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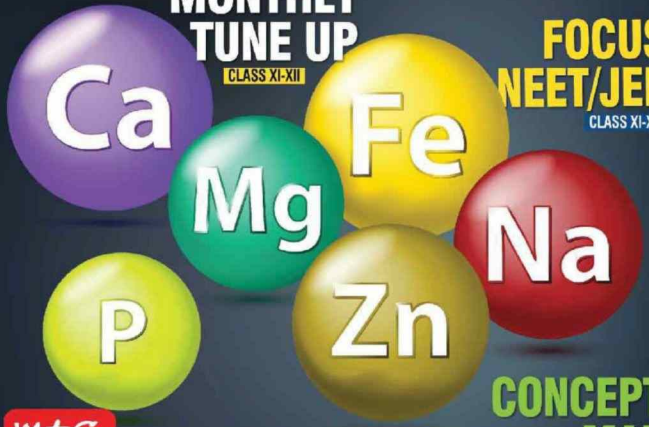
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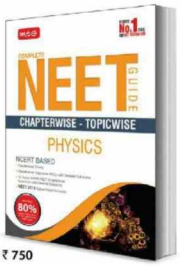
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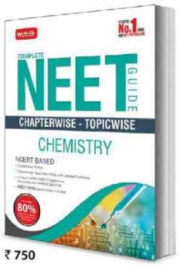
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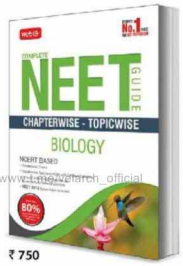
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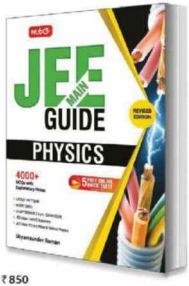
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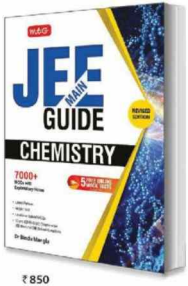
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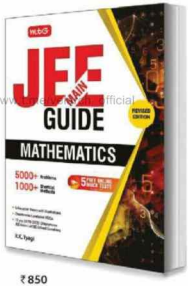
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Managing Editor
Mahabir Singh

Editor
Anil Ahlawat

Corporate Office:
Plot 99, Sector 44 Institutional area, Gurgaon -122 003 (HR).
Tel : 0124-6601200 e-mail : info@mtg.in website : www.mtg.in

Regd. Office:
406, Taj Apartment, Near Safdarjung Hospital, New Delhi - 110029.

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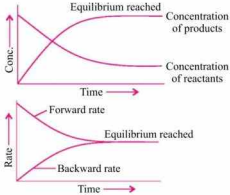
UNIT - 4 : Equilibrium | Redox Reactions

EQUILIBRIUM

- At equilibrium, two opposing processes (forward and reverse) take place at equal rates hence it is called dynamic equilibrium.
- Equilibrium can be established for both physical processes and chemical reactions.

Reversible Reactions

- A reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.



- Ultimately a stage comes in reversible reaction where concentration of both reactant and product becomes equal which is said to be equilibrium.

Law of Chemical Equilibrium

- Law of chemical equilibrium is a result obtained by applying the law of mass action to a reversible reaction in equilibrium.
- For example, consider a general reversible reaction, $aA + bB \rightleftharpoons cC + dD$

  $K_c = \frac{[C]^c[D]^d}{[A]^a[B]^b}$; where, K_c is equilibrium constant.

  K_c is specific for a reaction and this equation is known as law of chemical equilibrium .
- **Relations between equilibrium constants for a general reaction and its multiples :**

Chemical equation	Equilibrium constant
$aA + bB \rightleftharpoons cC + dD$	K_c
$cC + dD \rightleftharpoons aA + bB$	$K_c' = (1/K_c)$
$naA + nbB \rightleftharpoons ncC + ndD$	$K_c'' = (K_c)^n$

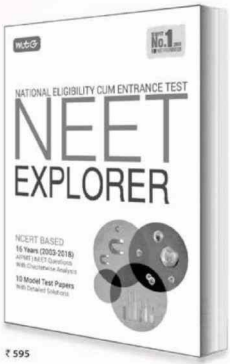
- For a gas phase reaction, $aA + bB \rightleftharpoons cC + dD$

  $K_p = \frac{(p_C)^c(p_D)^d}{(p_A)^a(p_B)^b}$ and $K_p = K_c(RT)^{\Delta n}$;

  where, $\Delta n = (n_{\text{gaseous products}} - n_{\text{gaseous reactants}})$

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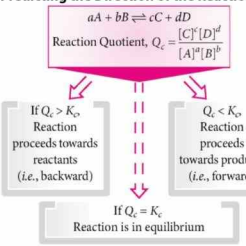
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- If $\Delta n_g = 0$, $K_p = K_c$
- If Δn_g = + ve (*i.e.*, $n_p > n_r$), $K_p > K_c$
- If Δn_g = –ve (*i.e.*, $n_p < n_r$), $K_p < K_c$

Predicting the Direction of the Reaction



Effect of Temperature on Equilibrium Constant

$$\frac{d\ln K_p}{dT} = \frac{\Delta H^\circ}{RT^2} \; ; \; \log\frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

- If $\Delta H = 0$, *i.e.*, no heat is evolved or absorbed in the reaction, $\log (K_2/K_1) = 0$, *i.e.*, $K_2/K_1 = 1$ or $K_2 = K_1$ *i.e.*, equilibrium constant does not change with temperature.
- If ΔH = + ve, *i.e.*, heat is absorbed in the reaction, then $\log (K_2/K_1)$ = + ve, or $\log K_2 > \log K_1$ or $K_2 > K_1$ *i.e.*, equilibrium constant increases with increase in temperature.
- If ΔH = – ve, *i.e.*, heat is evolved in the reaction, $\log (K_2/K_1)$ = – ve, *i.e.*, $\log K_2 < \log K_1$ or $K_2 < K_1$ *i.e.*, equilibrium constant decreases with increase in temperature.

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 :**

	Change imposed at equilibrium	Equilibrium shift
1.	Increase in the concentration of one or more reactants	in forward direction
2.	Increase in the concentration of one or more products	in backward direction
3.	Increase in temperature	towards endothermic reaction
4.	Decrease in temperature	towards exothermic reaction
5.	Increase in pressure	favours lesser number of gaseous moles
6.	Decrease in pressure	favours larger number of gaseous moles
7.	Addition of catalyst	has no effect
8.	Addition of inert gas (a) at constant volume	has no effect
	(b) at constant pressure	favours larger number of gaseous moles

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Ionic Equilibrium

- Those substances which conduct electricity in their aqueous solutions are called electrolytes. Faraday further classified electrolytes into two types :
  - Strong electrolytes on dissolution in water are ionized almost completely. They are excellent conductors of electricity, *e.g.*, HCl, HNO_3.
  - Weak electrolytes are partially ionized in their aqueous solution. They are poor conductors of electricity, *e.g.*, CH_3COOH, H_3PO_4, NH_4OH.

Ostwald's Dilution Law

- It is applicable for weak electrolytes only.
- Consider the dissociation of a weak electrolyte '*C*' moles of which has been dissolved in one litre and 'α' is its degree of dissociation, then

	AB	$\rightarrow$	A^+	+	B^-
Initial concentration	C		0		0
Concentration at equilibrium	$C - C\alpha$		$C\alpha$		$C\alpha$

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

In the case of weak electrolytes, $1 >> \alpha$, so $1 - \alpha = 1$

So, $K = \frac{C\alpha \times C\alpha}{C} = C\alpha^2$; $\alpha^2 = \frac{K}{C}$ or $\alpha = \sqrt{\frac{K}{C}}$

But *C* is concentration in moles/litre *i.e.*, n/V

If *n* is constant (for dilution), $\alpha \propto \sqrt{V}$

i.e., degree of ionization of weak electrolyte increases with dilution. The above expression is known as Ostwald's dilution law.

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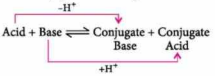
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Conjugate Acid-Base Pair

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



Ionization of Acids and Bases

$HA \rightleftharpoons H^+ + A^-$,
(Acid)

$K_a = \frac{[H^+][A^-]}{[HA]}$ and $\alpha = \sqrt{\frac{K_a}{C}}$

$BOH \rightleftharpoons B^+ + OH^-$,
Base

$K_b = \frac{[B^+][OH^-]}{[BOH]}$ and $\alpha = \sqrt{\frac{K_b}{C}}$

Greater the degree of ionization (α) or greater the dissociation constant (K_a or K_b), stronger is the acid or base.

- **The ionic product of water :**
$K_w = [H^+][OH^-] = 1.0 \times 10^{-14}$ at 298 K, where K_w is the ionic product of water.
The ionic product of water is constant only at constant temperature. With increase of temperature, the degree of ionization of water increases. Thus the concentration of H^+ and OH^- increases and hence the ionic product also increases.
- **The pH scale :** The pH of a solution is a measure of the acidity of a solution.
$pH = -\log[H^+]$
If pH < 7, acidic solution; if pH = 7, neutral solution; if pH > 7, basic solution.
$pK_w = pH + pOH = 14$
- **Relation between K_a and K_b :**
For a weak acid, $pK_a = -\log K_a$;
For a weak base, $pK_b = -\log K_b$
$pK_a + pK_b = pK_w = 14$ at 298 K

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Salt Hydrolysis

- 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	$K_h = \frac{K_w}{K_a}$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w + pK_a + \log C]$
Strong acid and Weak base	Cationic	Acidic pH < 7	$K_h = \frac{K_w}{K_b}$	$h = \sqrt{\frac{K_h}{C}}$	$pH = \frac{1}{2}[pK_w - pK_b - \log C]$
Weak acid and Weak base	Anionic and cationic both	Neutral, pH = 7 (If $K_a = K_b$)	$K_h = \frac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$pH = \frac{1}{2}[pK_w + pK_a - pK_b]$

Calculation of pH

	Types of solution	Formula
1.	Dilute aqueous solution of a strong acid or a strong base	$pH = -\log\{[H^+]_{acid} + [H^+]_{H_2O}\}$ $pOH = -\log\{[OH^-]_{base} + [OH^-]_{H_2O}\}$
2.	Highly concentrated solution of a strong acid or a strong base (concentration > 1 M)	pH of acidic solution is taken as 0. pH of basic solution is taken as 14.
3.	Solution of a weak acid or a weak base	$pH = -\log(C\alpha) = -\log(\sqrt{K_a C})$ $pOH = -\log(C\alpha) = -\log(\sqrt{K_b C})$
4.	Mixture of two or more strong monoprotic acids or strong bases	$pH = -\log\left(\frac{\Sigma NV}{\Sigma V}\right)$, $pOH = -\log\left(\frac{\Sigma NV}{\Sigma V}\right)$

5.	Mixture of an acid and a base	$pH = -\log\left(\frac{(N_1V_1)_{acid} - (N_2V_2)_{base}}{V_1 + V_2}\right)$ (if acid is in excess) $pOH = -\log\left(\frac{(N_2V_2)_{base} - (N_1V_1)_{acid}}{V_1 + V_2}\right)$ (if base is in excess)
6.	Amphiprotic system	$pH = \frac{pK_{a_1} + pK_{a_2}}{2}$

Solubility product

- It is defined as the product of molar concentration of its ions 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.

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

Applying law of mass action, $K_{eq} = \frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]}$

As conc. of $[A_xB_y]$ undissociated is almost constant.

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

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

Relation between solubility and solubility product

- If solubility of a sparingly soluble salt, A^xB^y is S moles/litre, then

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

S moles $\quad xS$ moles $\quad yS$ moles

Thus, $[A^{y+}] = xS$ and $[B^{x-}] = yS$

$\therefore \quad K_{sp} = [A^{y+}]^x\,[B^{x-}]^y = (xS)^x\,(yS)^y$ or $x^x.y^y.S^{(x+y)}$

Buffer Solutions

- The property of resisting change in pH of a solution when an acid or an alkali is added to it is known as buffer action and such solutions are called buffer solutions.
- Such solution usually consist a mixture of weak acid and salt of its conjugate base (acidic buffer) or weak base and salt of its conjugate acid (basic buffer) and a salt of a weak acid and a weak base, *e.g.*, ammonium acetate (CH_3COONH_4) has a buffer action.
- **Henderson-Hasselbalch equation**

For acidic buffer : $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

For basic buffer : $pOH = pK_b + \log\frac{[Salt]}{[Base]}$

or, $pH = pK_a + \log\frac{[Base]}{[Salt]}$

➢ On dilution, the ratio of concentrations of salt and acid or salt and base will still remain same thus pH will remain unchanged.

REDOX REACTIONS

Concept of Oxidation and Reduction

Oxidation

- Addition of oxygen or some other electronegative atom.
- Removal of hydrogen or some other electropositive atom.
- Loss of one or more electrons by an atom or an ion or a molecule.

Reduction

- Removal of oxygen or some electronegative atom.
- Addition of hydrogen or some other electropositive atom.
- Gain of one or more electrons by an atom or an ion or a molecule.
- **Oxidising agent :** The species, which gets reduced, *i.e.*, undergoes reduction and oxidises other species.
- **Reducing agent :** The species, which gets oxidised, *i.e.*, undergoes oxidation and reduces other species.

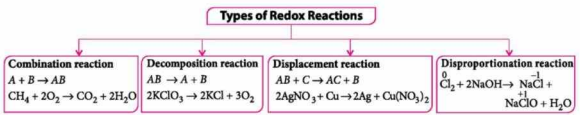
MONTHLY TUNE UP CLASS XII ANSWER KEY

1.	(a)	**2.**	(d)	**3.**	(c)	**4.**	(a)	**5.**	(d)
6.	(b)	**7.**	(b)	**8.**	(b)	**9.**	(b)	**10.**	(b)
11.	(d)	**12.**	(a)	**13.**	(c)	**14.**	(c)	**15.**	(b)
16.	(d)	**17.**	(c)	**18.**	(a)	**19.**	(a)	**20.**	(b,d)
21.	(a,b)	**22.**	(b,c,d)	**23.**	(a,d)	**24.**	(3)	**25.**	(6)
26.	(1.546)	**27.**	(a)	**28.**	(c)	**29.**	(a)	**30.**	(d)

Oxidation Number Rules

Applies to	Rule
Elements	The oxidation number of an atom in an element is zero.
Monoatomic ion	The oxidation number of an atom in a monoatomic ion equals the charge on the ion.
Oxygen	The oxidation number of oxygen is –2 in most of its compounds (an exception is O in H_2O_2 and other peroxides, where oxidation number is –1) and in oxygen fluoride (OF_2), it is +2.
Hydrogen	The oxidation number of hydrogen is +1 in most of its compounds. (The oxidation number of hydrogen is –1 in metallic hydrides such as CaH_2, NaH_2.)
Halogens	The oxidation number of fluorine is –1, in all of its compounds. Each of other halogens (Cl, Br, I) has an oxidation number of –1 in binary compounds, except when the other element is another halogen above it in the periodic table or the other element is oxygen.
Compounds and ions	The sum of the oxidation numbers of the atoms in a compound is zero. The sum of the oxidation number of the atoms in a polyatomic ion equals the charge on the ion.
Alkali metals	The oxidation number of alkali metals (Na, K, Li, etc) in compounds is +1.
Alkaline earth metals	The oxidation number of alkaline earth metals (Mg, Ca, Ba, Sr, etc.) in compounds is +2.
Sulphides	In all sulphides the oxidation number of sulphur is –2.
Transition elements and *p*-block elements	Variable oxidation number is most commonly shown by transition elements as well as *p*-block elements. *e.g.*, Fe (+2 and +3), Cu (+1 and +2), Mn (+7, +6, +5, +4, +3, +2), As (+3 and +5), Sb (+3 and +5), Sn (+2 and +4) etc.

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Balancing of Redox Reactions

Oxidation Number Method

- Identify atoms which undergo change in oxidation number in the reaction.
- Calculate the increase or decrease in the oxidation number per atom and multiply it by number of atoms undergoing that change, if increase or decrease is not equal then multiply by suitable number to make them equal.
- Add H^+ (if medium is acidic) or OH^- (if medium is basic) on the appropriate side so that the total ionic charges of reactants and products are equal.
- Make the number of hydrogen atoms in the expression on the two sides equal by adding H_2O to the reactants or products and finally check the number of oxygen atoms.

Half Reaction Method

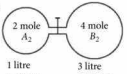
- Separate the equation into half-reactions.
- Balance the atoms other than O and H in each half-reaction individually.
- For reactions occurring in acidic medium, add H_2O to balance O atoms and H^+ to balance H atoms and for basic medium, H atoms are balanced by adding H_2O molecule to the side deficient in H atoms and equal number of OH^- ions are added to opposite side and then duplicacy is removed if any.
- Add electrons to one side of the half-reaction to balance the charges and make the number of electrons equal in two half-reactions by multiplying one or both half-reactions by appropriate number.
- Add two half-reactions to achieve the overall reaction and cancel the electrons on both sides.

Redox Reactions and Electrode Processes

- **Redox couple :** It is defined as having together the oxidised and reduced forms of a substance taking part in an oxidation or reduction half-reaction *i.e*, a metal dipped in the solution of its own ions.
- **Electrode potential :** The potential difference set up between the metal and its own ions in the solution is called the electrode potential. In general, it is the tendency of an electrode to gain or lose electrons.
- **Standard electrode potential (E°) :** If the concentration of each species taking part in the electrode reaction is unity and further the reaction is carried out at 298 K, then the potential of each electrode is called standard electrode potential.
  - Standard electrode potential of hydrogen is taken as 0.00 volts by convention.
  - Electrochemical series is a series in which a list of oxidising agents are arranged in decreasing order of their strength. It is also called activity or electromotive series.
  - A negative E° means that the redox couple is a stronger reducing agent than the H^+/H_2 couple.
  - A positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.



1. The gas A_2 in the left flask allowed to react with gas B_2 present in right flask as $A_{2(g)} + B_{2(g)} \rightleftharpoons 2AB_{(g)}$; $K_c = 4$ at 27 °C. What is the concentration of AB when equilibrium is established ?

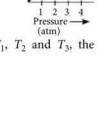


(a) 1.33 M (b) 2.66 M
(c) 0.66 M (d) 0.33 M

2. According to Bronsted–Lowry concept of acids and bases, mark the option in which conjugate pair is not correctly matched.

	Species	Conjugate acid	Conjugate base
(a)	HCO_3^-	CO_3^{2-}	H_2CO_3
(b)	HPO_4^{2-}	$H_2PO_4^-$	PO_4^{3-}
(c)	NH_3	NH_2^-	NH_4^+
(d)	HS^-	S^{2-}	H_2S

3. The preparation of $SO_{3(g)}$ by reaction, $SO_{2(g)} + 1/2\ O_{2(g)} \rightleftharpoons SO_{3(g)}$, is an exothermic reaction.
If the preparation follows the following temperature-pressure relationship for its % yield, then for temperatures T_1, T_2 and T_3, the correct option is



(a) $T_3 > T_2 > T_1$ (b) $T_1 > T_2 > T_3$
(c) $T_1 = T_2 = T_3$
(d) Nothing could be predicted about temperature from given information

4. Identify the compounds which are reduced and oxidised in the following reaction :

$$3N_2H_4 + 2BrO_3^- \rightarrow 3N_2 + 2Br^- + 6H_2O$$

(a) N_2H_4 is oxidised and BrO_3^- is reduced.
(b) BrO_3^- is oxidised and N_2H_4 is reduced.
(c) BrO_3^- is both reduced and oxidised.
(d) This is not a redox reaction.

5. From the given data, identify the most stable oxide of nitrogen.

(a) $2NO_{2(g)} \rightleftharpoons N_{2(g)} + 2O_{2(g)}$; $K = 6.7 \times 10^{16}$ mol L^{-1}
(b) $2N_2O_{5(g)} \rightleftharpoons 2N_{2(g)} + 5O_{2(g)}$;
$K = 1.2 \times 10^{24}$ mol^5 L^{-5}
(c) $2NO_{(g)} \rightleftharpoons N_{2(g)} + O_{2(g)}$; $K = 2.2 \times 10^{30}$
(d) $N_2O_{(g)} \rightleftharpoons 2N_{2(g)} + O_{2(g)}$; $K = 3.5 \times 10^{33}$ mol L^{-1}

6. Consider the following reaction,

Select the incorrect statement.
(a) It is not a disproportionation reaction.
(b) It is intramolecular redox reaction.
(c) OH^- is a reducing as well as oxidising agent.

(d) $\begin{matrix}\text{CHO}\\|\\\text{CHO}\end{matrix}$ is a reducing as well as oxidising agent.

7. The values of coefficients to balance the following reaction are

$$w\text{Cr(OH)}_3 + x\text{ClO}^- + a\text{OH}^- \rightarrow y\text{CrO}_4^{2-} + z\text{Cl}^- + b\text{H}_2\text{O}$$

	w	*x*	*y*	*z*
(a)	2	3	3	3
(b)	2	4	3	2
(c)	2	4	4	2
(d)	2	3	2	3

8. Consider the following reaction :

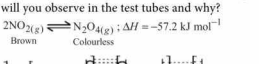
$2X_{(g)} + Y_{(g)} \rightleftharpoons 2Z_{(g)} + 80$ kcal

Which combination of pressure and temperature gives the highest yield of *Z* at equilibrium?

(a) 1000 atm and 500°C (b) 500 atm and 500°C
(c) 1000 atm and 100°C (d) 500 atm and 100°C

9. In an experiment, NO_2 gas is prepared and taken into three test tubes *X*, *Y* and *Z*. NO_2 gas which is brown in colour dimerises into N_2O_4 which is colourless. Test tube *X* is kept at room temperature, *Y* is kept in ice and *Z* is kept in hot water. What colour changes will you observe in the test tubes and why?

$$\underset{\text{Brown}}{2NO_{2(g)}} \rightleftharpoons \underset{\text{Colourless}}{N_2O_{4(g)}} ; \Delta H = -57.2 \text{ kJ mol}^{-1}$$



(a) In test tube *X*, brown colour intensifies since backward reaction is favoured at low temperature.
(b) In test tube *Y*, brown colour intensifies since backward reaction takes place at room temperature.
(c) In test tube *Z*, brown colour intensifies since high temperature favours the backward reaction.
(d) Brown colour of test tubes *X*, *Y* and *Z* remains same since there is no effect of change in temperature on the reaction.

10. What is the minimum pH required to prevent the precipitation of ZnS in a solution that is 0.01 M $ZnCl_2$ and saturated with 0.10 M H_2S ?
(Given : $K_{sp} = 10^{-21}$, $K_{a_1} \times K_{a_2} = 10^{-20}$)
(a) 0 (b) 1 (c) 2 (d) 4

11. What is the equivalent weight of NH_3 in the given reaction?

$3CuO + 2NH_3 \longrightarrow 3Cu + N_2 + 3H_2O$

(a) 17 (b) 17/4 (c) 17/2 (d) 17/3

12. Small quantities of aqueous solution of X_2, Y_2 and Z_2 are put separately in three test tubes. Now, small quantities of compounds *AX*, *AY* and *AZ* are added separately to each of the solution of X_2, Y_2 and Z_2. *AX* does not react with any of the three solutions. *AY* reacts with both X_2 and Z_2. *AZ* reacts with X_2. The decreasing order of ease of oxidation of the anions X^-, Y^- and Z^- is
(a) Y^-, Z^-, X^- (b) Z^-, X^-, Y^-
(c) Y^-, X^-, Z^- (d) X^-, Z^-, Y^-

13. The pK_a of a weak acid (*HA*) is 4.5. The pOH of an aqueous buffered solution of *HA* in which 50% of the acid is ionized, is
(a) 4.5 (b) 2.5 (c) 9.5 (d) 7.0

14. Which one of the following ionic species has the greatest proton affinity to form stable compound?
(a) I^- (b) HS^- (c) NH_2^- (d) F^-

15. The oxidation numbers of Fe and S in iron pyrites are respectively
(a) 3, – 1 (b) 2, – 1 (c) 3, – 1.5 (d) 4, – 2

16. The solubility of different sparingly soluble salts are given as follows:

S. No.	Formula Type	Solubility product
1.	*AB*	4.0×10^{-20}
2.	A_2B	3.2×10^{-11}
3.	AB_3	2.7×10^{-31}

The correct increasing order of solubility is
(a) 1, 3, 2 (b) 2, 1, 3 (c) 1, 2, 3 (d) 3, 1, 2

17. Using the standard electrode potential, find out the pair between which redox reaction is not feasible.
[E° values : $Fe^{3+}/Fe^{2+} = +0.77$ V; $I_2/I^- = +0.54$ V; $Cu^{2+}/Cu = +0.34$ V; $Ag^+/Ag = +0.80$ V]
(a) Fe^{3+} and I^- (b) Ag^+ and Cu
(c) Fe^{3+} and Cu (d) Ag and Fe^{3+}

18. pH of water is 7. When a substance *X* is dissolved in water, the pH becomes 13. The substance *X* is a salt of
(a) strong acid and strong base
(b) weak acid and weak base
(c) strong acid and weak base
(d) weak acid and strong base.

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19. In which of the following processes nitrogen is oxidised?
(a) $NH_4^+ \rightarrow N_2$ (b) $NO_3^- \rightarrow NO$
(c) $NO_2 \rightarrow NO_2^-$ (d) $NO_3 \rightarrow NH_4^+$

20. Which of the following statements is/are true?
(a) Weaker the acid, greater will be hydrolysis of its anion.
(b) Weaker the base, greater will be hydrolysis of its cation.
(c) Both (a) and (b). (d) None of these.

21. A compound of Xe and F is found to have 53.4% Xe (atomic mass 133). Oxidation number of Xe in this compound is
(a) 0 (b) +2 (c) +4 (d) +6

22. Pressure necessary to obtain 50% dissociation of PCl_5 at 500 K will be qual to
(a) K_p (b) $2K_p$ (c) $3K_p$ (d) $4K_p$

23. pOH of H_2O is 7.0 at 298 K. If water is heated at 350 K, which of the following statement should be true?
(a) pOH will decrease. (b) pOH will increase.
(c) pOH will remain 7.0.
(d) Concentration of H^+ ions will increase but that of OH^- will decrease.

24. 4.8 g of a sample of methanol was placed in an empty one litre vessel and heated to 250 °C. Methanol first changed into vapour and then decomposed into CO and H_2. After equilibrium was reached, a hole was made in the vessel. The gas effusing out showed that it contains 30 times as much H_2 as CH_3OH vapour. The equilibrium constant for this reaction at 250 °C is
(a) 1.1 (b) 2.2 (c) 3.3 (d) 4.4

25. Buffer capacity of a buffer solution is x, the volume of 1 M NaOH added to 100 mL of this solution if the change of pH by 1 is
(a) 0.1 x mL (b) 10 x mL
(c) 100 x mL (d) x mL.

SOLUTIONS

1. **(c)** :

	$A_{2(g)}$	+ $B_{2(g)}$	$\rightleftharpoons 2AB_{(g)}$
Initial moles	2	4	0
Moles at eqm	$2-x$	$4-x$	$2x$

$$K_c = \frac{4x^2}{(2-x)(4-x)} = 4 \Rightarrow x = 1.33 \text{ mole}$$

$$[AB_{(g)}] = \frac{2\times 1.33}{4} = 0.66 \text{ M}$$

2. **(b)**

3. **(b)** : For exothermic reactions, yield increases as temperature decreases *i.e.*, $T_1 > T_2 > T_3$

4. **(a)** : $3\overset{-2}{N_2}H_4 + 2\overset{+5}{Br}O_3^- \rightarrow 3\overset{0}{N_2} + 2\overset{-1}{Br}^- + 6H_2O$

5. **(a)** : The value of K_{eq} is the measure of extent of reaction. For most stable oxide, K_{eq} should be minimum.

6. **(c)** : One CHO is oxidised to COO^- and one CHO is reduced to CH_2OH.
Thus, it is not a disproportionation reaction. It is intramolecular redox reaction. Thus, options (a) and (b) are true and $\begin{vmatrix} CHO \\ | \\ CHO \end{vmatrix}$ is reducing as well as oxidising agent.

7. **(d)** : $Cr(OH)_3 + 5OH^- \rightarrow CrO_4^{2-} + 4H_2O + 3e^-] \times 2$
$ClO^- + H_2O \neq 2e^- \rightarrow Cl^- + 2OH^-] \times 3$
$2Cr(OH)_3 + 4OH^- + 3ClO^- \rightarrow 2CrO_4^{2-} + 3Cl^- + 5H_2O$

8. **(c)** : The reaction takes place with a reduction in number of moles (volume) and is exothermic. So high pressure and low temperature will favour the reaction in forward direction.

9. **(c)**

10. **(b)** : $K_{sp} = [Zn^{2+}][S^{2-}]$

$$[S^{2-}] = \frac{10^{-21}}{0.01} = 10^{-19}$$

$$H_2S \rightleftharpoons H^+ + HS^- \; ; \; K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

$$HS^- \rightleftharpoons H^+ + S^{2-} \; ; \; K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$K_{a_1}\cdot K_{a_2} = \frac{[H^+]^2[S^{2-}]}{[H_2S]}$$

$$10^{-20} = \frac{[H^+]^2 \times 10^{-19}}{0.1} \Rightarrow [H^+] = 0.1 \text{ or pH} = 1$$

11. **(d)** : $2NH_3 \rightarrow N_2 + 6e^-$ or, $NH_3 \rightarrow 1/2\, N_2 + 3e^-$
$\therefore$ Eq. wt. = $M/3 = 17/3$

12. **(a)** : Since AX does not react with any of the solutions, it means that X is least easily oxidized.
Since AY reacts with both X_2 and Z_2, *i.e.*,
$2Y^- + X_2 \rightarrow 2X^- + Y_2$ and $2Y^- + Z_2 \rightarrow 2Z^- + Y_2$,
therefore, Y^- is most easily oxidized.
Since AZ reacts with only X_2, *i.e.*,
$2Z^- + X_2 \rightarrow 2X^- + Z_2$, therefore, Z^- is more easily oxidized than X^-. Combining all the results, the decreasing order of oxidation of anions follows the order $Y^- > Z^- > X^-$

13. (c) : For buffer solution

$$pH = pK_a + \log\left[\frac{Salt}{Acid}\right] = 4.5 + \log\left[\frac{Salt}{Acid}\right]$$

As HA is 50% ionized, hence [Salt] = [Acid]

$pH = 4.5 \Rightarrow pOH = 14 - 4.5 = 9.5$

14. (c) : Strongest proton affinity will be for the species which is the strongest base or whose conjugate acid is the weakest. The conjugate acid of NH_2^- is NH_3 which is the weakest acid out of HI, H_2S, NH_3 and HF.

15. (d)

16. (a) : Solubility of $AB = \sqrt{K_{sp}} = 2\times10^{-10}$

Solubility of $A_2B = \sqrt[3]{\frac{K_{sp}}{4}} = 2\times10^{-4}$

Solubility of $AB_3 = \left[\frac{K_{sp}}{27}\right]^{1/4} = 10^{-8}$

17. (d) : For the reaction, $2Fe^{3+} + 2I^- \rightarrow 2Fe^{2+} + I_2$

$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{I_2/I^-} = 0.77 - (0.54) = +0.23$ V

Here, E°_{cell} is +ve so, the reaction is feasible.

For the reaction,

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

$E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu} = 0.80 - (0.34) = +0.46$ V

Here, E°_{cell} is +ve so, the reaction is feasible.

For the reaction, $2Fe^{3+} + Cu \rightarrow 2Fe^{2+} + Cu^{2+}$

$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Cu^{2+}/Cu} = 0.77 - (0.34) = +0.43$ V

Here, E°_{cell} is +ve so, the reaction is feasible.

For the reaction, $Ag + Fe^{3+} \rightarrow Ag^+ + Fe^{2+}$

$E^\circ_{cell} = E^\circ_{Fe^{3+}/Fe^{2+}} - E^\circ_{Ag^+/Ag} = 0.77 - (0.80) = -0.03$ V

Here, E°_{cell} is negative so, the reaction is not feasible.

18. (d) **19. (a)** **20. (c)**

21. (d) : Compound of Xe and F contains 53.4% Xe. Therefore, amount of Xe and F present are 53.4 g and 46.6 g respectively.

Molar ratio of Xe : F

$$= \frac{53.4}{133} : \frac{46.6}{19}$$

$$= 0.401 : 2.45$$

$$= 1 : 6$$

Thus, the empirical formula of the compound is XeF_6.

O. N. of Xe in $XeF_6 = +6$.

22. (c) :

	$PCl_5 \rightleftharpoons$	PCl_3	+ Cl_2
Initial moles	1	0	0
Moles at eqm.	1–0.5 = 0.5	0.5	0.5

Total = 1.5 moles

If P is the total required pressure, then

$$P_{PCl_5} = \frac{0.5}{1.5}\times P = \frac{P}{3},$$

$$P_{PCl_3} = \frac{0.5}{1.5}\times P = \frac{P}{3},\ P_{PCl_2} = \frac{0.5}{1.5}\times P = \frac{P}{3}$$

$$\therefore\ K_p = \frac{P_{PCl_3}\times P_{Cl_2}}{P_{PCl_5}} = \frac{(P/3)(P/3)}{P/3} = \frac{P}{3}$$

or $P = 3K_p$

23. (b) : $[OH^-] = \sqrt{K_w}$ in pure water.

As temperature increases K_w increases

$\Rightarrow$ $[OH^-]$ increases.

24. (a) :

	$CH_3OH_{(g)} \rightleftharpoons$	$CO_{(g)}$	+ $2H_{2(g)}$
Initial moles	4./32 = 0.15	0	0
Moles at eqm	(0.15 – x)	x	$2x$

Given, $30(0.15 - x) = 2x$

or $4.5 - 30x = 2x \Rightarrow 32x = 4.5 \Rightarrow x = 0.14$

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$$K_p = \frac{(0.14)(0.28)^2}{(0.15-0.14)} = 1.0976 = 1.1$$

25. (c) : Moles of NaOH required for 1 L solution = x

$\therefore$ Moles of NaOH required for 100 mL of solution = 0.1 x

Now, $0.1x = 1 \times V \Rightarrow V = 0.1\ x$ L = 100 x mL

For the SCIENTIST in YOU



Named after a mineral discovered in the Ural Mountains of Russia, perovskites have taken centre stage as a class of materials with properties that could be applied to future electronics and energy devices.

Semiconducting films made of perovskites promise flexible, light-weight solar cells that are cheap and easily made from abundant materials. While they are not yet available commercially – hurdles include making them more stable and durable – they may transform the solar energy industry in the next decade or two.

For scientists, perovskites also present an interesting puzzle: Start with any number of variations on the basic ingredients for making them – lead, iodide and methylammonium – and you end up with the same basic material. Yet, tweaks to the chemistry at various stages in the process can lead to perovskites with more desirable qualities for solar cells.

For researchers , the mystery and potential of perovskites converge in experiments where extremely bright X-rays are used to study the chemistry of the material in the very moments it is being formed.

Class XI

Be NEET READY

with exclusive and brain storming MCQs

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Practicing these MCQs helps to strengthen your concepts and give you extra edge in your NEET preparation

1. *A* is binary compound of an univalent metal. 1.422 g of *A* reacts completely with 0.321 g of sulphur in an evacuated and sealed tube to give 1.743 g of a white crystalline solid (*B*) that formed a hydrated double salt (*C*) with $Al_2(SO_4)_3$. *A* and *B* are respectively

(a) KO_2, K_2SO_4 (b) NaO_2, Na_2SO_4
(c) K_2O, K_2SO_4 (d) Na_2O, Na_2SO_4

2. IUPAC name of the following compound is

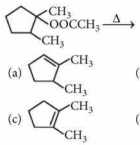


(a) 1-bromo-3, 5-epoxy-4, 4-dimethyl-2-hexanone
(b) 1-bromo-3, 3-dimethyl-2-oxo-2-hexanone
(c) 1-bromo-3, 3-dimethyl acetone
(d) 1-bromo-4, 4-dimethyl-5-oxo-hexanone.

3. For the equilibrium, $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$, the partial pressures of SO_3, SO_2 and O_2 gases at 650 K are respectively 0.3 bar, 0.6 bar and 0.4 bar. If the moles of both the oxides of sulphur are so adjusted as equal, what will be the partial pressure of O_2 ?

(a) 0.4 (b) 1.0 (c) 1.3 (d) 1.6

4. Which of the following is the product for the given reaction?



5. Amphoteric oxide (X) + 3C + Cl_2 ⟶ Poisonous gas + anhydrous chloride (Y)

Hydrated chloride $\xrightarrow{\Delta}$ Z

Element present in (Y) other than 'Cl' reacts with concentrated HCl but leads to passivation with conc. HNO_3. Select the correct option.

(a) $X = Z$ and Y on reacting with LiH forms strong oxidising agent.
(b) $X = Z$ and Y on reacting with LiH forms strong reducing agent.
(c) $X \neq Z$ and Y is used as a catalyst in Friedel—Crafts reaction.
(d) $X \neq Z$ and Y on reacting with LiH forms strong oxidising agent.

6. $N_2 + 3H_2 \longrightarrow 2NH_3$

Molecular weights of NH_3 and N_2 are x_1 and x_2, their equivalent weights are y_1 and y_2 respectively. Then $(y_1 - y_2)$ is

(a) $\left(\frac{2x_1 - x_2}{6}\right)$ (b) $(x_1 - x_2)$

(c) $(3x_1 - x_2)$ (d) $(x_1 - 3x_2)$

7. By what method the quantity of organic pollutants in water can be determined?
   (a) By measuring BOD
   (b) By pH measurement
   (c) By transparency measurement
   (d) By measuring the change of colour

8. From the observations given below, suggest the relation between X, Y and Z.

Experiment	Heat supplied	Work done	ΔE
I	100 J supplied to the system	200 J work done by the system	X Joules
II	200 J supplied to the system	200 J done on the system	Y Joules
III	400 J lost to the system	100 J work done by the system	Z Joules

(a) $X = Y = Z$ (b) $Y > X > Z$

(c) $Y > Z > X$ (d) $X > Z > Y$

9. $C_3H_{8(g)} + A \rightarrow$ syn gas $\xrightarrow[Fe_2O_3/Cr_2O_3]{X}$

$Y + Z \xrightarrow[\text{High } P]{\text{Cold water}} Z_{(g)}$ + a soln. of Y.

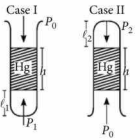
Z has low chemical reactivity at room temperature but under vigorous suitable conditions it reacts with other elements to form very useful compounds.
Z is also being looked upon as prospective source of energy for future. Which two substances are same ?

(a) X and Z (b) A and X

(c) A and Y (d) A and Z

10. Which of the following statements is incorrect?
    (a) Among O_2^+, O_2 and O_2^- the stability decreases as $O_2^+ > O_2 > O_2^-$.
    (b) He_2 molecule does not exist as the effect of bonding and anti-bonding molecular orbitals cancel each other.
    (c) C_2, O_2^{2-} and Li_2 are diamagnetic.
    (d) In F_2 molecule, the energy of $\sigma 2p_z$ is more than π_{2px} and π_{2py}.

11. A gas column is trapped between closed end of a tube and a mercury column of length (h) when this tube is placed with its open end upwards the length of gas column is (ℓ_1), the length of gas column becomes (ℓ_2) when open end of tube is held downwards. Find atmospheric pressure in terms of height of Hg column.



(a) $\frac{h(\ell_1 - \ell_2)}{(\ell_1 + \ell_2)}$ (b) $\frac{h(\ell_1 + \ell_2)}{\ell_2 - \ell_1}$

(c) $h\left(\frac{(\ell_1 \times \ell_2)}{\ell_2 - \ell_1}\right)$ (d) None of these

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12. For the element X, student Riya measured its radius as 102 nm, student Rajat as 203 nm. and Aman as 100 nm, using same apparatus. Their teacher explained that measurements were correct by saying that recorded values by three students were
    (a) crystal, van der Waal and covalent radii
    (b) covalent, crystal and van der Waal radii
    (c) van der Waal, ionic and covalent radii
    (d) none is correct.

13. The molar composition of polluted air is as follows :

Gas	At. wt.	Mole percentage
Oxygen	16	16%
Nitrogen	14	80%
Carbon dioxide	—	03%
Sulphur dioxide	—	01%

What is the average molecular weight of the given polluted air? (Given, atomic weights of C and S are 12 and 32 respectively.)

(a) 28.51 (b) 50.08 (c) 29.48 (d) 45.12

14. 0.395 g of an organic compound by Carius method for the estimation of sulphur gave 0.582 g of $BaSO_4$. The percentage of sulphur in the compound is
    (a) 20.24 (b) 35 (c) 40 (d) 45

15. An electron in a hydrogen like atom makes transition from a state in which its de-Broglie wavelength is λ_1 to a state where its de-Broglie wavelength is λ_2 then wavelength of photon (λ) generated will be

(a) $\lambda = \lambda_1 - \lambda_2$ (b) $\lambda = \frac{4mc}{h}\left\{\frac{\lambda_1^2\lambda_2^2}{\lambda_1^2 - \lambda_2^2}\right\}$

(c) $\lambda = \sqrt{\frac{\lambda_1^2\lambda_2^2}{\lambda_1^2 - \lambda_2^2}}$ (d) $\lambda = \frac{2mc}{h}\left\{\frac{\lambda_1^2\lambda_2^2}{\lambda_1^2 - \lambda_2^2}\right\}$

SOLUTIONS

1. **(a)** : B forms double salt with $Al_2(SO_4)_3$ and thus, may be K_2SO_4. $(A) + S \longrightarrow (B)\ K_2SO_4$

$\because$ 1.743 g K_2SO_4 is obtained by 1.422 g of A

$\therefore$ 174 g K_2SO_4 is obtained by $\frac{1.422 \times 174}{1.743} = 142$ g of A

$\therefore$ 174 g K_2SO_4 requires 32 g of S

$\therefore$ 1.743 g K_2SO_4 requires $\frac{32 \times 1.743}{174} = 0.32$ g of S

Thus, given data confirms that (B) is K_2SO_4.

Now, $2(A) + S \longrightarrow K_2SO_4$

(A) potassium salt

M. wt. of $(A) \times 2 = 142$ $\therefore$ M. wt. of $(A) = 71$

Since (A) is potassium salt

$\therefore$ Molecular weight of left component = 71 − 39 = 32

Thus, salt is KO_2.

2. **(a)**

3. **(d)** : The equilibrium given as,

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

$\therefore\ K_p = \frac{p_{SO_2}^2 p_{O_2}}{p_{SO_3}^2} = \frac{0.6 \times 0.6 \times 0.4}{0.3 \times 0.3} = 1.6$ bar

Upon adjustment, K_p does not change,

$\therefore\ 1.6 \text{ bar} = K_p = \frac{x^2 p_{O_2}}{x^2}$

Partial pressure of oxygen = 1.6 bar

4. **(b)**

5. **(b)** : $\underset{X}{Al_2O_3} + 3C + Cl_2 \longrightarrow \underset{Y}{2AlCl_3} + 3CO$

Hydrated chloride on heating gives

$2Al(H_2O)_6Cl_3 \xrightarrow[-400°C]{\text{strong heating}} ZAl_2O_3 + 9H_2O + 6HCl$

Al and Cl present in $AlCl_3$. Thus,

$2Al_{(s)} + 6HCl_{(aq)} \longrightarrow 2Al^{3+}_{(aq)} + 6Cl^-_{(aq)} + 3H_{2(g)}$

$2Al + 6HNO_{3(conc.)} \longrightarrow Al_2O_3 + 6NO_2 + 3H_2O$

Thin protective layer of Al_2O_3 on the surface of metal causes passivation.

$AlCl_3 + 4LiH \longrightarrow LiAlH_4 + 3LiCl$

6. **(a)** : For the given reaction, $N_2 + 3H_2 \longrightarrow 2NH_3$

Equivalent weight of $N_2(y_2) = x_2/6$

Equivalent weight of $NH_3(y_1) = x_1/3$

$y_1 - y_2 = \frac{x_1}{3} - \frac{x_2}{6} = \frac{2x_1 - x_2}{6}$

7. **(a)**

8. **(b)** : According to first two of thermodynamics, $\Delta E = q + w$

For experiment I $q = +100$ J $w = -200$ J

$\Delta E = 100 - 200 = -100$ J $= X$

For experiment II $q = +200$ J $w = +200$ J

$\Delta E = 200 + 200 = 400$ J $= Y$

For experiment III $w = -400$ J $w = -100$ J

$\Delta E = -400 - 100 = -500$ J $= Z$

Thus, $Y > X > Z$.

9. **(b)** : $\underset{(A)}{C_3H_{8(g)}} + 3H_2O_{(g)} \rightarrow \underbrace{3CO_{(g)} + 7H_{2(g)}}_{\text{Syn gas}}$

$CO_{(g)} + H_2O_{(g)} \xrightarrow[(X)]{Fe_2O_3/Cr_2O_3} \underset{(Y)}{CO_{2(g)}} + \underset{(Z)}{H_{2(g)}}$

10. **(d)**

11. **(b)** : For gas $P_1 = (P_0 + h)$ $P_2 = (P_0 - h)$

$V_1 = \pi r^2 \ell_1$ $V_2 = \pi r^2 \ell_2$

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at const. T and moles.

$P_1V_1 = P_2V_2$; $(P_0 + h)\ \pi r^2 \ell_1 = (P_0 - h)\ \pi r^2 \ell_2$

$P_0\ \ell_1 + h\ell_1 = P_0\ \ell_2 - h\ell_2$; $P_0\ \ell_2 - P_0\ell_1 = h\ell_1 + h\ell_2$

$P_0 = \left(\frac{h(\ell_1 + \ell_2)}{(\ell_2 - \ell_1)}\right)$ cm of Hg column

12. **(a)**

13. **(c)** : $M_{avg} = \frac{\sum_{j=1}^{j=n} n_j M_j}{\sum_{j=1}^{j=n} n_j}$ Here $\sum_{j=1}^{j=n} n_j = 100$

$M_{avg} = \frac{16 \times 32 + 80 \times 28 + 44 \times 3 + 64 \times 1}{100} = 29.48$

14. **(a)** : Mass of $BaSO_4 = 0.582$ g

We know, $\underset{233}{BaSO_4} = \underset{32}{S}$

233 g of $BaSO_4$ contains sulphur = 32 g

0.582 g of $BaSO_4$ contains sulphur $= \frac{32}{233} \times 0.582$

Percentage of sulphur $= \frac{\text{wt. of sulphur}}{\text{wt. of compound}} \times 100$

$= \frac{32 \times 0.582}{233 \times 0.395} \times 100 = 20.24\%$

15. **(d)** : $hc/\lambda = E_2 - E_1 = KE_2 - KE_1$

$\therefore\ \lambda = \frac{h}{mV}$, $(mV)^2 = \left(\frac{h}{\lambda}\right)^2$, $\frac{1}{2}\frac{m^2V^2}{m} = \frac{1}{2m}\frac{h^2}{\lambda^2}$

$\therefore\ \frac{hc}{\lambda} = \frac{h^2}{2m\lambda_2^2} - \frac{h^2}{2m\lambda_1^2}$ $\therefore\ \lambda = \frac{2mc}{h}\left\{\frac{\lambda_1^2\lambda_2^2}{\lambda_1^2 - \lambda_2^2}\right\}$

BRUSH UP YOUR CONCEPTS

Class XI

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

STRUCTURE OF ATOM

In continuation to the last article :

de Broglie's work (1924)

de Broglie suggested that all moving particles have wave character also, though it has no significance for macro particles.

Wave character of electrons is proved by diffraction (Davisson and Germer) while particle nature by scintillation on ZnS coated glass tube (opposite to cathode) in cathode ray tube.

$$\lambda_{\text{matter-wave}} = \frac{h}{\text{mass}(m) \times \text{velocity}(v)} = \frac{h}{\text{momentum}(p)}$$

$$\lambda_{\text{matter-wave}} = \frac{h}{\sqrt{2m \times \frac{1}{2}mv^2}} = \frac{h}{\sqrt{2m \cdot KE}}$$

KE is in joules. If q coulombs is the charge of a particle and potential V in volts, (1 CV = 1 J)

$$\lambda_{\text{matter-wave}} = \frac{h}{\sqrt{2m \cdot qV}}$$

$$\lambda_{\text{electronic motion}} = \frac{h}{\sqrt{2m \cdot eV}} \quad \text{(Here, } e = 1.6 \times 10^{-19} \text{ C)}$$

Heisenberg's work (1927)

Heisenberg gave the idea that determination of exact position (wave property) and exact momentum (particle property) of a microscopic object is not possible.

$$(\Delta x)(m\Delta v) = \Delta x \cdot \Delta p \geq \frac{h}{4\pi}$$

Δx is uncertainty (error) in measurement of position, Δv is uncertainty in measuring velocity and Δp is uncertainty in measuring momentum.

This principle had been one of the basis of failures of Bohr's view of definite circular paths for electrons in motion around nucleus.

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Wave mechanical model of atom

As in Newton's classical mechanics, the pivotal equation is, Force (F) = mass (m) × acceleration (a), in wave mechanical model of atom the pivotal equation is Schrodinger wave equation :

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V) = 0$$

or $\hat{H}\psi = E\psi$

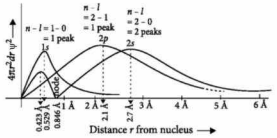
The solution of this equation is arrived at, for some definite values of ψ to get some definite sets of principal quantum number 'n', azimuthal quantum number 'l' and magnetic quantum number 'm', which are further used mathematically to know different details related to an electron in an atom. One more quantum number spin quantum number 's' is also used for the purpose of spin of electron. ψ, itself, has no significance except that it represents amplitude of electronic wave motion and now it is used to represent an orbital.

An orbital is the space around a nucleus where there is maximum probability of finding an electron.

The ψ^2, radial probability density value, which is always positive, is used to decide the number of nodes in an orbital.

Radial probability density function $4\pi r^2 \cdot dr \cdot \psi^2$ when plotted against distance from the nucleus r, gives the most probable radius of an orbital; for 1s it is 0.529 Å, for 2s it is 2.743 Å and for 2p it is 2.1 Å.

*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.



- **Very important for 1*s*, 2*s* and 2*p* orbitals:**
  (a) Size of orbitals : $1s < 2p < 2s$
  (b) Energy of orbitals : $1s < 2s < 2p$

Principal quantum number, *n* (*Niels Bohr*)

- It represents orbits or energy states or shells as 1, 2, 3, ...; also designated as *K*, *L*, *M*, ...
- Higher the *n* value, farther is the electron from nucleus, *i.e.*, $r_1 < r_2 < r_3 < .....$
- Energy of electron in n^{th} shell

$$= -1312\frac{Z^2}{n^2}\ \text{kJ mol}^{-1} = -1.312\times10^6\frac{Z^2}{n^2}\ \text{J mol}^{-1}$$

$$= -2.18\times10^{-18}\frac{Z^2}{n^2}\ \text{J atom}^{-1} = -13.6\frac{Z^2}{n^2}\ \text{eV atom}^{-1}$$

  (a) $E_1 < E_2 < E_3 < .....$
  (b) $(E_2 - E_1) > (E_3 - E_2) > .....$
- n^{th} shell has n subshells, n^2 orbitals and a maximum of $2n^2$ electrons.
- Angular momentum, $mvr = n\dfrac{h}{2\pi}$
- Spin (only) magnetic moment = $\sqrt{x(x+2)}$ B.M. Here, x is number of unpaired electrons.

$$1\ \text{B.M.} = \frac{eh}{4\pi m_e} = 9.273\times10^{-14}\ \text{J}$$

Azimuthal or secondary or subsidiary quantum number, *l* (*Sommerfeld*)

- It represents subshells.
- For n^{th} shell, l has n-values ($l = 0, 1, 2, ..., (n-1)$) *i.e.* n subshells.
  1st shell has only one subshell s with $l = 0$.
  2nd shell has two subshells s and p with $l = 0$ and $l = 1$.
- Shapes : s has spherically symmetrical shape.
  p has dumb-bell shape.
  d has clover leaf shape with d_{z^2} having baby soother or doughnut shape.
- Any subshell has $(2l + 1)$ orbitals and a maximum of $2(2l + 1)$ electrons. s-subshell ($l = 0$) has only one orbital with its capacity of 2 electrons. p-subshell ($l - 1$) has three orbitals (p_x, p_y and p_z), two electrons in each (maximum) and total maximum capacity of six electrons, etc.
- Orbital angular momentum of an electron in a subshell = $\sqrt{l(l+1)}\cdot\dfrac{h}{2\pi}$ B.M.

Magnetic quantum number *m* or m_l (*Lande*)

- For any value of l, m has $(2l + 1)$ values, *i.e.*, orbitals $-l, -(l-1), ..., 0, ..., (l-1), l$
- For $l = 0$, *i.e.*, s-subshell, there is only one orbital, s-orbital with $m = 0$.
  For $l = 1$, *i.e.*, p-subshell, there are three orbitals, if p_x or p_y has $l = -1$, then p_y or p_x has $l = +1$ and p_z has $l = 0$, etc.

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Spin quantum number *s* (*Uhlenbeck and Goudsmit*)

- It is used to represent the spin of electron, if clockwise, then +1/2 value and if anticlockwise, then −1/2 value.
- Spin angular momentum of electron

$$= \sqrt{s(s+1)}\cdot\frac{h}{2\pi}$$

- For x unpaired electrons, spin angular momentum is

$$\sqrt{\frac{x}{2}\left(\frac{x}{2}+1\right)}\cdot\frac{h}{2\pi}\ \text{B.M.}$$

National Talent Search Examination

The Schedule of NTSE-2018-19

Stage	Area	Tentative Dates
Stage-I (State)	Last Date for Submission of Application Form	To be notified by the respective State/UT. May vary from state to state.
	Examination in Mizoram, Meghalaya, Nagaland and Andaman and Nicobar Islands	03th November, 2018 (Saturday)
	Examination in All other States and Union Territories	04th November, 2018 (Sunday)
	West Bengal	18th November, 2018 (Sunday)
Stage-II (National)	Examination in All States and Union Territories	12th May, 2019 (Sunday)

Nodes

These are hypothetical points around a nucleus where there is no density of electrons. These may form radial (spherical) and angular (non-spherical) surfaces.

An orbital may have $(n - l - 1)$ radial/spherical and l angular/non-spherical and total $n - 1$ nodes.

1*s*, 2*p*, 3*d* and 4*f* do not have any radial/spherical nodes.

d_{z^2} has no nodes.

Writing electronic configuration

- **Aufbau principle :** In the ground state of an atom, all shells/subshells/orbitals are considered empty and electrons are fed to them one at a time according to increasing energies of subshells/orbitals, keeping in view Pauli's exclusion principle and Hund's rule. The sequence of subshells/orbitals in increasing energies obtained from Bohr-Bury's '$n + l$' rule.
- **'$n + l$' rule or Bohr-Bury's rule :** In the same atom, energies of two electrons/orbitals/subshells are compared by using '$n + l$' rule. Higher the '$n + l$' value, higher is the energy. If the two cases have the same value of '$n + l$' then higher the n value, higher is the energy.

  $1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p < 6s < 4f < 5d < 6p < 7s < 5f < 6d < 7p < ....$

  Note : H-atom is exception to this rule. Energies of all subshells/orbitals depend only on 'n' value.

  $1s < 2s = 2p < 3s = 3p = 3d < ....$
- **Pauli's exclusion principle :** No two electrons in an atom can have the same set of four quantum numbers.

  Corollary : An orbital can have at the most two electrons with opposite spins.
- **Hund's rule of maximum multiplicity :** Pairing of electrons in degenerate orbitals of *p*, *d* and *f* subshell starts only when they first gain one electron each with parallel spin. The new electron has opposite spin.
- It is very important to note that after atomic number 20, the electronic configurations are not written in accordance with the Aufbau principle. We follow certain more facts.
  (a) Melting point, magnetic moment, ionisation energy, etc. are given due weightage.
  (b) All subshells of a shell are written together.
  (c) Half filled and completely filled orbitals of a subshell give extra stability etc.

  Following elements have specially different setting of electronic configurations :

  Cr(Z = 24), Cu(Z = 29), Mo(Z = 42), Ag(Z = 47), Au(Z = 79), Nb (Z = 41), Ru(Z = 44), Rh(Z = 45), Pd(Z = 46), Pt(Z = 78), La(Z = 57), Ac(Z = 89) and some inner transition elements.

MULTIPLE CHOICE QUESTIONS

1. The period number of an element in periodic table is decided by _____ quantum number of the valence shell of electronic configuration.
   (a) principal (b) azimuthal
   (c) magnetic (d) spin
2. The shape of a subshell/orbital in an atom is decided by _____ quantum number.
   (a) principal (b) azimuthal
   (c) magnetic (d) spin
3. The orientation of an orbital is decided by _____ quantum number.
   (a) principal (b) azimuthal
   (c) magnetic (d) spin
4. Two electrons present in the same orbital in an atom can be distinguished by _____ quantum number.
   (a) principal (b) azimuthal
   (c) magnetic (d) spin
5. Which of the following set of quantum numbers is not allowed in an atom?

	n	l	m	s		n	l	m	s
(i)	2	3	1	$+\frac{1}{2}$	(ii)	3	2	3	$-\frac{1}{2}$
(iii)	2	1	3	$+\frac{1}{2}$	(iv)	4	0	1	$+\frac{1}{2}$

   (a) (ii) only (b) (iii) only
   (c) (iv) only (d) All of these
6. Which of electron, proton and alpha particle will have highest kinetic energy if their de Broglie wavelengths are the same?
   (a) Electron (b) Proton
   (c) Alpha-particle (d) All have equal K.E.
7. Which of the following is correct for the uncertainty of velocity if uncertainties of position and momentum are equal?

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(a) $\sqrt{\frac{mh}{2\pi}}$ (b) $\frac{h}{\sqrt{2m\pi}}$

(c) $\frac{1}{2m}\sqrt{\frac{h}{\pi}}$ (d) $\sqrt{\frac{2\pi m}{h}}$

8. If $m_{He} : m_H = 4 : 1$, ratio of uncertainties of velocity of alpha particle and proton for equal uncertainties of positions will be

(a) 1 : 2 (b) 1 : 4

(c) 4 : 1 (d) 2 : 1

9. The correct order of radii of 1*s*, 2*s* and 2*p* in an atom is

(a) $1s < 2s < 2p$ (b) $1s < 2p < 2s$

(c) $1s < 2s = 2p$ (d) $1s > 2s > 2p$

10. Which of the following is correct for energies in H-atom?

(a) $E_1 < E_2 < E_3 < ....$

(b) $(E_2 - E_1) > (E_3 - E_2)$

(c) $1s < 2s = 2p < 3s = 3p = 3d < ....$

(d) All are correct

11. If $\frac{h}{2\pi}$ is written as $\hbar$ direc-*h*, the orbital angular momentum of a *d*-subshell will be

(a) $\frac{\hbar}{\sqrt{2}}$ (b) $\frac{\hbar}{\sqrt{6}}$

(c) $\sqrt{6}\,\hbar$ (d) $2\sqrt{6}\,\hbar$

12. What is the spin only magnetic moment of Fe^{2+} ($Z = 26$)?

(a) 6.0 B.M. (b) 4.0 B.M.

(c) 9.4 B.M. (d) 4.9 B.M.

13. Which of the following is the correct value of spin angular momentum of Cr ($Z = 24$)?

(a) $\frac{h}{2\pi}$ B.M. (b) $\frac{h}{\sqrt{2}\,\pi}$ B.M.

(c) $\frac{\sqrt{2}\,h}{\pi}$ B.M. (d) $\frac{\sqrt{3}\,h}{\pi}$ B.M.

14. Which of the following does not have any radial/spherical nodes?

(a) 2*p* (b) 3*d*

(c) 4*f* (d) All of these

15. Which of the following has a total of three radial and angular nodes?

(a) 3*s* (b) 3*p*

(c) 3*d* (d) None of these

16. The maximum number of electrons with same spin in a subshell with $l = 2$ and $n = 4$ is

(a) 1 (b) 3

(c) 5 (d) 7

17. Which set of quantum number is correct for 19th electron of K ($Z = 19$)?

(a) 2, 1, 1, $+\frac{1}{2}$ (b) 3, 2, 2, $-\frac{1}{2}$

(c) 4, 0, 0, $+\frac{1}{2}$ (d) 4, 1, 0, $+\frac{1}{2}$

18. Which of the following electronic configuration is correct for Cr ($Z = 24$)?

(a) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2\ 3d^4$

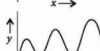
(b) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1\ 3d^5$

(c) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^4\ 4s^2$

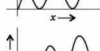
(d) $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$

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19. Which of the following plot between radial probability (distribution) density *y*-axis and distance from the nucleus *x*-axis for 4*s* orbit is correct?

(a) 

(b) 

(c) 

(d) 

20. Uncertainty in the position of an electron(mass = 9.1×10^{-31} kg) moving with velocity of 300 m s^{-1}, accurate upto 0.001%, will be ($h = 6.62 \times 10^{-34}$ J s)

(a) 1.92×10^{-2} m (b) 3.84×10^{-2} m

(c) 19.2×10^{-2} m (d) 5.76×10^{-2} m

SOLUTIONS

1. **(a) :** Period number of an element in periodic table is the same as the principal quantum number of the valence shell in its electronic configuration.

2. **(b) :** Azimuthal quantum number gives the shape of a subshell/orbital.

3. **(c) :** The orientation of an orbital with respect to co-ordinates is given by magnetic quantum number.

4. **(d)** : An orbital can have at the most two electrons with opposite spins +1/2 and −1/2. Other quantum numbers n, l and m for these electrons have to be the same.

5. **(d)** : The value of l is always less than that of n. The value of m can never be greater than l.

6. **(a)** : $K.E. = \frac{1}{2}mv^2$; $v = \frac{h}{m\lambda} \Rightarrow v^2 = \frac{h^2}{m^2\lambda^2}$

So, $K.E. = \frac{1}{2}\frac{h^2}{m\lambda^2}$

h and λ being same for all cases, $K.E. \propto \frac{1}{m}$.

Electron has the smallest mass among these cases.

7. **(c)** : $\Delta x = \Delta p$

$\Delta x \cdot \Delta p = \frac{h}{4\pi}$

$\Delta p \cdot \Delta p = \frac{h}{4\pi} \Rightarrow \Delta p = \sqrt{\frac{h}{4\pi}}$

So, $m\Delta v = \sqrt{\frac{h}{4\pi}} \Rightarrow \Delta v = \frac{1}{2m}\sqrt{\frac{h}{\pi}}$

8. **(b)** : $\frac{(\Delta x \cdot m \cdot \Delta v)_{He}}{(\Delta x \cdot m \cdot \Delta v)_H} = \frac{h/4\pi}{h/4\pi} = 1$

$\frac{m_{He}}{m_H} \times \frac{\Delta v_{He}}{\Delta v_H} = 1$; $\frac{\Delta v_{He}}{\Delta v_H} = \frac{m_H}{m_{He}} = \frac{1}{4}$

9. **(b)** **10.** **(d)**

11. **(c)** : For d-subshell, $l = 2$

Orbital angular momentum $= \sqrt{l(l+1)} \cdot \frac{h}{2\pi}$ B.M.

$= \sqrt{2(2+1)} \cdot \hbar$ B.M. $= \sqrt{6}\,\hbar$ B.M.

12. **(d)** : Fe$(Z = 26)$: [Ar] $3d^6\ 4s^2$

Fe^{2+} : [Ar] $\underset{3d_\varepsilon}{\boxed{\uparrow\downarrow \;\; \uparrow \;\; \uparrow \;\; \uparrow \;\; \uparrow}} \Rightarrow x = 4$

Spin only magnetic moment $= \sqrt{x(x+2)}$ B.M.

$= \sqrt{4(4+2)}$ B.M. $= \sqrt{24}$ B.M $= 4.9$ B.M.

13. **(d)** : Cr $(Z = 24)$: [Ar] $3d^5\ 4s^1 \Rightarrow x = 6$

Spin angular momentum $= \sqrt{\frac{x}{2}\left(\frac{x}{2}+1\right)} \cdot \frac{h}{2\pi}$ B.M.

$= \sqrt{3(3+1)} \cdot \frac{h}{2\pi}$ B.M. $= \frac{\sqrt{3} \cdot h}{\pi}$ B.M.

14. **(d)** : Number of radial/spherical nodes $= n - l - 1$

For $2p$, radial nodes $= 2 - 1 - 1 = 0$

For $3d$, radial nodes $= 3 - 2 - 1 = 0$

For $4f$, radial nodes $= 4 - 3 - 1 = 0$

15. **(d)** : Total number of radial and angular nodes $= n - 1 = 3 - 1 = 2$ (all given cases)

16. **(c)** : $n = 4$, $l = 2 \Rightarrow 4d$ subshell

It will have a maximum of five electrons with same spin.

17. **(c)** : K$(Z = 19)$: $1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 4s^1$

For 19^{th} electron : $n = 4$, $l = 0$, $m = 0$, $s = +1/2$

18. **(d)**

19. **(d)** : Number of peaks for an orbital on radial probability (distribution) density *vs* distance from nucleus is $n - l$.

Here, the number $= 4 - 0 = 4$

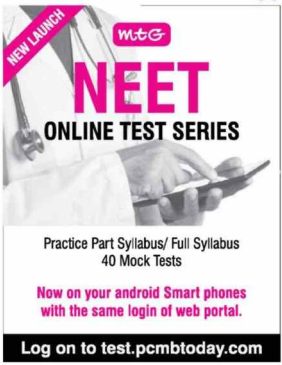
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20. **(a)** : $\Delta v = 0.001\%$ of $300 = \frac{0.001}{100} \times 300$

$= 0.003$ m s^{-1}

$\Delta x = \frac{h}{4\pi m\,\Delta v} = \frac{6.62 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 0.003}$

$= 1.92 \times 10^{-2}$ m



EXAMINER'S MIND CLASS XI

The questions given in this column have been prepared on the basis of pattern of Previous Years' Questions asked in JEE (Main & Advanced)/NEET/AIIMS exams.

CHEMICAL BONDING AND MOLECULAR STRUCTURE

SECTION - I

Only One Option Correct Type

1. A molecule XY_2 contains two σ-bonds, two π-bonds and one lone pair of electrons in valence shell of X. The arrangement of electron pairs around X is
(a) square pyramidal (b) linear
(c) trigonal planar (d) data insufficient.

2. In ICl_2^+, ICl_2^- and ICl_4^-, sum of the bond pairs and lone pairs on each iodine atom are respectively
(a) 2, 2 and 4 (b) 2, 3 and 2
(c) 4, 5 and 4 (d) 4, 5 and 6

3. The pair of species with similar shape is
(a) PCl_3, NH_3 (b) CF_4, SF_4
(c) $PbCl_2$, CO_2 (d) PF_5, IF_5

4. In which of the following, the central atom does not use sp^3 hybrid orbitals in its bonding?
(a) NO_3^- (b) H_3O^+ (c) NH_2^- (d) CH_3^-

5. $H-\overset{(I)}{N}\cdots\overset{(II)}{N}\cdots N$
In hydrogen azide (above) the bond orders of bonds (I) and (II) are

	(I)	(II)
(a)	> 2	< 2
(b)	< 2	< 2
(c)	< 2	> 2
(d)	> 2	> 2

(JEE Main Online 2018)

SECTION - II

More than One Options Correct Type

6. Which of the following is correct?
(a) During O_2^+ formation, one electron is removed from the bonding MO.
(b) During O_2^+ formation, one electron is removed from the anti-bonding MO.
(c) During O_2^- formation, one electron is added to the bonding MO.
(d) During C_2^- formation, one electron is added to the bonding MO.

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7. Identify the species which are non-planar.
(a) CH_3^+ (b) NH_4^+ (c) BF_4^- (d) C_2H_2

8. Which of the following statements are not correct?
(a) NaCl being an ionic compound is a good conductor of electricity in the solid state.
(b) In canonical structures there is difference in the arrangement of atoms.
(c) Hybrid orbitals are stronger than pure bonds.
(d) VSEPR theory can explain the square planar geometry of XeF_4.

9. In which of the following compound(s) F atom(s) can occupy any position around central atom?
(a) PCl_4F (b) CH_3F (c) BrF_3 (d) PCl_5F^-

10. According to molecular orbital theory,
(a) C_2^{2-} is expected to be diamagnetic
(b) O_2^{2+} is expected to have a longer bond length than O_2
(c) N_2^+ and N_2^- have the same bond order
(d) He_2^+ has the same energy as two isolated He atoms. *(JEE Advanced 2016)*

SECTION - III

Matching List Type

11. Match the following:

	List I		List II
A.	Paramagnetic	p.	CO
B.	Violation of octet rule	q.	CO^+
C.	Triangular planar structure	r.	BF_3
D.	Bond order is three	s.	PCl_5

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

12. Match the orbital overlap figures shown in List I with the description given in List II and select the correct answer using the codes given below the lists:

List I		List II	
A.		p.	p - d π-antibonding
B.		q.	d - d σ-bonding
C.		r.	p - d π-bonding
D.		s.	d - d σ-antibonding

	A	B	C	D
(a)	q	p	r	s
(b)	s	r	p	q
(c)	q	r	p	s
(d)	s	p	r	q

(JEE Advanced 2014)

SECTION - IV

Numerical Value Type

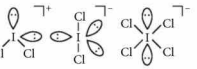
13. The number of molecules among the following which do not satisfy octet rule is BF_3, $AlCl_3$, H_2O_2, H_2SO_4, HNO_3, PCl_5, CO_2, CO, O_3, NO_2^-

14. The number of species among the following which have fractional bond order is
Li_2, He_2^+, N_2^+, N_2^{2-}, O_2^+, O_2^{2-}, O_2^-, CO_3^{2-}, C_6H_6, O_3

15. Among the triatomic molecules/ions, $BeCl_2$, N_3^-, N_2O, NO_2^+, O_3, SCl_2, ICl_2^-, I_3^- and XeF_2, the total number of linear molecule(s)/ion(s) where the hybridization of the central atom does not have contribution from the d-orbital(s) is
[Atomic number : S = 16, Cl = 17, I = 53 and Xe = 54]
(JEE Advanced 2015)

SOLUTIONS

1. (c) : Geometry of molecules depends only on sigma bonded electron pairs and lone pairs but not on π-bonded electron pairs.

2. (d) : 

3. (a)

4. (a) : No. of hybrid orbitals for

$NO_3^- = \frac{1}{2}[5 + 0 - 0 + 1] = 3$

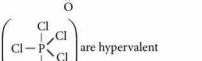
$\therefore$ Type of hybridization is sp^2.

5. (c) **6. (b, d)** **7. (b, c)** **8. (a,b)**

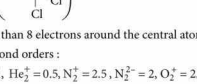
9. (b,d) : (a) One F atom must occupy axial position.
(b) F atom occupies any position because all the positions are identical in tetrahedral.
(c) Two F atoms occupy axial positions. One F atom occupies equatorial position.
(d) One F atom occupies any position around central atom because all the positions are identical in octahedral.

10. (a, c) **11. (b)** **12. (c)**

13. (4) : BF_3, $AlCl_3$ is electron deficient whereas



H_2SO_4 $(H-O-\overset{\overset{O}{\|}}{\underset{\underset{O}{\|}}{S}}-O-H)$,



PCl_5 $\left(Cl-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{P}}\overset{Cl}{\underset{Cl}{<}}\right)$ are hypervalent

(more than 8 electrons around the central atom).

14. (7) : Bond orders :

$Li_2 = 1$, $He_2^+ = 0.5$, $N_2^+ = 2.5$, $N_2^{2-} = 2$, $O_2^+ = 2.5$,

$O_2^{2-} = 1.0$, $O_2^- = 1.5$, $CO_3^{2-} = 1.33$, $C_6H_6 = 1.5$, $O_3 = 1.5$

15. (4) :

Molecule/ion	Hybridisation	Shape
$BeCl_2$	sp	linear
N_3^-	sp	linear
N_2O	sp	linear
NO_2^+	sp	linear
O_3	sp^2	bent
SCl_2	sp^3	bent
ICl_2^-	sp^3d	linear
I_3^-	sp^3d	linear
XeF_2	sp^3d	linear

Thus, there are total four linear molecules/ions where the hybridisation of the central atom does not have contribution from the d-orbitals.

CLASS XI

CBSE DRILL



Chapterwise practice questions for CBSE Exams as per the latest pattern and marking scheme issued by CBSE for the academic session 2018-19.

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 12 are short answer questions and carry 2 marks each.
(iv) Q. no. 13 to 24 are also short answer questions and carry 3 marks each.
(v) Q. no. 25 to 27 are long answer questions and carry 5 marks each.
(vi) Use log tables if necessary, use of calculators is not allowed.

Time Allowed : 3 hours | Maximum Marks : 70

Equilibrium | Redox Reactions

1. What is the oxidation number of S in S_2Cl_2?
2. For the reaction, $A_{2(g)} + 3B_{2(g)} \rightleftharpoons 2AB_{3(g)}$ + heat, on the basis of Le-Chatelier's principle, explain the conditions of temperature and pressure to yield maximum amount of AB_3.
3. The ionization constant of formic acid is 1.8×10^{-4}. Around what pH will its mixture with sodium formate give buffer solution of highest capacity?
4. Which compound amongst the following has the highest oxidation number for Mn?
   $KMnO_4$, K_2MnO_4, MnO_2 and Mn_2O_3
5. Which among the following are
   MnO_4^-, I^-, Ce^{4+}, $Cr_2O_7^{2-}$, Na, CrO_4^{2-}, HNO_3, Fe^{2+}, F_2
   (i) good oxidizing agents
   (ii) good reducing agents?
6. A solution of silver nitrate was stirred with iron rod. Will it cause any change in the concentration of silver and nitrate ions?
7. Which method can be used to find out strength of reductant/oxidant in a solution? Explain with an example.
8. State the condition in a chemical reaction in which
   (i) $Q_c < K_c$ (ii) $Q_c = K_c$
9. Why are the cations of group III precipitated as their hydroxides in the presence of ammonium chloride?

   OR

   A sample of pure PCl_5 was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl_5 was found to be 0.5×10^{-1} mol L^{-1}. If value of K_c is 8.3×10^{-3}, what are the concentrations of PCl_3 and Cl_2 at equilibrium?
10. Find out the oxidation states of two types of Fe atoms in $Fe_4[Fe(CN)_6]_3$ and rewrite the formula in stock notation form.
11. Show by giving example that oxidation-reduction reactions are complementary.

12. Reaction between acetic acid and ethyl alcohol attains a state of equilibrium in an open vessel but decomposition of $CaCO_3$ does not. Why?

13. (a) What are the net charges on the left and right sides of the following equations? Add electrons as necessary to make each of them balanced half-reactions.
    (i) $NO_3^- + 10H^+ \longrightarrow NH_4^+ + 3H_2O$
    (ii) $Cl_2 + 4H_2O \longrightarrow 2ClO_2^- + 8H^+$
    (b) What is a decomposition reaction? Give two examples.

14. The pH of blood stream is maintained by a proper balance of H_2CO_3 and $NaHCO_3$ concentrations. What volume of 5 M $NaHCO_3$ solution should be mixed with a 10 mL sample of blood which is 2 M in H_2CO_3, in order to maintain a pH of 7.4 ? K_a for H_2CO_3 in blood is 7.8×10^{-7}.

15. Which of the following reactions will get affected by increasing the pressure? Also, mention whether change will cause the reaction to go into forward or backward direction.
    (i) $COCl_{2(g)} \rightleftharpoons CO_{(g)} + Cl_{2(g)}$
    (ii) $CH_{4(g)} + 2S_{2(g)} \rightleftharpoons CS_{2(g)} + 2H_2S_{(g)}$
    (iii) $CO_{2(g)} + C_{(s)} \rightleftharpoons 2CO_{(g)}$
    (iv) $2H_{2(g)} + CO_{(g)} \rightleftharpoons CH_3OH_{(g)}$
    (v) $CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$
    (vi) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O_{(g)}$

16. (i) Why in Group V of qualitative analysis, sufficient NH_4OH solution should be added before adding $(NH_4)_2CO_3$ solution?
    (ii) Blood is buffer of H_2CO_3 and $[HCO_3^-]$ with pH = 7.40. Given K_1 of $H_2CO_3 = 4.5 \times 10^{-7}$. What will be the ratio of $[HCO_3^-]$ to $[H_2CO_3]$ in the blood?

17. Copper dissolves in dilute nitric acid but not in dilute HCl. Explain.

OR

Calculate the concentration of hypo ($Na_2S_2O_3.5H_2O$) solution in g dm^{-3} if 10.0 mL of this solution decolourised 15 mL of M/40 iodine solution.

18. The solubility product of AgCl is 1.5×10^{-10}. Predict whether there will be any precipitation by mixing 50 mL of 0.01 M NaCl and 50 mL of 0.01 M $AgNO_3$ solution.

19. At 817 °C, K_p for the reaction between $CO_{2(g)}$ and excess hot graphite(s) is 10 atm.
    (a) What are the equilibrium concentrations of gases at 817 °C and a total pressure of 5 atm?
    (b) At what total pressure, the gas contains 5% CO_2 by volume?

20. Both $Cr_2O_{7(aq)}^{2-}$ and $MnO_{4(aq)}^-$ can be used to titrate $Fe_{(aq)}^{2+}$. If in a given titration, 24.50 cm^3 of 0.1 M $Cr_2O_7^{2-}$ were used, then what volume of 0.1 M MnO_4^- solution would have been used for the same titration?

21. (i) A sample of AgCl was treated with 5.00 mL of 1.5 M Na_2CO_3 solution to give Ag_2CO_3. The remaining solution contained 0.0026 g of Cl^- per litre. Calculate the solubility product of AgCl. (K_{sp} for $Ag_2CO_3 = 8.2 \times 10^{-12}$).
    (ii) The solubility of $Pb(OH)_2$ in water is 6.7×10^{-6} M. Calculate the solubility of $Pb(OH)_2$ in a buffer solution of pH = 8.

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22. The K_{sp} of $Ca(OH)_2$ is 4.42×10^{-5} at 25°C. 500 mL of saturated solution of $Ca(OH)_2$ is mixed with equal volume of 0.4 M NaOH. How much $Ca(OH)_2$ in mg is precipitated?

23. Saccharin ($K_a = 2 \times 10^{-12}$) is a weak acid represented by formula HSac. A 4×10^{-4} mole amount of saccharin is dissolved in 200 cm^3 water of pH = 3. Assuming no change in volume, calculate the concentration of Sac^- ions in the resulting solution at equilibrium.

24. (i) What is the oxidation number of 'S' in H_2SO_5?
    (ii) Balance the following equation :
    $Zn_{(s)} + NO_{3(aq)}^- \longrightarrow Zn_{(aq)}^{2+} + NH_{4(aq)}^+ + H^+$
    (Acidic medium)

25. (i) The vapour density of N_2O_4 at a certain temperature is 30. Calculate the percentage dissociation of N_2O_4 at this temperature.
    (ii) The equilibrium constant for the reaction, $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$ is 4. What will be the composition of the equilibrium mixture when one mole of acetic acid is taken along with 4 moles of ethyl alcohol ?

OR

(i) Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) is represented by the formula HNic. Calculate its percentage dissociation in a solution which contains 0.10 mole of nicotinic acid per 2 litre of solution.
(ii) An aqueous solution contains 10% ammonia by mass and has a density of 0.99 g cm^{-3}. Calculate hydroxyl and hydrogen ion concentration in this solution. (K_a for $NH_4^+ = 5.0 \times 10^{-10}$)

26. At 450 K, $K_p = 2.0 \times 10^{10}$ bar^{-1} for the given reaction at equilibrium.

$$2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)} + 189.4 \text{ kJ}$$

(i) What is K_c at this temperature?

(ii) What is the value of K_c for the reverse reaction at the same temperature?

(iii) What would be the effect on equilibrium if

(a) more SO_2 is added

(b) pressure is increased

(c) the temperature is increased?

OR

Calculate the pH of the following solutions :

(i) 2 g of TlOH dissolved in water to give 2 litre of solution. (Given, atomic mass of Tl = 204.4)

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

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

(iv) H_3O^+ ion concentration of a water sample having pH = 6.58.

27. (i) Why HNO_3 acts only as oxidising agent while HNO_2 can act both as a reducing agent and an oxidising agent?

(ii) Balance the following equation by oxidation number method :

$$I_2 + NaOH \longrightarrow NaIO_3 + NaI + H_2O$$

OR

(i) Consider the reactions :

$$2S_2O_{3(aq)}^{2-} + I_{2(s)} \longrightarrow S_4O_{6(aq)}^{2-} + 2I_{(aq)}^-$$

$$S_2O_{3(aq)}^{2-} + 2Br_{2(l)} + 5H_2O_{(l)} \longrightarrow 2SO_{4(aq)}^{2-} + 4Br_{(aq)}^- + 10H_{(aq)}^+$$

Why does the same reductant, thiosulphate react differently with iodine and bromine?

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

(iii) The colour of KI solution containing starch turns blue when it is shaken with cold chlorine water. Why?

SOLUTIONS

1. The O.N. of S in S_2Cl_2 is +1 as shown

$$\overset{-1}{Cl}-\overset{+1}{S}-\overset{+1}{S}-\overset{-1}{Cl}$$

2. Increase in pressure and decrease in temperature will yield maximum amount of AB_3.

3. Buffer solution of highest capacity is formed at which, $pH = pK_a = -\log(1.8 \times 10^{-4}) = 3.74$.

4. $KMnO_4$ (+7), K_2MnO_4 (+6), MnO_2 (+4), Mn_2O_3 (+3) Thus, the highest oxidation number for Mn is in $KMnO_4$.

5. (i) MnO_4^-, Ce^{4+}, $Cr_2O_7^{2-}$, CrO_4^{2-}, HNO_3, F_2

(ii) I^-, Na, Fe^{2+}

6. Since $E°$ of Fe^{2+}/Fe (–0.44 V) is lower than that of Ag^+/Ag (+0.80 V) electrode, therefore Ag^+ gets reduced and Fe gets oxidised. As a result, concentration of Ag^+ ions decreases while that of NO_3^- ions remain unchanged.

$$2Ag_{(aq)}^+ + Fe_{(s)} \longrightarrow 2Ag_{(s)} + Fe_{(aq)}^{2+}$$

7. The method used is by connecting the redox couple of the given species with standard hydrogen electrode. Then the value of electrode potential will determine the strength of oxidant/reductant. If the value comes out to be positive then the species acts as the oxidant and if the value is negative then the species acts as the reductant. So, higher is the value of electrode potential higher is the strength of species to act as oxidant and vice versa. For example, when Zn^{2+}/Zn electrode is connected with SHE then the EMF of the cell is 0.76 V. Here, Zn^{2+}/Zn acts as anode and SHE as cathode.

$$\therefore \quad E°_{cell} = 0.76 \text{ V} = E°_{cathode} - E°_{anode}$$

$$0.76 = 0 - E°_{anode} \Rightarrow E°_{anode} = -0.76 \text{ V}$$

8. (i) If $Q_c < K_c$, the reaction tends towards forward direction to attain equilibrium.

(ii) If $Q_c = K_c$, no net reaction occurs. Reaction is at equilibrium.

9. Hydroxides of group III are precipitated by adding NH_4OH in presence of NH_4Cl. NH_4OH is a weak electrolyte, so it ionises to a small extent whereas NH_4Cl being a strong electrolyte ionises completely.

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

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

Due to common ion effect, the degree of dissociation of NH_4OH is suppressed and less OH^- ions are formed. This less concentration of OH^- is sufficient to precipitate group III cations but not the cations of higher groups since the K_{sp} of group III is lesser than K_{sp} of subsequent groups.

OR

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

Initial conc.	y	0	0
Conc. at equilibrium	$y - x$	x	x

But $y - x = 0.5 \times 10^{-1}$ mol L^{-1}

$$\therefore \quad K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{x.x}{(y-x)} = \frac{x^2}{0.5 \times 10^{-1}} = 8.3 \times 10^{-3}$$

$\Rightarrow \quad x = 2.04 \times 10^{-2}$ mol L^{-1}

$[PCl_3] = [Cl_2] = 2.04 \times 10^{-2}$ mol L^{-1}

10. The species Fe_4 which lies outside the complex ion, *i.e.*, $[Fe(CN)_6]_3$, is the +ve part while the complex ion itself is the –ve part. In other words, the +ve charge on 4Fe-atoms outside the coordination sphere is balanced by the –ve charge on the complex ion. Since, Fe has two oxidation states, *i.e.*, +2 and +3 and oxidation number of $CN^- = -1$, therefore, total – ve charge on the complex ion, $[Fe(CN)_6]_3 = 3[(+2 \times 1) + 6(-1)] = -12$

Total + ve charge on 4Fe-atoms = $4 \times (+3) = +12$

Fe in the complex ion has an O.N. + 2 while the Fe-atoms outside the coordination sphere have an O.N. of +3. Thus, the stock notation for $Fe_4[Fe(CN)_6]_3$ is $Fe_4^{III}[Fe^{II}(CN)_6]_3$.

11. Oxidation-reduction reactions are complementary reactions. Whenever any substance is oxidised, another substance is always reduced at the same time and vice versa. For example, consider the reaction

$2HgCl_2 + SnCl_2 \longrightarrow Hg_2Cl_2 + SnCl_4$

In this reaction, stannous chloride ($SnCl_2$) has been oxidised to stannic chloride ($SnCl_4$) due to addition of chlorine and $HgCl_2$ is reduced to Hg_2Cl_2 due to addition of mercury.

12. Acetic acid and ethyl alcohol are liquids and their products, ethyl acetate and water, are also liquids but one of the products of decomposition of $CaCO_3$ is gaseous (CO_2) which escape out in an open vessel and the reverse reaction cannot occur.

13. (a) (i) +9 charge on the left, +1 charge on the right

$NO_3^- + 10H^+ + 8e^- \longrightarrow NH_4^+ + 3H_2O$

(ii) No charge on the left, +6 charge on the right

$Cl_2 + 4H_2O \longrightarrow 2ClO_2^- + 8H^+ + 6e^-$

(b) Decomposition reactions : Decomposition reactions are the opposite of combination reactions. Precisely, a decomposition reaction leads to the breakdown of a compound into two or more components.

$\overset{+1+5-2}{2KClO_{3(s)}} \xrightarrow{\Delta} \overset{+1-1}{2KCl_{(g)}} + \overset{0}{3O_{2(g)}}$

$\overset{+2+4-2}{CaCO_{3(s)}} \xrightarrow{\Delta} \overset{+2-2}{CaO_{(s)}} + \overset{+4-2}{CO_{2(g)}}$

14. Let V mL of 5 M $NaHCO_3$ solution be mixed.

Total volume = $(V + 10)$ mL

Conc. of H_2CO_3 and $NaHCO_3$ in the solution becomes

$[NaHCO_3] = \frac{5 \times V}{(V+10)} M$ and $[H_2CO_3] = \frac{2 \times 10}{(V+10)} M$

Now applying Henderson's equation,

$pH = -\log K_a + \log \frac{[NaHCO_3]}{[H_2CO_3]}$

$7.4 = -\log (7.8 \times 10^{-7}) + \log \frac{5 \times V}{(V+10)} \times \frac{(V+10)}{2 \times 10}$

$7.4 = -\log (7.8 \times 10^{-7}) + \log \frac{V}{4}$

or $\log \frac{V}{4} = 7.4 + \log (7.8 \times 10^{-7}) \Rightarrow \log \frac{V}{4} = 7.4 - 6.10$

or $\log \frac{V}{4} = 1.3$ or $\frac{V}{4} = \text{antilog}\,(1.3) = 19.95$

$\Rightarrow \quad V = 19.95 \times 4 = 79.8$ mL

15. Reactions will be affected in those in which $(n_p \neq n_r)_{gaseous}$.

(i) $n_p = 2$, $n_r = 1$ *i.e.*, $n_p > n_r$, reaction will go in the backward direction.

(ii) $n_p = 3$, $n_r = 3$, *i.e.*, $n_p = n_r$, reaction will not be affected by pressure.

(iii) $n_p = 2$, $n_r = 1$ *i.e.*, $n_p > n_r$, reaction will go in the backward direction.

(iv) $n_p = 1$, $n_r = 3$ *i.e.*, $n_p < n_r$, reaction will go in the forward direction.

(v) $n_p = 1$, $n_r = 0$ *i.e.*, $n_p > n_r$, reaction will go in the backward direction.

(vi) $n_p = 10$, $n_r = 9$ *i.e.*, $n_p > n_r$, reaction will go in the backward direction.

16. (i) This is done to convert NH_4HCO_3 to $(NH_4)_2CO_3$ usually present in large amount along with $(NH_4)_2CO_3$.

$NH_4HCO_3 + NH_4OH \longrightarrow (NH_4)_2CO_3 + H_2O$

(ii) $H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$, $K_1 = \frac{[H^+][HCO_3^-]}{[H_2CO_3]}$

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

$pH = 7.40 \Rightarrow -\log[H^+] = 7.4$

or $\log[H^+] = -7.4$ or $[H^+] = 3.98 \times 10^{-8}$

$\frac{[HCO_3^-]}{[H_2CO_3]} = \frac{4.5 \times 10^{-7}}{3.98 \times 10^{-8}} = 11.3$

17. Since E° of Cu^{2+}/Cu electrode (+0.34 V) is higher than that of H^+/H_2 electrode (0.0 V), therefore, H^+ ions cannot oxidise Cu to Cu^{2+} ions and hence Cu does not dissolve in dil. HCl. In contrast, the electrode potential of NO_3^- ion, *i.e.*, NO_3^-/NO electrode (+0.96 V) is higher than that of copper electrode and hence it can oxidise Cu to Cu^{2+} ions and hence Cu dissolves in dil. HNO_3. Therefore, Cu dissolves in dil. HNO_3 due to oxidation of Cu by NO_3^- ions and not by H^+ ions.

OR

The balanced equation for the redox reaction is

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

From the balanced equation, it is evident that 2 moles of $Na_2S_2O_3 \equiv 1$ mole of I_2

$$\frac{M_1V_1}{n_1}(Na_2S_2O_3) = \frac{M_2V_2}{n_2}(I_2)$$

or $\dfrac{M_1 \times 10}{2} = \dfrac{15 \times 1}{1 \times 40}$ or $M_1 = \dfrac{15 \times 1 \times 2}{40 \times 10} = \dfrac{3}{40}$

Thus, the molarity of the hypo solution = 3/40 M

Mol. mass of $Na_2S_2O_3{\cdot}5H_2O = 248$ g mol^{-1}

$\therefore$ Concentration of $Na_2S_2O_3{\cdot}5H_2O = \dfrac{248 \times 3}{40}$

$= 18.6$ g dm^{-3}

18. Conc. of NaCl in 100 mL $= \dfrac{0.01 \times 50}{100} = 0.005$ M

Conc. of $AgNO_3$ in 100 mL $= \dfrac{0.01 \times 50}{100} = 0.005$ M

Now $NaCl_{(aq)} \rightleftharpoons Na^+_{(aq)} + Cl^-_{(aq)}$

and $AgNO_{3(aq)} \rightleftharpoons Ag^+_{(aq)} + NO^-_{3(aq)}$

$[Cl^-] = [NaCl] = 0.005$ M ; $[Ag^+] = [AgNO_3] = 0.005$ M

$\therefore$ Ionic product $= [Ag^+]\,[Cl^-] = 0.005 \times 0.005$

$= 2.5 \times 10^{-5}$

Since, ionic product is greater than its solubility product, precipitation will occur.

19. (a)

	$CO_{2(g)}$	+	$C_{(s)}$	$\rightleftharpoons$	$2CO_{(g)}$
Initial mole	1				0
Final	$1-\alpha$				2α

$p_{CO} = \dfrac{2\alpha}{1+\alpha} \times p \quad p_{CO_2} = \dfrac{1-\alpha}{1+\alpha} \times p$

$K_p = \dfrac{p^2_{CO}}{p_{CO_2}} = \left(\dfrac{2\alpha}{1+\alpha} \times p\right)^2 \times \dfrac{1+\alpha}{1-\alpha} \times \dfrac{1}{p} = \dfrac{4\alpha^2}{(1+\alpha)(1-\alpha)} \times p$

$p = 5$ atm $\quad K_p = 10$

$10 = \dfrac{20\alpha^2}{1-\alpha^2} \Rightarrow \alpha^2 = \dfrac{1}{3} \Rightarrow \alpha = \sqrt{\dfrac{1}{3}} = 0.577$

Moles of CO_2 at equilibrium $= 1 - \alpha = 1 - 0.577 = 0.423$

Moles of CO at equilibrium $= 2\alpha = 2 \times 0.577 = 1.154$

Total moles $= 0.423 + 1.154 = 1.577$

Ideal gas equation, $PV = nRT$

$5 \times V = 1.577 \times 0.0821 \times 1090 \quad \Rightarrow \quad V = 28.23$ L

$[CO_2] = \dfrac{0.423}{28.23} = 0.015$; $[CO] = \dfrac{1.154}{28.23} = 0.041$

(b) At 5% CO_2 by volume $p_{CO_2} = \dfrac{5}{100} \times p$

$p'_{CO} = \dfrac{95}{100} \times p$

$K_p = \dfrac{p'^2_{CO}}{p_{CO_2}} = \dfrac{95 \times 95}{100 \times 100} \times p^2 \times \dfrac{100}{5} \times \dfrac{1}{p} = 10$

$\Rightarrow \quad p = 0.554$ atm

20. The balanced redox reactions involving oxidation of Fe^{2+} ions by $Cr_2O_7^{2-}$ and MnO_4^- respectively are :

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

and $MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$

Suppose V_2 cm^3 of M_2 Fe^{2+} is titrated against 24.50 cm^3 of 0.1 M $Cr_2O_7^{2-}$ and V_1 cm^3 of 0.1 M MnO_4^- solutions, then,

$$\frac{24.5 \times 0.1}{1}(Cr_2O_7^{2-}) = \frac{M_2V_2}{6}(Fe^{2+}) \qquad ...(i)$$

and $$\frac{V_1 \times 0.1}{1}(MnO_4^-) = \frac{M_2V_2}{5}(Fe^{2+}) \qquad ...(ii)$$

Equation (i) and (ii), $V_1 = 24.5 \times \dfrac{6}{5} = 29.4$ cm^3

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21. (i) 1.5 M Na_2CO_3 gives $[CO_3^{2-}] = 1.5$ M

K_{sp} for $Ag_2CO_3 = [Ag^+]^2[CO_3^{2-}]$

$\therefore \quad [Ag^+] = \sqrt{\dfrac{K_{sp} \text{ for } Ag_2CO_3}{[CO_3^{2-}]}} = \sqrt{\dfrac{8.2 \times 10^{-12}}{1.5}}$

$= 2.34 \times 10^{-6}$ M

K_{sp} for AgCl $= [Ag^+]\,[Cl^-]$

$= (2.34 \times 10^{-6})\left(\dfrac{0.0026}{35.5}\right) = 1.71 \times 10^{-10}$

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

$\therefore \quad K_{sp} = [Pb^{2+}]\,[OH^-]^2 = s \times (2s)^2 = 4s^3$

$= 4 \times (6.7 \times 10^{-6})^3 = 1.20 \times 10^{-15}$

In a solution with pH = 8, $[H^+] = 10^{-8}$ and $[OH]^- = 10^{-6}$

$\therefore \quad 1.2 \times 10^{-15} = [Pb^{2+}] \times (10^{-6})^2$

or $\quad [Pb^{2+}] = \dfrac{1.2 \times 10^{-15}}{(10^{-6})^2} = 1.2 \times 10^{-3}$ M

22. Let S be the solubility of $Ca(OH)_2$ in saturated solution.

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

$K_{sp}\,Ca(OH)_2 = [Ca^{2+}]\,[OH^-]^2$

$4.42 \times 10^{-5} = s \times 4s^2 = 4s^3 \quad \Rightarrow \quad s = 0.0223$ mol L^{-1}

After mixing the two solutions, the total volume become 1 litre.

$[Ca^{2+}] = \dfrac{0.0223}{1000} \times 500 = 0.01115$ mol L^{-1}

$[OH^-] = \underset{\text{[From Ca(OH)}_2\text{]}}{\dfrac{0.0223 \times 2 \times 500}{1000}} + \underset{\text{(From NaOH)}}{\dfrac{0.4 \times 500}{1000}} = 0.2223$ mol L^{-1}

Under the high concentration of OH^- ions, some $Ca(OH)_2$ will be precipitated.

$[Ca^{2+}]_{left}[OH^-]^2 = K_{sp}$

$[Ca^{2+}]_{left} = \frac{4.42\times10^{-5}}{(0.2223)^2} = 8.94\times10^{-4}$ mol L^{-1}

Moles of $Ca(OH)_2$ precipitated = Moles of Ca^{2+} precipitated

$= [Ca^{2+}]_{initial} - [Ca^{2+}]_{left}$

$= 0.01115 - 8.94\times10^{-4} = 111.5\times10^{-4} - 8.94\times10^{-4}$

$= 102.56\times10^{-4}$ M $= 102.56\times10^{-4}\times74$ g

$= 7589.44\times10^{-4}$ g $= 758.944$ mg

23. Concentration of saccharin

$= \frac{4\times10^{-4}}{200}\times1000 = 2\times10^{-3}$ mol L^{-1}

$[H^+] = 10^{-pH} = 10^{-3}$ mol L^{-1}

$\underset{[(2\times10^{-3})-x]}{HSac} \rightleftharpoons \underset{(10^{-3}+x)}{H^+} + Sac^-$

$K_a = \frac{[H^+][Sac^-]}{[HSac]} = \frac{(10^{-3}+x)[Sac^-]}{[2\times10^{-3}-x]}$

$[Sac^-] = \frac{2\times10^{-12}\times(2\times10^{-3}-x)}{(10^{-3}+x)}$

Since, x is very small, it can be neglected.

$[Sac^-] = \frac{2\times10^{-12}\times2\times10^{-3}}{10^{-3}} = 4\times10^{-12}$ mol L^{-1}

24. (i)



Two oxygen atoms (peroxo linkage) *i.e.*, O. No. = –1

Let x be the O. No. of S,

thus, $3\times(-2) + 2(-1) + x + 2(+1) = 0 \quad \Rightarrow \quad x = +6$

(ii) $\overset{0}{Zn} + \overset{+5}{HNO_3} \longrightarrow \overset{+2}{Zn^{2+}} + \overset{-3}{NH_4^+} + H_2O$

(Oxidation: $0 \to +2$; Reduction: $+5 \to -3$)

$Zn \longrightarrow Zn^{2+} + 2e^-] \times 4$

$10H^+ + NO_3^- + 8e^- \longrightarrow NH_4^+ + 3H_2O$

$4Zn + NO_3^- + 10H^+ \longrightarrow 4Zn^{2+} + NH_4^+ + 3H_2O$

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

Mol. mass of $N_2O_4 = (28 + 64) = 92$

Vapour density, $D = \frac{92}{2} = 46$

Let the degree of dissociation be x

Given, $d = 30$

Applying the relationship,

$x = \frac{D-d}{d} = \frac{(46-30)}{30} = \frac{16}{30} = 0.533$

Percentage dissociation = 53.3%

(ii) $CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(l)} + H_2O_{(l)}$

Initial	1	4	0	0
At equilibrium	$1-x$	$4-x$	x	x

$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{x^2}{(1-x)(4-x)} = 4$

$x^2 = 4(1-x)(4-x) = 4[4 - 5x + x^2]$

$x^2 = 16 - 20x + 4x^2$ or, $3x^2 - 20x + 16 = 0$

$x = \frac{20 \pm \sqrt{400-192}}{6} = \frac{20 \pm 14.42}{6}$

$x = 0.93$ or 5.7366

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The value 5.7366 is not possible, hence $x = 0.93$

Thus, the composition of mixture at equilibrium is

$[CH_3COOH] = (1 - 0.93) = 0.07$ mole

$[C_2H_5OH] = (4 - 0.93) = 3.07$ mole

$[CH_3COOC_2H_5] = 0.93$ mole

$[H_2O] = 0.93$ mole

OR

(i) Suppose degree of dissociation of nicotinic acid = α

	HNic $\rightleftharpoons$	H^+ +	Nic^-
Initial amount	0.1 mole	0	0
Amount at equi.	$0.1 - 0.1\alpha$ $= 0.1(1-\alpha)$	0.1α	0.1α
Molar conc. at equi.	$= 0.1(1-\alpha)/2$	$0.1\alpha/2$	$0.1\alpha/2$

$K_a = \frac{[H^+][Nic^-]}{[HNic]}$ or $1.4\times10^{-5} = \frac{(0.1\alpha/2)(0.1\alpha/2)}{0.1(1-\alpha)/2}$

If $\alpha << 1$, then $1.4\times10^{-5} = \frac{(0.05\alpha)^2}{0.05} = 0.05\,\alpha^2$

or $\alpha^2 = 2.8\times10^{-4}$ or $\alpha = 1.67\times10^{-2}$

(ii) 10% ammonia by mass means 10 g NH_3 is present in 100 g of the solution.

$\therefore$ Molarity of the solution $= \frac{10}{17}\times\frac{1}{100/0.99}\times1000$

$= 5.82$ M

$NH_3 + H_2O \longrightarrow NH_4OH \rightleftharpoons NH_4^+ + OH^-$

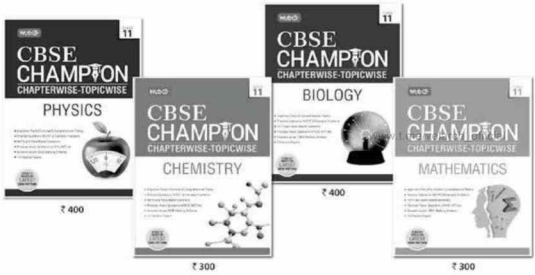
Initial	C mol L^{-1}		0	0
After dissociation	$C - C\alpha$		$C\alpha$	$C\alpha$

$\therefore \quad [OH^-] = C\alpha = C\sqrt{\frac{K_b}{C}} = \sqrt{K_bC} = \sqrt{\frac{K_w}{K_a}\times C}$

$= \sqrt{\frac{10^{-14}}{5.0\times10^{-10}}\times5.82} = 1.079\times10^{-2}$ M

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$\therefore [H^+] = \frac{K_w}{[OH^-]} = \frac{10^{-14}}{1.079 \times 10^{-2}} = 0.9268 \times 10^{-12}$ M

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

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

For the given reaction, $\Delta n_g = n_p - n_r = 2 - 3 = -1$

$K_p = 2 \times 10^{10}$ bar^{-1}

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

$K_c = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{2 \times 10^{10} \text{ bar}^{-1}}{(0.0831 \text{ L bar}^{-1}\text{mol}^{-1} \times 450 \text{ K})^{-1}}$

$= 2 \times 10^{10} \times 0.0831 \times 450 = 7.48 \times 10^{11}$ L mol^{-1}

(ii) For reverse reaction, K_c

$= \frac{1}{K_c \text{ (forward reaction)}} = \frac{1}{7.48 \times 10^{11}}$

$= 1.34 \times 10^{-12}$ L mol^{-1}

(iii) (a) If more SO_2 is added, rate of forward reaction increases and more SO_3 will be formed.

(b) If pressure is increased, the reaction will shift in forward direction *i.e.*, towards lesser number of moles.

(c) Increase in temperature will favour backward reaction.

OR

(i) Molar mass of TlOH = 221.4 g mol^{-1}

$\therefore n_{TlOH} = \frac{2 \text{ g}}{221.4 \text{ g mol}^{-1}} = 9.03 \times 10^{-3}$ mol

$[OH^-] = [TlOH] = \frac{9.03 \times 10^{-3} \text{ mol}}{2 \text{ L}} = 4.51 \times 10^{-3}$ M

pOH = $-\log(4.51 \times 10^{-3}) = 2.35$ and

pH = 14 – 2.35 = 11.65

(ii) $n_{Ca(OH)_2} = \frac{0.3 \text{ g}}{74 \text{ g mol}^{-1}} = 4.05 \times 10^{-3}$ mol

$[OH^-] = 2[Ca(OH)_2] = 2 \times \frac{4.05 \times 10^{-3} \text{ mol}}{0.5 \text{ L}}$

$= 1.62 \times 10^{-2}$ M

pOH = $-\log(1.62 \times 10^{-2}) = 1.79$ and

pH = 14 – 1.79 = 12.21

(iii) $M_1V_1 = M_2V_2$

13.6 mol L$^{-1} \times 1$ mL $= M \times 1000$ mL

$M_{HCl} = 0.0136$ mol L^{-1}

$[H^+] = [HCl] = 0.0136$ M

$\therefore$ pH = $-\log(0.0136) = 1.87$

(iv) pH = $-\log[H^+] = 6.58$

$\log[H^+] = -6.58$

$[H^+]$ or $[H_3O^+] = 2.63 \times 10^{-7}$ M

27. (i) The oxidation number of nitrogen in HNO_3 is +5 and increase in oxidation number beyond +5 cannot occur. Hence, HNO_3 cannot act as reducing agent. The oxidation number of nitrogen in HNO_3 can only decrease ; thus it acts as an oxidising agent. In HNO_2, the oxidation number of nitrogen is +3. Thus, it can increase or decrease within the range –3 to +5. Hence, it can act as an oxidising as well as a reducing agent.

(ii) $I_2 + NaOH \longrightarrow NaIO_3 + NaI + H_2O$

Writing oxidation numbers of all the atoms.

$\overset{0}{I_2} + \overset{+1}{Na}\overset{-2}{O}\overset{+1}{H} \longrightarrow \overset{+1}{Na}\overset{+5}{I}\overset{-2}{O_3} + \overset{+1}{Na}\overset{-1}{I} + \overset{+1}{H_2}\overset{-2}{O}$

The ox. no. of iodine has increased as well as decreased.

$\overset{0}{I} \longrightarrow \overset{+5}{NaIO_3}$ ...(i)

$\overset{0}{I} \longrightarrow \overset{-1}{NaI}$ ...(ii)

Increase in ox. no. of I = 5 units per I atom

Decrease in ox. no. of I = 1 unit per I atom

Eqn. (ii) should be multiplied by 5 as to make increase and decrease equal.

Then, adding the eqn. (i) with eqn. (ii)

$3I_2 \longrightarrow NaIO_3 + 5NaI$

To balance Na, 6 NaOH should be added on LHS.

$3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI$

To balance hydrogen and oxygen, $3H_2O$ should be added on RHS. Hence, the balanced equation is

$3I_2 + 6NaOH \longrightarrow NaIO_3 + 5NaI + 3H_2O$

OR

(i) The average O.N. of S in $S_2O_3^{2-}$ is +2 while in $S_4O_6^{2-}$ it is +2.5. The O.N. of S in SO_4^{2-} is +6. Since, Br_2 is a stronger oxidising agent, it oxidises S of $S_2O_3^{2-}$ to a higher oxidation state of +6 and hence, forms SO_4^{2-} ion. I_2, however, being a weaker oxidising agent oxidises S of $S_2O_3^{2-}$ ion to a lower oxidation state of + 2.5 in $S_4O_6^{2-}$ ion.

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

(iii) Cl_2 is stronger oxidising agent than I_2, therefore, when Cl_2 is passed through KI solution, Cl_2 gets reduced to Cl^- ions while I^- ions get oxidised to violet coloured iodine according to the equation,

$Cl_2 + 2I^- \longrightarrow 2Cl^- + I_2$

The iodine thus produced forms a blue coloured inclusion complex with starch and hence the solution turns blue.

Class XI

MONTHLY TUNE UP!



PRACTICE PROBLEMS

These practice problems enable you to self analyse your extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Performance analysis table given at the end will help you to check your readiness.

- States of Matter
- Thermodynamics

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

NEET / AIIMS

Only One Option Correct Type

1. For the given reaction following data is given
$C_2H_{6(g)} + 3.5\ O_{2(g)} \rightarrow 2CO_{2(g)} + 3H_2O_{(g)}$
$\Delta S_{vap}\ (H_2O, l) = x_1$ cal K^{-1} (boiling point = T_1)
$\Delta H_f\ (H_2O, l) = x_2$, $\Delta H_f\ (CO_2) = x_3$, $\Delta H_f\ (C_2H_6) = x_4$
Hence, ΔH for the reaction is
(a) $2x_3 + 3x_2 - x_4$
(b) $2x_3 + 3x_2 - x_4 + 3x_1T_1$
(c) $2x_3 + 3x_2 - x_4 - 3x_1T_1$
(d) $x_1T_1 + x_2 + x_3 - x_4$

2. 2 mole 'He' is mixed with 2 g of H_2. The molar heat capacity at constant pressure for the mixture is
(a) $\frac{17R}{6}$ (b) $\frac{11R}{6}$ (c) $4R$ (d) $\frac{3R}{2}$

3. N_2 is found in a litre flask under 100 kPa pressure and O_2 is found in another 3 litre flask under 320 kPa pressure. If the two flasks are connected, the resultant pressure is
(a) 310 kPa (b) 210 kPa
(c) 420 kPa (d) 265 kPa

4. For the process,
$H_2O_{(l)}$ (1 bar, 373 K) $\rightarrow H_2O_{(g)}$ (1 bar, 373 K),
the correct set of thermodynamic parameters is
(a) $\Delta G = 0, \Delta S = +ve$ (b) $\Delta G = 0, \Delta S = -ve$
(c) $\Delta G = +ve, \Delta S = 0$ (d) $\Delta G = -ve, \Delta S = +ve.$

5. For van der Waals' constants '*a*' and '*b*', the unit of the ratio $\frac{a}{b}$ will be
(a) atm $litre^{-1}$ (b) litre-atm mol^{-1}
(c) litre-atm mol^{-2} (d) litre mol^{-1}

6. Equal weights of ethane and hydrogen are mixed in an empty container at 25°C. The fraction of the total pressure exerted by hydrogen is
(a) 1 : 2 (b) 1 : 1 (c) 1 : 16 (d) 15 : 16

7. From the following data:

Substance	$\Delta H°$ (kJ/mol)	$\Delta S°$ (J/mol K)	$\Delta G°$ (kJ/mol)
$FeO_{(s)}$	−266.3	57.49	−245.12
C (Graphite)	0	5.74	0
$Fe_{(s)}$	0	27.28	0
$CO_{(g)}$	−110.5	197.6	−137.15

Determine at what temperature the following reaction is spontaneous?
$FeO_{(s)} + C_{(graphite)} \rightarrow Fe_{(s)} + CO_{(g)}$
(a) 298 K (b) 668 K
(c) 964 K
(d) $\Delta G°$ is +ve, hence the reaction will never be spontaneous.

8. The direct conversion of *A* to *B* is difficult, hence it is carried out as:
$$A \rightarrow C \rightarrow D \rightarrow B$$
Given, $\Delta S_{(A \rightarrow C)} = 50$ eU; $\Delta S_{(C \rightarrow D)} = 30$ eU; $\Delta S_{(B \rightarrow D)} = 20$ eU; where eU is entropy unit. Thus change in entropy in $(A \rightarrow B)$ is
(a) 100 eU (b) 60 eU
(c) −100 eU (d) −60 eU

9. Standard entropies of X_2, Y_2 and XY_3 are 60, 40 and 50 J $K^{-1}mol^{-1}$ respectively. For the reaction,

$$\frac{1}{2}X_2 + \frac{3}{2}Y_2 \rightleftharpoons XY_3 ; \Delta H = -30 \text{ kJ mol}^{-1}$$

to be at equilibrium, the temperature should be
(a) 750 K (b) 1000 K (c) 1250 K (d) 500 K

10. For one mole of an ideal gas, increasing the temperature from 10 °C to 20 °C
(a) increases the average kinetic energy by two times
(b) increases the *rms* velocity by $\sqrt{2}$ times
(c) increases the *rms* velocity by two times
(d) increases both the average kinetic energy and *rms* velocity, but not significantly.

11. For two gases P and Q with molecular weights M_P and M_Q it is observed that at a certain temperature T the mean velocity of P is equal to the root mean square velocity of Q. Thus, the root mean square velocity of P and Q will be equal if
(a) P is lowered to a temperature T_2 and $T_2 < T$ and Q is maintained at temperature T
(b) P is at a temperature T and Q at a temperature T_2 where $T > T_2$
(c) both P and Q are raised to higher temperature
(d) both P and Q are placed to lower temperature.

12. A 1 g sample of substance A at 100 °C is added to 100 mL of H_2O at 25 °C. Using separate 100 mL portions of H_2O, the procedure is repeated with substance B and then with substance C. The order of final temperature of different solutions will be
(Given specific heats for A, B and C are 0.6, 0.4, 0.2 J g^{-1} °C^{-1} respectively)
(a) $T_C > T_B > T_A$ (b) $T_B > T_A > T_C$
(c) $T_A > T_B > T_C$ (d) $T_A = T_B = T_C$

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**: Molar specific heat at constant volume of an ideal diatomic gas is $\left[\frac{3}{2}R + R\right]$.
Reason : On heating 1 mole of an ideal diatomic gas at constant pressure for 1°C rise in temperature, the increase in internal energy of gas is $\frac{5}{2}R$.

14. **Assertion**: When a real gas is allowed to expand adiabatically through a fine hole from a region of high pressure to a region of low pressure, the temperature of the gas falls.
Reason : Work is done at the cost of internal energy of the gas.

15. **Assertion**: The zeroth law of thermodynamics was known before the first law of thermodynamics.
Reason : The zeroth law concerning thermal equilibrium appeared before three laws (I, II and III) of thermodynamics and thus was named zeroth law.

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JEE MAIN / ADVANCED

Only One Option Correct Type

16. In an isobaric process, when temperature changes from T_1 to T_2, ΔS is equal to
(a) 2.303 $C_P \log (T_2/T_1)$ (b) 2.303 $C_P \ln (T_2/T_1)$
(c) $C_P \ln (T_1/T_2)$ (d) $C_V \ln (T_2/T_1)$

17. At a given temperature, density of gas x is twice as that of gas y and molar mass of x is one third of gas y. The ratio of their pressures will be
(a) $\frac{P_{(x)}}{P_{(y)}} = \frac{1}{4}$ (b) $\frac{P_{(x)}}{P_{(y)}} = 4$
(c) $\frac{P_{(x)}}{P_{(y)}} = 6$ (d) $\frac{P_{(x)}}{P_{(y)}} = \frac{1}{6}$

18. Calculate the energy (kJ mol^{-1}) of a C ≡ C bond in C_2H_2. (Given : The bond energy of a C – H bond = 350 kJ mol^{-1}).

$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$; $\Delta H = 225$ kJ mol^{-1}
$2C_{(s)} \longrightarrow 2C_{(g)}$; $\Delta H = 1410$ kJ mol^{-1}
$H_{2(g)} \longrightarrow 2H_{(g)}$; $\Delta H = 330$ kJ mol^{-1}

(a) 1165 (b) 837 (c) 865 (d) 815

19. A dry gas occupies 136.5 cm^3 at STP. If the same mass of the gas is collected over water at 27 °C at a total pressure of 725 torr, what volume does it occupy? (The vapour pressure of water at 27°C is 25 torr.)
(a) 157.3 cm^3 (b) 162.9 cm^3
(c) 159.2 cm^3 (d) 160.9 cm^3

More than One Options Correct Type

20. Which of the following statements are correct?
(a) Average velocity of molecules of a gas in a container is zero.
(b) All molecules in a gas are moving with the same speed.
(c) If an open container is heated from 300 K to 400 K, the fraction of air which goes out with respect to original present is 1/4.
(d) If compressibility factor of a gas at STP is less than unity then its molar volume is less than 22.4 L at STP.

21. Which of the following quantities are same for all ideal gases at the same temperature?
(a) The kinetic energy of 1 mole
(b) The kinetic energy of 1 g
(c) The number of molecules in 1 mole
(d) The number of molecules in 1 g

22. Boyle's law may be expressed as
(a) $\left(\frac{dP}{dV}\right)_T = \frac{K}{V}$ (b) $\left(\frac{dP}{dV}\right)_T = -\frac{K}{V^2}$
(c) $\left(\frac{dP}{dV}\right)_T = \frac{-K}{V}$ (d) $V \propto \frac{1}{P}$

23. The work done during adiabatic expansion or compression of an ideal gas is given by
(a) $nC_v\Delta T$ (b) $\frac{nR}{(\gamma-1)}(T_2 - T_1)$
(c) $-nRP_{ext}\left[\frac{T_2P_1 - T_1P_2}{P_1P_2}\right]$
(d) $-2.303\ RT \log V_2/V_1$

Numerical Value Type

24. The *K.E.* of *N* molecules of O_2 is *x* Joules at –123°C. Another sample of O_2 at 27°C has a *K.E.* of 2*x* Joules. The latter sample contains how many molecules of O_2 in multiple of *N*?

25. Calculate the entropy change when 1 kg of water is heated form 27°C to 200°C forming super heated steam under constant pressure. (Given, specific heat of water = 4180 J/kg-K and specific heat of steam = 1670 + 0.49 *T*J/kg-K and latent heat of vaporization = 23×10^5 J/kg).

26. At 20°C, two balloons of equal volume and porosity are filled to a pressure of 2 atm, one with 14 kg N_2 and other with 1 kg of H_2. The N_2 balloon leaks to a pressure of 1/2 atm in 1 hr. How long (in min) will it take for H_2 balloon to reach a pressure of 1/2 atm?

Comprehension Type

A gas bulb of 1 litre capacity contains 2.0×10^{21} molecules of nitrogen, exerting a pressure of 7.57×10^3 N m^{-2}. The ratio of the most probable speed to the root mean square speed is 0.82.

27. The root mean square speed of the gas molecules is
(a) 300.23 m s^{-1} (b) 494.16 m s^{-1}
(c) 507.45 m s^{-1} (d) 419.27 m s^{-1}

28. The temperature of the gas molecules is
(a) 200.15 K (b) 173.24 K
(c) 274.13 K (d) 225.10 K

Matrix Match Type

29. Match column I with column II and choose the correct option using the codes given below :

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Column I	Column II
(A) If temperature of given gas is increased.	(p) Average speed of gas will increase.
(B) If the pressure of a given gas is increased at constant temperature.	(q) Root mean square speed of gas molecules will increase.
(C) If the density of a given gas is lowered at constant temperature.	(r) Most probable speed of gas molecules will increase.
(D) If the volume of a given gas is increased at constant temperature.	(s) Speed of gas molecules will not change.

GLIMPSE OF NEXT ISSUE...

Focus NEET JEE (XI) : Hydrogen The *s* - Block Elements
Focus NEET JEE (XII) : Haloalkanes and Haloarenes Alcohols, Phenols and Ethers
Monthly Tune Up (XI) : Equilibrium
Monthly Tune Up (XII) : The *d* - and *f* - Block Elements Coordination Compounds
Concept Map : General Principles and Processes of Isolation of Elements



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

30. Match column I with column II and select the correct answer using the codes given below:

Column I	Column II
A. $\left(\frac{\delta G}{\delta P}\right)_T$	1. μ_{JT}
B. $\left(\frac{\delta H}{\delta T}\right)_P$	2. T
C. $\left(\frac{\delta H}{\delta S}\right)_P$	3. C_p
D. $\left(\frac{\delta T}{\delta P}\right)_H$	4. P
	5. V

	A	B	C	D
(a)	5	1	2	4
(b)	5	3	2	4
(c)	3	5	2	1
(d)	5	3	2	1



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		If your score is	
No. of questions attempted	.....	> 80%	Your preparation is going good, keep it up to get high score.
No. of questions correct	.....	60-80%	Need more practice, try hard to score more next time.
Marks scored in percentage	.....	<60%	Stress more on concepts and revise thoroughly.

Scientist of the Month



Sir Arthur Harden
(12 October, 1865 - 17 June, 1940)

Early Life and Education

Arthur was born to Scottish Prsebyterian businessman Albert Tyas Harden and Eliza Macalister. His early education was at a private school in Victoria Park. He went to study in 1877 at a Tettenhall College, Staffordshire, and entered Owens College in 1882 (now the University of Manchester) graduating in 1885. He studied chemistry under Professor Roscoe at Owens College and was influenced by J.B. Cohen.

After receiving a Ph.D. he returned to Manchester as a lecturer and demonstrator and taught along with Sir Philip Hartog. He researched the life and work of Dalton during these years. In 1895 he wrote a textbook on Practical Organic Chemistry along with F.C. Garrett. Harden continued to work at Manchester until 1897 when he was appointed chemist to the newly founded British Institute of Preventive Medicine, which later became the Lister Institute. He earned the degree Doctor of Science (D. Sc.) from the Victoria University in June 1902. Five years later, in 1907 he was appointed Head of the Biochemical Department, a position which he held until his retirement in 1930.

Contributions

- In 1886 Harden was awarded the Dalton Scholarship in Chemistry and spent a year working with Otto Fischer at Erlangen where he worked on the synthesis of β-nitroso- α -naphthylamine and studied its properties.
- At Manchester, Harden had studied the action of light on mixtures of carbon dioxide and chlorine, and when he entered the Institute he applied his methods to the investigation of biological phenomena such as the chemical action of bacteria and alcoholic fermentation. He studied the breakdown products of glucose and the chemistry of the yeast cell, and produced a series of papers on the antiscorbutic and anti-neuritic vitamins.

Honors

- He shared the Nobel Prize in Chemistry in 1929 with Hans Karl August Simon von Euler-Chelpin for their investigations into the fermentation of sugar and fermentative enzymes.
- He was a founding member of the Biochemical Society and editor of its journal for 25 years.
- Harden was knighted in 1926, and received several honorary doctorates. A Fellow of the Royal Society, he received the Davy Medal in 1935.

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Class XII

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UNIT - 4 : The *d* - and *f* - Block Elements | Coordination Compounds

THE *d*- AND *f*- BLOCK ELEMENTS

Transition Elements

Their general electronic configuration is $(n-1)d^{1-10}\,ns^{0-2}$ where, n is the outermost shell.

Series	Element
First transition series (3*d*-series)	Sc (At. no. 21) to Zn (At. no. 30)
Second transition series (4*d*-series)	Y (At. no. 39) to Cd (At. no. 48)
Third transition series (5*d*-series)	La (At. no. 57), Hf (At. no. 72) to Hg (At. no. 80)
Fourth transition series (6*d*-series)	Ac (At. no. 89), Rf (At. no. 104) to Cn (At. no. 112)

Metallic Character

- Metallic bonding is due to possession of one or two electrons in the outermost shell and relatively low ionisation energies. All the transition elements are metals having *hcp*, *ccp* or *bcc* lattice except mercury which is a liquid.

Oxidation States

- They show variable oxidation states due to involvement of $(n-1)d$ and outer *ns*-electrons in bonding as the energies of *ns* and $(n-1)d$ subshells are nearly equal.
- When *ns* and $(n-1)d$-electrons participate in bonding → show higher oxidation state.

Magnetic Properties

- Magnetic moment, $\mu_{eff} = \sqrt{n(n+2)}$ B.M. (where, n = number of unpaired electrons)
- Magnetic character ∝ n

Atomic and Ionic Radii

- Atomic radii decrease in the series with increase in atomic number because nuclear charge increases. After midway, decrease is small because of increased shielding effect of *d*-electrons. Ionic radii follow the same trend as the atomic radii.

Ionisation Energies

- $(IE)_1$ of 5*d*-elements are higher than those of the 3*d* and 4*d*-elements. This is due to greater effective nuclear charge acting on outer valence electrons because of the weak shielding of the nucleus by 4*f*-electrons.

Electrode Potential (E°)

- For the 3*d*-transition metals the $E^\circ(M^{2+}/M)$ values are :

V	Cr	Mn	Fe	Co	Ni	Cu
–1.18	–0.91	–1.18	–0.44	–0.28	–0.25	0.34 (Volts)

The irregular trend is due to variation in ionisation energies and sublimation energies. Except copper 3*d*-elements are good reducing agents but weaker than *s*-block elements.

Melting and Boiling Points

- These metals have very high melting and boiling points due to stronger metallic bonding.
- The melting point of the transition elements first rise to a maximum and then fall as the atomic number increases.

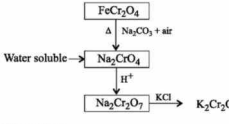
Alloy Formation

- Alloys are readily formed by these metals because of similar radii and other characteristics of transition metals.
- The alloys so formed are hard and have often high melting points and are also have considerable industrial importance.

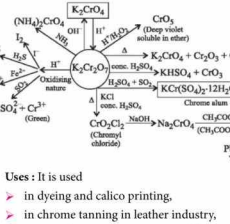
Some Important Compounds of Transition Elements

Potassium Dichromate ($K_2Cr_2O_7$)

- **Preparation :**



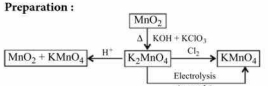
- **Properties :**



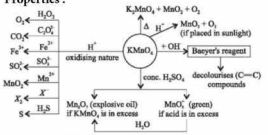
- **Uses :** It is used
  - in dyeing and calico printing,
  - in chrome tanning in leather industry,
  - as a volumetric reagent in laboratory for the estimation of ferrous ions, iodide ions, etc.

Potassium Permanganate ($KMnO_4$)

- **Preparation :**



- **Properties :**



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- **Uses :** It is used
  - as an oxidising agent in the laboratory and industry,
  - as a disinfectant and germicide,
  - in qualitative and quantitative analysis.

Inner Transition Elements

- Elements in which last electron enters into *f*-orbital are called *f*-block elements. *f*-block elements are also known as inner transition elements. There are two series of inner transition elements.
  (i) Lanthanoids (ii) Actinoids

Electronic Configuration

Element	Electronic configuration	Element	Electronic configuration
La (57)	$[Xe]5d^16s^2$	Ac (89)	$[Rn]6d^17s^2$
Ce (58)	$[Xe]4f^15d^16s^2$	Th (90)	$[Rn]6d^27s^2$
Pr (59)	$[Xe]4f^36s^2$	Pa (91)	$[Rn]5f^26d^17s^2$
Nd (60)	$[Xe]4f^46s^2$	U (92)	$[Rn]5f^36d^17s^2$
Pm (61)	$[Xe]4f^56s^2$	Np (93)	$[Rn]5f^46d^17s^2$
Sm (62)	$[Xe]4f^66s^2$	Pu (94)	$[Rn]5f^67s^2$
Eu (63)	$[Xe]4f^76s^2$	Am (95)	$[Rn]5f^77s^2$
Gd (64)	$[Xe]4f^75d^16s^2$	Cm (96)	$[Rn]5f^76d^17s^2$
Tb (65)	$[Xe]4f^96s^2$	Bk (97)	$[Rn]5f^97s^2$
Dy (66)	$[Xe]4f^{10}6s^2$	Cf (98)	$[Rn]5f^{10}7s^2$
Ho (67)	$[Xe]4f^{11}6s^2$	Es (99)	$[Rn]5f^{11}7s^2$
Er (68)	$[Xe]4f^{12}6s^2$	Fm (100)	$[Rn]5f^{12}7s^2$
Tm (69)	$[Xe]4f^{13}6s^2$	Md (101)	$[Rn]5f^{13}7s^2$
Yb (70)	$[Xe]4f^{14}6s^2$	No (102)	$[Rn]5f^{14}7s^2$
Lu (71)	$[Xe]4f^{14}5d^16s^2$	Lr (103)	$[Rn]5f^{14}6d^17s^2$

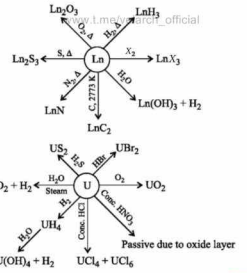
Lanthanoids Contraction

- A unique feature of lanthanoids is the decrease in atomic and ionic radii from lanthanum to lutetium. The gradual and steady decrease across the period is called Lanthanoid contraction.
- The difference in radii between two successive elements is not large but cumulative effect over 14 elements is nearly 14 pm in atomic radii and 20 pm in ionic radii of tripositive ions.
- **Cause of lanthanoid contraction :** From La to Lu atomic number increases, number of protons in the nucleus increases and electrons are added to 4*f* orbitals which have very poor shielding power. It shields the growing nuclear charge imperfectly. As a result effective nuclear charge increases and radius decreases.
  The decrease in atomic radii is irregular due to irregular electronic configuration. But ionic radii decrease in a regular manner.
- **Consequences of lanthanoid contraction :**
  - Atomic radii of 2nd and 3rd transition series elements are almost identical due to lanthanoid contraction. *e.g.,* Zr = 160 pm, Hf = 159 pm.
    As a result they occur in nature together and their separation from their mixture is difficult.
  - The slight difference in size of lanthanoids is responsible for difference in their properties like solubility, complex ion formation. This difference is utilised in their separation from the mixture of lanthanoids by solvent extraction or ion exchange.

Comparison of Lanthanoids and Actinoids

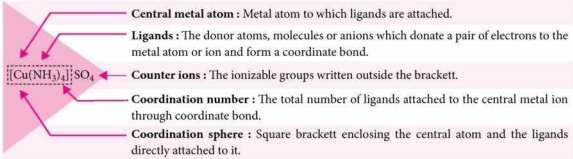
- Actinoid metals display greater variety of structures than lanthanoids. This is because irregularities in metallic radii are far greater than in lanthanoids.
- Magnetic susceptibility of actinoids vary with the number of 5*f* unpaired electrons roughly parallel to the corresponding lanthanoids. However magnetic susceptibility of lanthanoids are higher than those of actinoids.
- Actinoids resemble the lanthanoids in showing close similarities with each other and gradual variation in properties except oxidation state.

Chemical Properties of Lanthanoids and Actinoids



COORDINATION COMPOUNDS

Terms Related to Coordination Compounds



Werner's Theory

Proposed by Alfred Werner. The main postulates are :

- Primary valency corresponds to the oxidation state of the central metal. It is ionisable and satisfied by negative ions.
- Secondary valency is equal to the number of groups bound directly to the metal ion and is fixed for a metal. It is non-ionisable and is satisfied by neutral or negative ions.
- The ions/groups bound by the secondary linkages to the metal have characteristic spatial arrangements (called coordination polyhedra) corresponding to different coordination numbers.

IUPAC Rules for Naming Complexes

- The cations are named first.
- Within the coordination entity names are written in the following sequence :
  Number of ligands, Name of ligand, Name of central atom/ion, Oxidation state of central atom/ion.
- Number of ligands of each kind is indicated by numerical prefix di, tri, tetra, penta, hexa etc. for 2, 3, 4, 5, 6 .....
- For ligands containing any of these prefixes in their names, the number is indicated by prefix bis, tris, tetrakis etc. for 2, 3, 4, ... ligands respectively.
- Names of ligands are written in alphabetical order. The names of anionic ligands end as *o*. The suffix *ide*, *ite* or *ate* is replaced by *o* or suffix *–e* is replaced by *–o*.
- Names of neutral ligands are used as such. Some neutral ligands have special names. *e.g.*,
  en = ethylene diamine (ethane-1,2-diamine)
- **Names of central atom/ion :** When coordination entity is neutral or positive (cationic) then name of metal remains same. If the complex is anion, the name of central metal atom is made to end in *–ate*.
- Oxidation number of central atom is indicated in roman numerals just after name of central atom or ion in parenthesis.
- In case of ambidentate ligand the symbol of donor atom is indicated just after the name of metal.
  Examples :
  $[Cu(NH_3)_4]\,SO_4$: Tetraamminecopper(II) sulphate
  $[Ni(dmg)_2]$: *bis*(dimethylglyoximato)nickel(II)

Isomerism

Isomerism

Structural isomerism

Ionisation isomerism

Isomers which give different ions in solution due to the exchange of ions in coordination sphere and counter ions. *e.g.*, $[CoBr(NH_3)_5]SO_4$, $[CoSO_4(NH_3)_5]Br$

Hydrate isomerism

Isomers which differ in the number of water molecules attached to the metal atom or ion as ligands. *e.g.*, $[Cr(H_2O)_6]Cl_3$, $[Cr(H_2O)_5Cl]Cl_2{\cdot}H_2O$

Stereoisomerism

Linkage isomerism

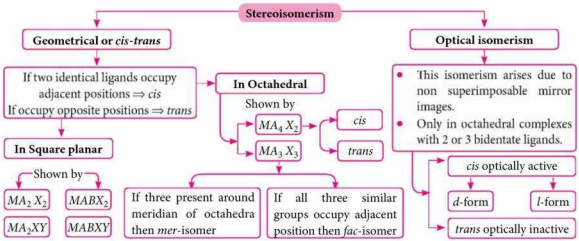
Isomers in which an ambidentate ligand attached to metal through different atoms. *e.g.*, $[Co(NO_2)(NH_3)_5]Cl$ $[Co(ONO)(NH_3)_5]Cl$

Coordination isomerism

When two isomers differ in the distribution of ligands in two complex ions. *e.g.*, $[Co(NH_3)_6][Cr(CN)_6]$, $[Co(CN)_6][Cr(NH_3)_6]$

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* Geometrical isomerism is not shown by tetrahedral complexes.

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Valence Bond Theory (VBT)

- Main postulates of this theory are
  - The central metal ion makes available as many number of empty orbitals as its coordination number in compound formation.
  - Appropriate vacant orbitals of metal undergoes hybridisation to give a definite geometry such as square planar(dsp^2), tetrahedral (sp^3), octahedral(d^2sp^3), etc.
  - Empty hybrid orbital of metal overlap with filled orbital of ligands containing lone pair to form $M \longleftarrow L$ coordinate bond.

Coordination Number	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)	$[FeF_6]^{3-}$, $[Fe(H_2O)_6]^{2+}$, $[Ni(NH_3)_6]^{2+}$

Crystal Field Theory (CFT)

- Main postulates of crystal field theory are
  - In a coordination compound there are electrostatic interaction between metal atom/ion and ligands.
  - In an isolated metal atom or ion all five d-orbitals have equal energy *i.e.*, they are degenerate.
  - When metal atom/ion gets surrounded by ligands, there occur interaction between d-electron cloud of metal atom/ion and ligands.
  - If the field due to ligand around metal atom is spherically symmetrical, the d-orbitals of metal remain degenerate.
  - If the field due to ligand surrounding metal is unsymmetrical (as in octahedral and tetrahedral complexes) the degeneracy of d-orbitals is splitted into two sets of orbitals.
  - Orbitals lying in the direction of ligands (point charges) are raised to higher energy state than

CONCEPT MAP

SOME BASIC CONCEPTS OF CHEMISTRY

Law of Conservation of Mass

- Proposed by the French Chemist Antoine Lavoisier (1789)
- Mass can neither be created nor destroyed in a chemical reaction.

OR

- For any chemical process in a closed system, the mass of the reactants must be equal to the mass of the products.

e.g., $C + O_2 = CO_2$

$12\ g + 32\ g = 44\ g$

Oxygen + Hydrogen → Water

32 g 4 g 36 g

Law of Definite Proportions

- Proposed by Louis Proust (1799)
- A chemical compound always consists of the same elements combined together in the same ratio, irrespective of the method of preparation or the source from it is taken.

In the formation of water compound, the ratio of the mass of hydrogen to the mass of oxygen is always 1 : 8, whatever be the source of water. Thus, if 9 g of water is decomposed, 1 g of hydrogen and 8 g of oxygen are always obtained.

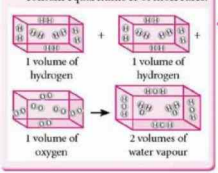
Law of Multiple Proportions

- Proposed by John Dalton (1804)
- When elements combine, they do so in the ratio of small whole numbers. *e.g.*, carbon and oxygen react to form CO or CO_2, but not $CO_{1.8}$.

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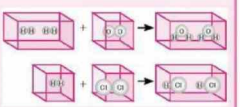
Avogadro's Law

- Proposed by Avogadro (1811)
- Equal volumes of gases at the same temperature and pressure should contain equal number of molecules.



Gay Lussac's Law of Gaseous Volumes

- Proposed by Gay Lussac (1808)
- At given temperature and pressure, the volumes of all gaseous reactants and products bear a simple whole number ratio to each other.

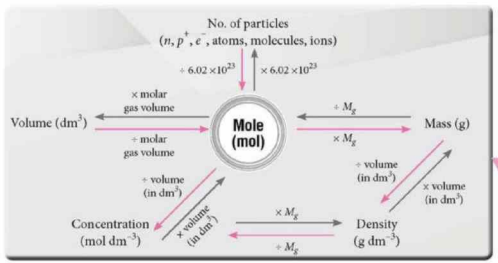


LAWS OF CHEMICAL COMBINATIONS

CONCENTR TERM

SO CO CH

MOLE CONCE



Concentration Terms

- Mass percent (%) = $\frac{w_{\text{solute}}}{w_{\text{solution}}} \times 100$
- Normality, $N = \frac{w_B \times 1000}{\text{eq. wt. of solute} \times V \text{ (in mL)}}$

  N = (Basicity or Acidity) $\times M$
- Molarity, $M = \frac{w_B \times 1000}{M_B \times V(\text{in mL})}$
- Relation between molarity and molality $\frac{1}{m} = \frac{d}{M} - \frac{M_B}{1000}$
- Molality, $m = \frac{w_B \times 1000}{M_B \times w_A(\text{in g})}$
- Mole fraction, $x_A = \frac{n_A}{n_A + n_B}$, $x_B = \frac{n_B}{n_A + n_B}$
- Relation between molality and mole fraction $m = \frac{x_B \times 1000}{(1 - x_B) \times M_A}$

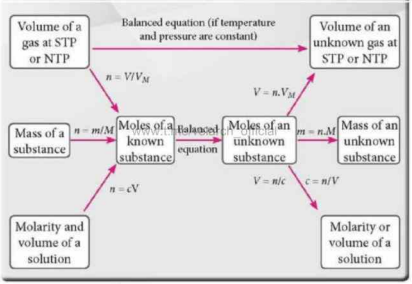
Limiting Reagent

The reactant which present in lesser amount and gets consumed and limits the amount of product formed is called limiting reagent.

e.g., $\underset{2\text{ g}}{H_2} + 1/2\underset{16\text{ g}}{O_2} \rightleftharpoons H_2O$

For every 16 g of oxygen, 2 g H_2 is required, if H_2 is present less than 2 g then it will be limiting reagent.

Mole Calculations



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STOICHIOMETRIC CALCULATIONS

ME BASIC
NCEPTS OF
HEMISTRY

EMPIRICAL FORMULA

PT

Empirical Formula

Mass % elements
↓ Assume 100 g sample
Calculate the grams of each element
↓ Use atomic weights
Calculate the moles of each element
↓ Calculate the molar ratio for each element
Assign empirical formula

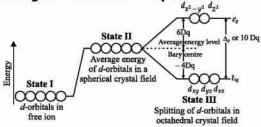
Molecular Formula

Empirical formula
↓
Empirical formula mass
↓ Use molecular mass
Calculate n = Molecular mass / Empirical mass
↓
Molecular formula = $n \times$ Empirical formula

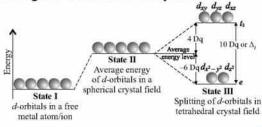
those orbitals lying between the ligands (point charges).

- The energy difference between two sets of orbitals is denoted by Δ_o and Δ_t for octahedral and tetrahedral complexes respectively.
- The magnitude of Δ_o or Δ_t depends upon the field strength of ligand around the metal.
- Ligands which cause large splitting (large Δ) are called strong field ligands while those which cause small splitting (small Δ) are called weak field ligands.

Splitting in Octahedral Complexes



Splitting in Tetrahedral Complexes



Calculation of CFSE

- CFSE = $(-0.4\,x + 0.6\,y)\,\Delta_o$
  where,
  x = number of electrons occupying t_{2g} orbitals.
  y = number of electrons occupying e_g orbitals.

Colour

- The energy difference for the first transition series generally falls in the visible region. Absorption of one colour in the visible spectrum results in the ion having the complementary colour.
- The amount of *d*-orbital splitting depends on the ligands, thus different ligands have different splitting energies (Δ_o values) and different colours result.

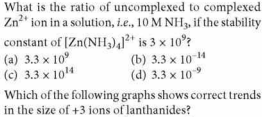
Applications of Coordination Compounds

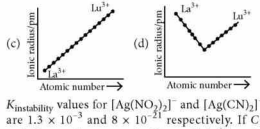
- Coordination compounds are of great importance in biological system. *e.g.*, chlorophyll, haemoglobin, myoglobin, etc. are coordinate compounds of Mg, Fe and Co respectively.
- The platinum complex, *cis*-$[PtCl_2(NH_3)_2]$ known as *cis*-platin is used in cancer treatment.
- EDTA is often used for treatment of lead poisoning.
- Coordination compounds are used as catalyst, *e.g.*, Wilkinson's catalyst, $(Ph_3P)_3RhCl$ is used for dehydrogenation of alkenes, Ziegler-Natta catalyst, $[TiCl_4 + (C_2H_5)_3Al]$ is used for polymerisation of ethene.

SPEED PRACTICE

1. What is the ratio of uncomplexed to complexed Zn^{2+} ion in a solution, *i.e.*, 10 M NH_3, if the stability constant of $[Zn(NH_3)_4]^{2+}$ is 3×10^9?
   (a) 3.3×10^{9} (b) 3.3×10^{-14}
   (c) 3.3×10^{14} (d) 3.3×10^{-9}

2. Which of the following graphs shows correct trends in the size of +3 ions of lanthanides?

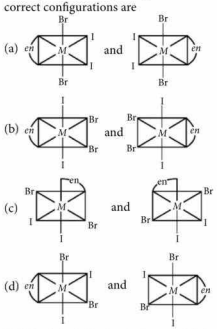




3. $K_{instability}$ values for $[Ag(NO_2)_2]^-$ and $[Ag(CN)_2]^-$ are 1.3×10^{-3} and 8×10^{-21} respectively. If C_1 and C_2 are the concentrations of Ag^+ ion in equimolar solutions of these two complexes respectively, then
   (a) $C_1 > C_2$ (b) $C_1 = C_2$
   (c) $C_1 < C_2$ (d) $C_1 = 2C_2$

4. What will be the charge on Fe^{x+} if the magnetic moment is $\sqrt{24}$?
   (a) +2 (b) +3
   (c) Zero (d) None of these

5. A complex ion has optically active isomers. Their correct configurations are



6. Which of the following is the most likely structure of $CrCl_3 \cdot 6H_2O$, if 1/3 of total chlorine of the compound is precipitated by adding $AgNO_3$ to its aqueous solution?
   (a) $CrCl_3 \cdot 6H_2O$
   (b) $[Cr(H_2O)_3Cl_3](H_2O)_3$
   (c) $[CrCl_2(H_2O)_4]Cl \cdot 2H_2O$
   (d) $[CrCl(H_2O)_5]Cl_2 \cdot H_2O$

7. If two moles of glycine NH_2CH_2COOH is added to a solution of one mole of aqueous copper acetate, which of the following observations is found?
   (a) Conductivity of solution increases.
   (b) Conductivity of solution decreases.
   (c) Conductivity of solution remains constant.
   (d) Conductivity of solution will be doubled.

8. Among the following transition metal ions, the one where all metal ions have $3d^2$ electronic configuration is
   (a) $Ti^{3+}, V^{2+}, Cr^{3+}, Mn^{4+}$ (b) $Ti^{+}, V^{4+}, Cr^{6+}, Mn^{7+}$
   (c) $Ti^{2+}, V^{3+}, Cr^{2+}, Mn^{3+}$ (d) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$

9. A transition metal exists in its highest oxidation state. It is expected to behave as
   (a) a chelating agent
   (b) a central metal in a coordination compound
   (c) an oxidizing agent
   (d) a reducing agent.

10. $Co^{2+}_{(aq)} + SCN^{-}_{(aq)} \rightarrow$ Complex (X)
    $Ni^{2+}_{(aq)}$ + Dimethyl glyoxime $\rightarrow$ Complex (Y)
    The coordination number of cobalt and nickel in complexes (X) and (Y) are four. The IUPAC names of the complexes (X) and (Y) are respectively
    (a) tetrathiocyanato-S-cobalt (II) and *bis*(dimethylglyoximate)nickel (II)
    (b) tetrathiocyanato-S-cobaltate (II) and *bis*(dimethylglyoximato)nickel (II)
    (c) tetrathiocyanato-S-cobaltate (II) and *bis*(dimethylglyoxime)nickel (II)
    (d) tetrathiocyanato-S-cobaltate (III) and *bis*(dimethylglyoximato)nickel (II).

11. An inorganic compound on strong heating gave a blackish brown powder and two oxides of sulphur. The powder was dissolved in HCl and a yellow solution was obtained which gave a blood red coloured solution with thiocyanate ions. The inorganic compound may be
    (a) $CuSO_4$ (b) $ZnSO_4$
    (c) $NiSO_4$ (d) $FeSO_4$

12. In which case racemic mixture is obtained on mixing its mirror images in 1 : 1 molar ratio?
    (a) $[Cr(en)_3]^{3+}$ (b) $[Ni(dmg)_2]$
    (c) *cis*-$[Cu(gly)_2]$ (d) All of these

13. Effective atomic number of $Co(CO)_4$ is 35 and hence it is less stable. It attains stability by
    (a) oxidation of Co (b) reduction of Co
    (c) dimerization (d) both (b) and (c).

14. Among the following transition elements, pick out the element with highest second ionization energy.
    (a) $V(Z = 23)$ (b) $Cr(Z = 24)$
    (c) $Mn(Z = 25)$ (d) $Cu(Z = 29)$

15. $[CoCl_2(NH_3)_4]^{+} + Cl^{-} \rightarrow [CoCl_3(NH_3)_3] + NH_3$
    If in this reaction two isomers of the product are obtained, which is true for the initial reactant complex?
    (a) Compound is in *cis*-form.
    (b) Compound is in *trans*-form.
    (c) Compound is in both *cis* and *trans* form.
    (d) Cannot be predicted.

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16. Increasing value of magnetic moments of I. $[Fe(CN)_6]^{4-}$, II. $[Fe(CN)_6]^{3-}$, III. $[Cr(NH_3)_6]^{3+}$, IV. $[Ni(H_2O)_4]^{2+}$ is
(a) I < II < III < IV (b) IV < III < II < I
(c) II < III < I < IV (d) I < II < IV < III

17. $[Cr(H_2O)_6]Cl_3$ has a magnetic moment of 3.87 B.M. The correct distribution of 3*d* electrons in chromium of the complex is
(a) $3d^3_{xy}, 3d^1_{yz}, 3d^2_z$ (b) $3d^1_{xy}, 3d^1_{yz}, 3d^1_{xz}$
(c) $3d^1_{(x^2-y^2)}, 3d^1_{z2}, 3d^1_{xz}$ (d) $3d^1_{xy}, 3d^1_{(x^2-y2)}, 3d^1_{yz}$

18. Which of the following pairs of transition metal ions are the stronger oxidizing agents in aqueous solution?
(a) V^{2+} and Cr^{2+} (b) Ti^{2+} and Cr^{2+}
(c) Mn^{3+} and Co^{3+} (d) V^{2+} and Fe^{2+}

19. A blue colouration is not obtained when
(a) ammonium hydroxide dissolves in copper sulphate
(b) copper sulphate solution reacts with $K_4[Fe(CN)_6]$
(c) ferric chloride reacts with potassium ferrocyanide
(d) anhydrous $CuSO_4$ is dissolved in water.

20. If excess of $AgNO_3$ solution is added to 100 mL of a 0.024 M solution of dichloro*bis*(ethylenediamine) cobalt(III) chloride, how many moles of AgCl be precipitated?
(a) 0.0012 (b) 0.0016
(c) 0.0024 (d) 0.0048

21. Among the following compounds whose optical activity does not depend on the orientation of the ligands around the metal cation?
I. $[CoCl_3(NH_3)_3]$
II. $[Co(en)_3]Cl_3$
III. $[Co(C_2O_4)_2(NH_3)_2]^-$
IV. $[CoCl_2(NH_3)_2(en)]^+$
(a) II and III (b) I, II and III
(c) II and IV (d) Only II

22. $FeCr_2O_4 \xrightarrow{I} Na_2CrO_4 \xrightarrow{II} Cr_2O_3 \xrightarrow{III} Cr$
I, II and III are

	I	II	III
(a)	Na_2CO_3/air	H^+/NH_4Cl	Al
(b)	NaOH/air	C	C
(c)	Na_2CO_3/air	C	C
(d)	NaOH/air	Al	C

23. Potassium permanganate acts as an oxidant in neutral, alkaline as well as acidic media. The final products obtained from it in the three conditions are, respectively
(a) MnO_2, MnO_2, Mn^{2+}
(b) MnO_2^{2-}, Mn^{3+}, Mn^{2+}
(c) MnO_2, MnO_4^{2-}, Mn^{3+}
(d) MnO, MnO_4, Mn^{2+}

24. An octahedral complex of cobalt contains five NH_3 groups, one chloride and one bromide group. This complex gives pale yellow precipitate with excess of $AgNO_3$. Then the ionization isomer of that complex is
(a) $[Co(NH_3)_5Cl]Br$ (b) $[Co(NH_3)_5Br]Cl$
(c) $[Co(NH_3)_4Cl_2]$ (d) $[Co(NH_3)_4ClBr]$

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25. Coordination compounds have great importance in biological systems. In this context which of the following statements is incorrect?
(a) Carboxypeptidase-A is an enzyme and contains zinc.
(b) Haemoglobin is the red pigment of blood and contains iron.
(c) Cyanocobalamin in B_{12} contains cobalt.
(d) Chlorophylls are green pigments in plants and contain calcium.

SOLUTIONS

1. **(b):** $Zn^{2+} + 4NH_3 \rightleftharpoons [Zn(NH_3)_4]^{2+}$

$$\frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}][NH_3]^4} = 3\times10^9$$

$$\frac{[Zn(NH_3)_4]^{2+}}{[Zn^{2+}]} = 3\times10^9\times10^4 = 3\times10^{13}$$

$$\frac{[Zn^{2+}]}{[Zn(NH_3)_4]^{2+}} = \frac{1}{3\times10^{13}} = 3.3\times10^{-14}$$

2. **(b):** On increasing the atomic number of lanthanide, there is regular decrease of ionic size due to poor shielding of 4*f* electrons (lanthanide contraction).

3. **(c):** Since instability constant 1.3×10^{-3} of $[Ag(NO_2)_2]^-$ is more, so it dissociates more than $[Ag(CN)_2]^-$ and hence, $C_1 < C_2$.

4. **(a):** If $\mu_B = \sqrt{24} = \sqrt{4(4+2)}$
thus, number of unpaired $e^- = 4$
∴ Fe must have +2 charge.

5. **(d)** : a, b and c have planes of symmetry.

6. **(c)**

7. **(b)** : Glycine forms a chelate $[Cu(gly)_2]$ which is a non-electrolyte. Acetic acid is produced which is also a weak electrolyte. Hence, the conductivity decreases.

8. **(d)** : $_{22}Ti = 3d^2\,4s^2$, $Ti^{2+} = 3d^2$
$_{23}V = 3d^3\,4s^2$, $V^{3+} = 3d^2$
$_{24}Cr = 3d^5\,4s^1$, $Cr^{4+} = 3d^2$
$_{25}Mn = 3d^5\,4s^2$, $Mn^{5+} = 3d^2$

9. **(c)** : In higher oxidation state a transition metal acts as an oxidizing agent.

10. **(b)** : $X = [Co(SCN)_4]^{2-}$
IUPAC name : tetrathiocyanato-*S*-cobaltate(II)
$Y = [Ni(dmg)_2]$
IUPAC name : *bis*(dimethylglyoximato)nickel (II)

11. **(d)** : $2FeSO_4 \xrightarrow{\Delta} \underset{\text{blackish brown}}{Fe_2O_3} + SO_2 + SO_3$

$Fe_2O_3 + 6HCl \rightarrow \underset{\text{Yellow soln.}}{2FeCl_3} + 3H_2O$

$FeCl_3 + 3CNS^- \rightarrow \underset{\text{Blood red coloured soln.}}{Fe(CNS)_3} + 3Cl^-$

12. **(a)** : (a) $[Cr(en)_3]^{3+}$ exists in *d*- and *l* – forms due to the absence of the symmetry element(s). So it will give racemic mixture when *d*- and *l*-forms are mixed in 1 : 1 molar ratio.
(b) $[Ni(dmg)_2]$ has square planar geometry and thus has mirror plane so optically inactive.
(c) *cis*-$[Cu(gly)_2]$ has square planar geometry and thus have mirror plane so optically inactive.

13. **(d)** : $Co(CO)_4$ gets the nearest inert gas configuration either by reduction or by dimerization.

14. **(d)** : Cu^+ has stable configuration, $[Ar]3d^{10}$.

15. **(a)** : *Cis*-isomer can produce two isomers *fac* and *mer* by the substitution of one NH_3 by Cl^- but not *trans*.

16. **(d)** : $[Fe(CN)_6]^{4-}$, unpaired electron = 0;
$[Fe(CN)_6]^{3-}$, unpaired electron = 1;
$[Cr(NH_3)_6]^{3+}$, unpaired electron = 3;
$[Ni(H_2O)_4]^{2+}$, unpaired electron = 2
Since, $\mu_B \propto$ no. of unpaired electrons (n)
Hence, the correct order is I < II < IV < III.

17. **(b)** : $3.87 = \sqrt{n(n+2)}$ so, $n = 3$
So, there are three unpaired e^-s. Based on crystal field splitting the orbital of t_{2g} set have one e^- each.

18. **(c)** : Mn^{3+} and Co^{3+} are stronger oxidizing agents because
(a) Mn^{2+} is stable than Mn^{3+} due to stable half filled d^5 configuration.
(b) In aqueous solution, Co^{2+} is more stable than Co^{3+}.

19. **(b)** : $2CuSO_4 + K_4[Fe(CN)_6] \rightarrow \underset{\text{Reddish brown vapour}}{Cu_2Fe(CN)_6} + 2K_2SO_4$

$4NH_4OH + CuSO_4 \rightarrow [Cu(NH_3)_4]SO_4 + 4H_2O$
Deep blue

$4FeCl_3 + 3K_4[Fe(CN)_6] \rightarrow \underset{\text{Ferric ferrocyanide (Prussian blue)}}{Fe_4[Fe(CN)_6]_3} + 12KCl$

$\underset{\text{Anhydrous}}{CuSO_4} + 5H_2O \rightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O}$

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20. **(c)** : The complex is $[Co(en)_2Cl_2]Cl$.
$[Co(en)_2Cl_2]Cl^- \rightarrow [Co(en)_2Cl_2]^+ + Cl^-$
Only one Cl^- which is precipitated as AgCl
100 mL of 0.024 M complex = 2.4 millimol
= 0.0024 mol

21. **(d)** : In $[Co(en)_3]Cl_3$ any change in the arrangement of ligands give same configuration because bidentate ligand can donate only to adjacent *cis* positions but not *trans*.

22. **(a)** : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Heat}} \underset{\text{(air)}}{8Na_2CrO_4} + 2Fe_2O_3 + 8CO_2$

$Na_2CrO_4 \xrightarrow{H^+/NH_4Cl} (NH_4)_2Cr_2O_7 \xrightarrow{\text{Heat}} N_2\uparrow + Cr_2O_3 \xrightarrow{Al} Cr + Al_2O_3$

23. **(a)** : In neutral medium :
$2KMnO_4 + 3MnSO_4 + 2H_2O \rightarrow K_2SO_4 + 2H_2SO_4 + 5MnO_2$
In alkaline medium :
$2KMnO_4 + H_2O \rightarrow 2MnO_2 + 2KOH + 3[O]$
In acidic medium :
$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

24. **(b)** : Since the complex is giving pale yellow precipitate with $AgNO_3$, the Br^- ion is in ionisation sphere. Its ionisation isomer should be $[Co(NH_3)_5Br]Cl$.

25. **(d)** : Chlorophyll a green pigment in plants contain Mg.

BRUSH UP YOUR CONCEPTS

Class XII

This specially designed column will help you to brush up your concepts by practicing questions. You can mail us your queries and doubts related to this topic at editor@mtg.in. The queries will be entertained by the author.*

ELECTROCHEMISTRY

- Electrochemistry deals with harnessing electric energy from Gibbs energy of indirect spontaneous chemical reactions using electrochemical cells and using electric energy to bring out non-spontaneous chemical reactions using electrolytic cells.
- A Daniell cell uses the reaction of $Zn_{(s)}$ with $Cu^{2+}_{(aq)}$ as :

$$Zn_{(s)} + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu_{(s)} \quad ...(i)$$

Anode/oxidation half reaction : $Zn_{(s)} \rightarrow Zn^{2+}_{(aq)} + 2e^-$

Cathode/reduction half reaction :

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

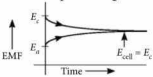
The cell is represented as :

$Zn_{(s)} \mid Zn^{2+}_{(aq)} \parallel Cu^{2+}_{(aq)} \mid Cu_{(s)}$

Anode or Left half cell | Cathode or Right half cell | [|| Shows salt bridge]

- $E_{cell} = E_c - E_a$

A cell works when $E_c > E_a$. EMF of half cell is directly proportional to concentration of metal ion. At cathode the concentration of metal ion decreases which decreases its emf. At anode the concentration of metal ion increases which increases its emf. The difference '$E_c - E_a$' goes on decreasing and after some time cell stops working.



Under standard conditions, when T = 298.15 K, molarity of solution 1 M, $E^\circ_{cell} = E^\circ_c - E^\circ_a$

For any other concentration, according to Nernst, the emf is :

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{n\mathcal{F}} \log Q$$

[n = electrons transferred]

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For Daniell cell from equation (i), $Q = \frac{[Zn^{2+}]}{[Cu^{2+}]}$

For the reaction,

$Ni_{(s)} + 2Ag^+_{(aq)} \rightarrow Ni^{2+}_{(aq)} + 2Ag_{(s)}$; $n = 2$

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF} \log \frac{[Ni^{2+}]}{[Ag^+]^2}$$

The value of $\frac{2.303RT}{F}$ in standard conditions = 0.059 V.

- The standard $E^\circ_{half\ cell}$ values are taken in terms of reduction potentials (IUPAC conventions) using Standard/Normal Hydrogen Electrode which consists of Pt-foil coated with Pt-black dipped in 1M $[H^+]$ concentrated acid on which pure $H_{2(g)}$ is passed at 1 atm. Its standard reduction potential is zero volt.
- **Salt Bridge :** It is inverted U-tube filled with a gel of an inert electrolyte KCl, KNO_3, NH_4NO_3, etc. with agar-agar, having its two ends immersed in electrolytes of two half cells. It has following functions :
  (a) It connects two half cells internally.
  (b) Only ions can pass through it.
  (c) It transports ions only and does not allow the two solutions to mix up.
- **Equilibrium Constant of Cell reaction and Work Done**

$$E_{cell} = E^\circ_{cell} - \frac{2.303RT}{nF}\left(\text{or } \frac{0.059}{n}\right) \log Q$$

*By **R.C. Grover**, having 45+ years of experience in teaching chemistry.

At equilibrium $Q = K_c$(Equilibrium constant), $E = 0$

$$\Rightarrow E^\circ_{cell} = \frac{2.303RT}{nF}\log K_c$$

Also $\Delta G^\circ = -nFE^\circ = -2.303\ RT \log K_c$ = Work done

Concentration Cell

When the two half cells of a cell are same, the cell will work if $[M^{x+}]_c > [M^{x+}]_a$. It is called concentration cell.

$$E_{cell} = \frac{0.059}{n}\log Q\text{; because } E^\circ_{cell} = 0$$

EMF Series and its Applications

When elements are arranged in decreasing order of emf from top to bottom it is called electrode potential series or activity series or EMF series or electromotive series or electrochemical series. Some of the applications of this series are :

(a) Metal of lower emf cannot be used to make a container for salt solution of metal of higher emf.

(b) When two half cells are joined to make an electrochemical cell, the metal of lower emf will work as anode and other as cathode.

$E_{cell} = E_{cathode} - E_{anode}$

(c) Lower the $E^\circ_{metal^{x+}/metal}$, better is the reducing power of the metal.

(d) The value of $E^\circ_{Li^+/Li}$ is the lowest –3.05 V, showing it to be the best reducing metal.

(e) The value of $E^\circ_{F_2/F^-}$ is the highest +2.87 V, showing it to be the best oxidising element.

(f) Metals having negative E° values can displace H_2 gas from acids.

Electrolysis

Sorting, shifting and deposition of ions on electrodes by passing electric current through electrolyte, is called electrolysis.

(a) Faraday's 1st Law of Electrolysis : The mass (m gram) of a substance consumed or deposited at an electrode is directly proportional to the quantity of charge (Q Coulombs) passed through the electrolyte during electrolysis.

mass $m \propto Q$ (Coulombs) $\propto I$ (ampere) $\times\ t$ (seconds)

$m = ZIt$

Z is proportionality constant known as electrochemical equivalent of a substance, which is the mass produced or consumed at electrode by passing one coulomb charge through electrolyte.

$H^+ + e^- \rightarrow H$ or $1/2\ H_2$

Practically, 0.000010364 g hydrogen is deposited by 1 C charge.

$\Rightarrow$ 1 g hydrogen is deposited by $\frac{1}{0.000010364}$ C charge

= 96488 C ≈ 96500 C = 1 F (Faraday)

Similarly, 1 mole of Na, Cu and Al will be collected from Na^+, Cu^{2+} and Al^{3+} by using 1 F, 2 F and 3 F charge respectively.

(b) Faraday's 2nd Law of Electrolysis : When the same quantity of charge is passed through different electrolytes, the ratio of masses deposited or consumed at electrodes to their equivalent weights is constant.

(c) Products of Electrolysis of Aqueous Solutions

1. Metal can be deposited at cathode only if its EMF is more than –0.83 V, otherwise H_2 is liberated.
2. Non metal is deposited at anode only if its EMF is less than 1.23 V, otherwise O_2 gas will be liberated.
3. Aqueous solutions of metal sulphates and metal nitrates, on electrolysis, produce O_2 gas at anode.
4. When two or more reactions are possible at an electrode, the reaction with lower discharge potential is preferred *i.e.*, at anode, reaction of lower reduction potential and at cathode, reaction of higher reduction potential will occur. It is called competing electrolysis.

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Applications of Electrolysis

(a) Determination of equivalent weight of elements
(b) Electrometallurgy
(c) Electrorefining of metals
(d) Electroplating
(e) Manufacture of compounds

MULTIPLE CHOICE QUESTIONS

1. If $Zn_{(s)} \mid Zn^{2+}_{(1\ M)} \parallel Cu^{2+}_{(1\ M)} \mid Cu$; $E^\circ_1 = 1.1$ V and $Cu_{(s)} \mid Cu^{2+}_{(1\ M)} \parallel Ag^+_{(1\ M)} \mid Ag_{(s)}$; $E^\circ_2 = 0.46$ V, What is the EMF of $Zn_{(s)} \mid Zn^{2+}_{(1\ M)} \parallel Ag^+_{(1\ M)} \mid Ag_{(s)}$?
   (a) 0.64 V (b) 0.08 V
   (c) 1.56 V (d) 1.74 V

2. Which of the following is the correct E_{cell} is the following if E°_{cell} is 3.17 V?
   $Mg_{(s)} \mid Mg^{2+}_{(0.2\ M)} \parallel Ag^+_{(0.001\ M)} \mid Ag_{(s)}$
   (a) 3.17 V (b) 3.318 V
   (c) 3.46 V (d) 3.01 V

3. The maximum work that a standard Daniell cell can do before it stops working is
[1 F = 96487 C mol^{-1} and E° = 1.1 V]
(a) 212.271 kJ mol^{-1} (b) 21.227 kJ mol^{-1}
(c) 721.221 kJ mol^{-1} (d) 71.222 kJ mol^{-1}

4. The value of equilibrium constant of Cu-Ag Galvanic cell will be
(E°_{cell} = 0.46 V, log 3.98 = 0.6)
(a) 3.98×10^{12} (b) 3.98×10^{13}
(c) 3.98×10^{14} (d) 3.98×10^{15}

5. If pH of acid in hydrogen electrode is 10, its potential will be
(a) 0.059 V (b) 0.59 V
(c) 0.0059 V (d) none of these.

6. Four half cells containing 1 M solution of each of $Mg(NO_3)_2$, $Cu(NO_3)_2$, $AgNO_3$ and $Hg_2(NO_3)_2$ are connected in series :
$E^\circ_{Mg^{2+}/Mg} = -2.37$ V ; $E^\circ_{Cu^{2+}/Cu} = +0.34$ V;
$E^\circ_{Ag^+/Ag} = +0.80$ V ; $E^\circ_{Hg_2^{2+}/Hg} = +0.79$ V
With increase in voltage, the sequence of deposition (decreasing order) of these metals would be (inert electrodes are used)
(a) Ag, Hg, Cu, Mg (b) Mg, Cu, Hg, Ag
(c) Cu, Hg, Ag (d) Ag, Hg, Cu

7. For the given three cells, select the correct option.
(i) $Cu_{(s)} \mid Cu^{2+}_{(1\ M)} \parallel Ag^+_{(1\ M)} \mid Ag_{(s)}$; E_1
(ii) $Cu_{(s)} \mid Cu^{2+}_{(10\ M)} \parallel Ag^+_{(10\ M)} \mid Ag_{(s)}$; E_2
(iii) $Cu_{(s)} \mid Cu^{2+}_{(0.1\ M)} \parallel Ag^+_{(0.1\ M)} \mid Ag_{(s)}$; E_3
(a) $E_1 > E_2 > E_3$ (b) $E_2 > E_1 > E_3$
(c) $E_3 > E_1 > E_2$ (d) $E_1 = E_2 = E_3$

8. For the given three cells, select the correct option.
(i) $Zn_{(s)} \mid Zn^{2+}_{(1\ M)} \parallel Cu^{2+}_{(1\ M)} \mid Cu_{(s)}$; E_1
(ii) $Zn_{(s)} \mid Zn^{2+}_{(10\ M)} \parallel Cu^{2+}_{(10\ M)} \mid Cu_{(s)}$; E_2
(iii) $Zn_{(s)} \mid Zn^{2+}_{(0.1\ M)} \parallel Cu^{2+}_{(0.1\ M)} \mid Cu_{(s)}$; E_3
(a) $E_1 > E_2 > E_3$ (b) $E_2 > E_1 > E_3$
(c) $E_3 > E_1 > E_2$ (d) $E_1 = E_2 = E_3$

9. In aqueous solution Cu^+ disproportionates as
$2Cu^+_{(aq)} \rightarrow Cu^{2+}_{(aq)} + Cu_{(s)}$
What is the E° value for this reaction if
$E^\circ_{Cu^{2+}/Cu^+} = 0.15$ V and $E^\circ_{Cu^{2+}/Cu} = 0.34$ V?
(a) 0.18 V (b) 0.28 V
(c) 0.38 V (d) 0.48 V

10. On passing a current of 6 amperes for 965 seconds through acidulated water. 0.56 L of H_2 gas was collected at cathode. The current efficiency is
(a) 3.338 % (b) 33.38 %
(c) 83.33 % (d) 95.55%

11. Which of the following is correct molar ratio of Na, Ca and Fe produced at cathode of three electrolytic cells connected in series and containing molten NaCl, $CaCl_2$ and $FeCl_3$, when 3F charge is passed?
(a) 1 : 2 : 3 (b) 3 : 2 : 1
(c) 2 : 3 : 6 (d) 6 : 3 : 2

12. Time taken to convert 1.0 L solution of 1 M NaCl to 1 M NaOH by passing 1.0 A current is
(a) 965 seconds (b) 9650 seconds
(c) 96500 seconds (d) none of these.

13. One litre of 1.0 M $CuSO_4$ solution is electrolysed by passing 1.5 F charge. Final molarity of the solution will be [At. wt. of Cu = 63.5]
(a) 0.20 M (b) 0.25 M (c) 0.30 N (d) 0.35 N

14. How long should a current of 0.25 amperes be passed through a molten metal salt to deposite that much weight of the metal which is equal to its electrochemical equivalent?
(a) 10 s (b) 12 s (c) 4 s (d) 8 s

15. How many coulombs of charge is required to convert 12.3 g of nitrobenzene to aniline?
(a) 57900 C (b) 95700 C
(c) 75900 C (d) 59700 C

16. What is the value of concentration quotient of Daniell cell at the condition of complete discharge?
E°_{cell} = 1.1 volt
(a) 37.3 (b) $10^{37.3}$ (c) $\frac{3}{37}$ (d) $\frac{37}{3}$

17. $Fe^{2+}_{(aq)}$, $Fe^{3+}_{(aq)}$ and some blocks of iron are kept together. Which of the following option is correct if $E^\circ_{Fe^{2+}/Fe} = -0.44$ V and $E^\circ_{Fe^{3+}/Fe^{2+}} = 0.77$ V?
(a) $[Fe^{3+}]$ increases (b) $[Fe^{3+}]$ decreases
(c) $[Fe^{2+}]$ decreases (d) $\frac{[Fe^{2+}]}{[Fe^{3+}]}$ is constant

18. Rusting follows the following reactions :
(i) $2H^+ + \frac{1}{2}O_2 + 2e^- \rightarrow H_2O$; $E^\circ = 1.23$ V
(ii) $Fe^{2+} + 2e^- \rightarrow Fe$; $E^\circ = -0.44$ V
The net work done is
(a) 122 kJ (b) 152 kJ (c) 222 kJ (d) 322 kJ

19. Which of the following is the correct representation of the EMF of the cell?

$Pt|H_{2(g)}\ (P_1)|H^+_{(aq)}|H_{2(g)}\ (P_2)|Pt$

(a) $\frac{RT}{F}\ln\frac{P_1}{P_2}$ (b) $\frac{RT}{2F}\ln\frac{P_1}{P_2}$

(c) $\frac{RT}{F}\ln\frac{P_2}{P_1}$ (d) $\frac{RT}{2F}\ln\frac{P_2}{P_1}$

20. Given that, $E^\circ_{Ce^{3+}|Ce} = -2.48$ V ; $E^\circ_{Cr^{3+}|Cr} = -0.74$ V and $E^\circ_{In^{3+}|In} = -0.34$ V ; the correct increasing order of oxidising power is

(a) $Ce^{3+} > Cr^{3+} > In^{3+}$ (b) $Ce^{3+} < Cr^{3+} < In^{3+}$

(c) $Ce < Cr < In$ (d) none of these

SOLUTIONS

1. **(c)** : Add the two sets (Cu-half cell is eliminated)

$E^\circ = E^\circ_1 + E^\circ_2 = 1.1 + 0.46 = 1.56$ V

2. **(d)** : $Mg_{(s)} + 2Ag^+_{(0.001\ M)} \rightarrow Mg^{2+}_{(0.2\ M)} + 2Ag_{(s)}$

$$Q = \frac{[Mg^{2+}]}{[Ag^+]^2} = \frac{0.2}{1\times10^{-6}} = 2\times10^5 \ ;\ n = 2$$

$$E_{cell} = E^\circ_{cell} - \frac{0.059}{n}\log Q$$

$$= 3.17 - \frac{0.059}{2}\log(2\times10^5)$$

$$= 3.17 - 0.0295\ [0.30 + 5]$$

$$= 3.17 - 0.0295 \times 5.30 = 3.17 - 0.156 = 3.01$$

3. **(a)** : Work done $= -\Delta G^\circ = nFE^\circ$

$= 2 \times 96487 \times 1.1\ J\ mol^{-1} = 212.271\ kJ\ mol^{-1}$

4. **(d)** : $E^\circ_{cell} = \frac{0.059}{n}\log K_c$; $n = 2$

$$\log K_c = \frac{2\times0.46}{0.059} = 15.6 = 0.6 + 15$$

K_c = (Antilog 0.6) $\times 10^{15} = 3.98 \times 10^{15}$

5. **(d)** : $pH = 10 \Rightarrow [H^+] = 10^{-10}$

$H^+ + e^- \rightarrow \frac{1}{2}H_2$; $P_{H_2} = 1$ atm

$$E_{half\ cell} = E^\circ_{half\ cell} - \frac{0.059}{n}\log\frac{[P_{H_2}]^{\frac{1}{2}}}{[H^+]}$$

$$= 0 - \frac{0.059}{1}\log\frac{1}{10^{-10}}$$

$= -0.059 \log 10^{10} = -0.059 \times 10 \log 10 = -0.59$ V

6. **(d)** : Mg cannot be extracted from aqueous $Mg(NO_3)_2$. For other cases, higher the E°, easier the deposition of metal.

7. **(b)** : Case (i), $E_1 = E^\circ$

Case (ii), $E_2 = E^\circ - \frac{0.059}{n}\log Q$

$$= E^\circ - \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$= E^\circ - 0.0295\log\frac{10}{100} = E^\circ - 0.0295\log10^{-1}$$

$= E^\circ + 0.0295$

$E_2 > E^\circ$, *i.e.*, $E_2 > E_1$

Case (iii), $E_3 = E^\circ - \frac{0.059}{2}\log\frac{0.1}{(0.1)^2}$

$= E^\circ - 0.0295\log10 = E^\circ - 0.0295$

$\Rightarrow \ E_3 < E^\circ$, *i.e.*, $E_3 < E_1$

8. **(d)** : Since, charges of Zn^{2+} and Cu^{2+} are equal and concentrations of ions at cathode and anode in each case are equal $E_1 = E_2 = E_3$ [$\because E^\circ_{cell}$ of cell (i)]

9. **(c)** : $Cu^{2+} \xrightarrow[\Delta G_1,\ E_1]{e^-} Cu^+ \xrightarrow[\Delta G_2,\ E_2]{e^-} Cu$

$2e^-,\ \Delta G_3,\ E_3$

$\Delta G_1 + \Delta G_2 = \Delta G_3$

$-n_1FE_1 - n_2FE_2 = -n_3FE_3$

$1 \times 0.15 + 1 \times E_2 = 2 \times 0.34 \Rightarrow E_2 = +0.53$ V

$Cu^+ + Cu^+ \longrightarrow Cu + Cu^{2+}$

Red., cathode, $E^\circ_c = +0.53$ V

Oxi., anode, $E^\circ_a = 0.15$ V

$E^\circ_{cell} = E^\circ_c - E^\circ_a = +0.53 - 0.15 = 0.38$ V

10. **(c)** : $H^+ + 1e^- \rightarrow \underset{1F}{\frac{1}{2}H_2}$

$\underset{11.2\ L}{}$

11.2 L $H_{2(g)}$, needs charge = 96500 C

0.56 L $H_{2(g)}$, needs charge = $\frac{96500\times0.56}{11.2}$ C

$$I = \frac{Q}{t} = \frac{96500\times0.56}{965\times11.2} = 5\ A$$

$$\text{Current efficiency} = \frac{I}{\text{Ammeter current}}\times100$$

$$= \frac{5}{6}\times100 = 83.33\,\%$$

11. **(d)** : $Na^+ + 1e^-(1F) \rightarrow Na(1\ Mole)$

3F charge will produce 3 moles of Na.

$Ca^{2+} + 2e^-(2F) \rightarrow Ca(1\ Mole)$

3F charge will produce $\frac{3}{2}$ moles of Ca.

$Fe^{3+} + 3e^-(3F) \rightarrow Fe(1\ Mole)$

3F charge will produce 1 mole of Fe.

The ratio of moles of Na, Ca and Fe $= 3 : \frac{3}{2} : 1$

$= 6 : 3 : 2$

12. **(c)** : From water 1 mole H^+ will change to $\frac{1}{2}$ mol H_2 and 1 mole OH^- will remain in solution by passing 1 F charge through $NaCl_{(aq)}$.

$It = Q = 96500$ C

$t = \frac{96500}{1}$ seconds $= 96500$ seconds

13. **(b)** : $Cu^{2+} + 2e^-$ (*i.e.*, 2F) $\rightarrow$ Cu

2F charge deposites 1 mole Cu

1.5 F charge deposites Cu $= \frac{1.5}{2} = 0.75$ mole

Left over copper in 1 L solution $= 1.0 - 0.75$

$= 0.25$ mole

Final molarity $= 0.25$ M

14. **(c)** : $W = Z\,I\,t$

$I\,t = \frac{W}{Z} = 1$ [$\because$ $W = Z$]

$t = \frac{1}{0.25}$ seconds $= 4$ seconds

15. **(a)** :



123 g (1 mole) nitrobenzene needs 6×96500 C

12.3 g nitrobenzene needs charge $= \frac{6 \times 96500 \times 12.3}{123}$

$= 57900$ C

16. **(b)** : At complete discharge, $E^\circ = \frac{0.059}{n} \log Q$

$\log_{10} Q = \frac{1.1 \times 2}{0.059} = 37.3$

[Here, $n = 2$ for Daniell cell]

Q, *i.e.*, $\frac{[Zn^{2+}]}{[Cu^{2+}]} = 10^{37.3}$

17. **(b)** : $(E^\circ_{Fe^{2+}/Fe} = -0.44\text{ V}) < (E^\circ_{Fe^{3+}/Fe^{2+}} = +0.77\text{ V})$

$\Rightarrow$ Fe changes to Fe^{2+} and Fe^{3+} changes to Fe^{2+}

$\Rightarrow$ $[Fe^{3+}]$ decreases

18. **(d)** : Work done $\Delta G^\circ = -nFE^\circ$

$= -2 \times 96500 \times [1.23 - (-0.44)]$ J

$= -2 \times 96500 \times 1.67$ J $= 322.3$ kJ

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19. **(b)** : Anode : $H_{2(a)}\,(P_1) \rightarrow 2H^+_{(a)} + 2e^-$

Cathode : $2H^+_{(c)} + 2e^- \rightarrow H_{2(c)}\,(P_2)$

$H_{2(a)}\,P_1 + 2H^+_{(c)} \rightarrow 2H^+_{(a)} + H_{2(c)}(P_2)$

$E = E^\circ - \frac{RT}{nF} \ln \frac{(P_2)}{(P_1)} = \frac{RT}{2F} \ln \frac{(P_1)}{(P_2)}$

20. **(b)** : Higher the reduction potential, higher is the oxidising power of the cation.

◈◈

3 AMAZING FACTS YOU MUST KNOW

1

Scientists didn't really exist until the 17th Century. Isaac Newton was a scientist before scientists even existed. Before the 17th century began, science and scientists were not truly recognized. At first, people like the 17th century genius Isaac Newton were called natural philosophers, because there was no concept of the word "scientist" at the time.



Isaac Newton

2

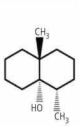
Dropping molten glass into cold water creates a tadpole-like shape called Prince Rupert's Drop.



The head is very strong and can withstand blows from a hammer, but if the tail is damaged at all, the whole structure will disintegrate explosively.

3

Geosmin has a distinct earthy flavour and aroma, and is responsible for the earthy taste of beets and a contributor to the scent (petrichor) in the air when rain falls after a dry spell of weather. It is produced by a type of Actinobacteria.





Class XII

Be JEE READY

with exclusive and brain storming MCQs

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Practicing these MCQs helps to strengthen your concepts and give you extra edge in your JEE preparation

1. Pure water is saturated with pure solid AgCl, a silver rod is placed in the solution and the potential is measured against normal calomel electrode at 25°C. This experiment is then repeated with a saturated solution of AgI. If the difference in potential is 0.177 V, what is the ratio of solubility product (K_{sp}) of AgCl and AgI at the temperature of the experiment ? (In both cases normal calomel electrode is cathode)

(a) 10^3 (b) 10^6 (c) 10^{-3} (d) 10^{-6}

2. pH of 0.1 M monobasic acid is measured to be 2. Its osmotic pressure at a given temperature T K is

(a) 0.1 RT (b) 0.11 RT

(c) 1.1 RT (d) 0.01 RT

3. Which of the following will produce isopropyl amine ?

I. $(CH_3)_2CO \xrightarrow{NH_2OH} X \xrightarrow{LiAlH_4}$

II. $CH_3-CH_2-CHO \xrightarrow[heat]{NH_3} X \xrightarrow{LiAlH_4}$

III. $(CH_3)_2CH-OH + PCl_5 \longrightarrow X \xrightarrow{NH_3}$

IV. $CH_3-CH_2-CH_2-NH_2 \xrightarrow{heat}$

(a) I, II (b) II, III

(c) I, III (d) IV only

4. Match each coordination compound in column I with an appropriate pair of characteristics in column II and select the correct answer using the code given below :

	Column I		Column II
A.	$[Cr(NH_3)_4Cl_2]Cl$	1.	Paramagnetic and exhibits ionisation isomerism
B.	$[Ti(H_2O)_5Cl](NO_3)_2$	2.	Diamagnetic and exhibits *cis-trans* isomerism
C.	$[Pt(en)(NH_3)Cl]NO_3$	3.	Paramagnetic and exhibits *cis-trans*-isomerism
D.	$[Co(NH_3)_4(NO_3)_2]NO_3$	4.	Diamagnetic and exhibits ionisation isomerism

	A	B	C	D
(a)	4	2	3	1
(b)	3	1	4	2
(c)	2	1	3	4
(d)	1	3	4	2

5. Read the following reactions :

I. $H_3C-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgBr(excess)}$

II. $H-\overset{O}{\overset{\|}{C}}-OEt \xrightarrow[(ii)\ H^+]{(i)\ PhMgBr\ (excess)}$

III. $H-\overset{\overset{O}{\|}}{C}-OEt \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgBr\ (excess)}$

IV. $ClCH_2COOEt \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgBr\ (excess)}$

In which set of the reactions the product will be 3° alcohol?

(a) I, II, III (b) I, III
(c) II, IV (d) I, IV

6. Consider the following isolation/purification processes.

I. Heating impure metal with I_2 at 150 – 200°C and passing the resulting volatile iodide on hot tungsten filament at 1400°C to get the pure metal.

II. Heating the sulphide ore in air until a part is converted to oxide and then further heating in the absence of air to let the oxide react unchanged metal sulphide to get the metal.

III. Electrolysis of the molten electrolyte containing metal oxide and cryolite or fluorspar to obtain the metal.

The processes used for obtaining aluminium, titanium and lead are respectively

(a) I, II and III (b) II, III and I
(c) III, I and II (d) II, I and III

7. An ester (*A*) with molecular formula, $C_9H_{10}O_2$ was treated with excess of CH_3MgBr and the complex so formed was treated with H_2SO_4 to give an olefin (*B*). Ozonolysis of (*B*) gave a ketone with molecular formula C_8H_8O which shows +ve iodoform test. The structure of (*A*) is

(a) $C_6H_5COOC_2H_5$
(b) $C_2H_5COOC_6H_5$
(c) $H_3COCH_2COC_6H_5$
(d) $p-H_3CO-C_6H_4-COCH_3$

8. A certain hypohalite on treating with hot and conc. NaOH forms anions *P* and *Q*. Stable anion among *P* and *Q* can be obtained by neutralising its conjugate acid *X*.

Upon heating to very high temperature a compound *Y* is formed, which is used in estimation of a toxic gas which have 300 times stronger affinity for haemoglobin than dioxygen. Then which of the following statements are true?

(a) *X* is HI.
(b) *Y* is Cl_2O_5
(c) Final product, *Y* has total no. of bonds 5.
(d) *Y* on reacting with the toxic gas produces a gas which is used in fire extinguisher.

9. The density of solid argon is 1.65 g/mL at –233°C. If the argon atom is assumed to be sphere of radius 1.54×10^{-8} cm, what percentage of solid argon is apparently empty space ?

(a) 62% (b) 38% (c) 50% (d) 84%

10. The pair of compounds in which both the compounds give positive test with Tollens' reagent is

(a) glucose and sucrose (b) fructose and sucrose
(c) acetophenone and hexanal
(d) glucose and fructose.

11. $4\,AgNO_3 + 2H_2O + H_3PO_2 \xrightarrow{boil} 4Ag + \text{'}X\text{'} + \text{'}Y\text{'}$

If *X* is oxyacid of nitrogen and *Y* is oxyacid of phosphorous then correct statement(s) is/are

(a) *X* is HNO_3 (b) *Y* is H_3PO_4
(c) the oxidation number of 'P' changed from + 1 to +5
(d) all of these.

12. Which compound in each of the following pairs is most reactive to the conditions indicated?

I.  and

II.  (KOH in CH_3OH)

III.  and

IV.  ($NaNH_2$ in NH_3)

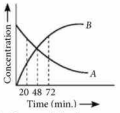
(a) I and III (b) II and III
(c) I and IV (d) II and IV

Quotable Quote

You cannot teach a man anything; you can only help him discover it in himself.

Galileo

13. For a first order reaction, $nA \longrightarrow B$ whose concentration vs time curve is as shown in the figure. If half life for the reaction is 24 minutes. Find out the value of n.



(a) 1 (b) 2 (c) 3 (d) 4

14. Select the correct statement.

(a) Langmuir adsorption isotherm is expected to be applicable at low gas pressure and moderately high temperature.

(b) The rate of an enzyme catalysed reaction depends upon enzyme concentration.

(c) A negative catalyst raises the activation energy barrier of a reaction and thus reduces its rate.

(d) Gases having lower critical temperature are adsorbed to a greater extent than those with higher critical temperature.

15. $FeCr_2O_4 + Na_2CO_3 + O_2 \xrightarrow{\text{Fusion}} (X) \xrightarrow[H_2O]{H^+} (Y)$

$\xrightarrow[H_2O_2]{H^+} (Z)$

Which of the following statement is true for the compounds (X), (Y) and (Z)?

(a) In all three compounds, the chromium is in +6 oxidation state.

(b) (Z) is a deep blue-violet coloured compound which decomposes rapidly in aqueous solution into Cr^{3+} and dioxygen.

(c) Saturated solution of (Y) gives bright orange compound, chromic anhydride, with concentrated H_2SO_4.

(d) All of these.

SOLUTIONS

1. **(b)** : $Ag \longrightarrow Ag^+ + e^-$

$E_1 = E_{oxid} + E_{calomel}$

$= E' - \frac{0.0591}{1}\log\sqrt{K_{sp_1}} + E_{calomel}$

$E_2 = E' - \frac{0.0591}{1}\log\sqrt{K_{sp_2}} + E_{calomel}$

$E_2 - E_1 = 0.177 = 0.0591\log\sqrt{\frac{K_{sp_1}}{K_{sp_2}}} \Rightarrow \frac{K_{sp_1}}{K_{sp_2}} = 10^6$

2. **(b)** :

	HA	$\rightleftharpoons$	H^+	+	A^-
$t = 0$	0		0		0
t_{eq}	C – Cα		Cα		Cα

$[H^+] = C\alpha$, $[H^+] = 10^{-pH}$

$\therefore \quad C\alpha = 10^{-2}$

$0.1\,\alpha = 10^{-2} \Rightarrow \alpha = 0.1$

$\alpha = \frac{i-1}{n-1}; 0.1 = \frac{i-1}{2-1}$

$i = 1.1$

$\therefore \quad \pi = iCRT = 1.1 \times 0.1 \times RT = 0.11\,RT$

3. **(c)** : $(CH_3)_2CO \xrightarrow{NH_2OH} (CH_3)_2C{=}N{-}OH \xrightarrow[LiAlH_4]{} (CH_3)_2CHNH_2$

$(CH_3)_2CHOH \xrightarrow{PCl_5} (CH_3)_2CHCl \xrightarrow{NH_3} (CH_3)_2CHNH_2$

4. **(b)** : (A) $[Cr(NH_3)_4Cl_2]Cl \rightarrow Cr^{+3}$ is d^3. It is paramagnetic and it shows *cis-trans* isomerism.

(B) $[Ti(H_2O)_5Cl](NO_3)_2 \rightarrow Ti^{+3}$ is d^1. It is paramagnetic and it show ionisation isomerism.

(C) $[Pt(en)(NH_3)Cl]NO_3 \rightarrow Pt^{+2}$ is d^8. But this complex is square planar and all electrons are paired. So it is diamagnetic. It exhibit ionisation isomerism.

(D) $[Co(NH_3)_4(NO_3)_2]NO_3 \rightarrow Co^{+3}$ is d^6. Since ligands are strong, so electron are paired. It is diamagnetic. It exhibit *cis-trans* isomerism.

5. **(d)** : I. $CH_3{-}\overset{O}{\overset{\|}{C}}{-}OEt \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgBr(excess)} CH_3{-}\overset{OH}{\overset{|}{C}}{-}CH_3$ (3° alcohol)

II. $H{-}\overset{O}{\overset{\|}{C}}{-}OEt \xrightarrow[(ii)\ H^+]{(i)\ PhMgBr\ (excess)} H{-}\overset{OH}{\overset{|}{C}}{-}Ph$ (2° alcohol)

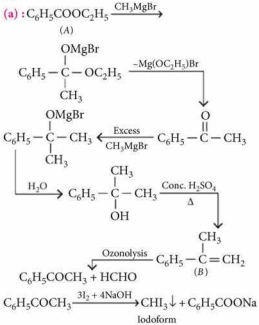
III. $H{-}\overset{O}{\overset{\|}{C}}{-}OEt \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgBr\ (excess)} H{-}\overset{OH}{\overset{|}{C}}{-}CH_3$ (2° alcohol)

IV. $ClCH_2COOEt \xrightarrow[(ii)\ H^+]{(i)\ CH_3MgBr\ (excess)} Cl{-}CH_2{-}\overset{OH}{\overset{|}{C}}{-}CH_3$ (3° alcohol)

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6. (c)

7. (a) : $C_6H_5COOC_2H_5 \xrightarrow[(A)]{CH_3MgBr}$



$$C_6H_5COCH_3 \xrightarrow{3I_2 + 4NaOH} CHI_3\downarrow + C_6H_5COONa$$

Iodoform

8. (d) : $IO^- \xrightarrow[\text{Hot and conc.}]{OH^-} \underset{P}{I^-} + \underset{Q}{IO_3^-}$

Q is more stable anion its conjugate acid is HIO_3.

$$\underset{X}{2HIO_3} \xrightleftharpoons{240\ ^\circ C} \underset{Y}{I_2O_5} + H_2O$$

$$I_2O_5 + 5CO \longrightarrow I_2 + 5CO_2$$

(Useful in fire extinguishing)

9. (a) : Volume of one atom of Ar $= \frac{4}{3}\pi r^3$

Also, number of atoms in 1.65 g or one mL

$$= \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$\therefore$ Total volume of all atoms of Ar in solid state

$$= \frac{4}{3}\pi r^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= \frac{4}{3} \times \frac{22}{7} \times (1.54 \times 10^{-8})^3 \times \frac{1.65}{40} \times 6.023 \times 10^{23}$$

$$= 0.380 \text{ cm}^3$$

Volume of solid argon = 1 cm^3

$\therefore$ % empty space $= \frac{[1 - 0.380]}{1} \times 100 = 62\%$

10. (d) : Glucose being an aldose responds to Tollens' test while fructose, although a ketose, undergoes rearrangement in presence of basic medium (provided by Tollens' reagent) to form glucose, which then responds to Tollens' test.

11. (d) : $4AgNO_3 + 2H_2O + H_3PO_2 \longrightarrow \underset{(X)}{4Ag} + \underset{(Y)}{4HNO_3 + H_3PO_4}$

12. (a) : In the first case the reaction gives side chain substitution product which is easier in A. In the second case the reaction will proceed by benzyne mechanism for which *ortho* position w.r.t. Cl must have H-atoms.

13. (c) : $\underset{a}{nA} \longrightarrow B$

$a - x \qquad x/n \qquad t_{1/2} = 24$ min

at $t = 48 \qquad a - x = \frac{x}{n}$

$$a = \frac{(1+n)x}{n} : \frac{na}{1+n} = x$$

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$$\frac{\ln 2}{24} = \frac{1}{48} \ln \frac{a}{a - \frac{na}{(1+n)}} \Rightarrow 4 = \frac{a(1+n)}{a} \Rightarrow n = 3$$

14. (c)

15. (d) : $4FeCr_2O_4 + 8Na_2CO_3 + 7O_2 \xrightarrow{\text{Fusion}} \underset{(X)}{Na_2CrO_4} \xrightarrow[H_2O]{H^+} \underset{(Y)}{Na_2Cr_2O_7} \xrightarrow{H^+/H_2O_2} \underset{(Z)}{CrO(O_2)_2} \xrightarrow{H_2O}$

(Deep blue violet)

$$O_2 + H_2O + Cr^{3+}$$

$$Na_2Cr_2O_7 + H_2SO_4 \xrightarrow{H_2O} \underset{\text{Chromic anhydride (bright orange)}}{2CrO_3}$$

COMIC CAPSULE

DON'T DRINK WATER WHILE STUDYING. BECAUSE CHEMISTRY SAYS THAT



CONCENTRATION DECREASES ON ADDING WATER

EXAMINER'S MIND CLASS XII

The questions given in this column have been prepared on the basis of pattern of Previous Years' Questions asked in JEE (Main & Advanced)/NEET/AIIMS exams.

CHEMICAL KINETICS

SECTION - I

Only One Option Correct Type

1. The rate constant is numerically the same for three reactions of first, second and third order respectively. Which one is true for rate of three reactions, if concentration of reactant is greater than 1 M?

(a) $r_1 = r_2 = r_3$ (b) $r_1 > r_2 > r_3$

(c) $r_1 < r_2 < r_3$ (d) All of these

2. In the following first order competing reactions where $t_1 = t_2$:

$A + \text{Reagent} \xrightarrow{k_1} \text{Product}$

$B + \text{Reagent} \xrightarrow{k_2} \text{Product}$

The ratio of $\frac{k_1}{k_2}$ if only 50% of B and 94% of A have been reacted is

(a) 4.06 (b) 0.246 (c) 2.06 (d) 0.06

3. The decomposition of N_2O_5 is a first order reaction represented by $N_2O_5 \rightleftharpoons N_2O_4 + \frac{1}{2}O_2$. After 15 minutes the volume of O_2 produced is 9 mL and at the end of the reaction 35 mL. The rate constant is equal to

(a) $\frac{1}{15}\ln\frac{35}{26}$ (b) $\frac{1}{15}\ln\frac{44}{35}$

(c) $\frac{1}{15}\ln\frac{35}{44}$ (d) $\frac{1}{15}\ln\frac{44}{26}$

4. The kinetic data for the given reaction, $A_{(g)} + 2B_{(g)} \xrightarrow{k} C_{(g)}$ is provided in the following table for three experiments at 300 K.

Ex. No.	[A/M]	[B/M]	Initial rate M(sec^{-1})
1.	0.01	0.01	6.930×10^{-6}
2.	0.02	0.01	1.386×10^{-5}
3.	0.02	0.02	1.386×10^{-5}

In another experiment starting with initial concentration of 0.5 M and 1 M respectively for A and B at 300 K, find the rate of reaction after 50 minutes from start of experiment (in M/sec).

(a) 6.93×10^{-4} (b) 0.25×10^{-7}

(c) 4.36×10^{-5} (d) 3.46×10^{-4}

5. Decomposition of H_2O_2 follows a first order reaction. In fifty minutes the concentration of H_2O_2 decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of H_2O_2 reaches 0.05 M, the rate of formation of O_2 will be

(a) 6.93×10^{-2} mol min^{-1}

(b) 6.93×10^{-4} mol L^{-1} min^{-1}

(c) 2.66 L min^{-1} at STP

(d) 1.34×10^{-2} mol min^{-1} *(JEE Main 2016)*

SECTION - II

More than One Options Correct Type

6. $A + B \rightleftharpoons C + D$; $\Delta H = -217$ kJ/mol

Mark out the incorrect statement (s) regarding the reaction.

(a) The rate of disappearance of B increases on increase of the concentration of A.

(b) The rate of formation of D increases on increasing temperature.

(c) The rate of formation of C increases on increasing temperature.

(d) The use of catalyst doesn't affect the rate of formation of C or D.

7. Rate constant for a reaction varies with temperature as, $\ln k(\text{sec}^{-1}) = 14.34 - \frac{1.25 \times 10^4}{T}$, which statement(s) is/are correct?

(a) The graph plotted in between $\ln k$ vs $1/T$ is straight line with $E_a = 24.83$ kcal

(b) Pre-exponential factor = $e^{14.34}$

(c) The rate constant at 500 K is 2.78×10^{-5} sec^{-1}
(d) $E_a = 30.63$ kcal

8. The rate of formation for $C_6H_6 + 3H_2 \underset{k_b}{\overset{k_f}{\rightleftharpoons}} C_6H_{12}$ for the forward reaction is first order with respect to C_6H_6 and H_2 each. Which of the following options are correct?

(a) $k_c = \dfrac{k_f}{k_b}$ (b) $k_c = \dfrac{[C_6H_{12}]}{[C_6H_6][H_2]^3}$

(c) $r_f = k_f[C_6H_6]\,[H_2]$ (d) $r_b = k_b[C_6H_{12}]\,[H_2]^{-2}$

9. Which of the following statements is/are correct about half-life period for a reaction?

(a) For a second order reactions $t_{1/2} \propto \dfrac{1}{a}$.

(b) For a zero order reactions $t_{1/2} \propto \dfrac{1}{a}$.

(c) Time taken for 75% completion of a first order reaction is twice to $t_{1/2}$.

(d) For third order reaction $t_{1/2} \propto a^2$.

10. In a biomolecular reaction, the steric factor P was experimentally determined to be 4.5. The correct option(s) among the following is(are)

(a) experimentally determined value of frequency factor is higher than that predicted by Arrhenius equation

(b) the value of frequency factor predicted by Arrhenius equation is higher than that determined experimentally

(c) the activation energy of the reaction is unaffected by the value of the steric factor

(d) since $P = 4.5$, the reaction will not proceed unless an effective catalyst is used.

(*JEE Advanced 2017*)

SECTION - III

Numerical Value Type

11. A reaction rate increases by a factor of 500 due to the presence of a catalyst at 37 °C. If the reaction is carried out in presence of a catalyst at 127 °C, by what factor compared to original rate in absence of catalyst at 27 °C, the rate will increase? Activation energy of original pathway is 106 kJ/mol.

12. Calculate the factor by which the rate of first order reaction is increased for a temperature rise of 10°C from 25°C to 35°C. The energy of activation is 35 kcal mol^{-1}.

13. Reaction $A + B \longrightarrow C + D$ follows, rate law, $r = k[A]^{1/2}\,[B]^{1/2}$ starting with 1 M of A and B each. What is the time taken for concentration of A to become 0.1 M? (Given $k = 2.303 \times 10^{-2}$ sec^{-1})

14. What will be the rate of a reaction if its rate constant is 10^{-3} min^{-1} and the concentration of reactant is 0.2 mol dm^{-3}?

15. Consider the following reversible reaction,

$A_{(g)} + B_{(g)} \rightleftharpoons AB_{(g)}$

The activation energy of the backward reaction exceeds that of the forward reaction by $2RT$ (in J mol^{-1}). If the pre-exponential factor of the forward reaction is 4 times that of the reverse reaction, the absolute value of ΔG° (in J mol^{-1}) for the reaction at 300 K is ___ .

(Given : ln(2) = 0.7, RT = 2500 J mol^{-1} at 300 K and G is the Gibbs energy)

(*JEE Advanced 2018*)

SOLUTIONS

1. **(c)** : $r_1 = k[A]^1$, $r_2 = k[A]^2$, $r_3 = k[A]^3$

If $[A] > 1$M ; then $r_3 > r_2 > r_1$

2. **(a)** : $k_2 = \dfrac{2.303}{t_2}\log\dfrac{100}{50}$ for 50% B reacted

$k_1 = \dfrac{2.303}{t_1}\log\dfrac{100}{6}$ for 94% of A reacted

$\therefore \quad \dfrac{k_2}{k_1} = \dfrac{t_1}{t_2} \times \dfrac{0.3010}{1.2218}$

Since $t_2 = t_1$, because 50% B has reacted when 94% A has reacted.

$\therefore \quad \dfrac{k_2}{k_1} = \dfrac{0.3010}{1.2218} = 0.246$ and $\dfrac{k_1}{k_2} = 4.06$

3. **(a)** : As at the completion of reaction 35 mL of O_2 is formed, hence 70 mL of N_2O_5 is present initially as from the reaction we can see that,

$N_2O_5 : N_2O_4 : O_2 :: 1 : 1 : \dfrac{1}{2}$

$$N_2O_5 \rightleftharpoons N_2O_4 + \frac{1}{2}O_2$$

Initial	70 mL	0	0
After 15 min.	70-18 mL	18 mL	9 mL

For first order reaction

$$k = \frac{1}{t}\ln\frac{a}{a-x} = \frac{1}{15}\ln\frac{70}{52} \text{ or } \frac{1}{15}\ln\frac{35}{26}$$

4. **(c)** : $r_1 = k[0.01]^a\,[0.01]^b = 6.93 \times 10^{-6}$ ...(i)

$r_2 = k[0.02]^a\,[0.01]^b = 1.386 \times 10^{-5}$ ...(ii)

$r_3 = k[0.02]^a\,[0.02]^b = 1.386 \times 10^{-5}$ ...(iii)

From data $a = 1$; $b = 0$

Overall order = 1 ; $k = 6.93 \times 10^{-4}$ sec^{-1}

$$6.93\times10^{-4} = \frac{1}{50\times60}\ln\frac{A_0}{A_t}\,;\; 2.07 = \ln\frac{A_0}{A_t}$$

$$\Rightarrow\quad 7.92 = \frac{A_0}{A_t}\;;\; A_t = \frac{0.5}{7.92}$$

$A_t = 0.0631$

Rate of reaction = $6.93 \times 10^{-4} \times 0.0631$

$= 4.36 \times 10^{-5}$ Ms^{-1}

5. **(b)**

6. **(b,c,d)** : Increase in temperature will shift the reaction in backward direction.

The use of catalyst lowers the activation energy for both forward as well as backward reactions, thus the rate of dissociation of reactants and formation of products both increase and help to attain the equilibrium earlier.

7. **(a,b,c)** : Comparing the given equation with

$$\ln k = \ln A - \frac{E_a}{RT}$$

we get, graph $\ln k$ vs $1/T$ is straight line with slope

$$\frac{E_a}{R} = 1.25\times10^4$$

or, $E_a = 1.25 \times 10^4 \times 1.987 \times 10^{-3} = 24.83$ kcal

$\ln A = 14.34$, $A = e^{14.34}$

and $k = e^{14.34}.\, e^{\frac{-24.83\times10^3}{2\times500}} = 2.78 \times 10^{-5}\ s^{-1}$

8. **(a,b,c,d)** : $K_c = \dfrac{k_f}{k_b} = \dfrac{[C_6H_{12}]}{[C_6H_6][H_2]^3}$

$$= \frac{[C_6H_{12}]}{[C_6H_6][H_2][H_2]^2}$$

$r_f = k_f \times [C_6H_6]\ [H_2]$

$r_b = k_b \times$ Unknown

at eq. $r_f = r_b$

$\therefore\quad k_f[C_6H_6]\ [H_2] = k_b \times$ Unknown

$\therefore\quad$ Unknown $= \dfrac{k_f}{k_b} \times [C_6H_6][H_2]$

$r_b = k_b \times \dfrac{k_f}{k_b} \times [C_6H_6][H_2]$

$= k_f \times [C_6H_6]\ [H_2] = k_b \times [C_6H_{12}]\ [H_2]^{-2}$

9. **(a, c)** **10.** **(a, c)**

11. **(5.05 × 10^6)** : $\ln\dfrac{k_c}{k_{uc}} = \dfrac{E_{uc} - E_c}{RT}$

$$\ln 500 = \frac{(106 - E_c)\times10^3}{8.314\times310} \Rightarrow\quad E_c = 90 \text{ kJ}$$

$$\ln k_c = \ln A - \frac{90\times10^3}{8.314\times400}$$

$$\ln k_{ac} = \ln A - \frac{106\times10^3}{8.314\times300}$$

$$\Rightarrow\quad \frac{k_c(127\,^\circ\text{C})}{k_{ac}(27\,^\circ\text{C})} = 5.05\times10^6$$

12. **(6.8)** : Given, $E_a = 35 \times 10^3$ cal mol^{-1}, $T_2 = 308$ K, $T_1 = 298$ K

$$\therefore\quad 2.303\log_{10}\frac{k_2}{k_1} = \frac{35\times10^3}{1.987}\left[\frac{308-298}{298\times308}\right]$$

or $\left(\dfrac{k_2}{k_1}\right) \approx 6.8$ or $k_2 = 6.813 \times k_1$

$\therefore\quad r_2 \approx 6.813 \times r_1 \qquad \left(\because\ \dfrac{r_2}{r_1} = \dfrac{k_2}{k_1}\right)$

13. **(100)** : $A \;+\; B \longrightarrow C + D$

$t=0$ 1 1

t $1-x$ $1-x$ x x

$r = k[A]^{1/2}[B]^{1/2}$

$$\frac{dx}{dt} = k\,(1-x)^{1/2}\,(1-x)^{1/2}$$

$$\frac{dx}{dt} = k(1-x) \Rightarrow\ t = \frac{1}{k}\ln\left(\frac{1}{1-x}\right)$$

$$t = \frac{2.303}{2.303\times10^{-2}}\log\left(\frac{1}{0.1}\right) = 100 \text{ sec}$$

14. **(2 × 10^4)** : Reaction is of first order as unit of rate constant is min^{-1}.

Rate = k[conc.] = 10^{-3} min^{-1} × 0.2 mol dm^{-3}

= 2×10^{-4} mol dm^{-3} min^{-1}

15. **(8500)**

MONTHLY TUNE UP CLASS XI — ANSWER KEY

1. (b)	**2.** (a)	**3.** (d)	**4.** (a)	**5.** (b)
6. (d)	**7.** (c)	**8.** (b)	**9.** (a)	**10.** (d)
11. (a)	**12.** (c)	**13.** (a)	**14.** (a)	**15.** (d)
16. (a)	**17.** (c)	**18.** (d)	**19.** (b)	**20.** (c,d)
21. (a,c)	**22.** (b,d)	**23.** (a,b,c)	**24.** (1)	
25. (7522.50)		**26.** (16)	**27.** (b)	**28.** (c)
29. (a)	**30.** (d)			

CLASS XII

CBSE DRILL



Chapterwise practice questions for CBSE Exams as per the latest sample paper issued by CBSE for the academic session 2018-19.

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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 12 are short answer questions and carry 2 marks each.
(iv) Q. no. 13 to 24 are also short answer questions and carry 3 marks each.
(v) Q. no. 25 to 27 are long answer questions and carry 5 marks each.
(vi) Use log tables if necessary, use of calculators is not allowed.

Time Allowed : 3 hours | Maximum Marks : 70

Haloalkanes and Haloarenes | Alcohols, Phenols and Ethers

1. Write the structure of the following compound:
2-(2-chlorophenyl)-1-iodooctane

2. Explain the completion of the following reactions with NaBr and conc. H_2SO_4.
(i) $CH_3CH_2CH_2OH$
(ii) 

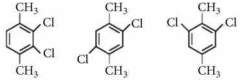
3. Account for the following :
Preparation of ethers by acid dehydration of secondary or tertiary alcohols is not a suitable method.

4. Phenols and alcohols behave as Bronsted acids. Explain.

5. What are the oxidation products of $(CH_3)_3COH$ using very strong oxidising agents?

6. Why is the reactivity of all the three classes of alcohols with conc. HCl and $ZnCl_2$ (Lucas reagent) different?

7. (i) Select the species with the highest melting point.



(I) (II) (III)

(ii) Select the species that undergoes faster S_N1 reaction.



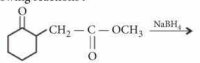
(I) (II)

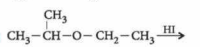
8. Explain why the dipole moment of chlorobenzene is lower than that of cyclohexyl chloride?

OR

Although chlorine is an electron withdrawing group, yet it is *ortho*-, *para*-directing in electrophilic aromatic substitution reactions. Why?

9. Write the structures of the products formed in the following reactions :

(i) 

(ii) 

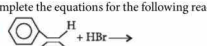
10. (i) Write the isomers of C_3H_5Br having
- (a) Br at vinylic position
- (b) Br at allylic position.

(ii) What is the advantage of using $SOCl_2$ in the preparation of $R-Cl$ from alcohol?

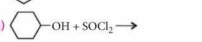
11. In Kolbe's reaction, instead of phenol, phenoxide ion is treated with carbon dioxide. Why?

12. Out of the various possible isomers of C_7H_7Cl containing benzene ring, suggest the structure with the weakest C — Cl bond.

13. Complete the equations for the following reactions :

(i) 

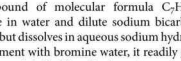
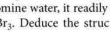
(ii) 

(iii) 

14. (i) Write complete reaction for the bromination of phenol in aqueous and non aqueous medium.

(ii) Explain why Lewis acid is not required in bromination of phenol?

15. (i) Of the two bromo derivatives, $C_6H_5CH(CH_3)Br$ and $C_6H_5CH(C_6H_5)Br$, which one is more reactive in S_N1 substitution reaction and why?

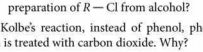
(ii) How would you account for the following :
- (a) Grignard reagents are prepared strictly under anhydrous conditions?
- (b)  undergoes faster S_N1 reaction than 

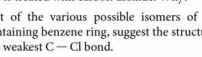
16. A compound of molecular formula C_7H_8O is insoluble in water and dilute sodium bicarbonate solution but dissolves in aqueous sodium hydroxide. On treatment with bromine water, it readily gives a precipitate of $C_7H_5OBr_3$. Deduce the structure of the compound.

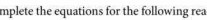
17. (i) Write the reactions of Williamson synthesis of 2-ethoxy-3-methylpentane starting from ethanol and 3-methylpentan-2-ol.

(ii) Explain why nucleophilic substitution reactions are not very common in phenols.

18. What would be the major products in each of the following reactions?

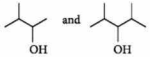
(i) 

(ii) 

(iii) 

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19. (i) Identify the chiral molecule in the following pair :



(I) (II)

(ii) Why is butan-1-ol optically inactive but butan-2-ol is optically active?

20. A compound $A(C_4H_{10}O)$ is found to be soluble in concentrated H_2SO_4 and does not react with sodium metal or $KMnO_4$. (A) when heated with excess of HI, it gives a single alkyl halide. Deduce the structure of the compound (A) and explain all the reactions involved.

OR

(i) The treatment of alkyl chloride with aqueous KOH leads to the formation of alcohol but in the presence of alcoholic KOH, alkene is the major product. Give reason.

(ii) Write the mechanism of the following reaction :

21. (i) Arrange the following compounds in the increasing order of the property indicated against each. Give reasons for your answers.
- (a) CH_3CH_2OH, CF_3CH_2OH, CCl_3CH_2OH (Acidic strength)
- (b) 2-Methyl-2-propanol, 1-butanol, 2-butanol (Reactivity towards sodium)

(ii) Which structural isomer of butanol cannot be dehydrogenated by copper at 573 K?

22. Name the reagents used in the following reactions :
- **(i)** Oxidation of primary alcohol to carboxylic acid
- **(ii)** Oxidation of primary alcohol to aldehyde
- **(iii)** Bromination of phenol to 2,4,6-tribromophenol
- **(iv)** Benzyl alcohol to benzoic acid
- **(v)** Dehydration of propan-2-ol to propene
- **(vi)** Butan-2-one to butan-2-ol

23. **(i)** One mole of an organic compound (*A*) having molecular formula C_2H_4O reacts with MeMgI to liberate one mole of methane. (*A*) reacts with CH_3COCl to yield a sweet smelling liquid (*B*). Identify (*A*) and (*B*).

(ii) Name the products when anisole is heated with HI.

24. **(i)** Arrange the following in increasing order of basicity : H_2O, OH^-, CH_3OH, CH_3O^-

(ii) Which of the following is the correct method for synthesising methyl *tert*-butyl ether and why?

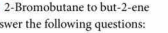
(a) $(CH_3)_3CBr + NaOCH_3 \longrightarrow$

(b) $CH_3Br + NaO\text{-}tert\text{-}butyl \longrightarrow$

(iii) Of the two hydroxy organic compounds *R*OH and *R'*OH, the first one is basic and the other is acidic in behaviour. How is *R* different from *R'*?

25. **(i)** How do you convert?
- **(a)** Chlorobenzene to biphenyl
- **(b)** 2-Bromobutane to but-2-ene

(ii) Answer the following questions:
- **(a)** What is meant by chirality of a compound? Give an example.
- **(b)** Which one of the following compounds is more easily hydrolysed by KOH and why? $CH_3CHClCH_2CH_3$ or $CH_3CH_2CH_2Cl$
- **(c)** Which one undergoes S_N2 substitution reaction faster and why?

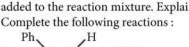


OR

(i) Why are alkyl halides generally not prepared in the laboratory by free radical halogenation of alkanes?

(ii) *R*Cl is hydrolysed slowly to *R*OH but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture. Explain.

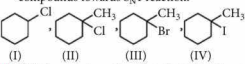
(iii) Complete the following reactions :

(a) 

(b) $C_6H_5C_2H_5 \xrightarrow[2.\ NaCN]{1.\ Br_2,\ Heat,\ Light}$

(c) $+ CHBr_3 + t - BuOK \longrightarrow$

26. **(i)** Predict the order of reactivity of the following compounds towards S_N1 reaction.



(ii) Which out of 2-cyclopentenol or 3-cyclopentenol has a chiral centre?

(iii) Racemisation occurs in S_N1 reactions. Why?

(vi) State one use each of DDT and iodoform.

(v) Racemic mixture is optically inactive.

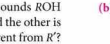
OR

(i) Which reaction in each pair shown below will show the faster rate of disappearance of starting material?

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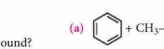
(a) **(I)** $(CH_3)_3CBr \xrightarrow[H_2O]{EtOH}$

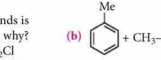
(II) $(CH_3)_3CBr \xrightarrow{EtOH}$

(b) **(I)**  $\xrightarrow{CH_3S^-}$

(II)  $\xrightarrow{(CH_3)_3CHS^-}$

(ii) Write the major product of the following reactions :

(a)  $\xrightarrow{\text{Anhyd. } AlCl_3}$

(b)  $\xrightarrow[AlCl_3]{\text{Anhyd.}}$

27. How will you convert :
- **(i)** Phenol to anisole
- **(ii)** Propan-2-ol to 2-methylpropan-2-ol
- **(iii)** Aniline to phenol
- **(iv)** 2-Methyl-1-pentene to 2-methylpentan-2-ol
- **(v)** Phenol to acetophenone?

OR

(i) Ethers are decomposed by HX. Arrange reactivity of ethers with HCl, HBr, HI in the increasing order.

(ii) Explain the reaction of $CH_3CH_2OCH_3$ with
- **(a)** limited amount of HI
- **(b)** excess of HI

(iii) Why boiling point of ethers are lower than isomeric alcohols?

SOLUTIONS

1. $IH_2C-CH-(CH_2)_5-CH_3$



2. (i) $NaBr + \text{conc. } H_2SO_4 \rightarrow NaHSO_4 + HBr$

$CH_3CH_2CH_2OH + HBr \rightarrow CH_3CH_2CH_2Br + H_2O$

(ii) Phenol is acidic in nature hence it does not react with HBr.

3. Acid dehydration of 2° and 3° alcohols give alkenes rather than ethers. Due to steric hindrance the nucleophilic attack by the alcohol molecule on the protonated alcohol molecule does not occur.

4. Bronsted acids are proton donors. Since, alcohols and phenols can donate protons, hence, they are Bronsted acids. Acids are converted to conjugate base.

5. $CH_3-\underset{\underset{CH_3}{|}}{\overset{CH_3}{|}}{C}-OH \xrightarrow[\text{conc. } HNO_3]{[O]} H_3C\diagdown \atop H_3C\diagup C=O \xrightarrow{[O]} CH_3COOH + HCOOH$

6. The reaction of alcohols with Lucas reagent occurs through carbocation formation. Order of ease of cleavage of C — OH bond and reactivity of different alcohols is : Tertiary > Secondary > Primary

Tertiary carbocation is most stable due to hyperconjugation and primary carbocation the least. Hence, on reaction with HCl and $ZnCl_2$ (Lucas reagent) tertiary alcohols react immediately to give cloudiness.

7. (i) All are derivatives of *p*-xylene.

(II) has maximum melting point since it is symmetrical and it fits into crystal lattice more easily than others and force of attraction is larger thus maximum melting point.

(ii) As benzyl carbocation  is resonance stabilised thus, II undergoes faster S_N1 reaction

8. There are two reasons :

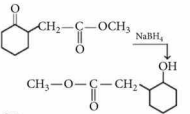
(a) In case of chlorobenzene, carbon to which chlorine is attached is sp^2-hybridised and is more electronegative than the corresponding carbon in cyclohexyl chloride which is sp^3- hybridised. So the net dipole moment is lower in chlorobenzene.

(b) In chlorobenzene C — Cl bond has some double bond character so its bond length is smaller. Hence, dipole moment is lower than cyclohexyl chloride which has a longer C—Cl single bond.

OR

Refer to answer 74 (ii), Page no. 205 (MTG CBSE Champion Chemistry Class 12)

9. (i)



(ii) $CH_3-\underset{\underset{OH}{|}}{\overset{CH_3}{|}}{CH}-O-CH_2CH_3 \xrightarrow{HI} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + CH_3CH_2I$

10. (i) (a) Br at vinylic position : $CH_3CH=CHBr$

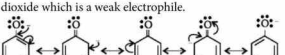
$CH_3C=CH_2$
$|$
Br

(b) Br at allylic position : $CH_2=CHCH_2Br$

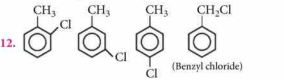
(ii) $R-OH + SOCl_2 \longrightarrow R-Cl + SO_2\uparrow + HCl\uparrow$

SO_2 and HCl in the gaseous form escape from the reaction mixture hence $R-Cl$ is isolated in pure form.

11. Phenoxide ion is more reactive than phenol towards electrophilic substitution reaction as O^- has greater ability to donate electrons to benzene ring and hence undergoes electrophilic substitution with carbon dioxide which is a weak electrophile.



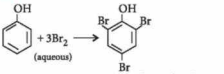
12.



Among these isomers, benzyl chloride has the weakest C — Cl bond. Because in all other isomers C — Cl bond has some double bond character due to resonance.

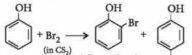
13. *Refer to answer 39, Page no. 202* (MTG CBSE Champion Chemistry Class 12)

14. (i) In aqueous medium



2, 4, 6 - Tribromophenol

(b) In non-aqueous medium



(ii) In bromination of benzene, Lewis acid is used to polarise Br_2 to form electrophile Br^+. In case of phenol polarisation of bromine takes place even in absence of Lewis acid as the O-atom of phenol itself polarises Br_2 molecule to form Br^+. Also, +*R*-effect of —OH group makes phenol highly activated towards electrophilic substitution reactions.

15. (i) $C_6H_5CH(C_6H_5)Br$ is more reactive than $C_6H_5CH(CH_3)Br$ for S_N1 reaction because its carbocation is resonance stabilised by two phenyl groups.

(ii) (a) Grignard reagents react with water to form alkanes.

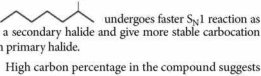
$$R-Mg-X + H_2O \longrightarrow R-H + Mg\begin{matrix}X\\OH\end{matrix}$$

So, they must be prepared under anhydrous conditions.

(b) 

undergoes faster S_N1 reaction as it is a secondary halide and give more stable carbocation than primary halide.

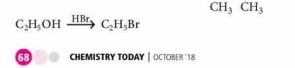
16. High carbon percentage in the compound suggests it to be aromatic and thus, the formula C_7H_8O represents the following four isomeric compounds.



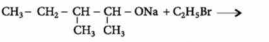
Since the compound is insoluble in water and dil. $NaHCO_3$ but dissolves in aqueous NaOH, it must be a phenol, *i.e.*, *o*-, *m*- or *p*-cresols. As on reaction with bromine water, it gives a precipitate of $C_7H_5OBr_3$.

Thus, it should be *m*-cresol.

17. (i)

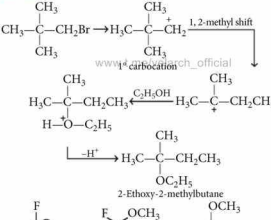


$$C_2H_5OH \xrightarrow{HBr} C_2H_5Br$$



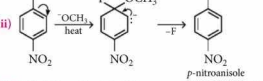
(ii) In phenols, oxygen atom of —OH group delocalise its lone pair of electrons over the benzene ring. This resonance phenomenon increases the electron density over benzene ring which makes it difficult for nucleophile to attack phenol molecule.

18. (i)



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(ii)



(iii) $CH_3CH_2 - Br + AgCN_{(alc.)} \longrightarrow CH_3CH_2N \rightleftarrows C$

19. (i)



(ii) *Refer to answer 74 (i), Page no. 204* (MTG CBSE Champion Chemistry Class 12)

20. The compound (*A*), $C_4H_{10}O$, may be an alcohol or ether. Since (*A*) does not react with Na metal or $KMnO_4$, it cannot be an alcohol. Since the compound dissolves in concentrated H_2SO_4, it may be an ether. Since ether (*A*) when heated with excess of HI gives a single alkyl halide, (*A*) must be symmetrical ether. The only symmetrical ether with molecular formula $C_4H_{10}O$ is diethyl ether, $C_2H_5 — O — C_2H_5$.

The reactions can be explained as follows :

$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} \xrightarrow{\text{conc. } H_2SO_4} \underset{\text{Oxonium salt (Soluble)}}{\left[C_2H_5-\overset{+}{O}(H)-C_2H_5\right]HSO_4^-}$$

$$\underset{\text{Diethyl ether}}{C_2H_5-O-C_2H_5} + \underset{\text{Excess}}{2HI} \xrightarrow{\text{heat}} \underset{\text{Ethyl iodide}}{2C_2H_5I} + H_2O$$

OR

(i) In aqueous solution, KOH is almost completely involved to give OH^- ion which being a better nucleophile gives a substitution reaction on alkyl halides to form alcohol. But an alcoholic solution of KOH containing alkoxide (RO^-) ions which being a much stronger base than OH^- ion preferentially snatches a H^+ ion from an alkyl chloride to form alkenes.

(ii) *Refer to answer 85, Page no. 206* (MTG CBSE Champion Chemistry Class 12)

21. (i) (a) Due to electron withdrawing effect (*–I* effect) of halogens, electron pair of O—H is drawn towards oxygen atom. This facilitates the release of hydrogen atom as proton. Thus, electron withdrawing groups increase the acidic character of alcohol. As F has higher *–I* effect than Cl, CF_3CH_2OH is stronger acid than CCl_3CH_2OH.

Thus, the acidic strength increase in the order :

$CH_3CH_2OH < CCl_3CH_2OH < CF_3CH_2OH$

(b) In the reaction of alcohol with Na, the O—H is cleaved and in such reactions, the reactivity of alcohols is in the order: primary > secondary > tertiary.

Therefore, reactivity of these alcohols towards sodium follows the order :

2-Methyl-2-propanol < 2-butanol < 1-butanol

(3°) (2°) (1°)

(ii) *t*-Butyl alcohol undergoes dehydrogenation instead of dehydrogenation.

$$\underset{\text{tert-Butyl alcohol}}{H_3C-\overset{CH_3}{\overset{|}{C}}(CH_3)-OH} \xrightarrow{\text{Cu, 573 K}} \underset{\text{2-Methylprop-1-ene}}{H_3C-\overset{CH_3}{\overset{|}{C}}=CH_2} + H_2O$$

22. (i) Alkaline $KMnO_4$

(ii) Pyridinium chlorochromate in chloromethane (CH_2Cl_2)

(iii) Br_2/H_2O **(iv)** Alkaline $KMnO_4$

(v) Conc. H_2SO_4 or H_3PO_4 at 433-443 K

(vi) H_2/Ni or $NaBH_4$ or $LiAlH_4$

23. (i) Since compound (*A*) with molecular formula C_2H_6O reacts with MeMgI to give one mole of CH_4, the compound (*A*) must be ethyl alcohol.

$$\underset{\text{Ethyl alcohol (A)}}{CH_3CH_2OH} + CH_3MgI \longrightarrow CH_4 + Mg(OCH_2CH_3)I$$

Compound *A*, *i.e.*, ethyl alcohol reacts with acetyl chloride (CH_3COCl) to form sweet smelling compound (*B*). Therefore, compound (*B*) must be ethyl acetate.

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Ethyl alcohol}}{HOCH_2CH_3} \longrightarrow \underset{\text{Ethyl acetate (B)}}{CH_3COOCH_2CH_3} + HCl$$

(ii) In anisole ($C_6H_5-O-CH_3$), C_6H_5-O bond has some double bond character due to resonance and hence more difficult to break. As a result, nucleophilic attack by I^- ion occurs on CH_3 group forming methyl iodide and phenol.

$$\underset{\text{Anisole}}{C_6H_5-O-CH_3} + HI \xrightarrow{373\ K} \underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Methyl iodide}}{CH_3I}$$

24. (i) Alkoxides are decomposed by water.

$$\underset{\text{Alkoxide}}{CH_3O^-} + H_2O \longrightarrow \underset{\text{Alcohol}}{CH_3OH} + OH^-$$

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Therefore, CH_3O^- is a stronger base than OH^- and CH_3OH is a stronger base than H_2O. Therefore, the order of basicity is as follows :

$H_2O < CH_3OH < OH^- < CH_3O^-$

(ii) Substitution and elimination reactions are always competitive reactions. Since tertiary (3°) alkyl halides preferentially undergo elimination and primary (1°) alkyl halides preferentially undergo substitution, therefore, reaction (a) will undergo elimination reaction to give *iso*-butylene and the reaction (b) will undergo substitution reaction to give methyl *tert*-butyl ether.

(iii) When *R* = alkyl, *R*OH behaves as a weak Bronsted base since it accepts a proton from strong acids such as HCl, H_2SO_4 etc.

$$R-\ddot{\underset{\cdot\cdot}{O}}-H + H^+ \longrightarrow R-\overset{+}{\underset{\cdot\cdot}{O}}\begin{matrix}H\\H\end{matrix}$$

However, when *R*′ = aryl, *R*′OH behaves as a weak Bronsted acid since it donates a proton to strong bases such as Na, NaOH, etc.

$$\underset{\text{Bronsted acid}}{R'-O-H} + NaOH \longrightarrow R'O^-Na^+ + H_2O$$

25. *Refer to answer 70 and 96, Page no. 204 and 207* (MTG CBSE Champion Chemistry Class 12)

OR

(i) Free radical halogenation of alkanes is not a suitable method to obtain an alkyl halide because :

(a) It gives a mixture of isomeric monohalogenated products whose boiling points are so close that their separation is difficult.

(b) Polyhalogenation may also occur making the product mixture more complex and hence, difficult to separate.

(ii) Iodide is a powerful nucleophile and therefore, it reacts rapidly with *R*Cl to form *R*I

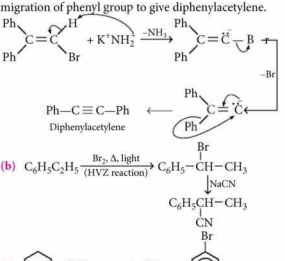
$$KI \longrightarrow K^+ + I^-$$

$$I^- + R\text{—}Cl \longrightarrow R\text{—}I + Cl^-$$

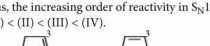
Also, I^- ion is a better leaving group than Cl^- ion and therefore, *R*I is more readily hydrolysed to form *R*OH.

$$HO^- + R\text{—}I \longrightarrow ROH + I^-$$

(iii) (a) Dehydrobromination takes place with the migration of phenyl group to give diphenylacetylene.

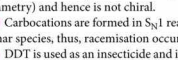


(b) $C_6H_5C_2H_5 \xrightarrow[\text{(HVZ reaction)}]{Br_2,\ \Delta,\ light} C_6H_5\text{—}\underset{Br}{\underset{|}{CH}}\text{—}CH_3 \xrightarrow{NaCN} C_6H_5\text{—}\underset{CN}{\underset{|}{CH}}\text{—}CH_3$

(c) 

26. (i) The first compound is a 2° alkyl halide while all others are 3° alkyl halide. Since 3° alkyl halides are more reactive than 2° alkyl halides in S_N1 reaction, therefore, first compound is the least reactive. Further reactivity increases in the order : chloride < bromide < iodide. Thus, the increasing order of reactivity in S_N1 reactions is (I) < (II) < (III) < (IV).

(ii)



2-Cyclopentenol has a chiral centre at C_1 while 3-cyclopentenol is symmetrical (*i.e.*, has a plane of symmetry) and hence is not chiral.

(iii) Carbocations are formed in S_N1 reaction which are planar species, thus, racemisation occurs.

(iv) DDT is used as an insecticide and iodoform is used as a mild antiseptic.

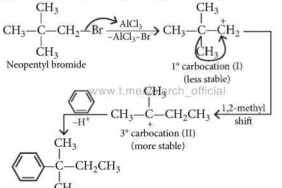
(v) Racemic mixture contains equal amount of *d*- and *l*-forms, hence rotation due to one enantiomer is cancelled by another.

OR

(i) (a) $EtOH/H_2O$ being more polar than EtOH facilitates ionization of $(CH_3)_3CBr$ and hence reaction (I) occurs faster than reaction (II).

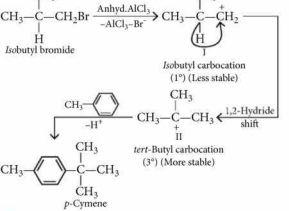
(b) $(CH_3)_2CHS^-$ being bigger in size than CH_3S^- causes steric hindrance and hence reaction (I) proceeds faster than reaction (II).

(ii) (a) The initially formed less stable 1° carbocation (I) undergoes 1,2-methyl shift to give the more stable 3° carbocation (II) which then attacks the benzene ring to give Friedels-Crafts alkylation product (III).



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(b) The initially formed less stable 1° carbocation (I) undergoes rearrangement by 1,2-hydride shift to form more stable 3° carbocation (II) which then attacks the toluene ring at the less hindered *p*-position to form *p*-cymene.



27. *Refer to answer 62 and 71, Page no. 222 and 224* (MTG CBSE Champion Chemistry Class 12)

OR

(i) $R\text{—}\underset{|}{\overset{|}{C}}\text{—}OR' + HX \xrightarrow{\text{High temp.}} R\text{—}X + R'OH$

$$R'OH + HX \xrightarrow{\text{High temp.}} R'\text{—}X + H_2O$$

Contd. on page no. 85

Class XII

MONTHLY TUNE UP!



PRACTICE PROBLEMS

These practice problems enable you to self analyse your extent of understanding of specified chapters. Give yourself four marks for correct answer and deduct one mark for wrong answer. Performance analysis table given at the end will help you to check your readiness.

p-Block Elements (Group 15 to 18)

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

NEET / AIIMS

Only One Option Correct Type

1. $(NH_4)_2Cr_2O_7$ on heating liberates a gas. The same gas will be obtained by
   (a) heating NH_4NO_2
   (b) heating NH_4NO_3
   (c) treating Mg_3N_2 with H_2O
   (d) heating H_2O_2 on $NaNO_2$.

2. Mixture of which gas produces blue liquid on cooling at –30°C?
   (a) $NO_2 + NO_2$ (b) $NO + O_2$
   (c) $N_2O + NO_2$ (d) $NO + NO_2$

3. Hydrolysis of one mole of peroxodisulphuric acid produces
   (a) two moles of sulphuric acid
   (b) two moles of peroxomonosulphuric acid
   (c) one mole of sulphuric acid and one mole of peroxomonosulphuric acid
   (d) one mole of sulphuric acid, one mole of peroxomonosulphuric acid and one mole of hydrogen peroxide.

4. The least stable oxo-anion among the following is
   (a) ClO^- (b) ClO_2^- (c) ClO_3^- (d) ClO_4^-

5. Identify the incorrect statement among the following.
   (a) Br_2 reacts with hot and strong NaOH solution to give NaBr and H_2O.
   (b) Ozone reacts with SO_2 to give SO_3.
   (c) Rhombic sulphur dissolves in boiling concentrated solution of sodium sulphite to form sodium thiosulphate.
   (d) Cl_2 reacts with excess of NH_3 to give N_2 and HCl.

6. The reaction of P_4 with X leads selectively to P_4O_6. X is
   (a) a dry O_2
   (b) a mixture of O_2 and N_2
   (c) moist O_2
   (d) O_2 in presence of aqueous NaOH.

7. Select correct order of dissociation constant (K_a) in aqueous solution at 298 K.
   (a) $H_2O > H_2S > H_2Se > H_2Te$
   (b) $H_2Te > H_2Se > H_2S > H_2O$
   (c) $H_2Te > H_2O > H_2Se > H_2S$
   (d) $H_2O > H_2Te > H_2Se > H_2S$

8. HI cannot be prepared by which of the following methods?
   (a) $PI_3 + H_2O \longrightarrow$
   (b) $KI + H_2SO_4$ (conc.) $\longrightarrow$
   (c) $H_2 + I_2 \longrightarrow$
   (d) $I_2 + H_2S \longrightarrow$

9. Select incorrect matching out of given.
   (a) N_2O : Colourless gas, neutral towards litmus
   (b) NO : Brown gas, neutral towards litmus
   (c) N_2O_3 : Blue, acidic
   (d) NO_2 : Brown, acidic

10. Which of the following is correct order of strength of H-bonding in the given compounds ?
(a) $HF < NH_3$ (b) $H_2O > H_2O_2$
(c) $H_2O_2 > H_2O$ (d) $NH_3 > H_2O$

11. Which of the following option is correct regarding XeF_6?
(a) It acts as Lewis acid when it reacts with RbF.
(b) It undergoes complete hydrolysis to give XeO_3.
(c) It fluorinates silica to give $XeOF_4$.
(d) All of the above.

12. Which one of the following reactions of xenon compounds is not feasible?
(a) $XeO_3 + 6HF \rightarrow XeF_6 + 3H_2O$
(b) $3XeF_4 + 6H_2O \rightarrow 2Xe + XeO_3 + 12HF + 1.5O_2$
(c) $2XeF_2 + 2H_2O \rightarrow 2Xe + 4HF + O_2$
(d) $XeF_6 + RbF \rightarrow Rb[XeF_7]$

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 :** The m.pt. / b.pt. of noble gases are quite low.
Reason : The inter-particle forces among noble gases in their liquid state are covalent forces.

14. **Assertion :** Nitrogen is unreactive at room temperature but becomes reactive at elevated temperature or in presence of a catalyst.
Reason : In nitrogen molecule there is extensive delocalization of electrons.

15. **Assertion :** Among nitrogen halides NX_3, the dipole moment is highest for NI_3 and lowest for NF_3.
Reason : Nitrogen halides NX_3, have trigonal pyramidal structure.

JEE MAIN / ADVANCED

Only One Option Correct Type

16. When a vapour , at atmospheric pressure was gradually heated from 25 °C its colour was found to deepen at first and then fade as the temperature was raised above 160 °C. At 600 °C, the vapour was almost colourless, but its colour deepened when the pressure was raised at this temperature. The vapour was

PUZZLE CORNER

CHEMDOKU

In this puzzle 5 × 5 grid is given, your objective is to fill the digits 1-5 so that each appear exactly once in each row and each column.

Notice that most boxes are part of a cluster. In the upper-left corner of each multibox cluster is a value that is addition, subtraction or multiple (as indicated) of its numbers. For example, if that value is 3× for a two-box cluster, you know that only 1 and 3 can go in there. But it is your job to determine which number goes where! A few cluster may have just one box and that is the number that fills that box.

Note : Atomic number of the given element to be considered as your answer.

Clues :

(a) Ratio of this gas with magnesium is important for better understanding the ionisation potentials in the solar atmosphere while the ratio with oxygen could potentially aid in determining the amount of the gas in the atmosphere of the Sun.

(b) Researchers first referred it as 'delirium' owing to the difficulties they encountered trying to isolate it.

a+		b×		
c×			d+	
e−	f×		g×	h−

(c) It has a low absorption cross section for neutrons and is therefore used for nuclear energy applications, such as for cladding fuel elements.

(d) Currently researchers found that the drugs that included this active non-metal were several times more active against various cancer stem cells and exhibited better stability than traditional cancer fighting drugs.

(e) Titan, the largest moon of Saturn, has this gas about 98% in its atmosphere. Titan is the only moon in our solar system known to have a dense atmosphere.

(f) As it is heavy gas, so it is also sealed between the glass of some double paned windows to help them trap heat.

(g) It radiates green shading on warming, making it attractive component for fireworks.

(h) The speed of sound in this gas is 3 times that in air, so when this gas is inhaled it excites the higher harmonics of the vocal tract.

Readers can send their responses at editor@mtg.in or post us with complete address. Solution Senders name with their valuable feedbck will be published in next issue. Hope our readers will enjoy solving Chemdoku.

Solution Senders of Chemistry Musing

Set - 62

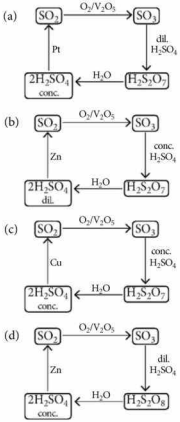
- Arpana Kaushik, Haryana
- Vinit Rao, Punjab

Winners of Unscramble Me

- Nitesh Sahoo, Odisha
- Devjit Acharjee, West Bengal

(a) the bromine
(b) a mixture of nitrogen dioxide and dinitrogen tetroxide
(c) pure nitrogen dioxide
(d) pure dinitrogen tetroxide.

17. Which of the following diagrams is correct for the change of sulphur compounds?



18. Which of the following compounds give paramagnetic gas on decomposition?
(I) $Pb(NO_3)_2$ (II) $LiNO_3$
(III) $NaNO_3$ (IV) NH_4NO_2
(a) (I), (II), (III) (b) (II), (III)
(c) (I), (II) (d) (III), (IV)

19. In which of the following reactions oxidation number of nitrogen does not change?
(a) Reaction of Ca_3N_2 with HCl
(b) Heating of NH_4NO_3
(c) Heating of NH_4NO_2
(d) Heating of $Ba(NO_3)_2$

More than One Options Correct Type

20. In which of the following options all species contains $X-O-X$ bond(s) in structure? (X = central atom)
(a) $H_2S_2O_8$, S_3O_9, $S_2O_6^{2-}$
(b) P_4O_{10}, P_4O_6, $H_4P_2O_7$
(c) N_2O_5, N_2O, N_2O_4 (d) S_3O_9, P_4O_6, $S_2O_5^{2-}$

21. $2MX + H_2SO_4(conc.) \longrightarrow 2HX + M_2SO_4$ (M = metal), above reaction is correct if 'X' is
(a) F^- (b) Cl^- (c) Br^- (d) I^-

22. Which of the following reactions can evolve phosphine?
(a) White P + $HNO_3 \longrightarrow$
(b) AlP + $H_2SO_4 \longrightarrow$
(c) $H_3PO_3 \xrightarrow{\Delta}$ (d) $PH_4I + NaOH \longrightarrow$

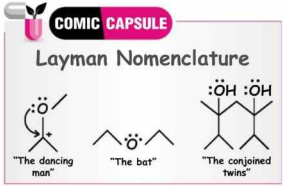
23. Which of the following arrangements do not give the correct picture of the trends indicated against it?
(a) $F_2 > Cl_2 > Br_2 > I_2$: Bond dissociation energy
(b) $F_2 > Cl_2 > Br_2 > I_2$: Electronegativity
(c) $F_2 > Cl_2 > Br_2 > I_2$: Oxidising nature
(d) $F_2 > Cl_2 > Br_2 > I_2$: Electron gain enthalpy

Numerical Value Type

24. When thiosulphate ion is oxidised by iodine, a new sulphur containing product (X) is formed. How many S — S linkage(s) is/are present in X?

25. The total number of diprotic acids among the following is
H_3PO_4 H_2SO_4 H_3PO_3 H_2CO_3 $H_2S_2O_7$
H_3PO_5 H_3PO_2 $H_2S_2O_6$ H_2SO_3

26. In a given sample of bleaching powder the percentage of available chlorine is 49. The volume of chlorine obtained if 10 g of sample is treated with HCl at N.T.P. is



Comprehension Type

Compared to the oxoacids of nitrogen, phosphorus presents a much more complicated picture particularly due to the formation of condensed phosphates. Phosphorus forms oxoacids in the oxidation numbers, +1, +3, +4 and +5. The three oxoacids, H_3PO_2, H_3PO_3 and H_3PO_4 are based on sp^3 hybridised phosphorus and may be formed from hypophosphorous acid by stepwise replacement of H by OH.

27. P_4(White) + *P* (an alkaline solution) ⟶ *Q*(reducing gas) + *R*

R + dil. H_2SO_4 ⟶ *T*(ppt.) + *S* (oxyacid of P)

T gives apple green colour in the flame.

Thus, *P*, *Q*, *R*, *S* and *T* respectively are

(a) $Ba(OH)_2$; PH_3; $Ba(H_2PO_2)_2$; H_3PO_2; $BaSO_4$

(b) $Ca(OH)_2$; P_2H_4; $Ca(H_2PO_2)_2$; H_3PO_2; $CaSO_4$

(c) $Ba(OH)_2$; PH_3; $Ba(H_2PO_2)_2$; H_3PO_3; $BaSO_4$

(d) $Ba(OH)_2$; P_2H_4; $Ba(H_2PO_2)_2$; H_3PO_3; $BaSO_4$

28. The hydrolysis of NCl_3 yields NH_3 and HOCl whereas the hydrolysis of PCl_3 yields H_3PO_3 and HCl. Because

(a) the hydrolysis of NCl_3 and PCl_3 both initiated by the abstraction of *lp* of oxygen to the vacant *d*-orbital of Cl

(b) the hydrolysis of NCl_3 is initiated by the abstraction of *lp* of electron of oxygen to the vacant *d*-orbital of N, whereas the hydrolysis of PCl_3 is initiated by the abstraction of *lp* of electrons of oxygen to vacant *d*-orbital of P

(c) the hydrolysis of NCl_3 is initiated by the abstraction of *lp* of electrons of oxygen to the vacant *d*-orbital of Cl, whereas the hydrolysis of PCl_3 is initiated by the abstraction of *lp* of electrons of oxygen to the vacant *d*-orbital of P

(d) all of these.

Matrix Match Type

29. Match column I with column II and choose the correct answer using the codes given below :

Column I	Column II
(A) $Cl_2 + NaOH_{(dil)} \xrightarrow[(Cold)]{0^\circ C}$	(p) Disproportionation reaction
(B) $Cl_2 + NaOH_{(conc)} \xrightarrow[(Hot)]{>50^\circ C}$	(q) Chloride (Cl^-) is produced
(C) $KClO_3 \xrightarrow[\Delta]{MnO_2}$	(r) Chlorate (ClO_3^-) is produced
(D) $ClO_2 + NaOH \longrightarrow$	(s) Hypochlorite (OCl^-) is produced
	(t) Chlorite (ClO_2^-) is produced

Codes :

	A	B	C	D
(a)	p,q,s	p,q,r	q	p,r,t
(b)	p,q	p,q,s	p,t	p,q,r
(c)	p,q,s	p,q,r	r	p,q
(d)	p,q,r	p,q,s	q	p,r,t

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30. Match the unbalanced chemical reactions given in column I with missing reagent or condition provided in column II and select the correct answer using the codes given below :

Column I	Column II
(A) $PbO_2 + H_2SO_4 \xrightarrow{?}$ $PbSO_4 + O_2$ + other product	(p) NO
(B) $Na_2S_2O_3 + H_2O \xrightarrow{?}$ $NaHSO_4$ + other product	(q) I_2
(C) $N_2H_4 \xrightarrow{?} N_2$ + other product	(r) Warm
(D) $XeF_2 \xrightarrow{?} Xe$ + other product	(s) Cl_2

Codes :

	A	B	C	D
(a)	s	q	r	p
(b)	r	q	p	s
(c)	p	s	q	r
(d)	r	s	q	p

◆◆

Keys are published in this issue. Search now! ☺

CHECK YOUR PERFORMANCE

		If your score is	
No. of questions attempted	.....	> 80%	Your preparation is going good, keep it up to get high score.
No. of questions correct	.....	60-80%	Need more practice, try hard to score more next time.
Marks scored in percentage	.....	<60%	Stress more on concepts and revise thoroughly.

CHEMISTRY MUSING

PROBLEM SET 63

Chemistry Musing was started from August '13 issue of Chemistry Today. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / JIPMER 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.

JEE MAIN/NEET

1. Consider the following reaction sequence :



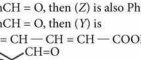
Choose the correct alternative.

(a) If (*X*) is PhCH = O, then (*Z*) is also PhCHO.

(b) If (*X*) is PhCH = O, then (*Y*) is

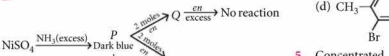
Ph — CH = CH — CH = CH — COOH

(c) If (*Z*) is 

then (*Y*) is 

(d) Both (a) and (c)

2.



Select incorrect statement.

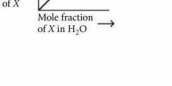
(a) *P*, *Q*, *R*, *S* are paramagnetic compounds.

(b) Number of t_{2g} electron $S > P = Q > P$.

(c) Both (*R*) and (*S*) show optical isomerism.

(d) (*Q*) and (*R*) are stereoisomers.

3. A gas '*X*' is present with saturated water vapour over water liquid at total pressure of 1.5 torr. Vapour pressure of H_2O at same temperature is 0.5 torr. What is the solubility of gas '*X*' in terms of moles in 10 mole $H_2O_{(l)}$.



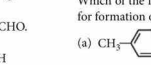
(a) 1×10^{-3} mole (b) 5×10^{-2} mole

(c) 2×10^{-3} mole (d) 1×10^{-2} mole

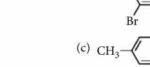
4. An azo compound *X* is cleaved at the azo linkage by $SnCl_2$ to form 3-bromo-4-amino toluene and 2-methyl-4-aminophenol.

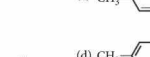
Which of the following is the suitable combination for formation of *X*?

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(a) 

(b) 

(c) 

(d) 

5. Concentrated sulphuric acid is added followed by heating of each of the test tubes (I to V) which contains:

Test tube I : Cane sugar
Test tube II : Sodium bromide
Test tube III : Copper nitrate
Test tube IV : Potassium ferrocyanide
Test tube V : Potassium chloride

Which of the following statements is incorrect?

(a) Evolution of reddish brown gas takes place in tube II and black substance in tube I.

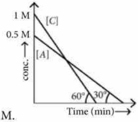
(b) Evolution of reddish brown gas takes place in tube III and blue solution forms.

(c) Evolution of neutral colourless gas takes place in tube IV which burns with blue flame.

(d) Evolution of yellowish green gas takes place in tube V and colourless solution forms.

JEE ADVANCED

6. For the two reactions $I: A \rightarrow B; II: C \rightarrow D$, following graph is obtained. Which of the following is true?



(a) If $[B] = [A]$ then at that time $[D] = 0.75$ M.
(b) If $[C] = [A]$ then at that time $[B] > [D]$.
(c) $(t_{100\%})_{\text{Reaction I}} = (t_{100\%})_{\text{Reaction II}}$
(d) $[A] = [C]$ at $t = \frac{\sqrt{3}}{2}$ min

COMPREHENSION

The allylic substitution on propene could be effectively carried out with halogen ($X_2 = Cl_2, Br_2$) at 400 °C or by using *N*-bromosuccinimide (NBS) in CCl_4 in presence of peroxide or light.

$$CH_3-CH=CH_2 + Cl_2 \xrightarrow[\text{gas phase}]{400\,°C} \underset{\underset{\text{allyl chloride}}{Cl}}{CH_2}-CH=CH_2 + HCl$$

$$CH_3-CH=CH_2 \xrightarrow{NBS/CCl_4, R_2O_2, h\upsilon} \underset{\underset{\text{allyl bromide}}{Br}}{CH_2}-CH=CH_2$$

The mechanism involves the free radical substitution. NBS is also useful for benzylic substitutions.

7. What is the final product in the following reaction sequence?

$$R-CH_2-CH=CH_2 \xrightarrow[CCl_4]{NBS} \xrightarrow[R_2O_2]{HBr} \xrightarrow[\Delta]{Mg}$$

(a) $R-CH=C=CH_2$
(b) $R-CH=CH-CH_3$
(c) 

(d) $\underset{Br}{CH}=C=CH_2 + RH$

8. The following products are observed in the reaction,

$$CH_3-CH_2-CH=CH_2 \xrightarrow[\text{high conc. } CCl_4, \Delta]{Br_2}$$

$$\underset{(A)}{CH_3-\overset{Br}{CH}-CH=CH_2} + \underset{(B)}{CH_3-CH=CH-CH_2-Br}$$

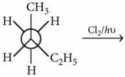
$$\underset{(C)}{CH_3-CH_2-\overset{Br}{CH}-CH_2Br}$$

Which of the following statement is incorrect?
(a) (*A*) is formed by allylic substitution.
(b) (*B*) is formed by allylic substitution via rearrangement.
(c) (*C*) is formed by electrophilic addition.
(d) Product (*C*) formation involves free radical intermediate.

INTEGER VALUE

9. Conductivity of a saturated solution of $Cu_2[Fe(CN)_6]$ after subtracting the conductivity of water is $6.4 \times 10^{-6}\ \Omega^{-1}cm^{-1}$. Solubility product of $Cu_2[Fe(CN)_6]$ is $x \times 10^{-15}$. Find out the value of '*x*'.
$[\Lambda_m^\infty(CuSO_4) = 260\ S\ cm^2\ mol^{-1}$,
$\Lambda_m^\infty(K_2SO_4) = 300\ S\ cm^2\ mol^{-1}$,
$\Lambda_m^\infty[K_4Fe(CN)_6] = 720\ S\ cm^2\ mol^{-1}]$

10. Calculate the total number of monochloroalkanes (including stereoisomer) formed in the following reaction.



CBSE board question paper pattern to change from 2020

According to media reports, CBSE is planning to make some changes in the examination pattern of class 10 and class 12 from 2020 as part of a revamp that would include changes in the examination schedule for vocational subjects as well as for the main subjects - among other changes. Citing MHRD sources, it is reported that the initiative of this pattern change is being taken to discourage students from rote learning. The new pattern would test students on their analytical skills and reasoning abilities instead of blind copy pasting of textbook text. The board has also claimed that this step will produce a better result and the academic quality of institutions will be renewed

Following are some of the major changes expected to be introduced in the new CBSE exam pattern 2020

- Question papers to be designed to check the problem-solving and analytical thinking of students
- Paper pattern to be revamped to include more short answer-type questions like those ranging from 1 to 5 marks
- Vocational course exams to be held in February, and the final board exams to conclude by March in around 15 days.
- Following the early wrapping up of boards, the results are likely to be declared earlier than the schedule followed in the current structure. This will give evaluators more time to check papers. Results, too, will likely be declared earlier.

Under the new plan, there is a vision for putting more emphasis on improved quality of academics in institutions such as teachers, learning outcomes and pedagogy. Respective state governments would be responsible for evaluating their schools' working criteria, infrastructure, and facilities, and their report will be the guide for CBSE to arrive at a decision. CBSE's renewed paper pattern also aims to simplify and shorten the rules of affiliation and renewal for schools.

ADVANCED CHEMISTRY BLOC

Fluorine, isolation, toxicity and properties

Mukul C. Ray, Odisha

Fluorine was recognized for the first time in fluorspar (CaF_2), a mineral. Toxic properties of fluorine compounds were studied for the first time in animal experiments in 1867. Because of fluorine's tight bonding as well as the toxicity of hydrogen fluoride, the element resisted many attempts to isolate it.

It could not be prepared for a long time from HF and metal fluorides due to the following reasons:

- Generally, we consider by oxidising halides, we can produce elemental halogens, such as production of bromine from HBr using concentrated sulphuric acid. Fluorine, however, being the strongest oxidising agent, no oxidising agent can oxidise fluorides (NaF or KF) to fluorine.
- Fluorine being highly reactive, attacks all materials of the apparatus such as glass, carbon, etc.
- It cannot be prepared by the electrolysis of anhydrous HF, as anhydrous HF is a bad conductor of electricity. Though aqueous solution of HF is good conductor of electricity but it does not give fluorine by electrolysis. This is because fluorine produced in this method reacts with water to produce HF once again. Note that electrolysis of aqueous solution of HCl produces chlorine.

Progress in isolating the element was slowed by the exceptional dangers of generating fluorine; several 19th century experimenters, the "fluorine martyrs", were killed or blinded. The English chemist Davy, as well as French chemist Louis Gay-Lussac and Louis Jacques Thenard, experienced severe pain from inhaling hydrogen fluoride gas; Davy's eyes were damaged. Irish chemist Thomas and George Knox developed fluorite apparatus for working with HF gas, but nevertheless were severely poisoned. Thomas nearly died and George was an invalid for three years. Belgian chemist Paulin Louyet and French chemist Jerome Nickles tried to follow the Knox work, but they died from hydrogen fluoride poisoning even though they were aware of the dangers.

Initial attempts to isolate the element were also hindered by material difficulties: the extreme corrosiveness and reactivity of hydrogen fluoride and fluorine gas as well as non- availability of suitable conducting liquid for electrolysis.

Fluorine was crudely prepared by Scheele, a Swedish, in 1771 and named by Ampere.

arch_official

Henry Moissan (a French man, was awarded Noble prize for this in 1906) first prepared this gas in 1886. A U-shaped tube fitted with two electrodes (made up of an alloy of platinum and iridium) is used as the cell. Anhydrous HF is used as the electrolyte. To make it good conductor, potassium hydrogen fluoride (KHF_2) is mixed with the hydrofluoric acid. Since fluorine gas attacks the glass vessel, hence to avoid it, the vessel is kept in boiling methyl chloride. Methyl chloride on evaporation lowers the temperature of the vessel to about –23°C.

On electrolysis, fluorine is liberated at the anode.

$KHF_2 \rightleftharpoons K^+ + H^+ + 2F^-$

$HF \rightleftharpoons H^+ + F^-$ (Practically unionized)

At cathode: $2H^+ + 2e^- \longrightarrow H_2$

At anode: $2F^- - 2e^- \longrightarrow F_2$

This method has few limitations such as the platinum-iridium alloy used is costly and the entire system is to be maintained at very low temperature, which is really difficult.

UNSCRAMBLED WORDS

SEPTEMBER 2018

1-d- OLIVINE	2-h- MARGARINE
3-j- JELUTONG	4-a- HUMECTANT
5-i- ELUTRIATION	6-b- AMETTRYST
7-e- PLEOCHROISM	8-c- CYCLONITE
9-g- COACERVATION	10-f- TETRATOGEN

Look at the following reaction:

$K_2MnF_6 + 2SbF_5 \longrightarrow 2KSbF_6 + MnF_3 + 1/2\ F_2$

This is an uncommon reaction giving elemental fluorine. You never find a reaction probably other than this where elemental fluorine is on the product side. As we have discussed early in this section that no oxidising agent can oxidise fluoride to fluorine but here we see preparation of fluorine from a fluoride. The success of this reaction lies in the thermodynamic instability of MnF_4. The SbF_5 is a very strong fluoride acceptor. It snatches fluoride from K_2MnF_6 to break it to MnF_4, which then decomposes to release elemental fluorine.

Physical Properties

It is a pale yellow irritating gas and is highly corrosive. It is non-combustible water soluble gas. Melting point 54.4 K, boiling point 84.9 K, density 1.5 g/cm^3, bond length 143 pm, bond dissociation energy 158.8 kJ/mol. As fluorine is most electronegative, it combines directly with all other elements (except nitrogen) and noble gases (except helium, neon and argon).

Important Chemical Reactions

Fluorine has very powerful oxidising ability, which is clear from its electrode potential.

$F_2 + 2e^- \longrightarrow 2F^- \quad E^o = +2.87\ V$

In molecular form, its oxidizing ability can be illustrated by the following partial equation :

$F_2 + H_2O \longrightarrow 2HF + O$

The complete equation for oxidation of bisulphate is

$F_2 + H_2O \longrightarrow 2HF + O$

$2KHSO_4 + O \longrightarrow K_2S_2O_8 + H_2O$

$F_2 + 2KHSO_4 + H_2O \longrightarrow K_2S_2O_8 + 2HF + H_2O$

Similarly, for chlorate:

$F_2 + H_2O \longrightarrow 2HF + O$

$KClO_3 + O \longrightarrow KClO_4$

$F_2 + KClO_3 + H_2O \longrightarrow KClO_4 + 2HF$

Oxidation of chromic salts can be written as:

$[F_2 + H_2O \longrightarrow 2HF + O] \times 3$

$Cr_2(SO_4)_3 + 4H_2O + 3O \longrightarrow H_2Cr_2O_7 + 3H_2SO_4$

$3F_2 + Cr_2(SO_4)_3 + 7H_2O \longrightarrow H_2Cr_2O_7 + 3H_2SO_4 + 6HF$

With dilute alkali, OF_2 is formed :

$2NaOH + 2F_2 \longrightarrow OF_2 + 2NaF + H_2O$

With concentrated alkali, oxygen is formed :

$4NaOH + 2F_2 \longrightarrow 4NaF + 2H_2O + O_2$

Exam Alert

The schedule of JEE Main and NEET examinations to be conducted by the National Testing Agency (NTA) till May 2019.

Examination: JEE Main I	
Mode of examination: Computer based	
Registration dates	1st to 30th Sept 2018
Downloading of admit cards	17th Dec 2018
Dates of examinations	6th to 20th Jan 2019
Date for announcing results	31st Jan 2019

Examinations will be organised on the weekends (Saturdays and Sundays) during the period of 6th to 20th January, 2019.

Examination: JEE Main II	
Mode of examination: Computer based	
Registration dates	8th Feb to 7th March 2019
Downloading of admit cards	18th March 2019
Dates of examinations	6th to 20th April 2019
Date for announcing results	30th April 2019

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Examination: NEET (UG)	
Mode of examination: Pen & Paper exam (in single session)	
Registration dates	1st Nov to 30th Nov 2018
Downloading of admit cards	15th April 2019
Date of examination	5th May 2019
Date for announcing result	5th June 2019

The NEET exam pattern will now be a single exam in pen-and-paper mode and in the same number of languages as has been conducted last year.

National Testing Agency (NTA) established a countrywide network of test practice centres (TPCs) for students of rural areas so that everyone will have an opportunity to practice before the exam. (2,697) Schools/engineering colleges with computer centres are being made available on every Saturday/Sunday starting from 1st September, 2018 and any student can use the facility free of charge. An App is being developed which will enable the students to choose the nearest TPC.

The TPCs will have a downloaded Computer Based Test (CBT) which will be similar to the actual test to be conducted on the exam day. The practice tests will help the candidates to familiarize themselves with logging into the system, going through the detailed instructions regarding the test, using the mouse or numeric keyboard on screen (virtual) for attempting each question, scrolling down to the next question, navigating between questions, reviewing and editing their options and submit questions.

YOU ASK WE ANSWER

Do you have a question that you just can't get answered?

Use the vast expertise of our MTG team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough. The best questions and their solutions will be printed in this column each month.

1. What is laughing gas and how it affects our body?

(Lakshay Sareen, Punjab)

Ans. Chemically laughing gas is nitrous oxide which is a colourless, sweet tasting gas, but when inhaled it can make people feel euphoric and relaxed. This happy feeling has led to it being nicknamed 'laughing gas'. It has low toxicity. But, long term and heavy use of nitrous oxide can lead to vitamin deficiency and anaemia as a result of the inactivation of vitamin B_{12}, if severe can lead to serious nerve damage and also depress formation of white blood cells. If the gas is consumed in an enclosed space then there is a risk of death due to lack of oxygen.

2. Why white phosphorus is thermodynamically less stable and chemically more reactive?

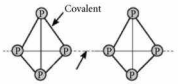
(Bhavya Pahwa, Punjab)

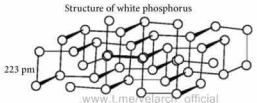
Ans. Thermodynamically black phosphorus is most stable, while white phosphorus is least stable. Thermodynamic stability of allotropic forms of phosphorus at room temperature increases as :

white < red < black

White phosphorus is made up of discrete P_4 tetrahedra, in which each P atom is bonded with other three P atoms by weak van der Waals' forces. The bond angle in P_4 particle is 60° which is significantly less. This high angular strain makes white phosphorus unstable and highly reactive. White P is so thermodynamically unstable that it combusts in air.

Black phosphorus is thermodynamically most stable form and has an orthorhombic structure. It is least reactive allotrope of phosphorus as a result of its lattice of interlinked six membered rings where each P atom is bonded to three other P atoms.





3. Is hydrogen a halogen?

(Pradeep Kumar, Jammu and Kashmir)

Ans. Though hydrogen resembles with halogens in many respects, it absolutely cannot be halogen because :

(i) Electronegativity decreases as we go down the group of the periodic table, and the element becomes more and more metallic. Hydrogen would have to be more electronegative than fluorine if it would be a halogen.

(ii) In most of the compounds, hydrogen exhibits mainly +1 oxidation state, whereas in most stable compounds of halogen, they have either –1 or a very high oxidation states like +7 or +5. An oxidation state of +1 is very unstable in halogens.

(iii) Oxides of halogens are acidic but the oxide of hydrogen, *i.e.*, H_2O is neutral.

(iv) Unlike halogen atom in halogen molecule, H-atom in hydrogen molecules do not possess any unshared pair of electrons.

(v) Hydrogen has less tendency to form H^- ions as compared to halogens which readily form halide (X^-) ions.

Thus it is evident that hydrogen displays unique behaviour that it does resemble and at the same time differ from halogens. Therefore, it is not justified to include hydrogen with halogens.

EXAM PREP

Useful for Medical/Engineering Examinations



*Arunava Sarkar

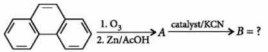
1. Identify the product.

$PhCH_2CH_2CH_3 \xrightarrow[(ii)\ H_2O]{(i)\ CrO_2Cl_2/CCl_4} ?$

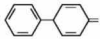
(a) PhCOOH (b) PhCHO

(c) $PhCH_2CHO$ (d) None of these

2.



(a)



(b)

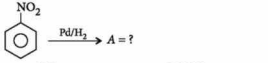


(c)



(d) None of these

3.



(a)



(b)

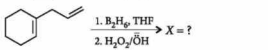


(c)

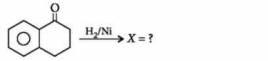


(d)

4.



5.



(a)



(b)

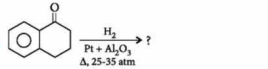


(c)



(d) None of these

6.



(a)



(b)



(c)



(d) None of these

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*Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

7. Identify the product.

$$CH_3-C\equiv C-CH=CH-R \xrightarrow{CrO_3 \text{ in } CH_3COOH} ?$$

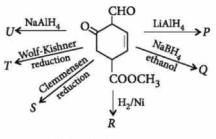
(a) $CH_3COOH + HOOC-COOH + RCOOH$

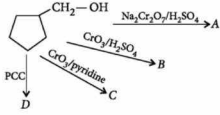
(b) $CH_3-C\equiv C-COOH + RCOOH$

(c) $CH_3-COOH + CO_2 + RCOOH$

(d) None of these

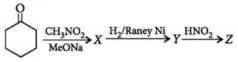
8. Identify the products in the following reactions.

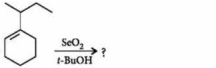


9. 

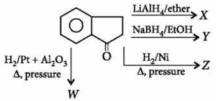
Identify *A*, *B*, *C*, *D*.

10. Identify *X*, *Y* and *Z*.

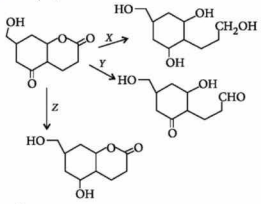


11. 

12. Identify *W*, *X*, *Y*, *Z*.



13. Identify *X*, *Y* and *Z*



14. 
This compound is known as *p*-benzoquinone.

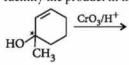
What happens when this is treated with

(a) $LiAlH_4$ (b) $NaBH_4$

(c) H_2, Pd (d) H_2 + Pd-C

(e) $LiAlH_4 + AlCl_3$ (f) Na, liq. NH_3, EtOH

15. Identify the product in the following reaction.



[* means ^{14}C]

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SOLUTIONS

1. **(d)** : You understand that this is an example or application of Etard reaction. Now, remember the following facts about Etard reaction :

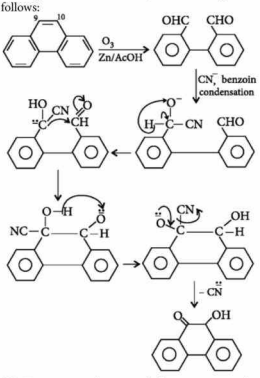
(1) It will not change the number of carbons.

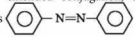
(2) Only terminal $-CH_3$ group will convert into $-CHO$.

So, $PhCH_2CH_2CH_3 \xrightarrow[\text{(ii) } H_2O]{\text{(i) } CrO_2Cl_2/CCl_4} PhCH_2CH_2CHO$

So, correct option is (d).

2. **(b)** : Given substance is phenanthrene. Here, C_9 and C_{10} are more active. So, the reaction goes as follows:



3. **(d)** : For getting the extended conjugation, the product here becomes 

(same as in the case with $LiAlH_4$)

∴ Correct option is (d).

4. **(c)** : This is hydroboration oxidation which adds a water molecule in anti-Markownikoff's fashion. Therefore, the correct option is (c).

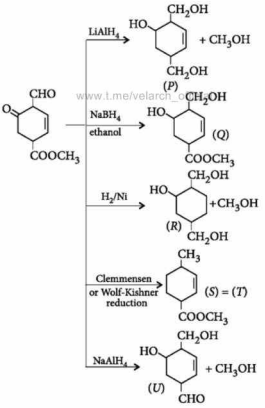
5. **(b)** : H_2/Ni is a powerful reducing agent. It will destroy the aromaticity of benzene ring by reducing it and also will convert $>C=O$ to $>CHOH$ group.

6. **(b)**

7. **(b)** : Remember that oxidation of triple bond is much slower than the oxidation of double bond. That is why '≡' bond remains silent when double bond undergoes oxidation.

$$\therefore\ CH_3-C\equiv C-CH=CH-R \xrightarrow{CrO_3 \text{ in } CH_3COOH} CH_3-C\equiv C-COOH + RCOOH$$

8.



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9. A = (1° alcohol converts to acid)



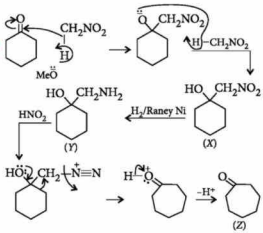
B = same as A

C = (1° alcohol to aldehyde)

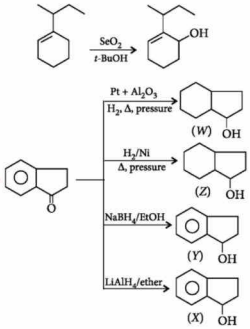


D = same as C

10.



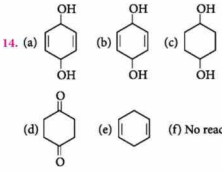
11. SeO_2 is used for allylic oxidation of alkenes. According to Guillemonat, hydroxylation takes place at the α-carbon adjacent to more crowded unsaturated carbon. So,



12.

13. Among the possible known reducing agents and the conversion of functional groups in the given question, we can say $X = LiAlH_4$, $Y = NaAlH_4$, $Z = NaBH_4$. Alcohols are not affected by any of the reducing agents. $NaAlH_4$ converts an ester into aldehyde and alcohol.

14. (a) (b) (c)



(d) (e) (f) No reaction

Points to be noted :

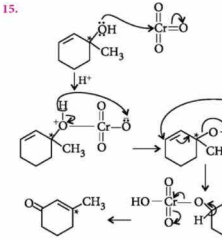
(1) H_2 + Pd reduces both double bond and carbonyl group.

(2) H_2, Pd + C reduces only double bond.

(3) $LiAlH_4 + AlCl_3$ reduces $>C=O$ to $>CH_2$

(4) Birch reduction is not applicable for $>C=O$ group.

15.





CHEMISTRY MUSING

SOLUTION SET 62

1. (a) : $C_2H_{6(g)} \rightleftharpoons C_2H_{4(g)} + H_{2(g)}$

Initial	4.0	0	0
pressure at equil:	$4.0 - x$	x	x

$$K_p = \frac{P_{C_2H_4} \times P_{H_2}}{P_{C_2H_6}} = \frac{x^2}{4.0 - x} = 0.04$$

$$\Rightarrow x^2 + 0.04x - 0.16 = 0$$

$$\therefore \quad x = \frac{-0.04 \pm \sqrt{(0.04)^2 + 4 \times 0.16}}{2}$$

$$= \frac{-0.04 \pm 0.801}{2} = -0.42 \text{ or } 0.38$$

Since, a negative value of x is impossible, the acceptable value of $x = 0.38$

The equilibrium partial pressure of C_2H_6 is $(4.0 - 0.38)$ atm $= 3.62$ atm

$$\text{The equilibrium molarity of ethane} = \frac{3.62}{RT}$$

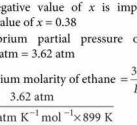
$$= \frac{3.62 \text{ atm}}{0.0821 \text{ L atm K}^{-1}\text{mol}^{-1} \times 899 \text{ K}}$$

$$= 4.9 \times 10^{-2} \text{ mol/L}$$

2. (c) : (a) Nearest neighbour of atom 2 are 1 and 3.

Distance between atoms 1 and 2 = a

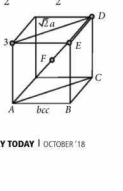
Distance between atoms 2 and 3 = $\sqrt{2}a$



(b) Nearest neighbours of atom D are E and F (F atom is in body centre)

Body diagonal $(AD) = \sqrt{3}a$

$$\text{Distance } DF = \frac{1}{2}(AD) = \frac{\sqrt{3}}{2}a$$



Distance $ED = a$.

(c) Option (c) is wrong. ZnS (wurtzite) and ZnS (zinc blende) are polymorphs.

Same substance occuring in different crystal forms is called polymorphism.

But in both the compounds, cations (Zn^{2+} ions) occupy alternate tetrahedral voids.

In both compounds S^{2-} occupies lattice points.

(d) Correct statement.

3. (b) : Gold obtained from extraction steps contains silver, copper, zinc and sometimes lead as impurities.

Cupellation ⟶ Zinc and lead are oxidised and ore blown off.

Parting process ⟶ Removal of impurities of silver and copper.

Miller's process ⟶ To refine gold to a high degree of purity (99.95%)

Electrolytic refining. ⟶ To improve purity to 99.999%

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4. (b) : The final temperature of the mixture can be calculated by equating the heat lost by the warmer sample with the heat gained by the cooler sample.

Let the final temperature be T.

The heat gained by the cooler sampler

$= 350 \times 1.00 \times (T - 5) = 350(T - 5)$ cal

The heat lost by the warm sample

$= 500 \times 1.00 \times (80 - T) = 500 \times (80 - T)$ cal

$\therefore \quad 350(T - 5) \text{ cal} = 500 \times (80 - T) \text{ cal} \Rightarrow T = 49.1$ °C

The temperature of the cold sample increases from 5 °C to 49.1°C.

$$\therefore \quad \Delta S_1 = 2.303 \times C \log \frac{T_f}{T_i}$$

$$= 2.303 \times 350 \text{ g} \times 1.00 \text{ cal deg}^{-1} \text{ g}^{-1} \times \log \frac{322.1\text{K}}{278\text{K}}$$

$$= 2.303 \times 350 \text{ cal deg}^{-1} \times (0.0639) = 51.5 \text{ cal deg}^{-1}$$

The temperature of the warm sample decreases from 80° C to 49.1° C.

$$\therefore \quad \Delta S_2 = 2.303 \times C \log \frac{T_f}{T_i}$$

$$= 2.303 \times 500 \text{ g} \times 1.00 \text{ cal deg}^{-1} \text{ g}^{-1} \times \log \frac{322.1 \text{ K}}{353 \text{ K}}$$

$$= 2.303 \times 500 \text{ cal deg}^{-1} \times (-0.04) = -46.1 \text{ cal deg}^{-1}$$

$\therefore$ Total change in entropy $= \Delta S = \Delta S_1 + \Delta S_2$

$= 51.5 \text{ cal deg}^{-1} - 46.1 \text{ cal deg}^{-1} = 5.4 \text{ cal deg}^{-1}$

5. (d):

$$PtF_6(g) + Xe(g) \longrightarrow Xe^+[PtF_6]^- \xrightarrow{PtF_6} [XeF]^+[PtF_6]^-$$

$$[XeF]^+[Pt_2F_{11}]^- \xleftarrow{PtF_6} [XeF]^+[PtF_6]^-$$

6. (b) : $(NH_4)_2CO_3 \rightarrow NH_2CONH_2 + 2H_2O$

Moles of $(NH_4)_2CO_3 = \frac{11.52}{96} = 0.12$ = moles of urea

$2MnO_4^- + 5C_2O_4^{2-} + 16\,H^+ \rightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$

Meq. of $(NH_4)_2C_2O_4$ = Meq. of $KMnO_4$

$\frac{W}{M/2} \times 1000 = 20 \times 1.6 \times 5$

Moles of $(NH_4)_2C_2O_4 = W/M = 0.08$

(i) $(CN)_2 + 4H_2O \rightarrow (NH_4)_2C_2O_4$
0.08 moles 0.08 moles

(ii) $(CN)_2 + 2H_2O \rightarrow NH_2CONH_2$
0.12 moles 0.12 moles

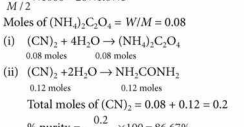
Total moles of $(CN)_2 = 0.08 + 0.12 = 0.2$

% purity $= \frac{0.2}{12/52} \times 100 = 86.67\%$

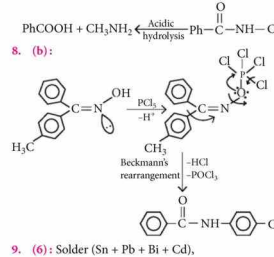
Progress in case (i) $\frac{0.08}{0.2} \times 100 = 40\%$

Progress in case (ii) $\frac{0.12}{0.2} \times 100 = 60\%$

7. (d):



8. (b):



9. (6) : Solder (Sn + Pb + Bi + Cd),
Gunmetal (Cu + Sn + Zn),
German Silver (Cu + Zn + Ni),
Nichrome (Ni + Cr + Fe), Monel metal (Cu + Ni)
Constantan (Cu + Ni), Bell metal (Cu + Sn)
Duralumin (Cu + Mn + Mg),
Type metal (Pb + Sn + Sb),
Invar (Ni + Fe), Alnico (Al + Ni + Co)

10. (4) : $Fe^{3+} = 3d^5$ and CN^- is strong ligand, paramagnetic.
$Co^{3+} = 3d^6$ and NH_3 is strong ligand, diamagnetic.
$Co^{3+} = 3d^6$ and $C_2O_4^{2-}$ is strong ligand, diamagnetic.
$Ni^{2+} = 3d^8$ and Ni octahedral complexes are always paramagnetic.
$Pt^{2+} = 5d^8$ and CN^- is a strong ligand, and have square planner complex, diamagnetic.
$Zn^{2+} = 3d^{10}$ and it is diamagnetic.

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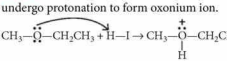
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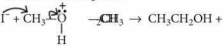
The cleavage of C—O bond in ethers takes place under drastic conditions with excess of H*X*. Order of reactivity of HCl, HBr, HI is

HCl < HBr < HI

(ii) (a) Step I : With limited amount of HI, ether undergo protonation to form oxonium ion.



Step II : Iodide is good nucleophile and attacks the least substituted carbon of the oxonium ion of step I and alcohol is displaced.



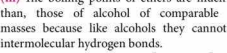
Thus, we get mixture of alcohol and alkyl iodide when HI reacts with mixed ether.

(b) With excess of HI alcohol formed is converted to alkyl iodide.

$CH_3-O-CH_2-CH_3 + HI \rightarrow CH_3CH_2OH + CH_3I$

$CH_3CH_2OH + HI \rightarrow CH_3CH_2I + H_2O$

(iii) The boiling points of ethers are much lower than, those of alcohol of comparable molar masses because like alcohols they cannot form intermolecular hydrogen bonds.



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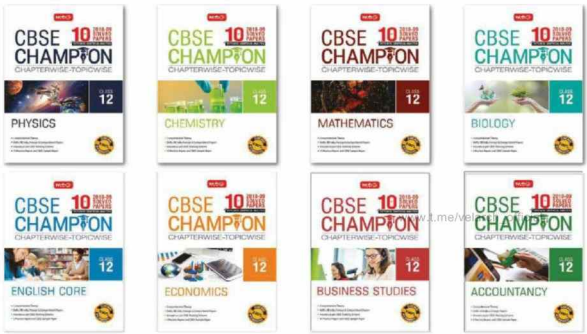
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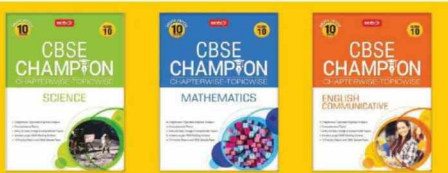
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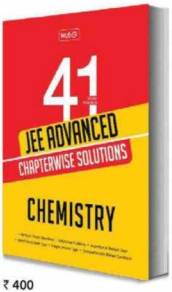
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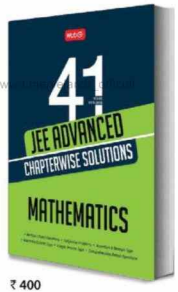
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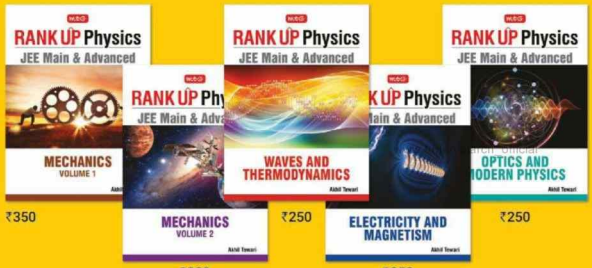
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