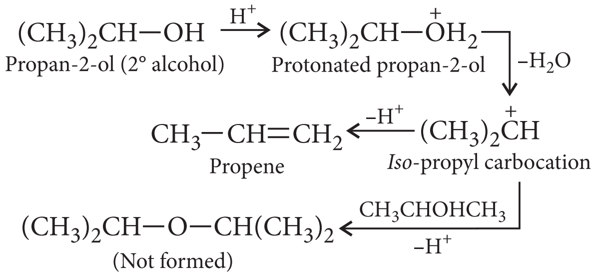
OR

Acid-catalysed dehydration of secondary and tertiary alcohols is not a suitable method for the preparation of ethers. Acid catalysed dehydration of 1° alcohols to ethers occurs by S_N2 reaction involving nucleophilic attack by the alcohol molecule on the protonated alcohol molecule.



$$CH_3CH_2CH_2\ddot{O}H + CH_3CH_2CH_2-\overset{+}{O}H_2 \xrightarrow{S_N2,\ -H_2O} CH_3CH_2CH_2-\ddot{O}-CH_2CH_2CH_3$$

Under these conditions, 2° and 3° alcohols, however give alkenes rather than ethers. The reason is that due to steric hindrance, nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur. Instead protonated 2° and 3° alcohols lose a water molecule to form stable 2° and 3° carbocations. These carbocations prefer to lose a proton to form alkenes rather than undergoing nucleophilic attack by alcohol molecule to form ethers.

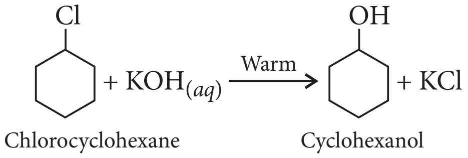


$$\underset{\text{Propan-2-ol (2° alcohol)}}{(CH_3)_2CH-OH} \xrightarrow{H^+} \underset{\text{Protonated propan-2-ol}}{(CH_3)_2CH-\overset{+}{O}H_2} \xrightarrow{-H_2O} \underset{\textit{Iso}\text{-propyl carbocation}}{(CH_3)_2\overset{+}{C}H}$$

$$\underset{\text{Iso-propyl carbocation}}{(CH_3)_2\overset{+}{C}H} \xrightarrow{-H^+} \underset{\text{Propene}}{CH_3-CH=CH_2}$$

$$(CH_3)_2\overset{+}{C}H \xrightarrow[-H^+]{CH_3CHOHCH_3} \underset{\text{(Not formed)}}{(CH_3)_2CH-O-CH(CH_3)_2}$$

25. (i) (a) Chlorobenzene and chlorocyclohexane : Add a small quantity of aqueous KOH to each compound. Acidify with dil. HNO_3 and add silver nitrate solution. Chlorocyclohexane when heated with aq. KOH undergoes hydrolysis to give potassium chloride. Potassium chloride reacts with silver nitrate to give white ppt. of AgCl.



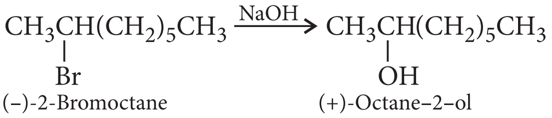
$$KCl + AgNO_3 \longrightarrow \underset{\text{(White ppt.)}}{AgCl} + KNO_3$$

Chlorobenzene does not undergo hydrolysis under these conditions to produce phenol and KCl with aq. KOH. Therefore, it does not give white ppt.

$$\underset{\text{Chlorobenzene}}{C_6H_5Cl} + KOH_{(aq)} \xrightarrow{\text{Heat}} \text{No reaction}$$

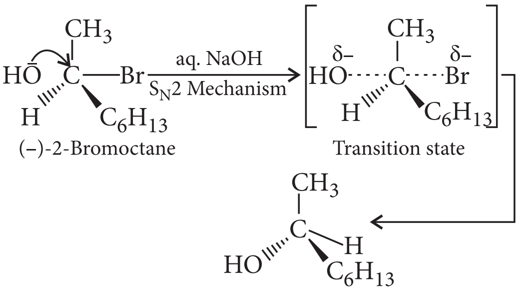
(b) 3-Bromopropene (allyl bromide) and 1-bromopropane (alkyl bromide) : Add a small amount of dil. alkaline $KMnO_4$ solution (Baeyer's reagent) to each compound and shake. 3-Bromopropene ($CH_2=CHCH_2Br$) decolourises pink colour of $KMnO_4$ while 1-bromopropane ($CH_3CH_2CH_2Br$) does not.

(ii)



$$CH_3\underset{\underset{Br}{|}}{C}H(CH_2)_5CH_3 \xrightarrow{NaOH} CH_3\underset{\underset{OH}{|}}{C}H(CH_2)_5CH_3$$

(−)-2-Bromoctane (+)-Octane–2–ol

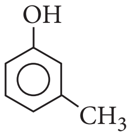


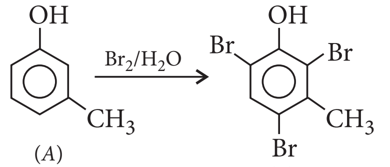
(−)-2-Bromoctane Transition state

(+)-Octane–2–ol

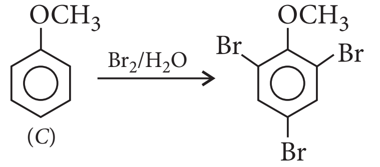
OR

(i) The aromatic compound (*A*) is





(*A*) (*B*)



(*C*) (*D*)

(ii) (a) Boiling point increases with increase in molecular mass. It also depends on the size and number of halogen atoms. Therefore, the arrangement of the given compounds in order of increasing boiling points is as follows :

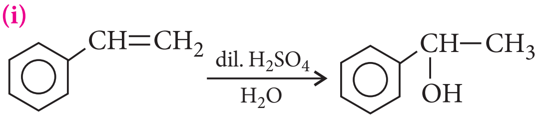
$CH_3Cl < CH_3Br < CH_2Br_2 < CHBr_3$

(b) For the same halogen, boiling point increases with increase in size of the alkyl group. Further the boiling point decreases as the branching increases. Therefore, the arrangement of the given compounds in the order of increasing boiling points is as follows :

$(CH_3)_2CHCl < ClCH_2CH_2CH_3 < ClCH_2CH_2CH_2CH_3$

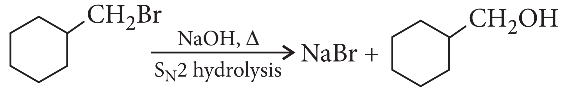
26. (i)

(a)



Ethenyl benzene 1-Phenylethanol

(b)



Cyclohexylmethyl bromide Cyclohexylmethanol

(c) $CH_3CH_2CH_2CH_2CH_2Br + NaOH$

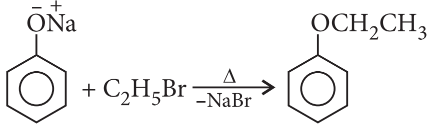
1-Bromopentane

$$\Big\downarrow \Delta \;\; S_N2 \text{ hydrolysis}$$

$NaBr + CH_3CH_2CH_2CH_2CH_2OH$

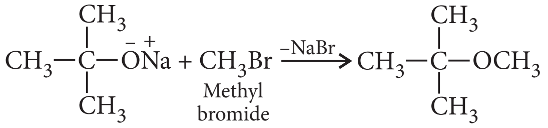
Pentan-1-ol

(ii) (a)



Sodium phenoxide Ethyl bromide Ethoxybenzene

(b)



$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{-}{O}\overset{+}{Na} + CH_3Br \xrightarrow{-NaBr} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OCH_3$$

Sodium *tert*-butoxide Methyl bromide 2-Methoxy-2-methyl propane

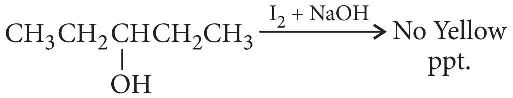
OR

(i) (a) On adding I_2 and NaOH, 2-pentanol will give yellow precipitate of iodoform whereas 3-pentanol will not give yellow precipitate.

$$CH_3-CH(OH)-CH_2CH_2CH_3 \xrightarrow{I_2 + NaOH} CHI_3 + CH_3CH_2CH_2CO\overset{-}{O}\overset{+}{Na}$$

2-Pentanol

Yellow ppt.



$$CH_3CH_2\underset{\underset{OH}{|}}{C}HCH_2CH_3 \xrightarrow{I_2 + NaOH} \text{No Yellow ppt.}$$

3-Pentanol

(b) Distinction between ethanol and phenol :

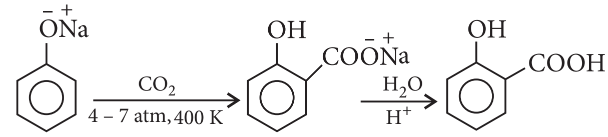
$FeCl_3$ test : Phenol gives a violet colouration with $FeCl_3$ solution while ethanol does not.

$3C_6H_5OH + FeCl_3 \longrightarrow (C_6H_5O)_3Fe + 3HCl$

Phenol Violet colouration

$C_2H_5OH + FeCl_3 \longrightarrow$ No violet colouration.

(ii) Kolbe's reaction : When sodium phenoxide is heated with carbon dioxide under pressure, it gives salicylic acid.



Sod. phenoxide Sod. salicylate Salicylic acid

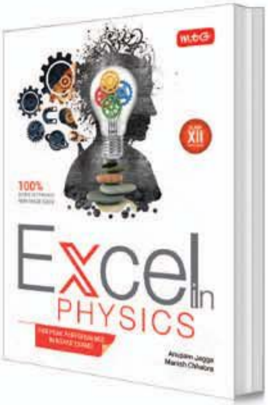
(iii) (a) Zinc dust

(b) Concentrated H_2SO_4

(c) Alkyl halide in the presence of anhydrous aluminium chloride, CH_3Cl and $AlCl_3$ (anhyd).

(d) Cu/573 K

◆◆



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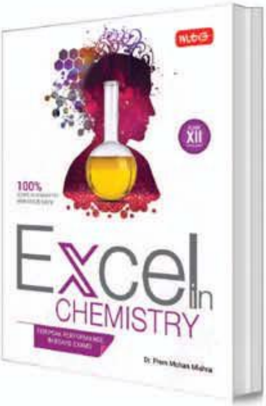

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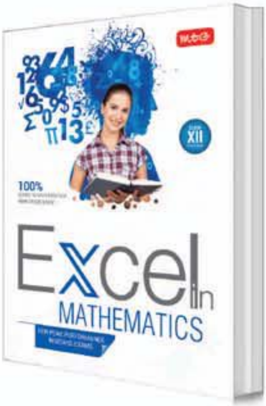

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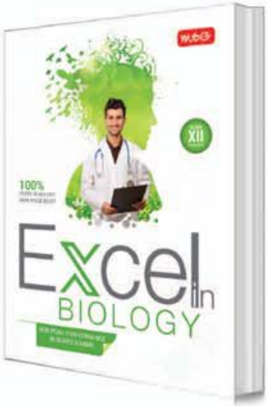

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MPP-4 MONTHLY Practice Problems


Class XII

This specially designed column enables students to self analyse their extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer.

Self check table given at the end will help you to check your readiness.

General Principles and Processes of Isolation of Elements
The *p*-Block Elements (Group 15 to 18)

Total Marks : 120 **Time Taken : 60 Min.**

NEET / AIIMS

Only One Option Correct Type

1. The correct order of decreasing acid strength of oxy acids of group 15 elements is
(a) $HNO_3 > H_3SbO_4 > H_3AsO_4 > H_3PO_4$
(b) $H_3PO_4 > H_3AsO_4 > H_3SbO_4 > HNO_3$
(c) $HNO_3 > H_3PO_4 > H_3AsO_4 > H_3SbO_4$
(d) $HNO_3 > H_3AsO_4 > H_3PO_4 > H_3SbO_4$

2. '925 Fine silver' mean
(a) 9.5% Ag + 90.75% Cu
(b) 92.5% Ag + 7.5% Cu
(c) 9.25% Cu + 90.75% Ag
(d) 7.5% Ag + 92.5% Cu

3. Hypo is used in photography to
(a) reduce AgBr grains to metallic Ag.
(b) convert metallic Ag to silver salt.
(c) remove undecomposed AgBr as soluble complex.
(d) remove reduced Ag.

4. The function of potassium ethyl xanthate in froth floatation process is to make the ore
(a) attracted towards water
(b) water repellant
(c) lighter
(d) heavier.

5. The reaction of the type, $2X_2 + S \longrightarrow SX_4$ is shown by sulphur when X is
(a) fluorine or chlorine
(b) chlorine only
(c) chlorine and bromine only
(d) F, Cl, Br all.

6. Which of the following statements is correct?
(a) Anthracite and chalcocite are both ores of copper.
(b) Anthracite and chalcocite are both sulphide ores.
(c) Both German silver and horn silver have zero percent silver content.
(d) Malachite and azurite are both basic copper carbonates.

7. CO_2 is passed through sodium metaborate solution. The states of hybridization of B in the product are
(a) sp^2
(b) sp^3d
(c) sp^3 and sp^2
(d) dsp^2

8. Consider the following reactions at 1000°C,

$$\text{I.}\quad Zn_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow ZnO_{(s)}\,;\Delta G° = -360\ \text{kJ mol}^{-1}$$

$$\text{II.}\quad C_{(\text{graphite})} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}\,;\Delta G° = -460\ \text{kJ mol}^{-1}$$

Choose the correct statement at 1000°C.
(a) Zinc can be oxidised by CO.
(b) Zinc oxide can be reduced by graphite.
(c) Both statements (a) and (b) are true.
(d) CO can be reduced by zinc.

9. In Fischer-Ringe's method of separation of noble gases mixture from air, the compound used is
(a) 90% $CaCO_3$ + 10% NH_2CONH_2
(b) coconut charcoal
(c) soda lime + potash solution
(d) 90% CaC_2 + 10% $CaCl_2$.

10. Si of high purity to be used in semiconductors can be prepared by following methods :

I. $SiO_2 + 2C \longrightarrow Si + 2CO$

II. $Si + 2Cl_2 \longrightarrow SiCl_4$

$SiCl_4 + 2Mg \longrightarrow Si + 2MgCl_2$

Better method is

(a) I (b) II

(c) both (I) and (II) (d) none of these.

11. $NH_4Cl_{(s)}$ is heated in a test tube. Vapours are brought in contact with red litmus paper, which changes to blue and then to red. It is because of

(a) formation of NH_4OH and HCl

(b) formation of NH_3 and HCl

(c) greater diffusion of NH_3 than HCl

(d) greater diffusion of HCl than NH_3.

12. Tempering of steel

(a) is heating the steel to appropriate temperature and then cooling it rapidly

(b) increases mechanical strength

(c) changes ratio of carbon in cementite

(d) all of the above.

Assertion & Reason Type

Directions : In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true 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 both assertion and reason are false.

13. **Assertion :** Conc. HNO_3 can be stored in Al vessel.

Reason : The surface of Al vessel gets coated with the impervious layer of Al_2O_3 on reaction with conc. HNO_3.

14. **Assertion :** Al cannot reduce MgO below 1500°C while Al can reduce MgO above 1500°C.

Reason : Mg is a liquid at less than 1500°C and gas at above 1500°C.

15. **Assertion :** Cl_2 or Br_2 changes KI into I_2 (violet in CCl_4 layer), Cl_2 changes KBr into Br_2 (orange-yellow in CCl_4 layer). Thus, Cl_2 would change mixture of KI and KBr into violet layer in CCl_4.

Reason : Oxidising power is in order : $I_2 < Br_2 < Cl_2 < F_2$.

JEE MAIN / JEE ADVANCED / PETs

Only One Option Correct Type

16. Roasting of sulphides gives the gas *X* as a byproduct. This is a colourless gas with choking smell of burnt sulphur and causes great damage to respiratory organs as a result of acid rain. Its aqueous solution is acidic, acts as a reducing agent and its acid has never been isolated. The gas *X* is

(a) H_2S (b) SO_2 (c) CO_2 (d) SO_3

17. A compound (*A*) forms an unstable pale blue coloured solution in water which rapidly decomposes even in the cold. The solution acts as reducing agent and decolourises bromine water. It also oxidises $SnCl_2$ in dil. HCl solution. It also shows complex forming ability. The compound (*A*) is

(a) HNO_3 (b) HNO_2 (c) $CuSO_4$ (d) N_2O_3

18. Oxygen is more electronegative than sulphur, yet H_2S is acidic while H_2O is neutral. This is because

(a) water is a highly associated compound

(b) H—S bond is weaker than H—O bond

(c) H_2S is a gas while H_2O is a liquid

(d) the molecular mass of H_2S is more than that of H_2O.

19. Identify *M* and *N* in the following reaction.

$$\text{Copper glance} \xrightarrow[\text{in presence of air}]{\text{controlled heating}} M + SO_2$$

$$M \xrightarrow{N} Cu + SO_2\uparrow$$

(a) $M = Cu_2O$; N = Self reduction

(b) $M = Cu_2O + Cu_2S$; N = Only heating

(c) $M = Cu_2O$; N = Carbon reduction

(d) $M = Cu_2O$; N = Electrolytic reduction

More than One Options Correct Type

20. N_2O_4 reacts with NaOH to produce a colourless solution. The correct statements among the following for this reaction are

(a) It can give the brown ring test for nitrate.

(b) It reacts with $AgNO_3$ to give white ppt.

(c) It decolourises $KMnO_4$ solution.

(d) After treatment with $AgNO_3$, ppt. is filtered and filtrate is treated with Zn + AcOH, and the resulting solution does not respond towards Grises-Ilosvay test.

21. Consider the following steps :

$$\text{Copper pyrite} \xrightarrow{\text{roast in air}} A + B + C$$

$$A + O_2 \longrightarrow D + C$$

Which of the following statements are correct?

(a) *A* is Cu_2S and *B* is FeS.
(b) *A* is Cu_2S and *B* is FeO.
(c) *C* is SO_2
(d) *D* is FeO.

22. The following side reaction in the production of N_2H_4,
$N_2H_4 + 2NH_2Cl \longrightarrow N_2 + 2NH_4Cl$
(a) is catalysed by traces of heavy metals as Cu^{2+}.
(b) is suppressed by addition of gelatin or glue.
(c) is made reversible by removing N_2.
(d) is made reversible by adding NaOH.

23. During the production of iron and steel,
(a) the oxide ore is primarily reduced to iron by solid coke according to the reaction,
$2Fe_2O_3 + 3C \longrightarrow 4Fe + 3CO_2$
(b) the oxide ore is reduced by the carbon monoxide according to the reaction,
$Fe_2O_3 + 3CO \longrightarrow 2Fe + 3CO_2$
(c) major silica impurities are removed as calcium silicate slag by addition of a fluxing agent limestone
(d) the silicate slag is used in manufacturing cement.

Integer Answer Type

24. Among the following metals, how many metals are extracted by self-reduction method from their respective ores?
Hg, Zn, Al, Mg, Pb, Fe, Sn, Cu

25. Among PbS, CuS, HgS, MnS, Ag_2S, NiS, CoS, Bi_2S_3 and SnS_2, the total number of black coloured sulphides is

26. Among the following, the number of ions/molecules having at least one atom *sp* hybridized is
C_3S_2, NO_2^-, NO_2^+, benzene, benzyne, diazonium cation, $C_6H_5^+$, C_3^{4-}, $Cr_2O_7^{2-}$, CaC_2,$(SCN)_2$

Comprehension Type

Peroxydisulphuric acid and its salts are powerful oxidising agents, thus can be used to estimate reducing agents and also to study the kinetics of the reaction.

27. Peroxydisulphuric acid
(a) is also called Marshall's acid
(b) has two peroxy linkages
(c) liberates I_2 with KI in a fast reaction
(d) has oxidation number of sulphur as +7.

28. As compared to H_2SO_5, $H_2S_2O_8$
(a) has two peroxy linkages
(b) liberates I_2 from KI solwly and thus, kinetics of oxidation of KI by $S_2O_8^{2-}$ can be studied.
(c) has different oxidation numbers
(d) reacts with $KMnO_4$.

Matrix Match Type

29. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I	Column II
(A) Chalcocite	(P) Bronze (Cu or Sn)
(B) Bauxite	(Q) Solder (Pb, Sn)
(C) Cassiterite	(R) Duralumin (Al, Cu, Mg, Mn)
(D) Carnalite	(S) Magnelium (Mg, Al)
	(T) German silver (Cu, Zn, Ni)

	A	B	C	D
(a)	P, R, T	R, S	P, Q	R, S
(b)	P, R, T	R, Q	P, Q	R, S
(c)	P, R, T	R, S	P, Q	R, Q
(d)	P, S, T	R, P	P, Q	R, S

30. Match the entries listed in Column I with appropriate entries listed in Column II.

Column I	Column II
(A) N_2O	(P) Neutral towards water
(B) NO	(Q) Acidic towards water
(C) N_2O_3 (unsymmetrical)	(R) N-N linkage is present.
(D) N_2O_4	(S) Molecule having the highest bond order of N–O bond.

	A	B	C	D
(a)	P, R	P, S	Q	Q, R
(b)	P, R	P, S	Q, R	Q, R
(c)	P, R	Q	Q, R	P, S
(d)	P, R	Q, R	Q	P, S

◆◆

Keys are published in this issue. Search now! ☺

SELF CHECK

No. of questions attempted ……
No. of questions correct ……
Marks scored in percentage ……

Check your score! If your score is

> 90%	EXCELLENT WORK !	You are well prepared to take the challenge of final exam.
90-75%	GOOD WORK !	You can score good in the final exam.
74-60%	SATISFACTORY !	You need to score more next time.
< 60%	NOT SATISFACTORY!	Revise thoroughly and strengthen your concepts.

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / PMTs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM
Set 39

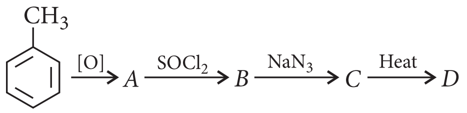
JEE MAIN/NEET

1. N_2O_4 dissociates as $N_2O_4 \rightleftharpoons 2NO_2$. At 55°C and one atmosphere, % decomposition of N_2O_4 is 50.3%. At what pressure (in atm) and same temperature, the equilibrium mixture will have the ratio of $N_2O_4 : NO_2$ as 1 : 8?
(a) 0.19 (b) 1.9 (c) 9.1 (d) 0.91

2. When K_2CrO_4 is added to $CuSO_4$ solution, there is the formation of $CuCrO_4$ as well as $CuCr_2O_7$. Formation of $CuCr_2O_7$ is due to
(a) basic nature of $CuSO_4$ solution which converts CrO_4^{2-} to $Cr_2O_7^{2-}$
(b) acidic nature of $CuSO_4$ solution which converts CrO_4^{2-} to $Cr_2O_7^{2-}$
(c) $CuSO_4$ has the typical property of converting $CuCrO_4$ formed to $CuCr_2O_7$
(d) no $CuCr_2O_7$ is formed.

3. A radioactive isotope $_{Z}A^{M}(t_{1/2} = 10 \text{ days})$ decays to give $_{Z-6}B^{M-12}$ stable atom along with α-particles. If *m* g of *A* are taken and kept in a sealed tube, the volume (in litre) of He accumulates in 20 days at STP is
(a) 40.5 (b) 50.4 (c) 5.04 (d) 5.40

4.



In the given sequence of reactions, what is *D*?
(a) Primary amine (b) An amide
(c) Phenyl isocyanate
(d) Chain lengthened hydrocarbon

5. A mixture of salts ($Na_2SO_3 + K_2Cr_2O_7$) in a test tube is treated with dil. H_2SO_4 and resulting gas is passed through lime water. Which of the following observations is correct about this test?
(a) Solution in test tube becomes green and lime water turns milky.
(b) Solution in test tube is colourless and lime water turns milky.
(c) Solution in test tube becomes green and lime water remains clear.
(d) Solution in test tube remains clear and lime water also remain clear.

JEE ADVANCED

6. A definite amount of $BaCl_2$ was dissolved in HCl solution of unknown normality. 20 mL of this solution was treated with 21.4 mL of N/10 NaOH for complete neutralisation. Further 20 mL of solution was added to 50 mL of N/10 Na_2CO_3 and the precipitate was filtered off. The filtrate reacted with 10.5 mL of 0.8 N/10 H_2SO_4 using phenolphthalein as indicator. The sum of strengths (in g litre^{-1}) of $BaCl_2$ and HCl in mixture is
(a) 109 (b) 20 (c) 15 (d) 10

COMPREHENSION

When a metal rod *M* is dipped into an aqueous colourless concentrated solution of compound *N*, the solution turns light blue. Addition of aqueous NaCl to the blue solution gives a white precipitate *O*. Addition of aqueous NH_3 dissolves *O* and gives an intense blue solution.

7. The metal rod *M* is
(a) Fe (b) Cu (c) Ni (d) Co

8. The final solution contains
(a) $[Pb(NH_3)_4]^{2+}$ and $[CoCl_4]^{2-}$
(b) $[Al(NH_3)_4]^{3+}$ and $[Cu(NH_3)_4]^{2+}$
(c) $[Ag(NH_3)_2]^{+}$ and $[Cu(NH_3)_4]^{2+}$
(d) $[Ag(NH_3)_2]^{3+}$ and $[Ni(NH_3)_6]^{2+}$

INTEGER VALUE

9. Same quantity of electricity being used to liberate iodine (at anode) and a metal (at cathode). The mass of metal liberated at cathode is 0.617 g and the liberated iodine completely reduced by 46.3 mL of 0.124 M sodium thiosulphate solution. If the equivalent weight of metal is 100 + *x* + 0.47, then the value of *x* is

10. The total number of *d*π-*p*π bonds formed in P_4O_{10} molecule is

◆ ◆

JEE Advanced

PRACTICE PAPER

SECTION - I

(Single Correct Answer Type)

This section contains 7 multiple choice questions. Each question has four choices (a), (b), (c) and (d) out of which only one is correct.

1. $Cl_{2(g)} + Ba(OH)_2 \rightarrow X_{(aq)} + BaCl_2 + H_2O$

$X + H_2SO_4 \rightarrow Y + BaSO_4$

$Y \xrightarrow[> 365\ K]{\Delta} Z + H_2O + O_2$

Compound Z can also be prepared by passing dry chlorine over freshly precipitated yellow mercuric oxide. It oxidizes HCl into Cl_2 and NH_3 into N_2 and NH_4Cl.

$Z + H_2O \rightarrow$ weak acid, linear shape.

Y, Z respectively, and magnetic behaviour exhibited by 'Z' are

(a) $HClO_4$, ClO_2, diamagnetic
(b) $HClO_3$, ClO_2, paramagnetic
(c) $HClO_3$, Cl_2O, diamagnetic
(d) $HClO_4$, Cl_2O_7, paramagnetic.

2. An ideal mixture of liquids A and B with 2 moles of A and 2 moles of B has a total vapour pressure of 1 atm at a certain temperature. Another mixture with 1 mole of A and 3 moles of B has vapour pressure greater than 1 atm. When 4 moles of C are added to 2nd mixture, the vapour pressure comes down to 1 atm. Vapour pressure of C in pure state $P^\circ_C = 0.8$ atm. What will be the vapour pressures of pure A and pure B?

(a) $P^\circ_A = 1.2$ atm, $P^\circ_B = 0.7$ atm
(b) $P^\circ_A = 1.2$ atm, $P^\circ_B = 0.6$ atm
(c) $P^\circ_A = 1.4$ atm, $P^\circ_B = 0.6$ atm
(d) $P^\circ_A = 0.6$ atm, $P^\circ_B = 1.4$ atm

3. Calculate the pH at which the following conversion (reaction) will be at equilibrium in basic medium.

$I_{2(s)} \rightleftharpoons I^-_{(aq)} + IO^-_{3(aq)}$

When the equilibrium concentrations at 300 K are $[I^-] = 0.10$ M and $[IO_3^-] = 0.10$ M given that

$\Delta G^\circ_f(I^-_{(aq)}) = -50$ kJ/mole,

$\Delta G^\circ_f(IO^-_{3(aq)}) = -123.5$ kJ/mole,

$\Delta G^\circ_f(H_2O_{(l)}) = -233$ kJ/mole,

$\Delta G^\circ_f(OH^-_{(aq)}) = -150$ kJ/mole $R = \frac{25}{3}$, $\log e = 2.3$

(a) 2 (b) 4
(c) 6 (d) 8

4. A hydrogen like species (atomic number Z) is present in a higher excited state of quantum number n. This excited atom can make a transition to the first excited state by successive emission of two photons of energies 10.20 eV and 17.0 eV respectively. Alternatively, the atom from the same excited state can make transition to the second excited state by successive emission of two photons of energy 4.25 eV and 5.95 eV respectively. The value of Z will be

(a) 1 (b) 2
(c) 3 (d) 4

5. Compound 'X', C_7H_8O, is insoluble in H_2O, dil. HCl and *aq*. $NaHCO_3$ but dissolves in dil. NaOH. When 'X' is treated with Br_2/H_2O, it is converted rapidly in to a compound of formula $C_7H_5OBr_3$. Then compound 'X' is

(a) *o*–Cresol (b) *p*–Cresol
(c) *m*–Cresol (d) anisole.

6. 1.0 g of a monobasic acid HA in 100 g water lowers the freezing point by 0.385 K. If 0.3 g, of

By : **Vidyalankar Institute**, Pearl Centre, Senapati Bapat Marg, Dadar (W), Mumbai - 28. Tel.: (022) 24306367

same acid requires 25 mL of N/5 NaOH solution for complete neutralisation, then % degree of ionization of acid is

(K_f of H_2O = 1.86 K kg mol^{-1}) :

(a) 18% (b) 24% (c) 42% (d) 64%

7. Some physical properties of four elements *L*, *M*, *Q* and *R* are given in the table below :

Physical property	***L***	***M***	***Q***	***R***
MP (°C)	–7	63	–189	1083
BP (°C)	58	766	–186	2582
Colour at STP	dark red	silvery	colourless	brown-red
Density at STP (g cm^{-3})	3.1	0.86	1.7×10^{-3}	8.9

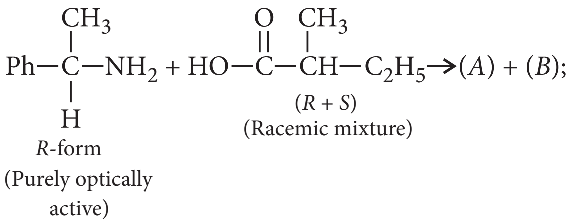
These elements in the order *L*, *M*, *Q* and *R* are from the following groups in the periodic table.

	L	***M***	***Q***	***R***
(a)	group I	transition elements	group VII	group zero
(b)	group VII	group I	group zero	transition elements
(c)	group VII	transition elements	group zero	group I
(d)	transition elements	group I	group VII	group zero

SECTION - II

(Multiple Correct Answer Type)

This section contains 4 multiple choice questions. Each question has four choices (a), (b), (c) and (d) out of which one or more may be correct.

8. 

$\mathrm{Ph-\underset{H}{\overset{CH_3}{C}}-NH_2 + HO-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{CH}-C_2H_5 \rightarrow (A) + (B);}$

R-form
(Purely optically active)

(*R* + *S*)
(Racemic mixture)

The correct statement regarding compounds (*A*) and (*B*) is/are

(a) both are optically active in nature

(b) relation between (*A*) and (*B*) is diastereomers

(c) (*A*) and (*B*) are meso compounds

(d) Out of (*A*) and (*B*) one is optically active and other is optically inactive.

9. Among the following, identify the correct statement(s)?

(a) The number of atoms in 100 g of an *fcc* crystal with density (ρ = 10 g cm^{-3}) and cell edge at 200 pm are 5×10^{24}.

(b) Sr–90 radioisotope ($t_{1/2}$ = 27 years) obtained as one of the fission products of uranium-235. The time required for 1.00 g of the isotope to be reduced to 0.2 g by decay is ≈ 63 years.

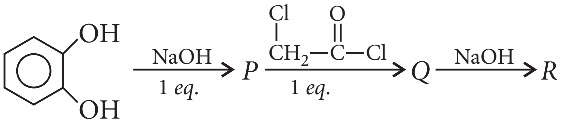
(c) The rate of uncatalysed reaction at 127 °C is equal to that of the catalysed reaction at 27 °C. The catalyst lowers the activation energy by 25%.

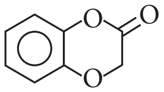
(d) Barium permanganate [$Ba(MnO_4)_2$] oxidises ferrous oxalate in dil.H_2SO_4 medium and itself is reduced to $MnSO_4$. The volume of 0.1 M $Ba(MnO_4)_2$ is needed to oxidise 50 mL of 0.2 M ferrous oxalate in acidic medium is 30 mL.

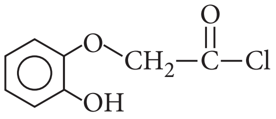
10. Decomposition of $3A_{(g)} \rightarrow 2B_{(g)} + 2C_{(g)}$ follows 1st order kinetics. Initially only *A* is present in the container. Pressure developed after 20 min and infinite time are 3.5 and 4 atm respectively. Which one is correct?

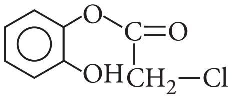
(a) $t_{50\%}$ = 20 min (b) $t_{75\%}$ = 40 min

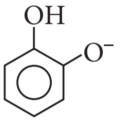
(c) $t_{99\%}$ = 64/3 min (d) $t_{87.5\%}$ = 60 min

11. 

(a) *R* = 

(b) *Q* = 

(c) *Q* = 

(d) *P* = 

SECTION - III

(Paragraph Type)

This section contains 2 paragraphs. Based upon one of the paragraphs 2 multiple choice questions and based on the other paragraph 3 multiple choice questions have to be answered. Each of these questions has four choices (a), (b), (c) and (d) out of which only one is correct.

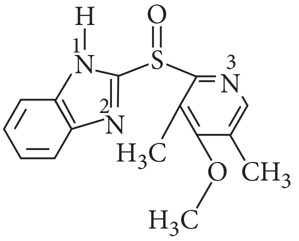
Paragraph for Q. No. 12 and 13

An average adult produces between 2 and 3 L of gastric juice daily. Gastric juice is a thin, acidic digestive fluid secreted by glands present in the stomach. It contains among other substances, hydrochloric acid. The pH of gastric juice is about 1.5. The purpose of the highly acidic medium within the stomach is to digest food and to activate certain digestive enzymes. Eating stimulates H^+ ion secretion. However, if the acid content is excessively high then the substances, which remove the excess acid and raise the pH to appropriate level in stomach are called antacids.

Some common commercial antacid preparations :

Commercial Name	**Active ingredients**
Alka – 2	$CaCO_3$
Alka-Seltzer	Aspirin, $NaHCO_3$, citric acid
Milk of Magnesia	$Mg(OH)_2$
Rolaids	Dihydroxy aluminum sodium carbonate

The reactions of active ingredients with stomach acid produce CO_2 causing the person to belch. The fizzing that takes place when an alka-seltzer tablet dissolves in water is caused by CO_2 which is released by the reaction between citric acid and $NaHCO_3$. In recent years omeprazole and lansoprazole are also marketed as antacids. These prevent formation of acid in the stomach.



12. One mole of active ingredients in Rolaid can react with moles of HCl.

(a) 2 (b) 4 (c) 3 (d) 6

13. During acidity HCl concentration in stomach rises from a normal of 8×10^{-2} M to 0.1 M HCl. One rolaid tablet contains 500 mg of active component. What percentage of tablet should be sufficient to return the molarity to normal if stomach contains 500 mL of the acid?

(a) 500 (b) 72 (c) 25 (d) 88

Paragraph for Q. No. 14 to 16

Piperine, $C_{17}H_{19}O_3N$ is an alkaloid found in black pepper. It is soluble in water, dilute acid and dilute base. When heated with alkali, it yields piperic acid, $C_{12}H_{10}O_4$, and the cyclic secondary amine piperidine, $C_5H_{11}N$. (a hydrogenated product of pyridine) Piperic acid ($C_{12}H_{10}O_4$) is insoluble in H_2O, but soluble in *aq*.NaOH and *aq*.$NaHCO_3$. It decolourises Br_2 / CCl_4 and consumes four bromine atoms. On careful oxidation with $KMnO_4$, it gives oxalic acid, tartaric acid and piperonylic acid, $C_8H_6O_4$. Its equivalent weight is 218.

When piperonylic acid is heated with *aq*. HCl at 200 °C it yields HCHO and protocatechuic acid (3, 4–dihydroxy benzoic acid).

Synthesis of piperine :

$$\text{Catechol} \xrightarrow[\text{KOH}]{CHCl_3} (C_7H_6O_3) \xrightarrow[\text{NaOH}]{CH_2I_2}$$

$$\text{‘}B\text{’}(C_8H_6O_3) \xrightarrow[\text{NaOH}, \Delta]{CH_3CHO} \text{‘}C\text{’}(C_{10}H_8O_3)$$

$$\xrightarrow[CH_3COONa, \Delta]{(CH_3CO)_2O} \text{piperic acid} \xrightarrow[SOCl_2]{PCl_5 \text{ or}}$$

$$\text{‘}D\text{’}(C_{12}H_9O_3Cl) \xrightarrow{\text{piperidine}} \text{piperine}$$

14. The number of isomers and nature of stereoisomerism exhibited by piperic acid

(a) 2, optical
(b) 4, geometrical
(c) 4, optical and geometrical
(d) 2, geometrical

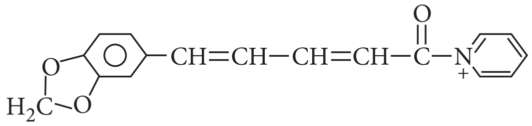
15. In the formation of piperic acid from catechol, the name reaction involving new carbon-carbon bond formation are

(a) Perkin, Riemer-Tiemann, Knoevenagel
(b) Claisen, Perkin, Cannizzaro
(c) Riemer-Tiemann, Claisen-Schmidt, Perkin
(d) Fries, Riemer-Tiemann, Perkin

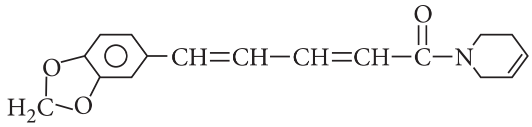
16. The structure of piperine is

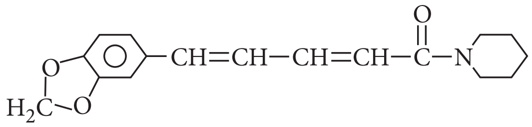
(a)

(b)



(c)



(d) 

SECTION - IV

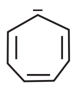
(Integer Answer Type)

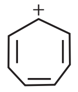
This section contains 7 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9. The bubble corresponding to the correct answer is to be darkened in the ORS.

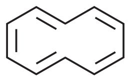
17. For a homogeneous gaseous phase reaction : $2A \rightarrow 3B + C$, the initial pressure of reactant was P° while pressure at time '*t*' was P. The pressure after time $2t$ is $xP^\circ - \dfrac{(yP^\circ - P)^z}{P^\circ}$. Assume first order reaction. Find $x \times y \times z$.

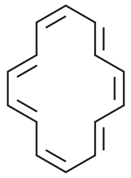
18. In a gravimetric determination of P, an aqueous solution of dihydrogen phosphate ion $H_2PO_4^-$ is treated with a mixture of ammonium and magnesium ions to precipitate magnesium ammonium phosphate $Mg(NH_4)PO_4 \cdot 6H_2O$. This is heated and decomposed to magnesium pyrophosphate, $Mg_2P_2O_7$, which is weighed. A solution of $H_2PO_4^-$ yielded 111/120 g of $Mg_2P_2O_7$. What weight of NaH_2PO_4 was present originally? (Na = 23, H = 1, P = 31, O = 16, Mg = 24)

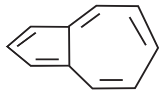
19. From the given species how many are aromatic.

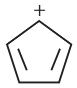

(I)


(II)


(III)


(IV)

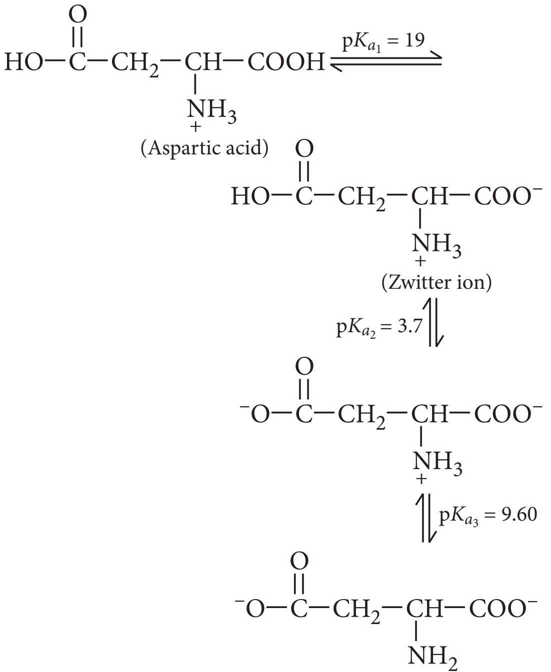

(V)


(VI)


(VII)


(VIII)

20. In following reaction chain,



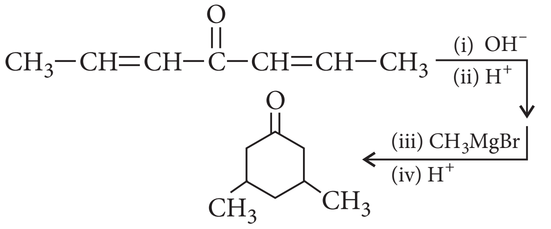
The isoelectric point of aspartic acid is

21. Count the total number of reactions in which hydrogen gas is liberated.

$LiH + H_2O \longrightarrow$	$LiH + C_2H_2OH \longrightarrow$
$LiH + NH_3 \longrightarrow$	$LiH + HCl \longrightarrow$
$6LiH + N_2 \longrightarrow$	$3CaH_2 + N_2 \longrightarrow$
$B_2H_6 + 2NaH \longrightarrow$	

22. On heating crystals of $K_2[Fe(CN)_6]$ with H_2SO_4 '*x*' mol of CO evolved per mol of $K_4[Fe(CN)_6]$. Identify '*x*'.

23. Consider the following reaction,



How many times Michael addition reaction can take place?

ANSWER KEY

1.	(b)	**2.**	(d)	**3.**	(d)	**4.**	(c)	**5.**	(c)
6.	(b)	**7.**	(b)	**8.**	(a,b)	**9.**	(a,b,c,d)		
10.	(a,b,d)	**11.**	(a,c,d)	**12.**	(b)	**13.**	(b)	**14.**	(b)
15.	(c)	**16.**	(d)	**17.**	(8)	**18.**	(1)	**19.**	(5)
20.	(3)	**21.**	(6)	**22.**	(6)	**23.**	(2)		

For detailed solutions
visit our website: www.vidyalankar.org

CONCEPT BOOSTER

My dear students, hope you all are doing well. I wish you all advanced Happy Durga Puja, Navaratri and as very very happy and colourful Diwali. I am presenting an article on 'Kinetic and Thermodynamic Enolate'. I hope you will like it! All the best!

*Arunava Sarkar

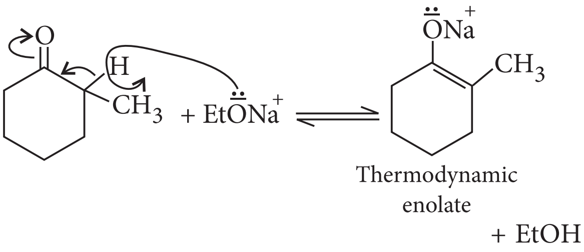
KINETIC AND THERMODYNAMIC ENOLATE

Role of Chlorotrimethyl Silane in Trapping Kinetic Enolate

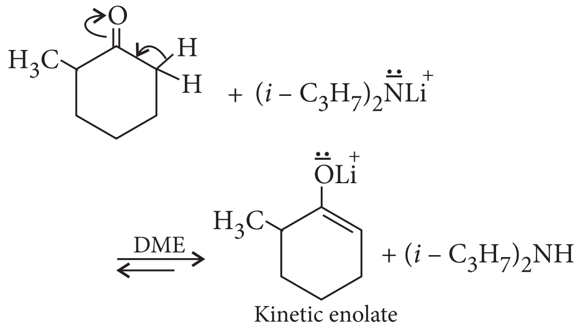
If an enolate is more substituted or highly substituted then it is formed predominantly under the conditions which establish an equilibrium. This type of enolate is known as thermodynamic enolate. For the formation of such enolate the following two conditions are necessary :

- Relatively weak or moderate bases as far as strength is concerned.
- Protic solvents like MeOH or EtOH, etc.

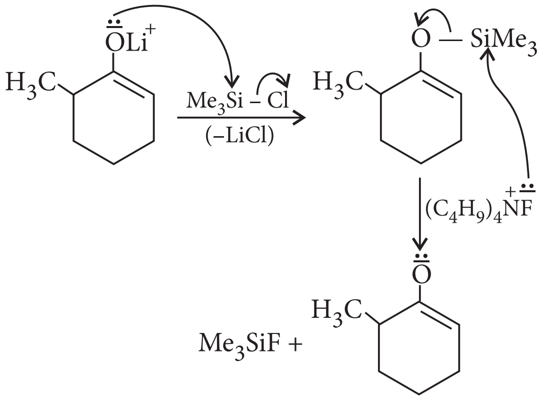
Take the following example :



On the other hand, there is another type of enolate with the less substituted double bond and it is formed faster as here the removal of hydrogen required to produce the enolate is less sterically hindered and predominant formation of this takes place when the reaction is kinetically controlled. This kind of enolate is known as kinetic enolate. The prerequisite for the formation of kinetic enolate is a strong, sterically hindered base which is keen to remove a hydrogen (proton) from less sterically hindered site. 1,2-Dimethoxyethane (DME) is a popular choice as solvent here.



Kinetic enolate can be trapped by converting it to the enol trimethyl silyl ether. Later on, through purification, this trimethyl silyl ether can be converted back to the enolate by treating the silyl ether with a solution containing fluoride ion, *e.g.*, tetrabutyl ammonium fluoride *i.e.*, $(C_4H_9)_4\overset{+}{\ddot{N}}F$. Reaction goes as below :



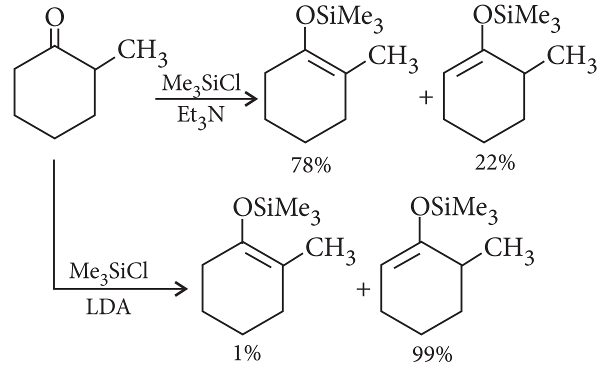
Remember that when you treat an enolate with chlorotrimethyl silane, silylation exclusively occurs at the oxygen atom.

This is a nucleophilic substitution which takes place at silicon atom by the oxygen atom. This process is highly exothermic process. Oxygen-silicon bond is thus found to be stronger than carbon-silicon bond. Also, the activation energy for the reaction at oxygen atom is lower than that of the reaction at carbon atom. So, the substitution at the oxygen atom is always more favourable than carbon atom in case of silylation.

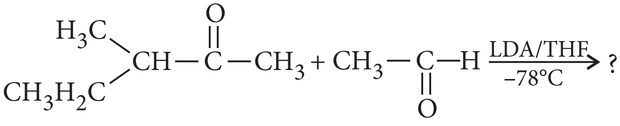
Now, the question is why are we using something which is containing fluoride ion (remember instead of tetrabutyl ammonium fluoride we can even use methyl lithium, this will also work).

Well, the straight answer to this, fluoride ions have high electron affinity towards silicon and Si—F bonds are very strong (594 kJ mol^{-1}).

The whole concept of the formation of thermodynamic and kinetic enolate can be understood if you look at the following observations :



Now, in this regard a very important concept is there which is directed aldol condensation. Let me show you an example.



$$\mathrm{(H_3C)(CH_3H_2C)CH-\overset{\displaystyle O}{\overset{\|}{C}}-CH_3 + CH_3-\underset{\displaystyle O}{\underset{\|}{C}}-H \xrightarrow[-78^\circ C]{LDA/THF} ?}$$

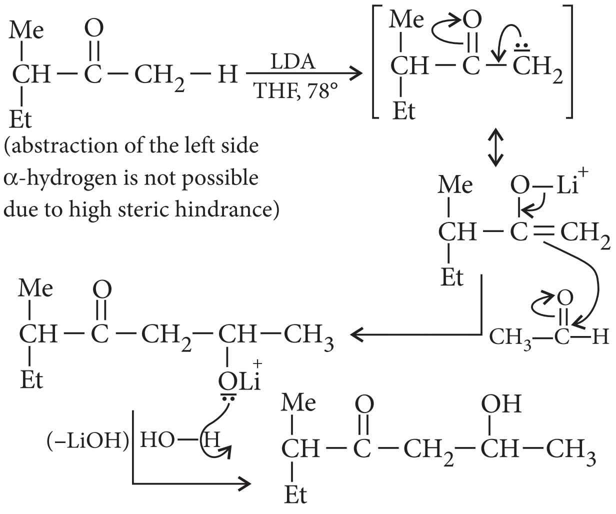
How many products are you expecting here?

Definitely more than one!! Crossed aldol condensation is supposed to take place here.

But answer is only one. Remember, crossed aldol reaction using strong bulky base in non-protic solvent like THF produces a single crossed aldol product through kinetic enolate. Let me show you this.

MPP-4 CLASS XII ANSWER **KEY**

1.	(c)	**2.**	(b)	**3.**	(c)	**4.**	(b)	**5.**	(a)
6.	(d)	**7.**	(c)	**8.**	(b)	**9.**	(d)	**10.**	(b)
11.	(c)	**12.**	(b)	**13.**	(a)	**14.**	(c)	**15.**	(a)
16.	(b)	**17.**	(b)	**18.**	(b)	**19.**	(b)	**20.**	(b,c)
21.	(a,c,d)	**22.**	(a,b)	**23.**	(b,c,d)	**24.**	(3)	**25.**	(7)
26.	(6)	**27.**	(a)	**28.**	(b)	**29.**	(a)	**30.**	(b)



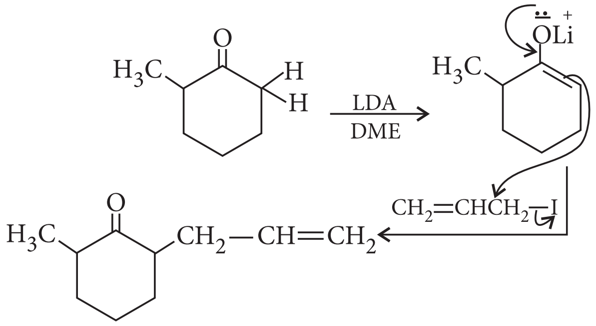
(abstraction of the left side α-hydrogen is not possible due to high steric hindrance)

2-Hydroxy-5-methylheptan-4-one
(A single crossed aldol product)

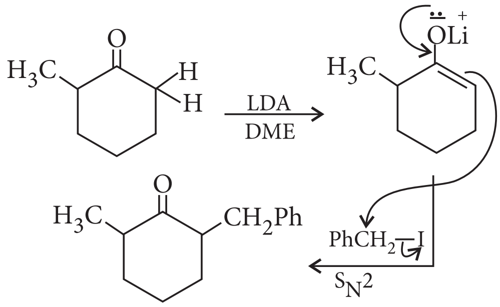
Direct Alkylation of Ketone with LDA via Lithium Enolate

This concept is now very easy for you to understand. Check the following two reactions :

- **Reaction-I :**



- **Reaction-II :**



So, we see that direct alkylation has taken place here. But, as the reaction proceeds via S$_N$2 path, so this reaction is successful with methyl or 1° alkyl halides, 1° benzyl halides as well as allyl halides (reaction I). But, the reaction is never successful with 3° or 2° halide where there is a chance of elimination reaction and of course elimination will take place here due to the fact that enolate ions are strong bases.

◆

ADVANCED CHEMISTRY BLOC

(LIMITS OF pH SCALE)

Mukul C. Ray, Odisha

The limits of pH scale are 15.7 and –1.7 rather than 14 and 0 as generally students consider. The strongest base that can survive in water is none other than hydroxide. And the solvents restrict the strength of acid or base that can be used in it. Read this small article to discover these nice points in chemistry.

- Consider the ionisation of an acid HA in water solution,

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

  The ionisation constant of acid is written as

  $$K_a = \frac{[H_3O^+][A^-]}{[HA]} \quad \dots (1)$$

  Concentration of H_2O is constant, which is 55.5 moles per litre.

  In a similar line of argument, we can write the following equation showing acidic behaviour of H_2O,

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

  $$K_a = \frac{[H_3O^+][OH^-]}{[H_2O]} \quad \dots (2)$$

  We know at 25°C, $[H_3O^+][OH^-]$ has a value of 1×10^{-14} and is known as the ionic product of water.

  From equation (2), we have

  $$K_a = \frac{10^{-14}}{55.5}$$

  $$\text{or} \quad pK_a = -\log K_a = -\log\left(\frac{10^{-14}}{55.5}\right) = 15.7 \quad \dots (3)$$

  So, pK_a of water is 15.7 at 25°C.

  When $[H_2O] = [OH^-]$

  From equation (2), we have

  $K_a = [H_3O^+]$

  or $-\log K_a = -\log[H_3O^+]$

  or $pH = pK_a = 15.7$

  So, when pH of water is 15.7, the concentrations of H_2O and OH^- are equal.

  Similarly, when $[H_2O] = [H_3O^+]$, from equation (2), we have

  $K_a = [OH^-]$

  $$\text{or} \quad K_a = \frac{K_w}{[H_3O^+]} \quad \text{or} \quad [H_3O^+] = \frac{K_w}{K_a}$$

  $$\text{or} \quad -\log[H_3O^+] = -\log\left(\frac{K_w}{K_a}\right)$$

  or $pH = -\{\log K_w - \log K_a\}$

  or $pH = -\{-14 + 15.7\} = -1.7$

  Thus, when pH of water is –1.7, the concentrations, of H_3O^+ and H_2O are equal.

  This defines the limits of pH scale.

- **Choice of solvents and limits of pK_a range of acids and bases that can be used in that solvent :**

  In water we can measure the pK_a of an acid only if the acid does not completely protonate water to give H_3O^+ or completely deprotonate to give OH^-. We are restricted roughly to pH –1.7 to 15.7 beyond which water is more than 50% protonated or deprotonated. The strength of acids and bases we can use in any solvent is limited by the acidity and basicity of the solvent itself.

  Say, you want to remove the proton from a compound with a high pK_a, say 25-30, it would be impossible to do this in water since the strongest base we can use in water is hydroxide. If you add a base stronger than hydroxide, it won't deprotonate your compound, rather it will deprotonate water to give hydroxide, any way. Likewise acids, stronger than H_2O can't exist in water, they just protonate water completely to make H_3O^+. If you need a stronger base than OH^- or stronger acid than H_3O^+ you have to use a solvent other than water. This is the reason why we use NH_2^- in liquid NH_3 solvent. Got it? Let me show you once again.

  Imagine you add $NaNH_2$ in water with a desire to use NH_2^- as a base in water medium. Now NH_2^- will rather deprotonate water to produce OH^-. So, the strongest base that can survive in water medium is OH^-. Similarly, if you add $HClO_4$ to H_2O, the perchloric acid will protonate water completely. The strongest acid that can survive in water is thus, H_3O^+.

- **The levelling effect :**

  The phenomenon discussed above is in terms of solvent water, but are general to any solvent, leading to what is known as levelling effect.

  The levelling effect states that,

  - An acid stronger than the conjugate acid of the solvent cannot exist in any appreciable concentration in that solvent.
  - A base stronger than the conjugate base of the solvent cannot exist in any appreciable concentration in that solvent.

  The levelling effect creates a limitation of the strengths of acids and bases that can be used in particular solvents.

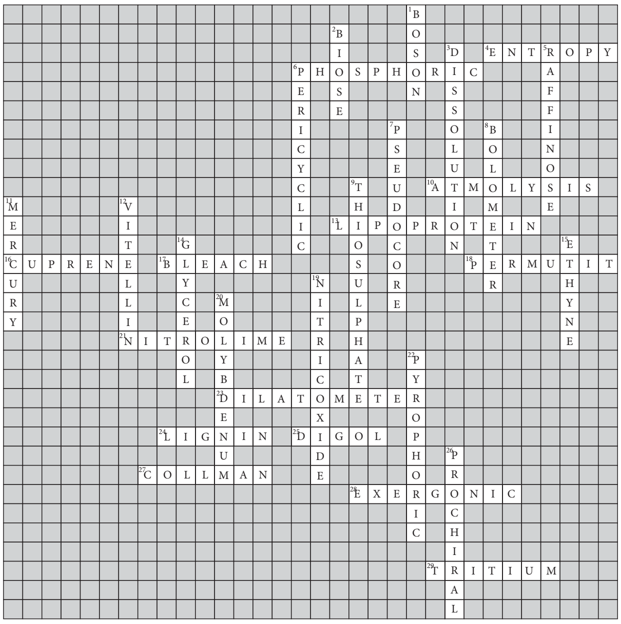
- **The pK_a's of acids :**

  Now we conclude, the pK_a's of acids stronger than the conjugate acid of the solvent cannot be measured in that solvent. The pK_a's of acids whose conjugate bases are stronger than the conjugate base of the solvent cannot be measured in that solvent.

  So, then how do we measure pK_a of HCl (pK_a = –7)? Mostly by extrapolating or calculation or using other solvents like acetic acid, we create path out of no paths.

◆

SOLUTIONS OF SEPTEMBER 2016 CROSSWORD



Winners of September 2016 Crossword

- Sakshi Madan, Mumbai
- Neha Khanna, Ranchi

Winners of August 2016 Crossword

- Devjit Acharjee, West Bengal

Solution Senders of Chemistry Musing

Set - 38

- Swastik Biswas, Kolkata
- Sayak Mandal, West Bengal
- Baidurya Nayak, West Bengal

Set - 37

- Yakaiah Chennori, Telangana

CHEMISTRY MUSING

SOLUTION SET 38

1. (b) : Work required to lift the plane = *mgh*

$= 6.3 \times 10^7 \times 981 \times 8 \times 10^5$ erg

$= 4.9442 \times 10^{16}$ erg

$$= \frac{4.9442\times10^{16}}{4.18\times10^{7}}\text{ cal} = 1.1828\times10^{9}\text{ cal}$$

∵ Efficiency of fuel is 40%.

∴ Work obtained by 1 mole of fuel $= \frac{1300\times40}{100}$ kcal

∴ Number of moles of fuel required to do 1.1828×10^6 kcal of work

$$= \frac{1.1828\times10^{6}\times100}{40\times1300} = 2.274\times10^{3}\text{ moles}$$

$= 2.274 \times 10^3 \times 114 \text{ g} = 2.59 \times 10^5$ g

∴ Volume of fuel $= \frac{2.59\times10^{5}}{d} = \frac{2.59\times10^{5}}{0.705}$ mL

$= 3.673 \times 10^5 \text{ mL} = 3.673 \times 10^2$ L

∴ Cost of fuel = 367.3 × 3 = ₹ 1101.9

2. (a) : At boiling point, $P_{\text{mixture}} = 736$ mm

At boiling point, $p'_{H_2O} = 526$ mm

∴ $p'_l = 736 - 526 = 210$ mm

Also, $p'_l = P_{\text{mixture}} \times x_{(\text{in vapour phase})}$ ...(1)

Let *a* g of liquid and *a* g of water is collected or this is the amount of vapours at equilibrium.

Thus, wt. of liquid vapours $= \frac{2.5\times a}{3.5}$

wt. of water vapours $= \frac{a}{3.5}$

Now for liquid, from eq. (1),

$$210 = \frac{736\times\frac{2.5a}{3.5\times M}}{\frac{a}{3.5\times18}+\frac{2.5a}{3.5\times M}} \quad ...(2)$$

where *M* is mol. wt. of liquid.

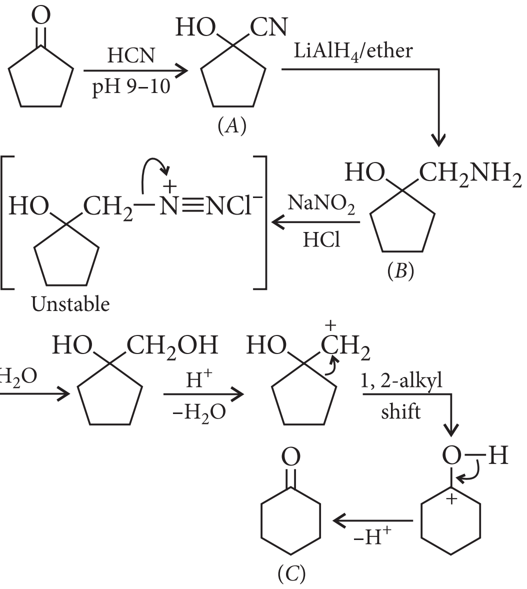
For H_2O, from eq. (1),

$$526 = 736\times\frac{\frac{a}{3.5\times18}}{\frac{a}{3.5\times18}+\frac{2.5a}{3.5\times M}} \quad ...(3)$$

Thus, from eqs. (2) and (3) $\frac{210}{526} = \frac{18\times2.5}{M}$

$M = 112.7 \text{ g mol}^{-1}$

3. (a) :



4. (b) : The colourless inorganic salt (*A*) is ammonium nitrate.

$$\underset{(A)}{NH_4NO_3} \xrightarrow{\Delta} \underset{(B)}{N_2O} + \underset{(C)}{2H_2O}$$

Product (*B*) N_2O is a neutral gas, product (*C*) H_2O is liquid and neutral to litmus.

$$\underset{(B)}{10N_2O} + P_4 \longrightarrow \underset{\text{(Dehydrating agent)}}{P_4O_{10}} + 10N_2$$

5. (a) : As volume of the species is proportional to their concentration thus,

	H_2	+	I_2	⇌	$2HI$
Initial volume	25		18		0
Volume at equilibrium	$(25 - x)$		$(18 - x)$		$2x(= 30.8)$
	$(25 - 15.4)$		$(18 - 15.4)$		30.8
	= 9.6		= 2.6		$\left(x = \frac{30.8}{2} = 15.4\right)$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(30.8)^2}{9.6\times2.6} = 38.01$$

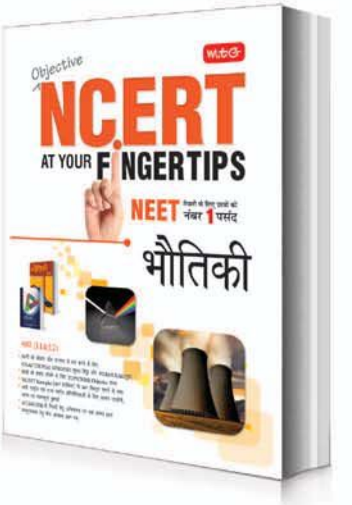
Now, if the dissociation of HI is carried out at the same temperature, degree of dissociation *x*′, we have

	$2HI$	⇌	H_2	+	I_2
Initial mole	1		0		0
Moles at equilibrium	$(1 - x')$		$\frac{x'}{2}$		$\frac{x'}{2}$

Equilibrium constant, $K'_c = \frac{1}{K_c} = \frac{1}{38.01}$

$$K'_c = \frac{\left(\frac{x'}{2}\right)\left(\frac{x'}{2}\right)}{(1-x')^2} = \frac{1}{38.01}$$

$x' = 0.245$



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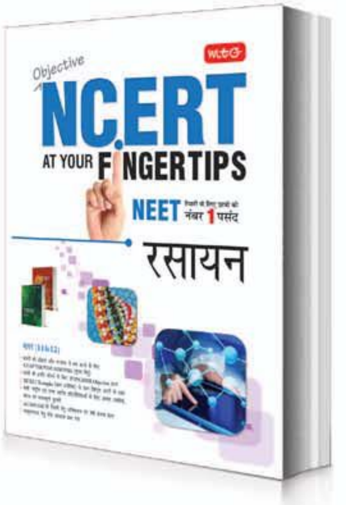

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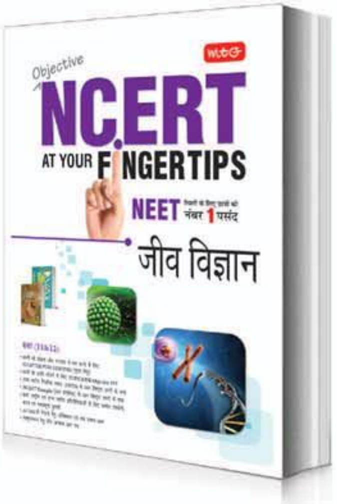

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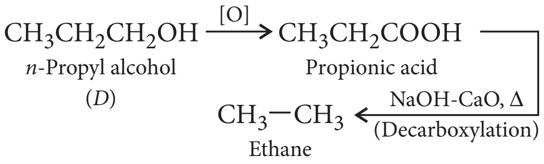
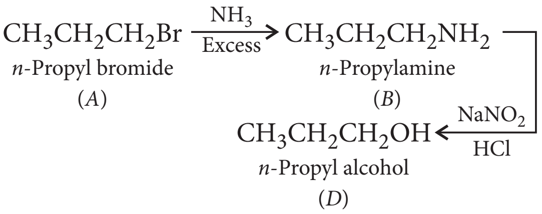
6. (d) : Since, ethane is obtained by decarboxylation of an acid which is obtained by oxidation of a 1° alcohol, *i.e.*, *n*-propyl alcohol. Therefore, the acid must be propionic acid.



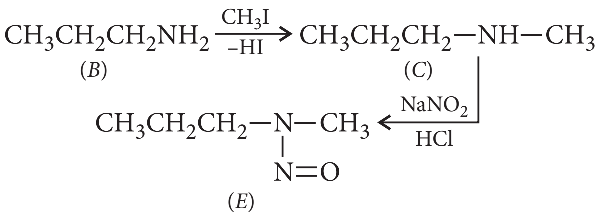
$$\underset{\substack{n\text{-Propyl alcohol}\\(D)}}{CH_3CH_2CH_2OH} \xrightarrow{[O]} \underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[\text{(Decarboxylation)}]{\text{NaOH-CaO, }\Delta} \underset{\text{Ethane}}{CH_3-CH_3}$$

Since *n*-propyl alcohol (*D*) is obtained by the action of $NaNO_2$/HCl, on *B*, which, in turn, is obtained from alkyl bromide (*A*) by action of NH_3, therefore, (*A*) must be *n*-propyl bromide and (*B*) must be *n*-propylamine.



$$\underset{\substack{n\text{-Propyl bromide}\\(A)}}{CH_3CH_2CH_2Br} \xrightarrow[\text{Excess}]{NH_3} \underset{\substack{n\text{-Propylamine}\\(B)}}{CH_3CH_2CH_2NH_2} \xrightarrow[HCl]{NaNO_2} \underset{\substack{n\text{-Propyl alcohol}\\(D)}}{CH_3CH_2CH_2OH}$$

Since (*C*) is obtained by the action of one equivalent of CH_3I on (*B*), therefore, (*C*) must be *n*-propylmethylamine and the compound (*E*) which it gives on treatment with $NaNO_2$/HCl must be its *N*-nitroso derivative.



$$\underset{(B)}{CH_3CH_2CH_2NH_2} \xrightarrow[-HI]{CH_3I} \underset{(C)}{CH_3CH_2CH_2-NH-CH_3} \xrightarrow[HCl]{NaNO_2} \underset{(E)}{CH_3CH_2CH_2-\underset{\substack{|\\N=O}}{N}-CH_3}$$

7. (b) : $2CuFeS_2 + O_2 \xrightarrow{\text{Roasting}} Cu_2S + 2FeS + SO_2$

8. (b) : In the given metals, only Cu undergoes auto reduction.

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

9. (6) : The formula $M_{0.97}O_{1.00}$ shows that if there are 100 oxide ions, then there are 97 *M* atoms (present as M^{2+} and M^{3+}).

Charge on 100 O^{2-} ions = 200 units

Suppose M^{2+} present = x

Then, M^{3+} present = $97 - x$

Total charge on M^{2+} and M^{3+} = $2x + 3(97 - x)$
$= 291 - x$

As metal oxide is neutral, total charge on cations = total charge on anions.

Hence, $291 - x = 200$ or $x = 91$

$\therefore$ % of M as M^{2+} = $\frac{91}{97} \times 100 = 93.8\%$

% of M as M^{3+} = $100 - 93.8 = 6.2\% \approx 6\%$

10. (5) : H—O—O bond angle in H_2O_2 is 94.8°. Therefore, $x = 100 - 94.8 = 5.2 \approx 5$

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CROSS WORD

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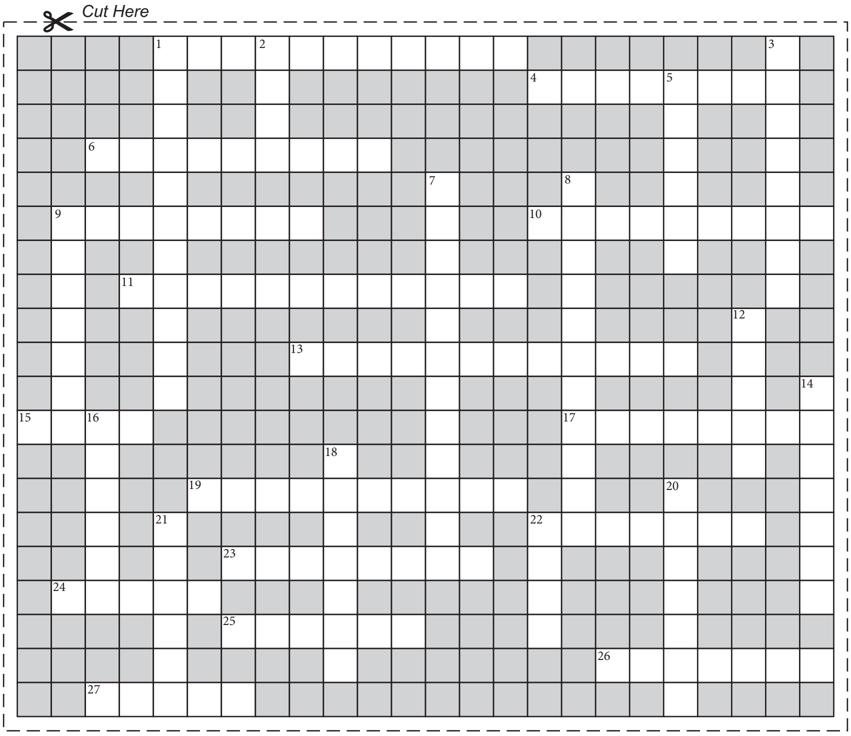

ACROSS

1. A hard refractory material made by heating carbon and silicon to 2000°C. (11)
4. A parameter empirically relating [Surface tension]$^{1/4}$ and molecular volume. (8)
6. The solids which have extremely low conductivity. (9)
9. The process of removal of material from the surface of an object by vaporisation. (8)
11. The process of decomposing or changing a substance, usually in solution or as a melt, by the passage of an electric current. (12)
13. The process of emission of light by a substance that has absorbed light or other electromagnetic radiation. (12)
15. The Palladium-catalyzed C—C coupling between aryl halides or vinyl halides and activated alkenes in the presence of a base is known as ___ reaction. (4)
16. The bluish-green plating formed on copper or bronze on exposure to the atmosphere. (9)
17. A widely distributed igneous rock composed essentially of plagioclase feldspar and augite. (8)
19. The principal ore of tungsten. (10)
22. A chemical that binds to a receptor and activates the receptor to produce a biological response. (7)
23. The individual component sheets of graphite. (8)
24. A colourless soluble organic substance used in the form of its sulphate, as a photographic developer. (5)
25. A phosphoprotein which occurs in the milk of mammals as a suspension of calcium caseinate. (6)
26. A commercial name for solid CO_2. (7)
27. A naked anionic clusters of main group elements. (5)

DOWN

1. Water soluble proteins present in eye lenses. (11)
2. The emission of a nuclear electron as a neutron decays to a proton is known as ____ decay. (4)
3. The fragmentation reaction of alkanes with very high temperature is called ___. (8)
5. A long-chain polymer of an N-acetylglucosamine. (6)
7. The law of __________ of matter and energy states that matter can neither be created nor be destroyed but can only be changed from one form to another. (12)
8. NMR effect that has signals at lower field (down field). (11)
9. One of the three mineral forms of titanium oxide. (7)
12. A poisonous protein of the lectin class from the seeds of the castor bean. (5)
14. A subatomic particle with half-integral spin. (7)
16. A resin obtained from the Mexican tree (*Achras sapita*) and used in chewing gum manufacture. (6)
18. Three closely spaced transitions in a spectrum. (7)
20. A volatile hydrocarbon mixture obtained from petroleum, used as a solvent. (7)
21. A vitamin which is present in yeast, egg yolk, liver and other tissues. (6)
22. A double sulphate salts, used in fire extinguishers to smother chemical and oil fires. (4)

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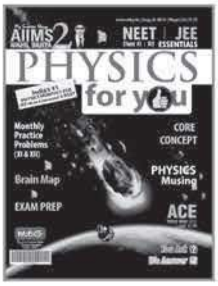

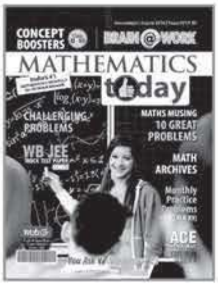

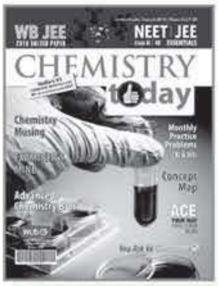

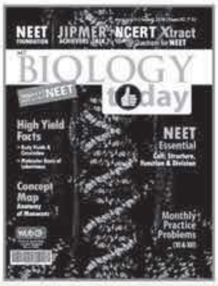

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