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HIGHLIGHTS

- NCERT-based • Chapterwise • Topicwise • 11 years' solved previous test papers (all major medical entrance exams) • Concise summary at the start of each chapter for quick revision of key concepts
- Analysis of importance of topics basis historical examination pattern • Test papers for self-assessment

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today



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Managing Editor

Mahabir Singh

Editor

Anil Ahlawat

Corporate Office:

Plot 99, Sector 44 Institutional area, Gurugram -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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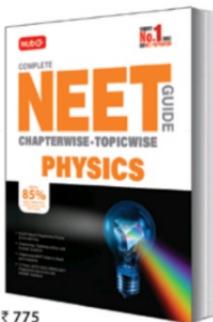
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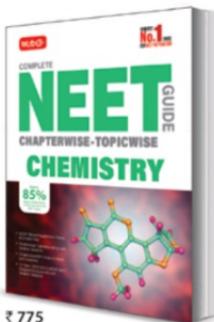
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Presenting India's No.1 NEET Guides

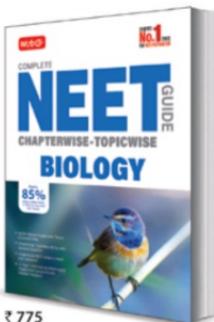
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HIGHLIGHTS:

- 100% NCERT based
- Comprehensive Chapterwise theory complemented with concept maps, flowcharts and easy-to-understand illustrations
- Last 11 years' questions (2010-2020) of AIPMT/NEET
- Chapterwise - Topicwise MCQs with detailed explanations and solutions
- Approx. 85% same or similar MCQs in NEET are from MTG NEET Books



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NEET

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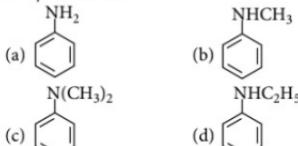
We are happy to inform our readers that out of the 45 questions asked in NEET 2020, more than 85% questions were either exactly same or of similar type from the **MTG Books**.

Here, the references of few are given :

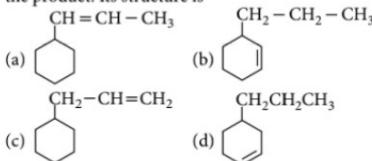
Exam Q. No.	MTG Book	Q. No.	P. No.	Exam Q. No.	MTG Book	Q. No.	P. No.
1	NEET Champion (XII)	60	287	22	NEET Champion (XI)	47	110
5	NEET Champion (XII)	125	51	26	NEET Champion (XII)	114	128
7	NEET Guide (XI)	69	11	28	NEET Champion (XII)	138	225
11	NEET Guide (XI)	92	130	31	NEET Champion (XI)	143	232
12	NCERT Fingertips (XII)	54	9	34	NEET Guide (XII)	156	79
13	NCERT Fingertips (XII)	54	81	35	NEET Champion (XII)	57	23
14	NEET Champion (XII)	20	217	37	NCERT Fingertips (XII)	23	315
15	NEET Champion (XI)	32	59	41	NEET Champion (XII)	54	345
17	NEET Champion (XI)	12	45	42	NEET Guide (XI)	183	202
20	NEET Champion (XII)	103	174	43	NCERT Fingertips (XI)	82	71

and more such questions

1. Which of the following amines will give the carbalamine test?



2. An alkene on ozonolysis gives methanal as one of the product. Its structure is



3. Match the following and identify the correct option.

- | | |
|--|---|
| (A) $\text{CO}_{(g)} + \text{H}_2_{(g)}$ | (i) $\text{Mg}(\text{HCO}_3)_2 + \text{Ca}(\text{HCO}_3)_2$ |
| (B) Temporary hardness of water | (ii) An electron deficient hydride |
| (C) B_2H_6 | (iii) Synthesis gas |
| (D) H_2O_2 | (iv) Non-planar structure |

- (A) (B) (C) (D)

- (a) (iii) (i) (ii) (iv)
 (b) (iii) (ii) (i) (iv)
 (c) (iii) (iv) (ii) (i)
 (d) (i) (iii) (ii) (iv)

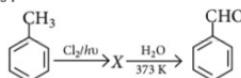
4. The freezing point depression constant (K_f) of benzene is $5.12 \text{ K kg mol}^{-1}$. The freezing point depression for the solution of molality 0.078 m containing a non-electrolyte solute in benzene is (rounded off upto two decimal places)

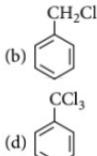
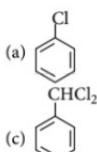
- (a) 0.20 K (b) 0.80 K
 (c) 0.40 K (d) 0.60 K

5. On electrolysis of dil. sulphuric acid using platinum (Pt) electrode, the product obtained at anode will be

- (a) hydrogen gas (b) oxygen gas
 (c) H_2S gas (d) SO_2 gas.

6. Identify compound X in the following sequence of reactions :





7. Which one of the followings has maximum number of atoms?
- $1\text{ g of } \text{Ag}_{(g)}$ [Atomic mass of Ag = 108]
 - $1\text{ g of } \text{Mg}_{(s)}$ [Atomic mass of Mg = 24]
 - $1\text{ g of } \text{O}_{2(g)}$ [Atomic mass of O = 16]
 - $1\text{ g of } \text{Li}_{(s)}$ [Atomic mass of Li = 7]
8. Identify the correct statement from the following :
- Wrought iron is impure iron with 4% carbon.
 - Blister copper has blistered appearance due to evolution of CO_2 .
 - Vapour phase refining is carried out for Nickel by van Arkel method.
 - Pig iron can be moulded into a variety of shapes.
9. A tertiary butyl carbocation is more stable than a secondary butyl carbocation because of which of the following?
- I effect of $-\text{CH}_3$ groups
 - +R effect of $-\text{CH}_3$ groups
 - R effect of $-\text{CH}_3$ groups
 - Hyperconjugation
10. Urea reacts with water to form A which will decompose to form B. When passed through $\text{Cu}^{2+}_{(aq)}$, deep blue colour solution C is formed. What is the formula of C from the following?
- CuSO_4
 - $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 - $\text{Cu}(\text{OH})_2$
 - $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$
11. A mixture of N_2 and Ar gases in a cylinder contains 7 g of N_2 and 8 g of Ar. If the total pressure of the mixture of the gases in the cylinder is 27 bar, the partial pressure of N_2 is
[Use atomic masses (in g mol^{-1}) : N = 14, Ar = 40]
- 9 bar
 - 12 bar
 - 15 bar
 - 18 bar.
12. An element has a body centered cubic (bcc) structure with a cell edge of 288 pm. The atomic radius is
- $\frac{\sqrt{3}}{4} \times 288\text{ pm}$
 - $\frac{\sqrt{2}}{4} \times 288\text{ pm}$
 - $\frac{4}{\sqrt{3}} \times 288\text{ pm}$
 - $\frac{4}{\sqrt{2}} \times 288\text{ pm}$

13. The rate constant for a first order reaction is $4.606 \times 10^{-3}\text{ s}^{-1}$. The time required to reduce 2.0 g of the reactant to 0.2 g is
- 100 s
 - 200 s
 - 500 s
 - 1000 s
14. Reaction between acetone and methylmagnesium chloride followed by hydrolysis will give
- iso-propyl alcohol
 - sec-butyl alcohol
 - tert-butyl alcohol
 - iso-butyl alcohol.
15. Which of the following set of molecules will have zero dipole moment?
- Ammonia, beryllium difluoride, water, 1, 4-dichlorobenzene
 - Boron trifluoride, hydrogen fluoride, carbon dioxide, 1, 3-dichlorobenzene
 - Nitrogen trifluoride, beryllium difluoride, water, 1, 3-dichlorobenzene
 - Boron trifluoride, beryllium difluoride, carbon dioxide, 1, 4-dichlorobenzene
16. What is the change in oxidation number of carbon in the following reaction?
- $$\text{CH}_4_{(g)} + 4\text{Cl}_{2(g)} \rightarrow \text{CCl}_4_{(l)} + 4\text{HCl}_{(g)}$$
- + 4 to + 4
 - 0 to + 4
 - 4 to + 4
 - 0 to - 4
17. Match the following :
- | Oxide | Nature |
|-----------------------------|-----------------|
| (A) CO | (i) Basic |
| (B) BaO | (ii) Neutral |
| (C) Al_2O_3 | (iii) Acidic |
| (D) Cl_2O_7 | (iv) Amphoteric |
- Which of the following is correct option?
- | (A) | (B) | (C) | (D) |
|-----------|-------|-------|-------|
| (a) (i) | (ii) | (iii) | (iv) |
| (b) (ii) | (i) | (iv) | (iii) |
| (c) (iii) | (iv) | (i) | (ii) |
| (d) (iv) | (iii) | (ii) | (i) |
18. Which of the following is not correct about carbon monoxide?
- It forms carboxyhaemoglobin.
 - It reduces oxygen carrying ability of blood.
 - The carboxyhaemoglobin (haemoglobin bound to CO) is less stable than oxyhaemoglobin.
 - It is produced due to incomplete combustion.
19. Measuring zeta potential is useful in determining which property of colloidal solution?
- Viscosity
 - Solubility
 - Stability of the colloidal particles
 - Size of the colloidal particles

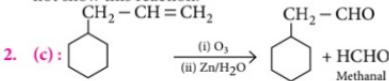


- 20.** Which of the following is the correct order of increasing field strength of ligands to form coordination compounds?
- $\text{SCN}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{CN}^-$
 - $\text{SCN}^- < \text{F}^- < \text{CN}^- < \text{C}_2\text{O}_4^{2-}$
 - $\text{F}^- < \text{SCN}^- < \text{C}_2\text{O}_4^{2-} < \text{CN}^-$
 - $\text{CN}^- < \text{C}_2\text{O}_4^{2-} < \text{SCN}^- < \text{F}^-$
- 21.** Elimination reaction of 2-bromopentane to form pent-2-ene is
- β -Elimination reaction
 - Follows Zaitsev rule
 - Dehydrohalogenation reaction
 - Dehydration reaction
- | | |
|-------------------|-------------------|
| (a) (A), (B), (C) | (b) (A), (C), (D) |
| (c) (B), (C), (D) | (d) (A), (B), (D) |
- 22.** The correct option for free expansion of an ideal gas under adiabatic condition is
- $q = 0, \Delta T = 0$ and $w = 0$
 - $q = 0, \Delta T < 0$ and $w > 0$
 - $q < 0, \Delta T = 0$ and $w = 0$
 - $q > 0, \Delta T > 0$ and $w > 0$
- 23.** Identify the incorrect statement.
- $\text{Cr}^{2+}(d^4)$ is a stronger reducing agent than $\text{Fe}^{2+}(d^6)$ in water.
 - The transition metals and their compounds are known for their catalytic activity due to their ability to adopt multiple oxidation states and to form complexes.
 - Interstitial compounds are those that are formed when small atoms like H, C or N are trapped inside the crystal lattices of metals.
 - The oxidation states of chromium in CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ are not the same.
- 24.** Identify the incorrect match.
- | Name | IUPAC Official Name |
|-----------------|---------------------|
| (A) Unnilunium | (i) Mendelevium |
| (B) Unniltrium | (ii) Lawrencium |
| (C) Unnilhexium | (iii) Seaborgium |
| (D) Unununnum | (iv) Darmstadtium |
| (a) (A), (i) | (b) (B), (ii) |
| (c) (C), (iii) | (d) (D), (iv) |
- 25.** Reaction between benzaldehyde and acetophenone in presence of dilute NaOH is known as
- Aldol condensation
 - Cannizzaro's reaction
 - Cross Cannizzaro's reaction
 - Cross Aldol condensation.
- 26.** Which of the following oxoacid of sulphur has — O — O — linkage
- H_2SO_3 , sulphurous acid
 - H_2SO_4 , sulphuric acid
 - $\text{H}_2\text{S}_2\text{O}_8$, peroxodisulphuric acid
 - $\text{H}_2\text{S}_2\text{O}_7$, pyrosulphuric acid
- 27.** HCl was passed through a solution of CaCl_2 , MgCl_2 and NaCl . Which of the following compound(s) crystallise(s)?
- Both MgCl_2 and CaCl_2
 - Only NaCl
 - Only MgCl_2
 - NaCl , MgCl_2 and CaCl_2
- 28.** Anisole on cleavage with HI gives
- | | | | |
|-----|----------------------------------|-----|-----------------------------------|
| (a) | + CH_3I | (b) | + CH_3OH |
| (c) | + $\text{C}_2\text{H}_5\text{I}$ | (d) | + $\text{C}_2\text{H}_5\text{OH}$ |
- 29.** Identify the correct statements from the following :
- $\text{CO}_{2(g)}$ is used as refrigerant for ice-cream and frozen food.
 - The structure of C_{60} contains twelve six carbon rings and twenty five carbon rings.
 - ZSM-5, a type of zeolite, is used to convert alcohols into gasoline.
 - CO is colourless and odourless gas.
- | | | | |
|---------------------------|----------------------|----------------------|----------------------|
| (a) (A), (B) and (C) only | (b) (A) and (C) only | (c) (B) and (C) only | (d) (C) and (D) only |
|---------------------------|----------------------|----------------------|----------------------|
- 30.** For the reaction, $2\text{Cl}_{(g)} \rightarrow \text{Cl}_{2(g)}$, the correct option is
- $\Delta_rH > 0$ and $\Delta_rS > 0$
 - $\Delta_rH > 0$ and $\Delta_rS < 0$
 - $\Delta_rH < 0$ and $\Delta_rS > 0$
 - $\Delta_rH < 0$ and $\Delta_rS < 0$
- 31.** Paper chromatography is an example of
- adsorption chromatography
 - partition chromatography
 - thin layer chromatography
 - column chromatography.
- 32.** Which of the following alkane cannot be made in good yield by Wurtz reaction?
- n*-Hexane
 - 2, 3-Dimethylbutane
 - n*-Heptane
 - n*-Butane

33. An increase in the concentration of the reactants of a reaction leads to change in
 (a) activation energy (b) heat of reaction
 (c) threshold energy (d) collision frequency.
34. The number of Faradays (F) required to produce 20 g of calcium from molten CaCl_2 (Atomic mass of Ca = 40 g mol^{-1}) is
 (a) 1 (b) 2 (c) 3 (d) 4
35. The mixture which shows positive deviation from Raoult's law is
 (a) ethanol + acetone (b) benzene + toluene
 (c) acetone + chloroform (d) chloroethane + bromoethane.
36. Hydrolysis of sucrose is given by the following reaction:
 $\text{Sucrose} + \text{H}_2\text{O} \rightleftharpoons \text{Glucose} + \text{Fructose}$
 If the equilibrium constant (K_C) is 2×10^{13} at 300 K, the value of $\Delta_g G^\circ$ at the same temperature will be
 (a) $-8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$
 (b) $8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$
 (c) $8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(3 \times 10^{13})$
 (d) $-8.314 \text{ J mol}^{-1}\text{K}^{-1} \times 300 \text{ K} \times \ln(4 \times 10^{13})$
37. Sucrose on hydrolysis gives
 (a) β -D-glucose + α -D-fructose
 (b) α -D-glucose + β -D-glucose
 (c) α -D-glucose + β -D-fructose
 (d) α -D-fructose + β -D-fructose.
38. The calculated spin only magnetic moment of Cr^{2+} ion is
 (a) 3.87 BM (b) 4.90 BM
 (c) 5.92 BM (d) 2.84 BM
39. Which of the following is a natural polymer?
 (a) *cis*-1, 4-polyisoprene
 (b) poly (Butadiene-styrene)
 (c) polybutadiene
 (d) poly (Butadiene-acrylonitrile)
40. Which of the following is a basic amino acid?
 (a) Serine (b) Alanine
 (c) Tyrosine (d) Lysine
41. Which of the following is a cationic detergent?
 (a) Sodium lauryl sulphate
 (b) Sodium stearate
 (c) Cetyltrimethyl ammonium bromide
 (d) Sodium dodecylbenzene sulphonate
42. Find out the solubility of Ni(OH)_2 in 0.1 M NaOH . Given that the ionic product of Ni(OH)_2 is 2×10^{-15} .
- (a) $2 \times 10^{-13} \text{ M}$ (b) $2 \times 10^{-8} \text{ M}$
 (c) $1 \times 10^{-13} \text{ M}$ (d) $1 \times 10^8 \text{ M}$
43. Identify a molecule which does not exist.
 (a) He_2 (b) Li_2 (c) C_2 (d) O_2
44. The following metal ion activates many enzymes, participates in the oxidation of glucose to produce ATP and with Na, is responsible for the transmission of nerve signals.
 (a) Iron (b) Copper
 (c) Calcium (d) Potassium
45. The number of protons, neutrons and electrons in ^{175}Lu , respectively, are
 (a) 71, 104 and 71 (b) 104, 71 and 71
 (c) 71, 71 and 104 (d) 175, 104 and 71

SOLUTIONS

1. (a) : Aliphatic and aromatic primary amines give carbylamine test. Secondary and tertiary amines do not show this reaction.

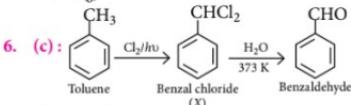


3. (a)

4. (c) : Given : $K_f = 5.12 \text{ K kg mol}^{-1}$, $m = 0.078 \text{ m}$
 $\Delta T_f = K_f \times m = 5.12 \times 0.078 = 0.39936 \approx 0.40 \text{ K}$

5. (b) : During electrolysis of dilute sulphuric acid the following reaction takes place at anode.

$2\text{H}_2\text{O}_{(l)} \rightarrow \text{O}_{2(g)} + 4\text{H}_{(aq)}^+ + 4e^-$; $E_{\text{cell}}^\circ = +1.23 \text{ V}$
i.e., $\text{O}_{2(g)}$ will be liberated at anode.



7. (d) : 1 mole of substance = N_A atoms

$$108 \text{ g of Ag} = N_A \text{ atoms}$$

$$\Rightarrow 1 \text{ g of Ag} = \frac{N_A}{108} \text{ atoms}$$

$$24 \text{ g of Mg} = N_A \text{ atoms}$$

$$\Rightarrow 1 \text{ g of Mg} = \frac{N_A}{24} \text{ atoms}$$

$$32 \text{ g of O}_2 = N_A \text{ molecules} = 2 N_A \text{ atoms}$$

$$\Rightarrow 1 \text{ g of O}_2 = \frac{N_A}{16} \text{ atoms}$$

$$7 \text{ g of Li} = N_A \text{ atoms}$$

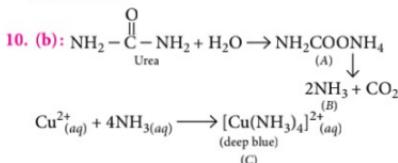
$$\Rightarrow 1 \text{ g of Li} = \frac{N_A}{7} \text{ atoms}$$

Therefore, 1 g of $\text{Li}_{(s)}$, has maximum number of atoms.

8. (d): (a) Pig iron is impure iron with 4% carbon.
 (b) Blister copper has blistered appearance due to evolution of SO_2 .
 (c) Vapour phase refining is carried out for nickel by Mond's process.
 (d) Pig iron can be moulded into a variety of shapes.

9. (d): *tert*-Butyl carbocation, $(\text{CH}_3)_3\overset{+}{\text{C}}$ is more stable than *sec*-butyl carbocation $(\text{CH}_3)_2\overset{+}{\text{CH}}$ due to hyperconjugation.

$(\text{CH}_3)_3\overset{+}{\text{C}}$ has nine C — H bonds while $(\text{CH}_3)_2\overset{+}{\text{CH}}$ has six C — H bonds. Thus, there is more hyperconjugative structures in *tert*-butyl carbocation.



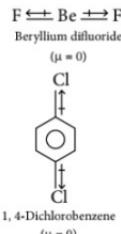
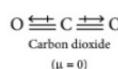
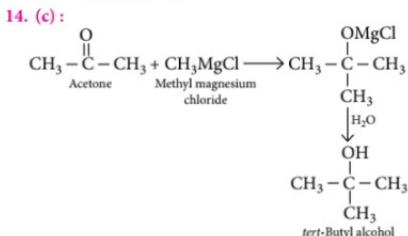
11. (c) : Number of moles of $\text{N}_2 = \frac{7}{28} = 0.25 \text{ mol}$
 Number of moles of Ar = $\frac{8}{40} = 0.2 \text{ mol}$
 Mole fraction of $\text{N}_2 = \frac{0.25}{0.25 + 0.2} = \frac{0.25}{0.45} = 0.55$
 Partial pressure of N_2 gas = mole fraction \times total pressure
 $= 0.55 \times 27 = 14.85 \approx 15 \text{ bar}$

12. (a) : For *bcc* structure, $r = \frac{\sqrt{3}}{4}a$, where a is the unit cell edge length and r is the radius of the sphere (atom).
- $$r = \frac{\sqrt{3}}{4} \times 288 \text{ pm}$$

13. (c) : For a first order reaction,

$$k = \frac{2.303}{t} \log \frac{[R]_0}{[R]}$$

$$\Rightarrow t = \frac{2.303}{4.606 \times 10^{-3} \text{ s}^{-1}} \log \left(\frac{2}{0.2} \right) = \frac{2.303 \times 10^3}{4.606} = 500 \text{ s}$$



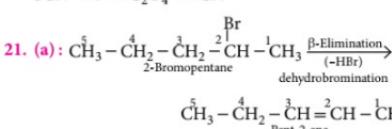
16. (c) : In CH_4 , oxidation number of carbon is -4 while in CCl_4 , oxidation number of carbon is $+4$. Thus, the change in oxidation number of carbon in the given reaction is from -4 to $+4$.

17. (b) : CO — neutral, BaO — basic, Al_2O_3 — amphoteric and Cl_2O_7 — acidic.

18. (c) : The carboxyhaemoglobin is about 300 times more stable than oxyhaemoglobin.

19. (c) : Measuring zeta potential is useful in determining stability of the colloidal particles.

20. (a) : According to spectrochemical series, order of increasing field strength is :
 $\text{SCN}^- < \text{F}^- < \text{C}_2\text{O}_4^{2-} < \text{CN}^-$



(More substituted alkene is formed, Zaitsev's rule.)

22. (a) : For free expansion of an ideal gas, $P_{ex} = 0$, $w = -P_{ex}\Delta V = 0$

For adiabatic process, $q = 0$

According to first law of thermodynamics,

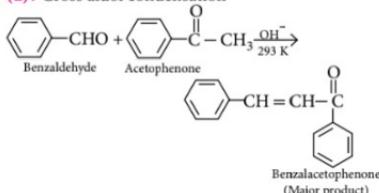
$$\Delta U = q + w = 0$$

As internal energy of an ideal gas is a function of temperature, $\Delta U = 0$, $\therefore \Delta T = 0$

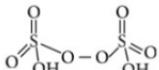
23. (d) : The oxidation states of Cr in CrO_4^{2-} and $\text{Cr}_2\text{O}_7^{2-}$ is same i.e., $+6$.

24. (d) : Unnilonium — Mendelevium \Rightarrow (a)-(i)
 Unniltrium — Lawrencium \Rightarrow (b)-(ii)
 Unnilhexium — Seaborgium \Rightarrow (c)-(iii)
 Unununium — Roentgenium \Rightarrow (d) \times (iv)

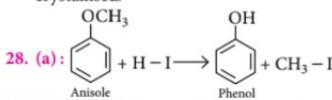
25. (d): Cross aldol condensation



26. (c): Peroxodisulphuric acid, $H_2S_2O_8$ has $-O-O-$ linkage.



27. (b): $CaCl_2$ and $MgCl_2$ are more soluble than $NaCl$. Thus, when HCl was passed through a solution containing $CaCl_2$, $MgCl_2$ and $NaCl$, only $NaCl$ got crystallised.



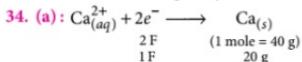
29. (d): (A) Solid CO_2 (dry ice) is used as refrigerant for ice-cream and frozen food.
(B) The structure of C_{60} contains twenty six-membered rings and twelve five-membered rings.
(C) and (D) are correct statements.

30. (d): In the reaction, $2Cl_{(g)} \rightarrow Cl_{2(g)}$, the randomness decreases as 2 moles of $Cl_{(g)}$ are converted to 1 mole of $Cl_{2(g)}$, thus, $\Delta_r S < 0$. And this is an exothermic reaction, thus, $\Delta_r H < 0$.

31. (b): Paper chromatography is a type of partition chromatography.

32. (c): Wurtz reaction is used for the preparation of higher alkanes containing even number of C-atoms. Thus this reaction cannot be used for the preparation of *n*-heptane.

33. (d): Collision frequency \propto no. of reacting molecules or atoms. Higher the concentration of reactant molecules, higher is the probability of collision and so the collision frequency.



Thus, one Faraday is required to produce 20 g of calcium from molten $CaCl_2$.

35. (a): Mixture of ethanol and acetone shows positive deviation from Raoult's law.

In pure ethanol, molecules are hydrogen bonded. On adding acetone, its molecules get in between the host molecules and break some of the hydrogen bonds between them. Due to weakening of interactions, the solution shows positive deviation from Raoult's law.

36. (a): $\Delta G = \Delta G^\circ + RT \ln Q$

At equilibrium, $\Delta G = 0$ and $Q = K_C$

$$\therefore 0 = \Delta G^\circ + RT \ln K_C \Rightarrow \Delta G^\circ = -RT \ln K_C \\ = -8.314 \text{ J K}^{-1} \text{ mol}^{-1} \times 300 \text{ K} \times \ln(2 \times 10^{13})$$

37. (c): In sucrose, two monosaccharides are held together by a glycosidic linkage between C-1 of $\alpha-D$ -glucose and C-2 of $\beta-D$ -fructose.

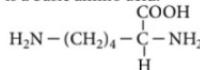


38. (b): $Cr: 3d^5 4s^1, Cr^{2+}: 3d^4$ has four unpaired electrons.

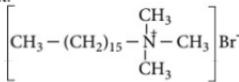
$$\mu = \sqrt{n(n+2)} = \sqrt{4(4+2)} = \sqrt{24} = 4.90 \text{ B.M.}$$

39. (a): *cis*-1, 4-polyisoprene is a natural rubber.

40. (d): Lysine is a basic amino acid.

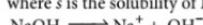


41. (c): Cetyltrimethyl ammonium bromide is a cationic detergent.



42. (a): $Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$

where s is the solubility of $Ni(OH)_2$.



0.1 M 0.1 M 0.1 M

$$[OH^-] = 2s + 0.1 \approx 0.1 \quad (\because 2s < < 0.1)$$

Ionic product of $Ni(OH)_2 = [Ni^{2+}][OH^-]^2$

$$2 \times 10^{-15} = s(0.1)^2$$

$$s = \frac{2 \times 10^{-15}}{0.1 \times 0.1} = 2 \times 10^{-13} \text{ M}$$

43. (a): He_2 does not exist as it has zero bond order.



$$\text{Bond order} = \frac{1}{2}(N_b - N_a) = \frac{1}{2}(2 - 2) = 0$$

44. (d): Potassium ions are the most abundant cations within cell fluids, where they activate many enzymes, participate in the oxidation of glucose to produce ATP and, with sodium, are responsible for the transmission of nerve signals.

45. (a): $^{175}_{71}\text{Lu}$, Number of protons = Number of electrons
= Atomic number = 71

Number of neutrons = Mass number - Atomic number
= 175 - 71 = 104



JEE Advanced

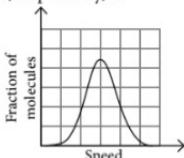
SOLVED PAPER 2020

PAPER - I

SECTION 1 (Maximum Marks : 18)

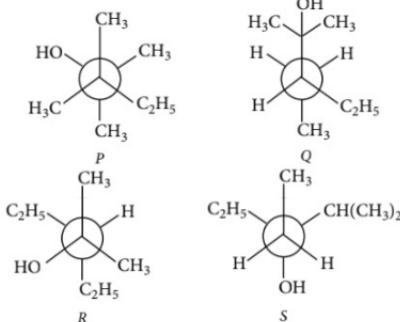
- This section contains SIX (06) questions.
- Each question has FOUR options. ONLY ONE of these four options is the correct answer.
- For each question, choose the option corresponding to the correct answer.
- Answer to each question will be evaluated according to the following marking scheme :
 - Full Marks : +3 If ONLY the correct option is chosen;
 - Zero Marks : 0 If none of the options is chosen (i.e., the question is unanswered);
 - Negative Marks : -1 In all other cases.

1. If the distribution of molecular speeds of a gas is as per the figure shown below, then the ratio of the most probable, the average, and the root mean square speeds, respectively, is



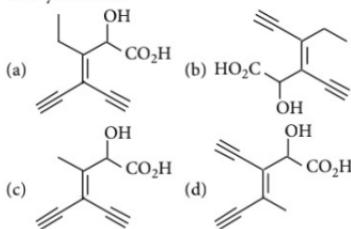
- (a) 1 : 1 : 1 (b) 1 : 1 : 1.224
 (c) 1 : 1.128 : 1.224 (d) 1 : 1.128 : 1
- 2. Which of the following liberates O₂ upon hydrolysis?
 (a) Pb₃O₄ (b) KO₂ (c) Na₂O₂ (d) Li₂O₂
- 3. A colourless aqueous solution contains nitrates of two metals, X and Y. When it was added to an aqueous solution of NaCl, a white precipitate was formed. This precipitate was found to be partly soluble in hot water to give a residue P and a solution Q. The residue P was soluble in aq. NH₃ and also in excess sodium thiosulphate. The hot solution Q gave a yellow precipitate with KI. The metals X and Y, respectively, are

- (a) Ag and Pb (b) Ag and Cd
 (c) Cd and Pb (d) Cd and Zn
4. Newman projections P, Q, R and S are shown below :

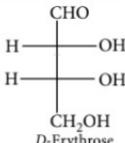


Which one of the following options represents identical molecules?

- (a) P and Q (b) Q and S
 (c) Q and R (d) R and S
- 5. Which one of the following structures has the IUPAC name 3-ethynyl-2-hydroxy-4-methylhex-3-en-5-ynoic acid?



6. The Fischer projection of *D*-erythroose is shown below :



D-Erythroose and its isomers are listed as P, Q, R, and S in Column-I. Choose the correct relationship of P, Q, R, and S with *D*-erythroose from Column-II.

	Column-I	Column-II
P.		1. Diastereomer
Q.		2. Identical
R.		3. Enantiomer
S.		

- (a) P \rightarrow 2, Q \rightarrow 3, R \rightarrow 2, S \rightarrow 2
- (b) P \rightarrow 3, Q \rightarrow 1, R \rightarrow 1, S \rightarrow 2
- (c) P \rightarrow 2, Q \rightarrow 1, R \rightarrow 1, S \rightarrow 3
- (d) P \rightarrow 2, Q \rightarrow 3, R \rightarrow 3, S \rightarrow 1

SECTION 2 (Maximum Marks : 24)

- This section contains SIX (06) questions.
- Each question has FOUR options. ONE OR MORE THAN ONE of these four option(s) is (are) correct answer(s).
- For each question, choose the option(s) corresponding to (all) the correct answer(s).
- Answer to each question will be evaluated according to the following marking scheme :

Full Marks : +4 If only (all) the correct option(s) is (are) chosen.

Partial Marks : +3 If all the four options are correct but ONLY three options are chosen.

Partial Marks : +2 If three or more options are correct but ONLY two options are chosen, both of which are correct.

Partial Marks : +1 If two or more options are correct but ONLY one option is chosen and it is a correct option.

Zero Marks : 0 If none of the options is chosen (i.e., the question is unanswered).

Negative Marks : -2 In all other cases.

7. In thermodynamics, the *P* – *V* work done is given by
 $w = -\int dV P_{ext}$.

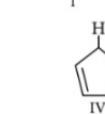
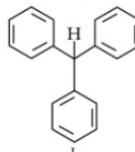
For a system undergoing a particular process, the work done is,

$$w = -\int dV \left(\frac{RT}{V-b} - \frac{a}{V^2} \right)$$

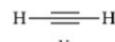
This equation is applicable to a

- (a) system that satisfies the van der Waals equation of state
- (b) process that is reversible and isothermal
- (c) process that is reversible and adiabatic
- (d) process that is irreversible and at constant pressure.

8. With respect to the compounds I-V, choose the correct statement(s).



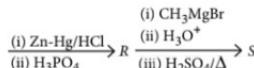
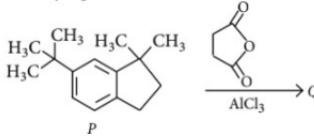
III



II

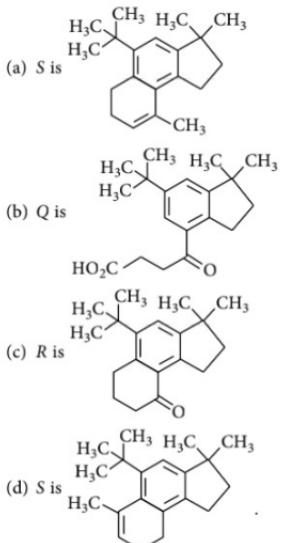
- (a) The acidity of compound I is due to delocalization in the conjugate base.
- (b) The conjugate base of compound IV is aromatic.
- (c) Compound II becomes more acidic, when it has a $-\text{NO}_2$ substituent.
- (d) The acidity of compounds follows the order I > IV > V > II > III.

9. In the reaction scheme shown below, Q, R, and S are the major products.

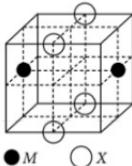


The correct structure of





10. Choose the correct statement(s) among the following.
- $[\text{FeCl}_4]^-$ has tetrahedral geometry.
 - $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ has 2 geometrical isomers.
 - $[\text{FeCl}_4]^-$ has higher spin-only magnetic moment than $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$.
 - The cobalt ion in $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ has $sp^3 d^2$ hybridization.
11. With respect to hypochlorite, chlorate and perchlorate ions, choose the correct statement(s).
- The hypochlorite ion is the strongest conjugate base.
 - The molecular shape of only chlorate ion is influenced by the lone pair of electrons of Cl.
 - The hypochlorite and chlorate ions disproportionate to give rise to identical set of ions.
 - The hypochlorite ion oxidises the sulphite ion.
12. The cubic unit cell structure of a compound containing cation M and anion X is shown below. When compared to the anion, the cation has smaller ionic radius. Choose the correct statement(s).



- The empirical formula of the compound is MX .
- The cation M and anion X have different coordination geometries.
- The ratio of M-X bond length to the cubic unit cell edge length is 0.866.
- The ratio of the ionic radii of cation M to anion X is 0.414.

SECTION 3 (Maximum Marks : 24)

- This section contains SIX (06) questions. The answer to each question is a NUMERICAL VALUE.
- For each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, truncate/round-off the value to TWO decimal places.
- Answer to each question will be evaluated according to the following marking scheme :

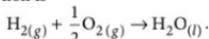
Full Marks :	+4 If ONLY the correct numerical value is entered.
Zero Marks :	0 In all other cases.

13. 5.00 mL of 0.10 M oxalic acid solution taken in a conical flask is titrated against NaOH from a burette using phenolphthalein indicator. The volume of NaOH required for the appearance of permanent faint pink colour is tabulated below for five experiments. What is the concentration, in molarity, of the NaOH solution?

Exp. No.	Vol. of NaOH (mL)
1.	12.5
2.	10.5
3.	9.0
4.	9.0
5.	9.0

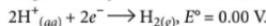
14. Consider the reaction, $A \rightleftharpoons B$ at 1000 K. At time t' , the temperature of the system was increased to 2000 K and the system was allowed to reach equilibrium. Throughout this experiment the partial pressure of A was maintained at 1 bar. Given below is the plot of the partial pressure of B with time. What is the ratio of the standard Gibbs energy of the reaction at 1000 K to that at 2000 K?
-

15. Consider a 70% efficient hydrogen-oxygen fuel cell working under standard conditions at 1 bar and 298 K. Its cell reaction is



The work derived from the cell on the consumption of 1.0×10^{-3} mol of $\text{H}_{2(g)}$ is used to compress 1.00 mol of a monoatomic ideal gas in a thermally insulated container. What is the change in the temperature (in K) of the ideal gas?

The standard reduction potentials for the two half-cells are given below :



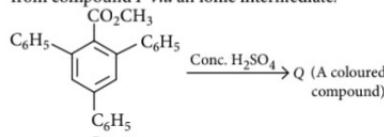
$$\text{Use } F = 96500 \text{ C mol}^{-1}, R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}.$$

16. Aluminium reacts with sulphuric acid to form aluminium sulphate and hydrogen. What is the volume of hydrogen gas in liters (L) produced at 300 K and 1.0 atm pressure, when 5.4 g of aluminium and 50.0 mL

of 5.0 M sulphuric acid are combined for the reaction? (Use molar mass of aluminium as 27.0 g mol⁻¹, $R = 0.082 \text{ atm L mol}^{-1} \text{ K}^{-1}$)

17. ^{238}U is known to undergo radioactive decay to form ^{206}Pb by emitting alpha and beta particles. A rock initially contained 68×10^{-6} g of ^{238}U . If the number of alpha particles that it would emit during its radioactive decay of ^{238}U to ^{206}Pb in three half-lives is $Z \times 10^{18}$, then what is the value of Z ?

18. In the following reaction, compound Q is obtained from compound P via an ionic intermediate.



What is the degree of unsaturation of Q?

PAPER - II

SECTION 1 (Maximum Marks : 18)

- This section contains SIX (06) questions.
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, BOTH INCLUSIVE.
- For each question, enter the correct integer corresponding to the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer.
- Answer to each question will be evaluated according to the following marking scheme :

Full Marks : +3 If ONLY the correct integer is entered.

Zero Marks : 0 If the question is unanswered;

Negative Marks : -1 In all other cases.

1. The 1st, 2nd, and the 3rd ionization enthalpies, I_1 , I_2 , and I_3 , of four atoms with atomic numbers n , $n + 1$, $n + 2$, and $n + 3$, where $n < 10$, are tabulated below. What is the value of n ?

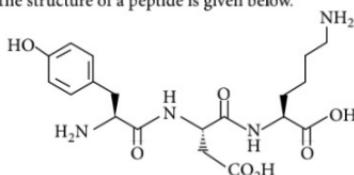
Atomic number	Ionization Enthalpy (kJ/mol)		
	I_1	I_2	I_3
n	1681	3374	6050
$n + 1$	2081	3952	6122
$n + 2$	496	4562	6910
$n + 3$	738	1451	7733

2. Consider the following compounds in the liquid form : O_2 , HF , H_2O , NH_3 , H_2O_2 , CCl_4 , CHCl_3 , C_6H_6 , $\text{C}_6\text{H}_5\text{Cl}$. When a charged comb is brought near their flowing stream, how many of them show deflection as per the following figure?

-
3. In the chemical reaction between stoichiometric quantities of KMnO_4 and KI in weakly basic solution, what is the number of moles of I_2 released for 4 moles of KMnO_4 consumed?

4. An acidified solution of potassium chromate was layered with an equal volume of amyl alcohol. When it was shaken after the addition of 1 mL of 3% H_2O_2 , a blue alcohol layer was obtained. The blue colour is due to the formation of a chromium(VI) compound 'X'. What is the number of oxygen atoms bonded to chromium through only single bonds in a molecule of X?

5. The structure of a peptide is given below.

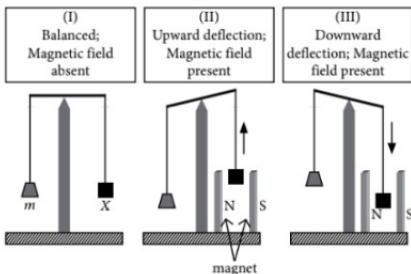


- If the absolute values of the net charge of the peptide at pH=2, pH=6, and pH=11 are $|z_1|$, $|z_2|$, and $|z_3|$, respectively, then what is $|z_1|+|z_2|+|z_3|$?
6. An organic compound ($C_8H_{10}O_2$) rotates plane-polarized light. It produces pink colour with neutral $FeCl_3$ solution. What is the total number of all the possible isomers for this compound?

SECTION 2 (Maximum Marks : 24)

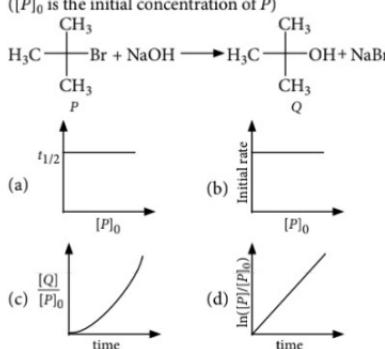
- This section contains SIX (06) questions.
 - Each question has FOUR options. ONE OR MORE THAN ONE of these four option(s) is (are) correct answer(s).
 - For each question, choose the option(s) corresponding to (all) the correct answer(s).
 - Answer to each question will be evaluated according to the following marking scheme :
- | | |
|-------------------------|--|
| Full Marks : | + 4 If only (all) the correct option(s) is (are) chosen; |
| Partial Marks : | + 3 If all the four options are correct but ONLY three options are chosen; |
| Partial Marks : | + 2 If three or more options are correct but ONLY two options are chosen, and both of which are correct; |
| Partial Marks : | + 1 If two or more options are correct but ONLY one option is chosen and it is a correct option; |
| Zero Marks : | 0 If none of the options is chosen (i.e., the question is unanswered); |
| Negative Marks : | - 2 In all other cases. |

7. In an experiment, m grams of a compound X (gas/liquid/solid) taken in a container is loaded in a balance as shown in figure I below. In the presence of a magnetic field, the pan with X is either deflected upwards (figure II), or deflected downwards (figure III), depending on the compound X . Identify the correct statement(s).



- (a) If X is $H_2O(l)$, deflection of the pan is upwards.
 (b) If X is $K_4[Fe(CN)_6]_{(s)}$, deflection of the pan is upwards.
 (c) If X is $O_2(g)$, deflection of the pan is downwards.
 (d) If X is $C_6H_6(l)$, deflection of the pan is downwards.

8. Which of the following plots is(are) correct for the given reaction?
 $([P]_0)$ is the initial concentration of P)



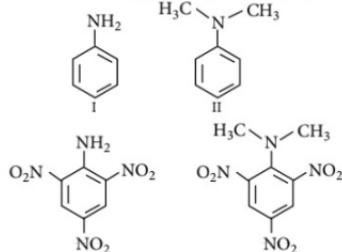
9. Which among the following statement(s) is(are) true for the extraction of aluminium from bauxite?

- (a) Hydrated Al_2O_3 precipitates, when CO_2 is bubbled through a solution of sodium aluminate.
 (b) Addition of Na_3AlF_6 lowers the melting point of alumina.
 (c) CO_2 is evolved at the anode during electrolysis.
 (d) The cathode is a steel vessel with a lining of carbon.

10. Choose the correct statement(s) among the following.

- (a) $SnCl_2 \cdot 2H_2O$ is a reducing agent.
 (b) SnO_2 reacts with KOH to form $K_2[Sn(OH)_6]$.
 (c) A solution of $PbCl_2$ in HCl contains Pb^{2+} and Cl^- ions.
 (d) The reaction of Pb_3O_4 with hot dilute nitric acid to give PbO_2 is a redox reaction.

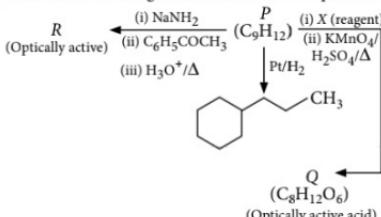
11. Consider the following four compounds I, II, III, and IV.



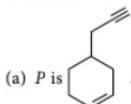
Choose the correct statement(s).

- (a) The order of basicity is II > I > III > IV.
- (b) The magnitude of pK_b difference between I and II is more than that between III and IV.
- (c) Resonance effect is more in III than in IV.
- (d) Steric effect makes compound IV more basic than III.

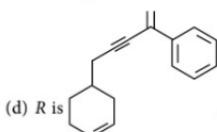
12. Consider the following transformations of a compound P.



Choose the correct option(s).



(b) X is Pd-C/quinoline/ H_2 .

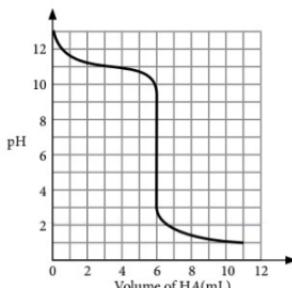


SECTION 3 (Maximum Marks : 24)

- This section contains SIX (06) questions. The answer to each question is a NUMERICAL VALUE.
 - For each question, enter the correct numerical value of the answer using the mouse and the on-screen virtual numeric keypad in the place designated to enter the answer. If the numerical value has more than two decimal places, truncate/round-off the value to TWO decimal places.
 - Answer to each question will be evaluated according to the following marking scheme:
- Full Marks : +4** If ONLY the correct numerical value is entered;
- Zero Marks : 0** In all other cases.

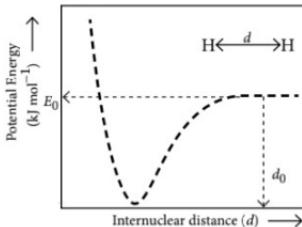
13. A solution of 0.1 M weak base (B) is titrated with 0.1 M of a strong acid (HA). The variation of pH

of the solution with the volume of HA added is shown in the figure below. What is the pK_b of the base? The neutralization reaction is given by $B + \text{HA} \rightarrow \text{BH}^+ + \text{A}^-$.



14. Liquids A and B form ideal solution for all compositions of A and B at 25°C . Two such solutions with 0.25 and 0.50 mole fractions of A have the total vapour pressures of 0.3 and 0.4 bar, respectively. What is the vapour pressure of pure liquid B in bar?

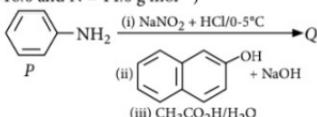
15. The figure below is the plot of potential energy versus internuclear distance (d) of H_2 molecule in the electronic ground state.



What is the value of the net potential energy E_0 (as indicated in the figure) in kJ mol^{-1} , for $d = d_0$ at which the electron-electron repulsion and the nucleus-nucleus repulsion energies are absent? As reference, the potential energy of H atom is taken as zero when its electron and the nucleus are infinitely far apart. Use Avogadro constant as $6.023 \times 10^{23} \text{ mol}^{-1}$.

16. Consider the reaction sequence from P to Q shown below. The overall yield of the major product Q from P is 75%. What is the amount in grams of

Q obtained from 9.3 mL of P? (Use density of $P = 1.00 \text{ g mL}^{-1}$; Molar mass of C = 12.0, H = 1.0, O = 16.0 and N = 14.0 g mol $^{-1}$)



17. Tin is obtained from cassiterite by reduction with coke.

Use the data given below to determine the minimum temperature (in K) at which the reduction of cassiterite by coke would take place.

$$\begin{aligned}\text{At } 298 \text{ K : } \Delta_f H^\circ(\text{SnO}_{2(s)}) &= -581.0 \text{ kJ mol}^{-1}, \\ \Delta_f H^\circ(\text{CO}_{2(g)}) &= -394.0 \text{ kJ mol}^{-1}, \\ S^\circ(\text{SnO}_{2(s)}) &= 56.0 \text{ J K}^{-1}\text{mol}^{-1}, \\ S^\circ(\text{Sn}_{(s)}) &= 52.0 \text{ J K}^{-1}\text{mol}^{-1}, \\ S^\circ(\text{C}_{(s)}) &= 6.0 \text{ J K}^{-1}\text{mol}^{-1}, \\ S^\circ(\text{CO}_{2(g)}) &= 210.0 \text{ J K}^{-1}\text{mol}^{-1}.\end{aligned}$$

Assume that the enthalpies and the entropies are temperature independent.

18. An acidified solution of 0.05 M Zn²⁺ is saturated with 0.1 M H₂S. What is the minimum molar concentration (M) of H⁺ required to prevent the precipitation of ZnS?

Use $K_{sp}(\text{ZnS}) = 1.25 \times 10^{-22}$ and overall dissociation constant of H₂S, $K_{\text{NET}} = K_1 K_2 = 1 \times 10^{-21}$.

SOLUTIONS

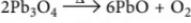
PAPER - I

1. (b): Graph represents symmetrical distribution of speed and hence, the most probable and the average speed should be same. But the root mean square speed must be greater than average speed as it is calculated by the square root of the average of the squares of the speeds of molecules.

2. (b): Only KO₂ upon hydrolysis liberates O₂ gas.



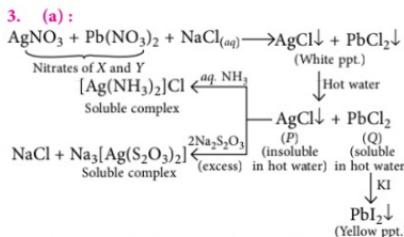
Pb₃O₄ on thermal decomposition produces O₂ gas.



Na₂O₂ on hydrolysis produces NaOH and H₂O₂.

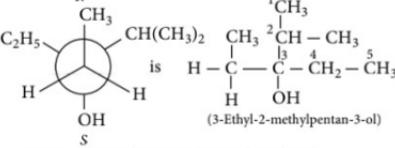
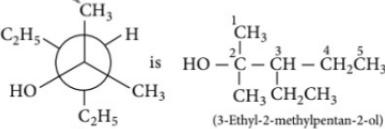
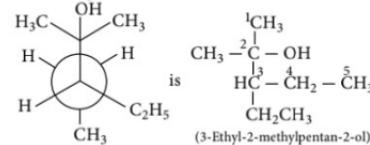
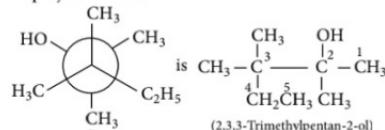


Similarly,



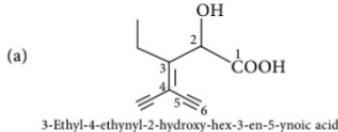
Thus, metal 'X' is Ag and metal 'Y' is Pb.

4. (c) : Write the structures for each Newman projections as :

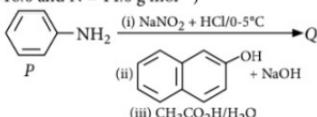


Hence, Q and R are identical molecules.

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SOLUTIONS

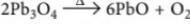
PAPER - I

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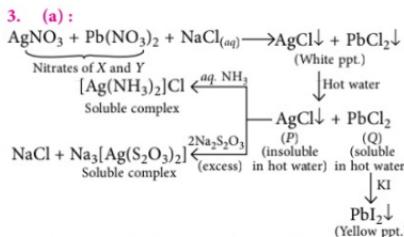
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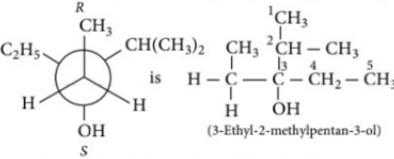
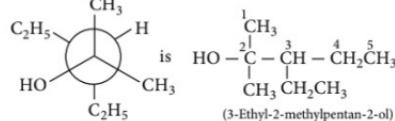
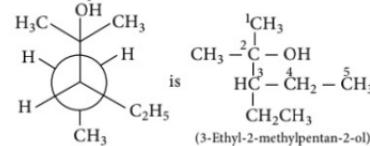
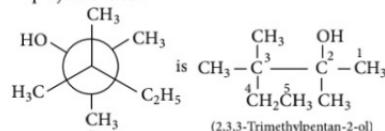


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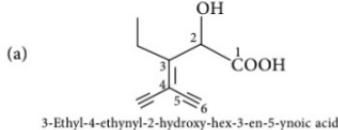
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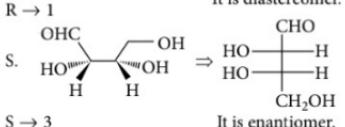
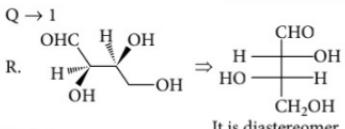
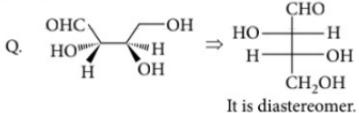
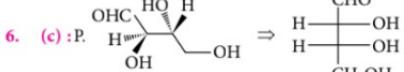
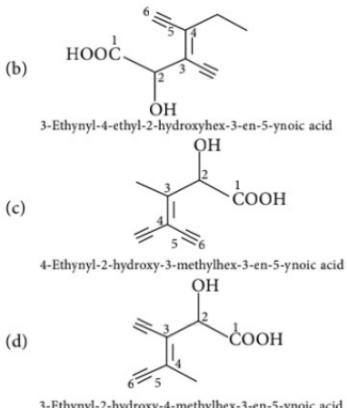
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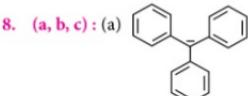


7. (a, b, c) : The following expression of $P \cdot V$ work done
 $w = -\int p_{ext} dV$

is applicable for reversible isobaric as well as isothermal and adiabatic processes. If p_{ext} is substituted for a van der Waals equation then it becomes

$$w = -\int \left(\frac{RT}{V-b} - \frac{a}{V^2} \right) dV$$

But it is not applicable for irreversible processes which are carried out very fast. So, work done is calculated assuming final pressure remains constant throughout the process.



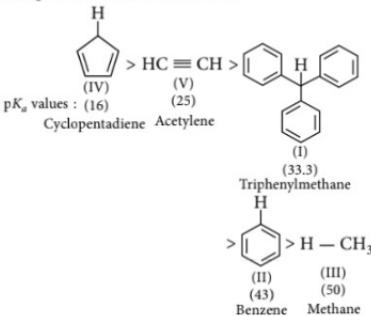
Conjugate base of compound (I) is stabilised due to delocalisation of -ve charge among three benzene rings. As a result of which (I) is acidic in nature.



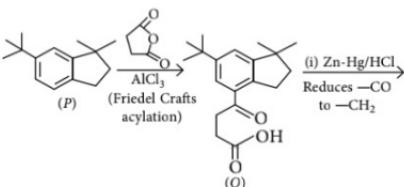
Conjugate base of compound (IV) is aromatic in nature due to planarity and $(4n + 2) \pi$ -electrons (i.e., 6 π -electrons).

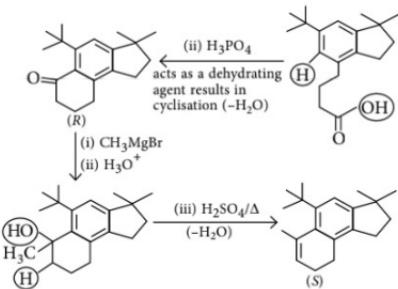
(c) --NO_2 is an electron withdrawing group thus, it increases the acidic strength of any compound to which it is attached.

(d) pK_a values give the order of acidic strength of given compounds. Smaller the pK_a value, more acidic will be the compound. The acidity of given compounds follows the order :



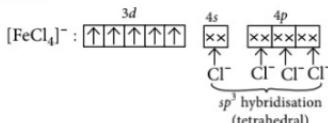
9. (b, d) :





Thus, (b) and (d) are correct options.

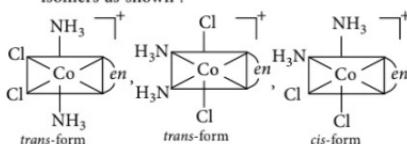
- 10. (a, c)** : (a) $[\text{FeCl}_4]^-$; Co^{3+} : $3d^5 4s^0$



As Cl is a weak field ligand, no pairing of electrons takes place. Thus, $[\text{FeCl}_4]^-$ has tetrahedral geometry with sp^3 hybridisation.

Thus, (a) is correct statement.

(b) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ has three geometrical isomers as shown :

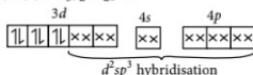


Thus, (b) is incorrect statement.

(c) $[\text{FeCl}_4]^-$ has five unpaired electrons thus, it has higher spin-only magnetic moment than $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ which has zero unpaired electron. Thus, (c) is the correct statement.

(d) $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$; Co^{3+} : $3d^6 4s^0$

$[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$:

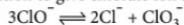


As en and NH_3 are strong field ligands, pairing of electrons takes place. Thus, Co^{3+} ion in $[\text{Co}(\text{en})(\text{NH}_3)_2\text{Cl}_2]^+$ has d^2sp^3 hybridisation. Hence, option (d) is incorrect statement.

- 11. (a, b, d)** : (a) Hypochlorous acid (HOCl) is the weakest acid among oxoacids of chlorine, thus, its conjugate base (OCl^-) is the strongest base. Thus, (a) is the correct statement.

(b) In chloride ion, bond angle decreases due to the presence of lone pair of electrons on chlorine-atom.

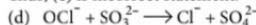
(c) Hypochlorite ions disproportionate in basic solution to give chloride ion and perchlorate ion.



The chlorate ions disproportionate in basic solution to give chloride ion and perchlorate ion.



Thus, (c) is incorrect statement.



Thus, hypochlorite ion oxidises sulphite ion to sulphate ion. Hence, (d) is the correct statement.

- 12. (a, c)** : Contribution of $M = \frac{1}{2} \times 2 = 1$

$$\text{Contribution of } X = \frac{1}{4} \times 4 = 1$$

$$\therefore \text{Empirical formula} = MX$$

Distance between M and X , i.e., bond length of $M-X$ bond

$$= \sqrt{\frac{a^2 + a^2}{4}} = \sqrt{\frac{3}{4}}a = \frac{\sqrt{3}}{2}a = 0.866a$$

Both cation, M and anion, X have same coordination number i.e., 8.

Assuming, anions are in contact, the ratio of ionic radii of cation M to anion X is 0.732, the minimum radius ratio for a cubical void.

- 13. (0.11)** : Given : $M_1 = 0.10 \text{ M}$, $V_1 = 5.00 \text{ mL}$, $M_2 = ?$, $V_2 = 9.0 \text{ mL}$

$$(M_1 V_1)_{\text{oxalic acid}} = \frac{1}{2} \times (M_2 V_2)_{\text{NaOH}}$$

$$0.10 \times 5.00 = \frac{1}{2} \times (M_2 \times 9.0)$$

$$M_2 = \frac{2 \times 0.10 \times 5.00}{9.0} = 0.11 \text{ M}$$

- 14. (0.25)** : Given : $T_1 = 1000 \text{ K}$, $T_2 = 2000 \text{ K}$, $p_A = 1 \text{ bar}$, $(p_B)_{\text{initial}} = 10 \text{ bar}$ and $(p'_B)_{\text{final}} = 100 \text{ bar}$

For reaction, $A \rightleftharpoons B$

$$K_{P_1} = \frac{P_B}{P_A} = \frac{10}{1} \text{ and } K_{P_2} = \frac{P'_B}{P_A} = \frac{100}{1}$$

At equilibrium, $\Delta G^\circ = -RT \ln K_p$

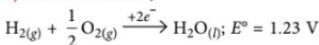
$$\Delta G_1^\circ = -RT_1 \ln K_{P_1} \quad \dots(i)$$

$$\Delta G_2^\circ = -RT_2 \ln K_{P_2} \quad \dots(ii)$$

On dividing equation (i) by (ii), we get

$$\begin{aligned}\frac{\Delta G_1^\circ}{\Delta G_2^\circ} &= \frac{T_1}{T_2} \times \frac{\ln K_{P_1}}{\ln K_{P_2}} \\ &= \frac{1000}{2000} \times \frac{\ln(10)}{\ln(100)} = \frac{1}{2} \times \frac{2.303}{2.303 \times 2} \\ &= \frac{1}{2} \times \frac{1}{2} = \frac{1}{4} = 0.25\end{aligned}$$

15. (13.32): For the reaction,



$$\Delta_r G^\circ = -nFE_\text{cell} = -2 \times 96500 \times 1.23 \text{ J mol}^{-1}$$

Work derived from this cell,

$$\begin{aligned}w &= \left(\frac{70}{100} \right) \times (-\Delta_r G^\circ) \times 1 \times 10^{-3} \text{ mol} \\ &= 0.7 \times (2 \times 96500 \times 1.23 \text{ J mol}^{-1}) \times 1 \times 10^{-3} \text{ mol} \\ &= 166.173 \text{ J} \\ \therefore w &= 166.173 \text{ J}\end{aligned}$$

This work done = Change in internal energy of monoatomic gas ($\because q = 0$)

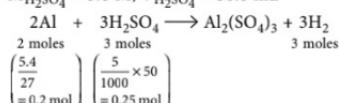
$$\therefore w = \Delta U$$

$$w = nC_{v,m} \cdot \Delta T$$

$$\begin{aligned}166.173 &= 1 \times \frac{3}{2} R \times \Delta T \\ (\because C_{v,m} &= \frac{3R}{2} \text{ for monoatomic gas}) \\ \Delta T &= \frac{166.173 \times 0.66}{8.314} = 13.32 \text{ K}\end{aligned}$$

16. (6.15): Given : $T = 300 \text{ K}$, $P = 1 \text{ atm}$, $w_{\text{Al}} = 5.4 \text{ g}$

$$M_{\text{H}_2\text{SO}_4} = 5.0 \text{ M}, V_{\text{H}_2\text{SO}_4} = 50.0 \text{ mL}$$



Thus, for 2 moles of Al, 3 moles of H_2SO_4 is required i.e., for 0.2 mol of Al, 0.3 mol of H_2SO_4 is required but the moles of H_2SO_4 available is 0.25 mol thus, H_2SO_4 is the limiting reagent. So, 0.25 mol of H_2 will be produced i.e., $n = 0.25 \text{ mol}$.

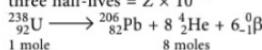
$$PV = nRT$$

$$1 \times V = 0.25 \times 0.082 \times 300$$

$$V = 6.15 \text{ L}$$

17. (1.20): Given : Mass of $^{238}_{92}\text{U} = 68 \times 10^{-6} \text{ g}$.

Number of ^4He particles (α -particles) emitted in three half-lives = $Z \times 10^{18}$



$$\text{Moles of } ^{238}_{92}\text{U} = \frac{68 \times 10^{-6}}{238} = 0.286 \times 10^{-6} \text{ mol}$$

$$= 0.286 \times 10^{-6} \times N_A \text{ particles}$$

$$= 0.286 \times 10^{-6} \times 6.023 \times 10^{23} \text{ particles}$$

$$= 1.72 \times 10^{17} \text{ particles/atoms}$$

Amount of the substance left after ' n ' half lives

$$= \frac{[N]_0}{2^n}$$

$$\text{Amount of } ^{238}_{92}\text{U left after 3 half-lives} = \frac{1.72 \times 10^{17}}{(2)^3}$$

$$= 0.215 \times 10^{17}$$

Thus, amount of $^{238}_{92}\text{U}$ decayed

$$= 1.72 \times 10^{17} - 0.215 \times 10^{17} = 1.505 \times 10^{17}$$

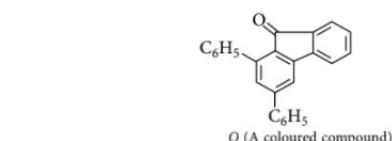
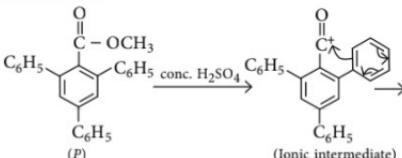
Hence, number of α -particles produced

$$= 8 \times 1.505 \times 10^{17} = 12.04 \times 10^{17}$$

$$= 1.204 \times 10^{18} \approx Z \times 10^{18}$$

$$\therefore Z = 1.204 \approx 1.20$$

18. (18.00):



Degree of unsaturation = $(2 \times \text{no. of Carbon atoms}) + 2 - \text{no. of Hydrogen atoms}$

$$= \frac{(2 \times 25) + 2 - 16}{2} = \frac{36}{2} = 18$$

(Oxygen has no effect on degree of unsaturation)

Thus, degree of unsaturation in Q = 18.

PAPER II

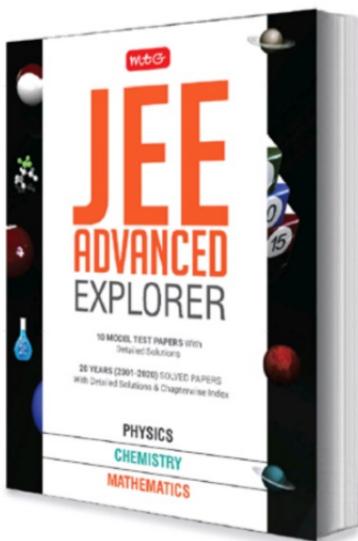
ANSWER KEY

- | | | | |
|--------------|--------------|----------------|-----------|
| 1. (9) | 2. (6) | 3. (6) | 4. (4) |
| 5. (5) | 6. (6) | 7. (a,b,c) | 8. (a) |
| 9. (a,b,c,d) | 10. (a,b) | 11. (c,d) | 12. (b,c) |
| 13. (3.00) | 14. (0.20) | 15. (-5246.03) | |
| 16. (18.60) | 17. (935.00) | 18. (0.20) | |



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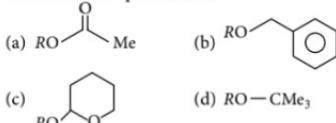
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JEE MAIN 2020

1. Which of the following derivatives of alcohol is unstable in an aqueous base?



2. The values of the crystal field stabilization energies for a high spin d^6 metal ion in octahedral and tetrahedral fields, respectively, are

(a) $-0.4 \Delta_o$ and $-0.6 \Delta_t$ (b) $-2.4 \Delta_o$ and $-0.6 \Delta_t$
 (c) $-1.6 \Delta_o$ and $-0.4 \Delta_t$ (d) $-0.4 \Delta_o$ and $-0.27 \Delta_t$

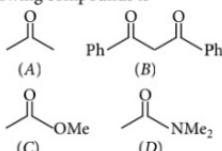
3. Consider the following reaction :



For each of the following cases (1, 2), the direction in which the equilibrium shifts is

- (1) temperature is decreased
 (2) pressure is increased by adding N_2 at constant T .
 (a) (1) towards product, (2) towards reactant
 (b) (1) towards reactant, (2) towards product
 (c) (1) towards reactant, (2) no change
 (d) (1) towards product, (2) no change.

4. The increasing order of the acidity of the α -hydrogen of the following compounds is

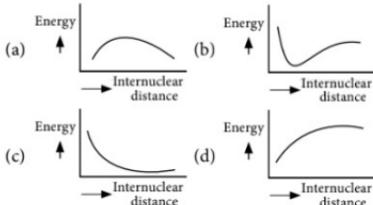


- (a) (D) < (C) < (A) < (B)
 (b) (B) < (C) < (A) < (D)
 (c) (A) < (C) < (D) < (B)
 (d) (C) < (A) < (B) < (D)

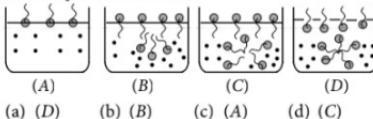
5. A diatomic molecule X_2 has a body-centred cubic (*bcc*) structure with a cell edge of 300 pm. The density of the molecule is 6.17 g cm^{-3} . The number of molecules present in 200 g of X_2 is (Avogadro constant (N_A) = $6 \times 10^{23} \text{ mol}^{-1}$)

(a) $40 N_A$ (b) $8 N_A$ (c) $4 N_A$ (d) $2 N_A$

6. The potential energy curve for the H_2 molecule as a function of internuclear distance is



7. Identify the correct molecular picture showing what happens at the critical micellar concentration (CMC) of an aqueous solution of a surfactant (● polar head; ○ non-polar tail; • water).



8. The difference between the radii of 3rd and 4th orbits of Li^{2+} is ΔR_1 . The difference between the radii of 3rd and 4th orbits of He^+ is ΔR_2 . Ratio $\Delta R_1 : \Delta R_2$ is

(a) 8 : 3 (b) 3 : 8
 (c) 2 : 3 (d) 3 : 2

9. In the sixth period, the orbitals that are filled are

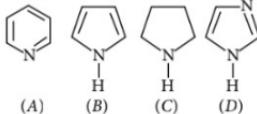
(a) 6s, 4f, 5d, 6p (b) 6s, 5d, 5f, 6p
 (c) 6s, 5f, 6d, 6p (d) 6s, 6p, 6d, 6f

10. The most appropriate reagent for conversion of C_2H_5CN into $CH_3CH_2CH_2NH_2$ is
 (a) $NaBH_4$ (b) CaH_2
 (c) $LiAlH_4$ (d) $Na(CN)BH_3$

11. If a person is suffering from the deficiency of nor-adrenaline, what kind of drug can be suggested?
 (a) Anti-inflammatory (b) Antidepressant
 (c) Antihistamine (d) Analgesic
12. Which of the following is not an essential amino acid?
 (a) Tyrosine (b) Leucine
 (c) Valine (d) Lysine

13. The correct electronic configuration and spin-only magnetic moment (BM) of Gd^{3+} ($Z = 64$), respectively, are
 (a) $[Xe] 4f^7$ and 8.9 (b) $[Xe] 4f^7$ and 7.9
 (c) $[Xe] 5f^7$ and 8.9 (d) $[Xe] 5f^7$ and 7.9

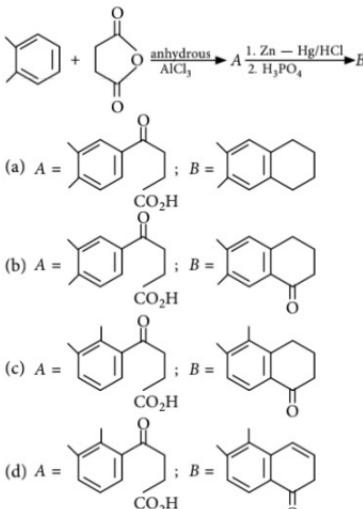
14. The increasing order of basicity of the following compounds is



- (A) $(A) < (B) < (C) < (D)$ (B) $(B) < (A) < (D) < (C)$
 (C) $(D) < (A) < (B) < (C)$ (D) $(B) < (A) < (C) < (D)$

15. A flask contains a mixture of compounds *A* and *B*. Both compounds decompose by first-order kinetics. The half-lives for *A* and *B* are 300 s and 180 s, respectively. If the concentrations of *A* and *B* are equal initially, the time required for the concentration of *A* to be four times that of *B* (in s) is (Use $\ln 2 = 0.693$)
 (a) 180 (b) 900 (c) 300 (d) 120

16. The structure of PCl_5 in the solid state is
 (a) tetrahedral $[PCl_4]^+$ and octahedral $[PCl_6]^-$
 (b) square planar $[PCl_4]^+$ and octahedral $[PCl_6]^-$
 (c) square pyramidal (d) trigonal bipyramidal.
17. An Ellingham diagram provides information about
 (a) the conditions of pH and potential under which a species is thermodynamically stable
 (b) the temperature dependence of the standard Gibbs energies of formation of some metal oxides
 (c) the pressure dependence of the standard electrode potentials of reduction reactions involved in the extraction of metals
 (d) the kinetics of the reduction process.
18. In the following reaction sequence the major products *A* and *B* are



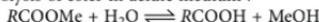
19. The equation that represents the water-gas shift reaction is
 (a) $\text{CH}_4(g) + \text{H}_2\text{O}(g) \xrightarrow[1270 \text{ K}]{\text{Ni}} \text{CO}(g) + 3\text{H}_2(g)$
 (b) $2\text{C}_{(s)} + \text{O}_{2(g)} + 4\text{N}_{2(g)} \xrightarrow[1273 \text{ K}]{\text{Ni}} 2\text{CO}_{(g)} + 4\text{N}_{2(g)}$
 (c) $\text{C}_{(s)} + \text{H}_2\text{O}_{(g)} \xrightarrow[1270 \text{ K}]{\text{Ni}} \text{CO}_{(g)} + \text{H}_{2(g)}$
 (d) $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \xrightarrow[673 \text{ K}]{\text{Catalyst}} \text{CO}_{2(g)} + \text{H}_{2(g)}$
20. The condition that indicates a polluted environment is
 (a) eutrophication
 (b) 0.03% of CO_2 in the atmosphere
 (c) BOD value of 5 ppm
 (d) pH of rain water to be 5.6.
21. The minimum number of moles of O_2 required for complete combustion of 1 mole of propane and 2 moles of butane is _____.
 22. The total number of coordination sites in ethylene diaminetetraacetate (EDTA $^{4-}$) is _____.
 23. The number of chiral carbon(s) present in peptide, Ile-Arg-Pro, is _____.
 24. A soft drink was bottled with a partial pressure of CO_2 of 3 bar over the liquid at room temperature. The partial pressure of CO_2 over the solution approaches a value of 30 bar when 44 g of CO_2 is dissolved in 1 kg of water at room temperature. The approximate pH of the soft drink is $\text{log } 2 = 0.3$; density of the soft drink = 1 g mL $^{-1}$;
 $\text{log } 2 = 0.3$; density of the soft drink = 1 g mL $^{-1}$)

25. An oxidation-reduction reaction in which 3 electrons are transferred has a ΔG° of $17.37 \text{ kJ mol}^{-1}$ at 25°C . The value of E_{cell}° (in V) is $\underline{\quad} \times 10^{-2}$. ($1 \text{ F} = 96,500 \text{ C mol}^{-1}$)

SOLUTIONS

1. (a) : Hydrolysis of esters occur in both acidic and basic medium.

Hydrolysis of ester in acidic medium :



The reaction is in equilibrium so reaction does not go to completion.

Hydrolysis of ester in basic medium :

In this case carboxylic acid is neutralized by the base as fast as it is formed. According to Le-Chatelier's principle, this pull the position of equilibrium to the right.



Thus, yield is 100%. Therefore, esters are unstable in basic medium.

2. (a) : For high spin complex,

$$d^6 \text{ (In octahedral field)} = t_{2g}^4 e_g^2$$

$$d^6 \text{ (In tetrahedral field)} = e^3 t_2^3$$

$$\text{CFSE in octahedral field} = (-0.4x_{t_{2g}} + 0.6y_{e_g})\Delta_o$$

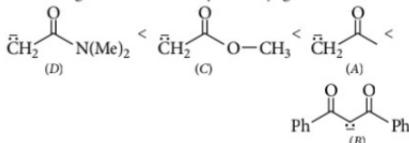
$$= (-0.4(4) + 0.6(2))\Delta_o = -0.4 \Delta_o$$

$$\text{CFSE in tetrahedral field} = (-0.6x_e + 0.4y_{t_2})\Delta_t$$

$$= (-0.6(3) + 0.4(3))\Delta_t = -0.6 \Delta_t$$

3. (c) : The given reaction is endothermic. According to Le-Chatelier's principle, the increase of temperature will favour the forward reaction while the decrease of temperature will favour the backward reaction. On increasing pressure by adding inert gas at constant temperature, equilibrium will not shift.

4. (a) : Acidity \propto stability of conjugate base. The increasing order of stability of conjugate base is



This is the correct order of acidic strength of α hydrogen of the given compounds.

5. (c) : Edge length, $a = 300 \text{ pm}$, density, $d = 6.17 \text{ g cm}^{-3}$

$$\text{For bcc, } Z = 2, \text{ Density, } d = \frac{Z \times M}{a^3 \times N_A}$$

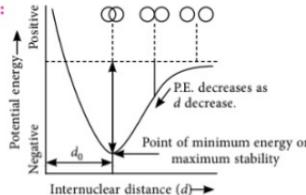
$$6.17 = \frac{2 \times M}{6.02 \times 10^{23} \times (300 \times 10^{-10})^3} = \frac{2M}{6.02 \times 2.7}$$

$$M = 50 \text{ g/mol}$$

$$\text{Number of moles} = \frac{\text{Mass}}{\text{Molar mass}} = \frac{200 \text{ g}}{50 \text{ g/mol}} = 4 \text{ mol}$$

$$\therefore \text{Number of molecules} = 4 N_A$$

6. (b) :



The minima in the curve corresponds to the most stable state of H_2 .

7. (a) : At CMC, the anions are pulled into the bulk of the solution and they aggregate to form a spherical shape with their hydrocarbon chain pointing towards the centre of the sphere with COO^- part remaining outward on the surface of sphere.

8. (c) : For H-like particles, the radii for n^{th} orbit is given by, $r_n = \frac{a_0 n^2}{Z}$

where, $a_0 = 52.9 \text{ pm}$; n = energy level and Z = atomic number

$$\text{For Li}^{2+} \text{ ion, } (r_{\text{Li}^{2+}})_{n=4} - (r_{\text{Li}^{2+}})_{n=3} = \frac{52.9(16-9)}{3} = \Delta R_1$$

$$\text{For He}^+ \text{ ion, } (r_{\text{He}^+})_{n=4} - (r_{\text{He}^+})_{n=3} = \frac{52.9(16-9)}{2} = \Delta R_2$$

$$\therefore \frac{\Delta R_1}{\Delta R_2} = \frac{2}{3} \text{ or } \Delta R_1 : \Delta R_2 = 2 : 3$$

9. (a) : Order of energy of orbitals : $6s < 4f < 5d < 6p$



11. (b) : If a person is suffering from the deficiency of nor-adrenaline, then the signal sending activity becomes low and the person suffers from depression. In such situations, anti-depressant drugs are required. These drugs inhibit the enzymes which catalyse the degradation of nor-adrenaline.

12. (a) : Tyrosine is a non-essential amino acid.

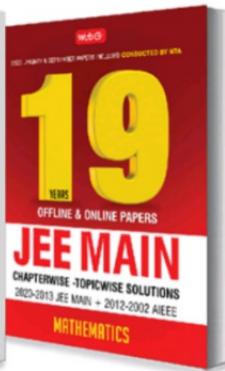
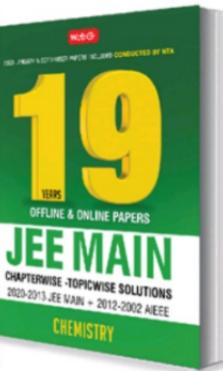
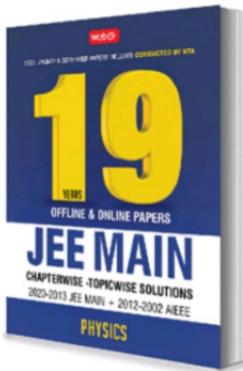
13. (b) : Electronic configuration of Gd^{3+} : $[\text{Xe}]4f^7$

- \therefore Number of unpaired electrons = 7

$$\text{Magnetic moment, } \mu = \sqrt{n(n+2)} \text{ B.M.}$$

$$= \sqrt{7(7+2)} \text{ B.M.} = 7.93 \text{ B.M.}$$

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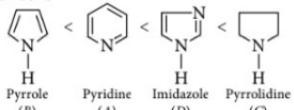


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14. (b): The increasing order of basicity of the given compounds is



Pyrrolidine is the strongest base among the given compounds because it does not have the double bond and not aromatic in nature. So lone pair of electrons on nitrogen (N) is easily available for donation. Imidazole is stronger base than pyridine because protonated imidazole has two resonance forms such that both nitrogens contribute equally in carrying the positive charge whereas pyridinium cation has only one nitrogen to stabilize the positive charge. In pyrrole, lone pair of electrons on N gets involved with carbon-carbon double bond to form a conjugated system of π -electrons, leading to greater stability of system which makes it more stable.

15. (b): For first-order kinetics, $t_{1/2} = \frac{\ln 2}{k}$

$$\therefore k_A = \frac{\ln 2}{300}; k_B = \frac{\ln 2}{180}$$

For first order kinetics

$$R_t = R_0 e^{-kt}, (R_t)_A = (R_0)_A e^{-k_A t}, (R_t)_B = (R_0)_B e^{-k_B t}$$

$$\frac{(R_t)_A}{(R_t)_B} = \frac{(R_0)_A}{(R_0)_B} e^{(-k_A + k_B)t}$$

$$4 = e^{(k_B - k_A)t}, 2 \ln 2 = \left(\frac{\ln 2}{180} - \frac{\ln 2}{300} \right)t$$

$$2 = \left(\frac{120}{180 \times 300} \right)t \Rightarrow t = \frac{2 \times 180 \times 300}{120} = 900 \text{ sec}$$

16. (a): In the solid state, PCl_3 exists as an ionic solid $[\text{PCl}_4]^+ [\text{PCl}_6]^-$. In this, the cation $[\text{PCl}_4]^+$ is tetrahedral and the anion $[\text{PCl}_6]^-$ is octahedral.

17. (b): Ellingham diagram is a graph of ΔG° vs T of some metal oxides.

18. (b):



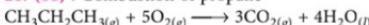
19. (d): $\text{CO}_{(g)} + \text{H}_2\text{O}_{(g)} \xrightarrow[\text{Catalyst}]{673 \text{ K}} \text{CO}_{2(g)} + \text{H}_{2(g)}$

This is called water-gas shift reaction.

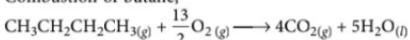
20. (a): Eutrophication is a process in which a water body overly enriched with minerals and nutrients induce excessive growth of algae. This process may result in oxygen depletion of water body. Consequently aquatic life is adversely affected.

The permissible value of CO_2 in atmosphere is 0.03% by volume. More than this value of CO_2 can cause air pollution. Clean water should have BOD value of 5 ppm whereas highly polluted water could have a BOD value of 17 ppm or more. pH of rain water should be 5.6. Less than this value of increases the acidity of water.

21. (18): Combustion of propane

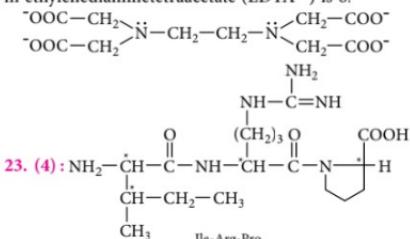


Combustion of butane,



Hence, the total number of moles of O_2 required for complete combustion of 1 mole of propane and 2 moles of butane = $5 + 13 = 18$ moles.

22. (6): The ethylenediaminetetraacetate is an hexadentate ligand. Therefore, the total number of coordination sites in ethylenediaminetetraacetate (EDTA $^{4-}$) is 6.

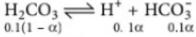


23. (4): $\text{NH}_2-\overset{\cdot}{\underset{\text{CH}_3}{\text{CH}}}(\text{CH}_2)_3-\overset{\cdot}{\underset{\text{CH}_2-\text{CH}_3}{\text{CH}}}(\text{CH}_2)_3-\overset{\cdot}{\underset{\text{CH}_3}{\text{C}}}(\text{H})-\text{N}^+(\text{C}_5\text{H}_5)_2-\text{COOH}$
Ile-Arg-Pro

24. (37): At 30 bar pressure, mass of CO_2 in 1 kg of water = 44 g

At 3 bar pressure, mass of CO_2 in 1 kg of water = 4.4 g

\therefore Moles of CO_2 in 1 kg water = 0.1



$$K_{a_1} = \frac{[\text{H}]^+[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}; 4.0 \times 10^{-7} = \frac{0.1\alpha^2}{1-\alpha} = 0.1\alpha^2$$

$$\alpha = 2 \times 10^{-3}, [\text{H}^+] = 0.1\alpha = 2 \times 10^{-4}$$

$$\therefore \text{pH} = -\log (2 \times 10^{-4}) = 3.7 \text{ or } 37 \times 10^{-1}$$

25. (-6): As $\Delta G^\circ = -nFE_{\text{cell}}^\circ$

$$17.37 \times 10^3 = -3 \times 96500 \times E_{\text{cell}}^\circ$$

$$\therefore E_{\text{cell}}^\circ = -\frac{17.37 \times 10^3 \text{ J mol}^{-1}}{3 \times 96500 \text{ C mol}^{-1}} = -0.06 \text{ V} = -6 \times 10^{-2} \text{ V}$$





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Unit
4

d- and f-Block Elements | Coordination Compounds

d- and f-Block Elements

TRANSITION ELEMENTS

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

GENERAL CHARACTERISTICS

TRANSITION METAL

Physical Properties

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

Chemical Properties

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

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

SOME IMPORTANT COMPOUNDS

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

INNER TRANSITION ELEMENTS

☞ **Lanthanoids** : The elements with atomic numbers 58 to 71 i.e., cerium to lutetium (which come immediately after lanthanum, $Z = 57$) are called *lanthanoids*.

☞ **Actinoids** : The elements with atomic number 90

to 103 i.e., thorium to lawrencium (which come immediately after actinium, $Z = 89$) are called *actinoids*.

They are called *f*-block elements because last electron enters into *f*-orbital.

General electronic configuration : $(n - 2)f^{1-14}$ $(n - 1)d^{0-1} ns^2$

Therapeutic and Diagnostic Applications of Lanthanides !

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



GENERAL CHARACTERISTICS

INNER TRANSITION ELEMENTS

LANTHANOIDS

ACTINOIDS

- They show mainly +3 oxidation state. +2 and +4 oxidation states also exist. They have greater shielding effect as compared to actinoids. Most of their ions are coloured. They are paramagnetic and their magnetic properties can be easily explained. Less tendency to form complexes. Except promethium, these are non-radioactive substances. These are less basic.
- The regular decrease in the size of lanthanoid atoms and ions from La/La³⁺ to Lu/Lu³⁺ is known as *lanthanoid contraction*. It is due to greater effect of the increased nuclear charge than that of the screening effect, which is attributed to the imperfect shielding of one electron by another in the same sub-shell.

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

CONSEQUENCES OF LANTHANOID CONTRACTION

- Separation of lanthanoids is difficult because of small difference in their size. Therefore, lanthanoids are mainly separated by ion exchange method.
- Basic strength of hydroxides decreases from Ce to Lu. Thus, La(OH)₃ is most basic whereas Lu(OH)₃ is least basic.

- Radii of elements in same group from 4th to 12th groups in 4d and 5d series are very close and these elements in each group are called *chemical twins*. e.g., Zr and Hf, Nb and Ta, etc.
- The properties of complex formation increases from La to Lu because of decrease in size and increase in "charge : size" ratio.
- There is a very slight increase in electronegativity from La to Lu.

Coordination Compounds

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

Double Salt	Co-ordination Compound
<ol style="list-style-type: none">These exist only in solid state and dissociate into constituent species in their solution.They lose their identity in dissolved state.Their properties are essentially the same as those of their constituent species.In double salts' the metal atom/ion exhibit normal valency.	<ol style="list-style-type: none">They retain their identity in solid as well as in solution state.They do not lose their identity in dissolved state.Their properties are different from those of their constituents. For example, K₄[Fe(CN)₆] does not show the test of Fe²⁺ and CN⁻ ions.In co-ordination compounds, the number of negative ions or molecules surrounding the central metal atom is different from its normal valency.

WERNER'S COORDINATION THEORY

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



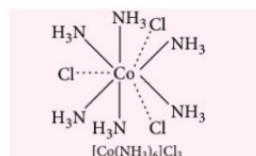
When a polydentate ligand coordinates to a metal ion through more than one electron pairs of donor site simultaneously, is called **chelation**. The resulting complex has ring like structure and such ligand is called chelating ligand.
Chelating ligands form more stable complexes than similar ordinary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

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

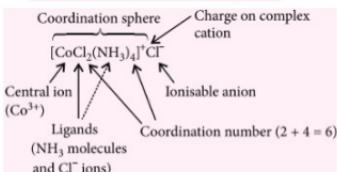
IUPAC NOMENCLATURE

Naming and writing formulas of coordination compounds -

- ☛ The cation comes first, then the anion(s)
 - diammine silver(I) chloride $[\text{Ag}(\text{NH}_3)_2]\text{Cl}$
 - potassium hexacyanoferrate(III) $\text{K}_3[\text{Fe}(\text{CN})_6]$
- ☛ Complex ion is enclosed in brackets
- Ligands are named first in alphabetical order followed by metal atom.
 - **Anionic ligands** : End in -o e.g., Cl^- : Chlorido
 - **Neutral ligands** : Retain their names with a few exceptions e.g., NH_3 : Ammine
 - **Cationic ligands** : End in -ium, e.g., NO_2^+ : Nitronium
 - **Ambidentate ligands** : Named by using



Representation of $[\text{CoCl}_3(\text{NH}_3)_6]\text{Cl}_3$ complex according to Werner's theory



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

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

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

different names of ligands or by placing the symbol of donor atom. e.g., $-\text{SCN}^-$ (Thiocyanato-S or Thiocyanato), $-\text{ONO}^-$ (Nitrito-O or Nitrito), $-\text{NO}_2^-$ (Nitrito-N or Nitro), $-\text{NCS}^-$ (Thiocyanato-N or Isothiocyanato).

- Metal is written first in the formula
- Naming is started with a small letter and complex part is written as one word.
- Metal oxidation state in roman numerals in parentheses after the metal ion.
- A space only between cation and anion.
- When coordination sphere is anionic, name of central metal ends in -ate. For e.g.,
 - tetraamminecopper(II) sulphate $[\text{Cu}(\text{NH}_3)_4]\text{SO}_4$
 - hexaammincobalt(III) chloride $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$

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

2	di	bis	4	tetra	tetrakis
3	tri	tris	5	penta	pentakis

6	hexa	hexakis	8	octa	octakis
7	hepta	heptakis	9	nona	nonakis
10	deca				decakis

Some examples -

Sodium bis(thiosulphato) argentate (I) : $\text{Na}_3[\text{Ag}(\text{S}_2\text{O}_3)_2]$
tris(ethylene diamine) cobalt (III) ion : $[\text{Co}(\text{en})_3]^{3+}$

ISOMERISM

ISOMERISM

Structural isomerism

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

Ionisation isomerism : Isomers that give different ions in solution. e.g., $[\text{Co}(\text{NH}_3)_5\text{Br}]\text{Cl}$; $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Br}$.

Hydrate isomerism : Isomers having different number of H_2O as a ligand and as water of hydration. e.g., $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$; $[\text{CrCl}(\text{H}_2\text{O})_5]\text{Cl}_2 \cdot \text{H}_2\text{O}$, $[\text{CrCl}_2(\text{H}_2\text{O})_4]\text{Cl} \cdot 2\text{H}_2\text{O}$.

Coordination isomerism : The ligands are interchanged in both the cationic and anionic ions. e.g., $[\text{Co}(\text{NH}_3)_6][\text{Cr}(\text{CN})_6]$; $[\text{Cr}(\text{NH}_3)_6][\text{Co}(\text{CN})_6]$

Linkage isomerism : This type of isomerism exists when ambidentate ligand is coordinated with its different donor atoms. e.g., $[\text{Co}(\text{NH}_3)_5\text{ONO}]\text{Cl}_2$; $[\text{Co}(\text{NH}_3)_5\text{NO}_2]\text{Cl}_2$.

Stereoisomerism

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

Geometrical isomerism

Arises due to different possible geometric arrangement of ligands.

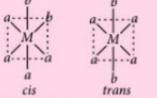
In octahedral complex $[\text{Ma}_3\text{b}_3]$

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

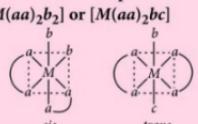


Meridional (mer) : When the positions are around the meridian.

In octahedral complex $[\text{Ma}_3\text{b}_2]$



In octahedral complex $[\text{M}(aa)_2\text{b}_2]$ or $[\text{M}(aa)_2\text{bc}]$



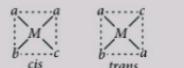
In square planar complex $[\text{Ma}_2\text{b}_2]$

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



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

In square planar complex $[\text{Ma}_2\text{bc}]$



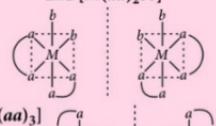
In square planar complex $[\text{Mabcd}]$

These isomers are obtained by selecting 1 ligand, (a) and then placing the remaining 3 ligands (b, c and d), one by one, trans to ligand (a). These type of complex shows three isomers – two *cis* and one *trans*. **Geometrical isomerism** is not possible in tetrahedral complexes.

Optical isomerism

Shown by molecule which do not have plane of symmetry.

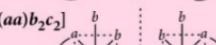
Optical isomerism in $[\text{M}(aa)_2\text{b}_2]$ and $[\text{M}(aa)_2\text{bc}]$



Optical isomerism in $[\text{M}(aa)_3]$



Optical isomerism in $[\text{M}(aa)\text{b}_2\text{c}_2]$



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

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

BONDING IN COORDINATION COMPOUNDS

Valence Bond Theory : According to this theory, the metal atom/ion makes available empty orbitals equal to its coordination number.

- The orbitals may be inner orbitals (Low spin) i.e., $(n - 1)d$, ns and np or outer orbitals (High spin) i.e., nd , ns and np depending upon the strength of ligand.
- The vacant orbitals undergo hybridisation to yield a set of equivalent orbitals of definite geometry such as octahedral, tetrahedral and square planar.
- These hybridised orbitals are allowed to overlap with ligand orbitals that can donate electron pairs for bonding.

C. No.	Type of hybridisation	Geometry	Examples
2	sp	Linear	$[\text{Ag}(\text{NH}_3)_2]^+$, $[\text{Ag}(\text{CN})_2]^-$
3	sp^2	Trigonal planar	$[\text{HgI}_3]^-$
4	sp^3	Tetrahedral	$\text{Ni}(\text{CO})_4$, $[\text{NiX}_4]^{2-}$, $[\text{ZnCl}_4]^{2-}$, $[\text{CuX}_4]^{2-}$ where X = Cl^- , Br^- , I^-
	dsp^2	Square planar	$[\text{Ni}(\text{CN})_4]^{2-}$, $[\text{Cu}(\text{NH}_3)_4]^{2+}$, $[\text{Ni}(\text{NH}_3)_4]^{2+}$
5	dsp^3	Trigonal bipyramidal	$[\text{Fe}(\text{CO})_5]$, $[\text{CuCl}_5]^{3-}$
	sp^3d	Square pyramidal	$[\text{SbF}_5]^{2-}$
6	d^2sp^3	Octahedral (Inner orbital)	$[\text{Cr}(\text{NH}_3)_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$
	sp^3d^2	Octahedral (Outer orbital)	$[\text{FeF}_6]^{3-}$, $[\text{Fe}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{NH}_3)_6]^{2+}$

Magnetic properties :

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

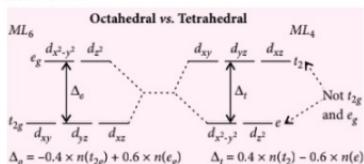
Crystal Field Theory : This theory is based on the assumption that the metal ion and the ligands act as a point charges and the interaction between them is purely electrostatic, i.e., metal-ligand bonds are 100% ionic.

➤ $\Delta_o > P$ (low spin complex)

➤ $\Delta_o < P$ (high spin complex)

$$\Delta_t = \frac{4}{9} \Delta_o$$

➤ **Spectrochemical series :** Arrangement of ligands in the order of increasing field strength. $\Gamma < \text{Br}^- < \text{S}^{2-} < \text{SCN}^- < \text{NO}_3^- < \text{F}^- < \text{OH}^- < \text{ox}^{2-} < \text{O}^{2-} < \text{H}_2\text{O} < \text{NCS}^- < \text{py} = \text{NH}_3 < \text{en} < \text{dipy} < \text{O} - \text{phen} < \text{CN}^- < \text{CO}$.



STABILITY OF COORDINATION COMPOUNDS

Stability depends on

Charge on the central metal ion (oxidation state) : Greater the charge on central metal ion, more is the stability.

Basic nature of ligand : More the basic strength of ligand, more is the stability of complex.

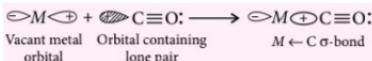
Presence of chelate rings : Formation of chelate ring increases the stability of complex.

Size of the metal ion : Smaller the size of metal ion, more is the stability.

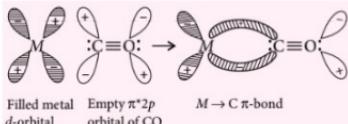
Electronegativity and polarising power of the central metal ion : More is the electronegativity and polarising power of the metal ion, more stable is the complex.

BONDING IN METAL CARBONYLS

There is an overlap of filled π_{2p} orbital of CO with suitable empty orbital of metal resulting in the formation of sigma bond.



Then there is a π -overlap involving filled metal d -orbital and empty antibonding π^{*}_{2p} orbital of same CO. This results in formation of $M \rightarrow C$ π -bond. This is also called *back bonding*.



APPLICATIONS OF COORDINATION COMPOUNDS

Complex *cis*-[PtCl₂(NH₃)₂] known as *cis*-platin is used in cancer treatment.

Coordination compounds are also used in electroplating, photography, dyes, etc.

Hardness of water can be estimated by complex formation using EDTA.

Coordination compounds are used as catalyst, e.g., Wilkinson's catalyst, (Ph₃P)₃RhCl Ziegler-Natta catalyst, [TiCl₄ + (C₂H₅)₃Al]

EDTA is often used for treatment of lead poisoning.

Coordination compounds are of great importance in biological system, e.g., chlorophyll, haemoglobin, myoglobin, etc. are coordinate compounds of Mg, Fe and Co respectively.

ORGANOMETALLIC COMPOUNDS

Compounds having one or more metal carbon bonds.

Types of organometallic compounds :

Based on nature of metal - carbon bond, they are classified into :

➤ σ -bonded organometallic compounds:

e.g.; R-Mg-X, (C₂H₅)₂Zn, etc.

➤ π -bonded organometallic compounds

(π complexes) : e.g.; Zeise's salt, K[PtCl₃(η^2 -C₂H₄)]; ferrocene, [Fe(η^5 -C₅H₅)₂], etc.

➤ σ - and π -bonded organometallic compounds (Metal carbonyls) : e.g., [Fe(CO)₅], [Ni(CO)₄].



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A Balancing Act : Stability versus Reactivity of Mn(O) Complexes !

A large class of heme and non-heme metalloenzymes utilize O₂ or its derivatives (e.g., H₂O₂) to generate high-valent metal-oxo intermediates for performing challenging and selective oxidations. Due to their reactive nature, these intermediates are often short-lived and very difficult to characterize. Synthetic chemists have sought to prepare analogous metal-oxo complexes with ligands that impart enough stability to allow for their characterization and an examination of their inherent reactivity. The challenge in designing these molecules is to achieve a balance between their stability, which should allow for their *in situ* characterization or isolation, and their reactivity, in which they can still participate in interesting chemical transformations. This account focuses on our recent efforts to generate and stabilize high-valent manganese-oxo porphyrinoid complexes and tune their reactivity in the oxidation of organic substrates.



- Geometrical shapes of the complexes formed by the reaction of Ni^{2+} with Cl^- , CN^- and H_2O , respectively, are
 - octahedral, tetrahedral and square planar
 - tetrahedral, square planar and octahedral
 - square planar, tetrahedral and octahedral
 - octahedral, square planar and octahedral.
- The correct order of magnetic moments (spin only values in B.M.) among is
 - $[\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-}$
 - $[\text{MnCl}_4]^{2-} > [\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-}$
 - $[\text{Fe}(\text{CN})_6]^{4-} > [\text{MnCl}_4]^{2-} > [\text{CoCl}_4]^{2-}$
 - $[\text{Fe}(\text{CN})_6]^{4-} > [\text{CoCl}_4]^{2-} > [\text{MnCl}_4]^{2-}$.

(Atomic no.: Mn = 25, Fe = 26, Co = 27)
- Among $[\text{Ni}(\text{CO})_4]$, $[\text{NiCl}_4]^{2-}$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, $\text{Na}_3[\text{CoF}_6]$, Na_2O_2 and CsO_2 , the total number of paramagnetic compounds is
 - 2
 - 3
 - 4
 - 5

(JEE Advanced 2016)
- Select the incorrect statement.
 - Ionisation energies of 5d elements are greater than those of 3d and 4d elements.
 - Cu(I) is diamagnetic while Cu(II) is paramagnetic.
 - $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ is coloured while $[\text{Sc}(\text{H}_2\text{O})_6]^{3+}$ is colourless.
 - Transition elements cannot form complexes.
- Which of the following will exhibit optical isomerism?
 - $[\text{Cr}(\text{en})(\text{H}_2\text{O})_4]^{3+}$
 - $[\text{Cr}(\text{en})_3]^{3+}$
 - $[\text{trans-}[\text{Cr}(\text{en})_2\text{Cl}_2]]^+$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
- Which one of the following species is stable in aqueous solution?
 - Cr^{2+}
 - MnO_4^{2-}
 - MnO_3^{3-}
 - Cu^+

(JEE Main 2016)
- In $\text{Fe}(\text{CO})_5$, the Fe – C bond possesses
 - π -character only
 - both σ and π characters
 - ionic character
 - σ -character only.
- The correct order of ionic radii of Y^{3+} , La^{3+} , Eu^{3+} and Lu^{3+} is
 (Atomic number of Y = 39, La = 57, Eu = 63, Lu = 71)

$$\text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+} < \text{Y}^{3+}$$
- (b) $\text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+} < \text{Y}^{3+}$
 (c) $\text{Y}^{3+} < \text{La}^{3+} < \text{Eu}^{3+} < \text{Lu}^{3+}$
 (d) $\text{Y}^{3+} < \text{Lu}^{3+} < \text{Eu}^{3+} < \text{La}^{3+}$
- Consider the complex ions, *trans*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (A) and *cis*- $[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (B). The correct statement regarding them is
 - both (A) and (B) cannot be optically active
 - (A) can be optically active, but (B) cannot be optically active
 - both (A) and (B) can be optically active
 - (A) cannot be optically active, but (B) can be optically active.

(JEE Main 2020)
- Among the following statements which one is correct?
 - Cr^{2+} is a reducing agent.
 - Mn^{2+} is a reducing agent.
 - Both Cr^{2+} and Mn^{2+} exhibit d^4 electronic configuration.
 - When Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration.
- Consider the following complex $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$. The coordination number, oxidation number, number of d -electrons and number of unpaired d -electrons on the metal are respectively
 - 6, 3, 6, 0
 - 7, 2, 7, 1
 - 7, 1, 6, 4
 - 6, 2, 7, 3
- The geometry and magnetic behaviour of the complex $[\text{Ni}(\text{CO})_4]$ are
 - square planar geometry and diamagnetic
 - tetrahedral geometry and diamagnetic
 - square planar geometry and paramagnetic
 - tetrahedral geometry and paramagnetic.

(NEET 2018)
- In the complexes $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$ and $[\text{FeCl}_6]^{3-}$, more stability is shown by
 - $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$
 - $[\text{Fe}(\text{CN})_6]^{3-}$
 - $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$
 - $[\text{FeCl}_6]^{3-}$
- Four successive members of the first row transition elements are listed below with their atomic numbers. Which one of them is expected to have the highest third ionization enthalpy?
 - La = 57
 - Eu = 63
 - Lu = 71
 - Gd = 72

- (a) Vanadium ($Z = 23$)
 (b) Chromium ($Z = 24$)
 (c) Iron ($Z = 26$)
 (d) Manganese ($Z = 25$)
- 15.** Identify the correct trend given below :
 (Atomic no. : Ti = 22, Cr = 24 and Mo = 42)
 (a) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and
 Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (b) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} > [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and
 Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (c) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and
 Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} > [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
 (d) Δ_0 of $[\text{Cr}(\text{H}_2\text{O})_6]^{2+} < [\text{Mo}(\text{H}_2\text{O})_6]^{2+}$ and
 Δ_0 of $[\text{Ti}(\text{H}_2\text{O})_6]^{3+} < [\text{Ti}(\text{H}_2\text{O})_6]^{2+}$
- (JEE Main 2016)
- 16.** The actinoids exhibit more number of oxidation states in general than the lanthanoids. This is because
 (a) the $5f$ orbitals extend farther from the nucleus than the $4f$ orbitals.
 (b) the $5f$ orbitals are more buried than the $4f$ orbitals.
 (c) there is a similarity between $4f$ and $5f$ orbitals in their angular part of the wave function.
 (d) the actinoids are more reactive than the lanthanoids.
- 17.** Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 \AA .)
 (a) $[\text{Fe}(\text{CO})_4]^{2-}$ (b) $[\text{Mn}(\text{CO})_6]^+$
 (c) $[\text{Ni}(\text{CO})_4]$ (d) $[\text{Co}(\text{CO})_4]^-$
- (NEET 2016)
- 18.** The manganate and permanganate ions are tetrahedral, due to
 (a) the π -bonding involves overlap of d -orbitals of oxygen with d -orbitals of manganese
 (b) the π -bonding involves overlap of p -orbitals of oxygen with d -orbitals of manganese
 (c) there is no π -bonding
 (d) the π -bonding involves overlap of p -orbitals of oxygen with p -orbitals of manganese.
- (NEET 2019)
- 19.** Which one of the following complexes will consume more equivalents of aqueous solution of AgNO_3 ?
 (a) $\text{Na}_2[\text{CrCl}_5(\text{H}_2\text{O})]$ (b) $\text{Na}_3[\text{CrCl}_6]$
 (c) $[\text{Cr}(\text{H}_2\text{O})_5\text{Cl}] \text{Cl}_2$ (d) $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$
- 20.** The complex ion which has no d electrons in the central metal atom is
 (a) $[\text{MnO}_4]^-$ (b) $[\text{Co}(\text{NH}_3)_6]^{3+}$
 (c) $[\text{Fe}(\text{CN})_6]^{3-}$ (d) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$
- 21.** Cerium ($Z = 58$) is an important member of the lanthanides. Which of the following statements about cerium is incorrect?
 (a) The common oxidation states of cerium are +3 and +4.
 (b) Cerium (IV) acts as an oxidising agent.
 (c) The +4 oxidation state of cerium is not known in solutions.
 (d) The +3 oxidation state of cerium is more stable than the +4 oxidation state.
- 22.** Which of the following complexes is diamagnetic?
 (a) $[\text{Mn}(\text{H}_2\text{O})_6]^{2+}$ (b) $[\text{Cu}(\text{H}_2\text{O})_6]^{3+}$
 (c) $[\text{Co}(\text{NH}_3)_6]^{3+}$ (d) $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$
- 23.** If M is an element of actinoids series, the degree of complex formation decreases in the order
 (a) $M^{4+} > M^{3+} > MO_2^{2+} > MO_2^+$
 (b) $MO_2^+ > MO_2^{2+} > M^{3+} > M^{4+}$
 (c) $M^{4+} > MO_2^{2+} > M^{3+} > MO_2^+$
 (d) $MO_2^{2+} > MO_2^+ > M^{4+} > M^{3+}$
- 24.** Which of the following has largest number of isomers? (R = alkyl group, en = ethylenediamine)
 (a) $[\text{Ru}(\text{NH}_3)_4\text{Cl}_2]^+$ (b) $[\text{Co}(\text{NH}_3)_5\text{Cl}]^{2+}$
 (c) $[\text{Ir}(\text{PR}_3)_2\text{H}(\text{CO})]^{2+}$ (d) $[\text{CoCl}_2(en)_2]^+$
- 25.** Iron exhibits +2 and +3 oxidation states. Which of the following statements about iron is incorrect?
 (a) Ferrous oxide is more basic in nature than the ferric oxide.
 (b) Ferrous compounds are relatively more ionic than the corresponding ferric compounds.
 (c) Ferrous compounds are less volatile than the corresponding ferric compounds.
 (d) Ferrous compounds are more easily hydrolysed than the corresponding ferric compounds.
- 26.** Oxidation number of Cr in the following complex is

$$\left[(\text{H}_2\text{O})_6\text{Cr} \begin{array}{c} \text{O}_2 \\ \diagup \quad \diagdown \\ \text{O} - \text{O} \end{array} \text{Cr}(\text{H}_2\text{O})_6 \right]^{3+}$$
 (a) 3 (b) 6 (c) 4 (d) 5
- 27.** MnO_4^- is of intense pink colour, though Mn is in (+7) oxidation state. It is due to
 (a) oxygen gives colour to it.
 (b) charge transfer when oxygen gives its electron to Mn making it Mn (+VI) hence, coloured.
 (c) charge transfer when Mn gives its electron to oxygen.
 (d) none of the above is correct.

28. Which one of the following complex species does not obey the EAN rule?

 - $[\text{Cu}(\text{CN})_4]^{3-}$
 - $[\text{Cr}(\text{NH}_3)_6]^{3+}$
 - $[\text{Fe}(\text{CN})_6]^{4-}$
 - $[\text{Ni}(\text{CO})_4]$

29. A change in oxidation number is observed when

 - aqueous solution of CrO_4^{2-} is acidified.
 - SO_2 gas is passed into $\text{Cr}_2\text{O}_7^{2-}/\text{H}^+$.
 - $\text{Cr}_2\text{O}_7^{2-}$ solution is made alkaline.
 - CrO_2Cl_2 is dissolved in NaOH.

30. Black coloured solid (A) $\xrightarrow[\Delta]{\text{KNO}_3 + \text{KOH}}$ green colour solution (B) $\xrightarrow{\text{CO}_2}$ (C) + (A)
pink

Pink compound (C) is decolourised by Fe^{2+} . The compound A, B and C are

- (a) MnO_2 , K_2MnO_4 , KMnO_4
- (b) MnO_2 , KMnO_4 , K_2MnO_4
- (c) KMnO_4 , MnO_2 , K_2MnO_4
- (d) K_2MnO_4 , MnO_2 , KMnO_4

SOLUTIONS

6. (b): $\text{Cr}^{2+}(d^4)$ is unstable and oxidised to $\text{Cr}^{3+}(d^3 \text{ i.e., } t_{2g}^3)$ which is more stable.

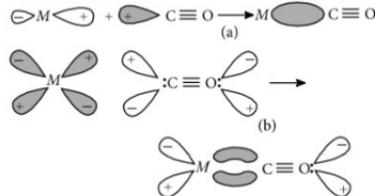
Cu^+ is unstable and is oxidised to Cu^{2+} which has more negative enthalpy of hydration.

Similarly, $Mn^{3+}(d^4)$ in MnO_3^{3-} is unstable and is reduced to $Mn^{2+}(d^5)$.

MnO₄⁻ ion is far more likely to exist in a very high pH solution and is stable for a few hours in alkalies.

7. (b): In a metal carbonyl, the metal carbon bond possesses both the σ - and π -character. A σ -bond between metal and carbon atom is formed when a vacant hybrid bond of the metal atom overlaps with an orbital of C atom of carbon monoxide containing a lone pair of electrons.

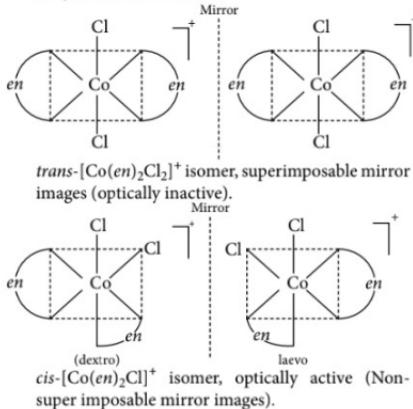
Formation of π -bond is caused when a filled orbital of the metal atom overlaps with a vacant antibonding π^* orbital of C atom of CO. This overlap is also called back donation of electrons by metal atom to carbon.



- (a) The formation of the metal \leftarrow carbon σ -bond using an unshared pair of the C atom. (b) The formation of the metal \rightarrow carbon π -bond.

8. (d)

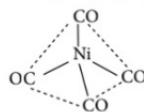
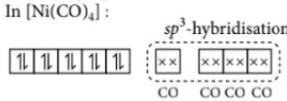
9. (d): *trans*-[Co(en)₂Cl₂]⁺ isomer cannot be optically active as it possesses plane of symmetry but *cis*-[Co(en)₂Cl₂]⁺ isomer can be optically active as it is unsymmetrical molecule.



10. (a): Cr^{2+} is a reducing agent, it gets oxidised to Cr^{3+} ($3d^3$ or t_{2g}^3 , stable half-filled configuration).

- 11. (a):** In $[\text{Co}(\text{NH}_3)_5\text{CO}_3]\text{ClO}_4$, C.N. of Co = 6;
 $\text{O.N.} = x + 5x(0) + 1x(-2) + 1x(-1) = 0 \therefore x = +3$
 Electronic configuration of Co^{3+} : $[\text{Ar}]3d^64s^0$;
 Number of d-electrons = 6
 All d-electrons are paired due to strong ligand
 hence, no unpaired electrons.

12. (b) Ni(28) : [Ar]3d⁸4s²
 ∴ CO is a strong field ligand, so, unpaired electrons get paired.



Thus, the complex is sp^3 hybridised with tetrahedral geometry and diamagnetic in nature.

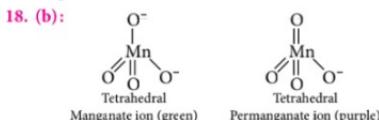
13. (c) : $[\text{Fe}(\text{C}_2\text{O}_4)_3]^{3-}$. The iron is present in the highest oxidation state Fe^{3+} and $\text{C}_2\text{O}_4^{2-}$ is a chelating ligand. Chelates are always more stable complexes.

14. (d)

15. (c) : Δ_o increases from $3d$ -series to $4d$ -series. Thus, $[\text{Cr}(\text{H}_2\text{O})_6]^{2+}$ has lower Δ_o value than that of $[\text{Mo}(\text{H}_2\text{O})_6]^{2+}$. Also, for a metal ion having lesser number of d -electrons, Δ_o value increases. Thus, $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ has greater Δ_o value than that of $[\text{Ti}(\text{H}_2\text{O})_6]^{2+}$.

16. (a) : More the distance between nucleus and outer orbitals, lesser will be force of attraction on them. Distance between nucleus and $5f$ orbitals is more as compared to distance between $4f$ orbital and nucleus. So actinoids exhibit more number of oxidation states in general than the lanthanoids.

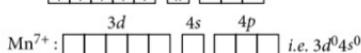
17. (a) : The greater the negative charge on the carbonyl complex, the more easy it would be for the metal to permit its electrons to participate in the back bonding, the higher would be the $M - \text{C}$ bond order and simultaneously there would be larger reduction in the $\text{C} - \text{O}$ bond order. Thus, $[\text{Fe}(\text{CO})_4]^{2-}$ has the lowest $\text{C} - \text{O}$ bond order means the longest bond length.



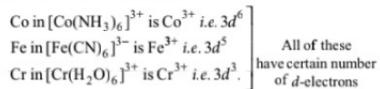
In manganese and permanganate ions, π -bonding takes place by overlap of p -orbitals of oxygen with d -orbitals of manganese.

19. (d) : Chloride ions outside the coordination sphere are ionisable only. Hence, $[\text{Cr}(\text{H}_2\text{O})_6]\text{Cl}_3$ will give 3Cl^- ions in aqueous solution which consume more equivalents of AgNO_3 .

20. (a) : In MnO_4^- , the O.S. of Mn is +7 i.e. Mn^{7+}



In other species, we have



21. (c)

22. (c) :

Mn^{2+}	Cu^{3+}	Co^{3+}	Co^{2+}
$[\text{Ar}]3d^5$	$[\text{Ar}]3d^8$	$[\text{Ar}]3d^6$	$[\text{Ar}]3d^7$
No pairing of e^-	No pairing of e^-	Pairing of e^-	No pairing of e^-
Paramagnetic	Paramagnetic	Diamagnetic	Paramagnetic

23. (c) : The higher the charge on the metal ion, smaller is the ionic size and more is the complex forming ability. Thus, the degree of complex formation decreases in the order



The higher tendency of complex formation of MO_2^{2+} as compared to M^{3+} is due to high concentration of charge on metal atom M in MO_2^{2+} .

24. (d) : Among the given complexes, $[\text{CoCl}_2(\text{en})_2]^+$ is a $[\text{M}(\text{AA})_2\text{B}_2]$ type complex, thus, it is possible for it to exhibit geometrical as well as optical isomerism, which is not possible in case of other given complexes. Thus, it exhibits largest number of isomers.

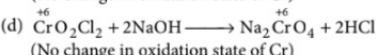
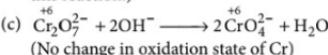
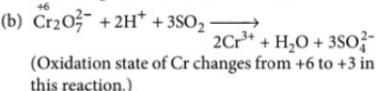
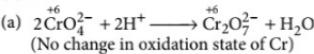
25. (d) : Greater the covalent nature, more easily they are hydrolysed. Thus, FeCl_3 is more easily hydrolysed than FeCl_2 . Thus, statement (d) is incorrect.

26. (a)

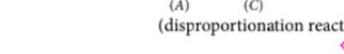
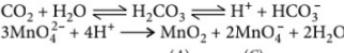
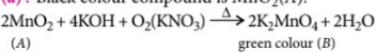
27. (b) : The colour arise by charge transfer. In MnO_4^- , an electron is momentarily transferred from oxygen to the metal and thus oxygen changes from O^{5-} to O^- and Mn from (+7) to (+6).

28. (b)

29. (b) :



30. (a) : Black colour compound is $\text{MnO}_2(A)$.





CBSE warm-up!

CLASS-XII

Practice questions for CBSE Exams as per the reduced syllabus, latest pattern and marking scheme issued by CBSE for the academic session 2020-21.

Series 4

CHAPTERWISE PRACTICE PAPER :
d & f-Block Elements and Coordination Compounds

Time Allowed : 3 hours
Maximum Marks : 70

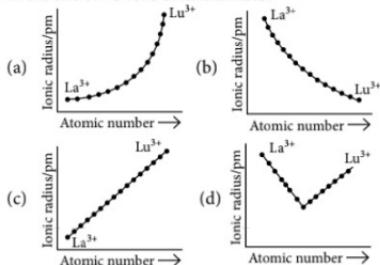
GENERAL INSTRUCTIONS

Read the following instructions very carefully and strictly follow them :

- (i) Question paper comprises two parts A and B.
 - (ii) Part A : Q. no. 1 to 26 are objective type questions.
 - Q. no. 1 to 19 are objective type questions carrying one mark each.
 - Q. no. 20 to 24 are objective type questions carrying two marks each.
 - Q. no. 25 to 26 are case based objective type questions carrying three marks each.
 - (iii) Part B : Q. no. 27 to 37 are subjective/descriptive type questions.
 - Q. no. 27 to 30 are short answer type-I questions carrying two marks each.
 - Q. no. 31 to 34 are short answer type-II questions carrying three marks each.
 - Q. no. 35 to 37 are long answer type questions carrying five marks each.
 - (iv) There is no overall choice in the question paper. However, internal choices have been provided in both part A and Part B.
 - (v) Use of calculators and log tables is not permitted.

PART - A

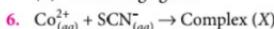
1. Which of the following graphs shows correct trends in the size of +3 ions of lanthanides?



- (a) Conductivity of solution increases.
 (b) Conductivity of solution decreases.
 (c) Conductivity of solution remains constant.
 (d) Conductivity of solution will be doubled.
5. 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) $Ti^{2+}, V^{3+}, Cr^{4+}, Mn^{5+}$

OR

- 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.



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(dimethylglyoximate)nickel (II)
 (c) tetrathiocyanato-S-cobaltate (II) and bis(dimethylglyoxime)nickel (II)
 (d) tetrathiocyanato-S-cobaltate (III) and bis(dimethylglyoximate)nickel (II).

7. 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) $Cu(Z = 29)$

OR

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+}

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

OR

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.

9. Among d -block elements, the most abundant element belongs to the
 (a) first transition series
 (b) second transition series
 (c) third transition series
 (d) fourth transition series.

10. Which of the following complexes has magnetic moment of 2.83 B.M.?
 (a) $[Ni(NH_3)_6]^{2+}$ (b) $[Ni(CN)_4]^{2-}$
 (c) $TiCl_4$ (d) $[CoCl_6]^{3-}$

11. The basic character of the transition metal monoxides follows the order

- (a) $CrO > VO > FeO > TiO$
 (b) $TiO > FeO > VO > CrO$
 (c) $TiO > VO > CrO > FeO$
 (d) $VO > CrO > TiO > FeO$

12. The hypothetical complex chlorodiaquatriamminecobalt(III) chloride can be represented as
 (a) $[CoCl(NH_3)_3(H_2O)_2]Cl_2$
 (b) $[Co(NH_3)_3(H_2O)Cl]$
 (c) $[Co(NH_3)_3(H_2O)_2Cl]Cl$
 (d) $[Co(NH_3)_3(H_2O)_3]Cl_3$

OR

Which of the following factors may be regarded as the main cause of lanthanide contraction?

- (a) Poor shielding of $4f$ -electrons in compare to other electrons in the sub-shell.
 (b) Effective shielding of one of the $4f$ -electrons by another in the sub-shell.
 (c) Poor shielding of $5d$ -electrons by $4f$ -electrons.
 (d) Greater shielding of $5d$ -electrons by $4f$ -electrons.

13. Which of the following statements is not correct?
 (a) $La(OH)_3$ is less basic than $Lu(OH)_3$.
 (b) In lanthanide series ionic radius of Ln^{3+} ion decreases.
 (c) La is actually an element of transition series rather lanthanide.
 (d) Atomic radius of Zr and Hf are same because of lanthanide contraction.

- 14.** A solution containing 2.675 g of $\text{CoCl}_3 \cdot 6\text{NH}_3$ (molar mass = 267.5 g mol⁻¹) is passed through a cation exchanger. The chloride ions obtained in solution were treated with excess of AgNO_3 to give 4.75 g of AgCl (molar mass = 143.5 g mol⁻¹). The formula of the complex is
 (a) $[\text{CoCl}_3(\text{NH}_3)_3]$ (b) $[\text{CoCl}(\text{NH}_3)_5]\text{Cl}_2$
 (c) $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$ (d) $[\text{CoCl}_2(\text{NH}_3)_4]\text{Cl}$

Question 15 to 19 (Assertion/Reason)

Directions : In the following questions (15-19), a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both Assertion (A) and Reason (R) are correct and Reason (R) is the correct explanation of Assertion (A).
 (b) If both Assertion (A) and Reason (R) are correct but Reason (R) is not the correct explanation of Assertion (A).
 (c) If Assertion (A) is correct but Reason (R) is incorrect.
 (d) If Assertion (A) is incorrect and Reason (R) is correct.

15. Assertion : Mercury is liquid at room temperature.

Reason : In mercury, there is no unpaired d -electron and thus metallic bonding is weakest.

16. Assertion : As compared to non-chelated complexes, chelated complexes are more stable.

Reason : Labile complexes are the complexes which contain ligands that can be easily replaced by other ligands.

OR

Assertion : $[\text{CoF}_6]^{3-}$ ion shows magnetic moment corresponding to zero unpaired electrons.

Reason : It undergoes sp^3d^2 hybridisation.

17. Assertion : E° value of $\text{Mn}^{3+} | \text{Mn}^{2+}$ is more positive than for $\text{Cr}^{3+} | \text{Cr}^{2+}$.

Reason : Cr^{3+} is more stable than Cr^{2+} but Mn^{3+} is less stable than Mn^{2+} .

18. Assertion : Copper metal gets covered with a green layer of basic copper carbonate.

Reason : Copper metal is unaffected when exposed to atmospheric CO_2 and moisture.

OR

Assertion : CrO_3 reacts with HCl to form chromyl chloride gas.

Reason : Chromyl chloride (CrO_2Cl_2) has tetrahedral structure.

19. Assertion : The oxidation number of platinum in Zeise's salt is +4.

Reason : Zeise's salt is an ionic complex.

20. Among $[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$, $[\text{Fe}(\text{CN})_6]^{3-}$, $[\text{Fe}(\text{Cl})_6]^{3-}$ species, the hybridisation state of the Fe atom are, respectively

- (a) $d^2sp^3, d^2sp^3, sp^3d^2$ (b) $sp^3d^2, d^2sp^3, d^2sp^3$
 (c) $sp^3d^2, d^2sp^3, sp^3d^2$ (d) none of these.

OR

Increasing order of Δ_0° of the following complex is

- (a) $[\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{H}_2\text{O})_6]^{3+} < [\text{Cr}(\text{NO}_2)_6]^{3-}$
 (b) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} > [\text{Cr}(\text{NH}_3)_6]^{3+} > [\text{Cr}(\text{NO}_2)_6]^{3-}$
 (c) $[\text{Cr}(\text{H}_2\text{O})_6]^{3+} < [\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{NO}_2)_6]^{3-}$
 (d) $[\text{Cr}(\text{NH}_3)_6]^{3+} < [\text{Cr}(\text{NO}_2)_6]^{3-} < [\text{Cr}(\text{H}_2\text{O})_6]^{3+}$

21. Which of the following pairs have both the elements showing highest oxidation states equal to

$[ns + (n - 1)d]$ electrons

- (a) Ti and Fe (b) Cr and Co
 (c) Cr and Mn (d) Co and Ni.

22. 0.001 mol of $[\text{Co}(\text{NH}_3)_5(\text{NO}_3)(\text{SO}_4)]$ was passed through a cation exchanger and the acid coming out of it required 20 mL of 0.1 M NaOH for neutralisation. Hence, the complex is

- (a) $[\text{Co}(\text{NH}_3)_5\text{SO}_4]\text{NO}_3$
 (b) $[\text{Co}(\text{NH}_3)_5\text{NO}_3]\text{SO}_4$
 (c) $[\text{Co}(\text{NH}_3)_5]\text{NO}_3\text{SO}_4$
 (d) none of these.

23. Out of vanadium (V), chromium (Cr), manganese (Mn) and iron (Fe), which one is expected to have the highest second ionisation enthalpy?

- (a) V (b) Cr (c) Mn (d) Fe

OR

In which of the following ions, the colour is not due to $d-d$ transition?

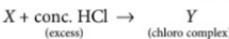
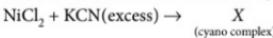
- (a) $[\text{Ti}(\text{H}_2\text{O})_6]^{3+}$ (b) $[\text{Cu}(\text{NH}_3)_4]^{2+}$
 (c) $[\text{CoF}_6]^{3-}$ (d) CrO_4^{2-}

24. If excess of AgNO_3 solution is added to 100 mL of a 0.024 M solution of dichlorobis(ethylenediamine) cobalt(III) chloride, how many moles of AgCl be precipitated?

- (a) 0.0012 (b) 0.0016
 (c) 0.0024 (d) 0.0048

Read the following passage and answer the questions 25 and 26.

The coordination number of nickel (II) ion is 4.



25. The IUPAC names for the complexes X and Y are respectively,
- potassium tetracyanonickel(II), potassium tetrachloronickel(II).
 - tetracyanonickel(II), tetrachloronickel(II).
 - tetracyano potassium nickelate(II), tetra chloro potassium nickelate(III).
 - potassium tetracyanonickelate(II), potassium tetrachloronickelate (II).
26. The hybridisation of X and Y are
- sp^3d^2, dsp^2
 - dsp^2, sp^3
 - sp^3, sp^3
 - sp^3, dsp^3

PART - B

27. Explain the following observations :

- Many of the transition elements are known to form interstitial compounds.
- There is a general increase in density from titanium ($Z = 22$) to copper ($Z = 29$).

28. The sum of first and second ionisation energies and those of third and fourth ionisation energies of nickel and platinum are given below :

$IE_1 + IE_2$ (kJ mol $^{-1}$)	$IE_3 + IE_4$ (kJ mol $^{-1}$)
Ni : 2.49×10^3	8.80×10^3
Pt : 2.66×10^3	6.70×10^3

Taking these values into account, answer the following :

- The most common oxidation state for Ni and Pt.
 - The name of the metal which can form compounds in +4 oxidation state more easily, and why?
29. The hexaaquamanganese (II) ion contains five unpaired electrons while hexacyano ion contains only one unpaired electron. Explain using crystal field theory.

OR

- What is meant by chelate effect?
 - NH_2NH_2 although possesses two electron pairs for donation but not acts as chelating agent.
30. Answer the following :
- Why are Sm^{2+} , Eu^{2+} and Yb^{2+} good reducing agents?
 - Can lanthanum ($Z = 57$) exhibit +4 oxidation state?
31. (a) Why are different colours observed in octahedral and tetrahedral complexes for the same metal and same ligands?

(b) What is the relationship between observed colour of the complex and the wavelength of light absorbed by the complex?

32. (A), (B) and (C) are three complexes of chromium (III) with the empirical formula $H_{12}O_6Cl_3Cr$. All the three complexes have water and chloride ion as ligands. Complex (A) does not react with concentrated H_2SO_4 , whereas complexes (B) and (C) lose 6.75% and 13.5% of their original weight respectively, on treatment with concentrated H_2SO_4 . Identify (A), (B) and (C) and explain.

33. For M^{2+}/M and M^{3+}/M^{2+} systems, the E° values for some metals are as follows :

Cr^{2+}/Cr	-0.9 V	Cr^{3+}/Cr^{2+}	-0.4 V
Mn^{2+}/Mn	-1.2 V	Mn^{3+}/Mn^{2+}	+1.5 V
Fe^{2+}/Fe	-0.4 V	Fe^{3+}/Fe^{2+}	+0.8 V

Use this data to comment upon :

- The stability of Fe^{3+} in acid solution as compared to Cr^{3+} or Mn^{3+} .
- The ease with which iron can be oxidised as compared to a similar process for either chromium or manganese metal.

OR

Write the chemical reactions involved in developing of a black and white photographic film. An aqueous $Na_2S_2O_3$ solution is acidified to give a milky white turbidity. Identify the product and write the balanced chemical reaction for it.

34. Explain the following :

- Low spin octahedral complexes of nickel are not known.
- π -complexes are known for transition elements only.
- CO is a stronger ligand than NH_3 for many metals.

35. (i) What are the different oxidation states exhibited by the lanthanoids?

- What happens when
 - potassium ferricyanide is added to ferrous sulphate?
 - excess of potassium iodide is added to mercuric chloride?
 - green vitriol is strongly heated?
 - silver chloride is treated with aqueous sodium cyanide and the product thus formed is allowed to react with zinc in alkaline medium?

OR

Explain the following giving suitable reason :

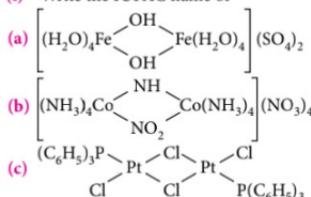
- Yellow coloured aqueous solution of sodium chromate changes to orange red when CO_2 is passed under pressure.
- Ce^{3+} can be easily oxidised to Ce^{4+} .
- E° for $\text{Mn}^{3+}/\text{Mn}^{2+}$ couple is more positive than for $\text{Fe}^{3+}/\text{Fe}^{2+}$ couple.
- (iv) Lu(OH)_3 is a weaker base than La(OH)_3 .

36. Explain why :

- $[\text{Cr}(\text{NH}_3)_6]^{3+}$ is paramagnetic while $[\text{Ni}(\text{CN})_4]^{2-}$ is diamagnetic.
- A solution of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ is green but $[\text{Ni}(\text{CN})_4]^{2-}$ is colourless.
- The low spin tetrahedral complexes are rarely observed.

OR

(i) Write the IUPAC name of



- $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ is blue in colour while CuSO_4 is colourless. Why?

37. (i) (a) Out of the ions Ag^+ , Co^{2+} and Ti^{4+} which will be coloured in aqueous solution?
 (b) If each one of the above ionic species is placed in a magnetic field, how will they respond and why?
 (ii) Explain the following :
 (a) Why *d*-block elements exhibit more oxidation states than *f*-block elements?
 (b) The enthalpies of atomization of the transition metals are high. Explain.

OR

- What is Lanthanoid contraction? Write down its two consequences?
- Arrange the following complexes in the increasing order of conductivity of their solutions : $[\text{Co}(\text{NH}_3)_3\text{Cl}_3]$, $[\text{Co}(\text{NH}_3)_4\text{Cl}_2]\text{Cl}$, $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$, $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$.

SOLUTIONS

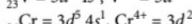
- (b) : On increasing the atomic number of lanthanide, there is regular decrease of ionic size due to poor shielding of $4f$ electrons (lanthanide contraction).

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

- (c)

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

- (d) : $_{22}\text{Ti} = 3d^2 4s^2$, $\text{Ti}^{2+} = 3d^2$

**OR**

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

- (b) : $X = [\text{Co}(\text{SCN})_4]^{2-}$

IUPAC name : tetrathiocyanato-S-cobaltate(II)



IUPAC name : bis(dimethylglyoximato)nickel (II)

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

OR

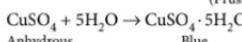
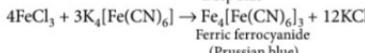
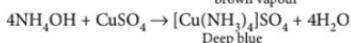
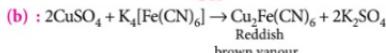
(c) : Mn^{3+} and Co^{3+} are stronger oxidizing agents because

- Mn^{2+} is stable than Mn^{3+} due to stable half filled d^5 configuration.

- In aqueous solution, Co^{2+} is more stable than Co^{3+} .

- (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.

OR

- (a)

- (a) : 2.83 B.M. implies two unpaired electrons according to the expression, $\mu = \sqrt{n(n+2)}$ B.M. The species Ni^{2+} , Ni^{2+} , Ti^{4+} and Co^{3+} in the given complexes have $3d^8$, $3d^8$, $3d^0$, and $3d^6$ electronic configurations, respectively. CN^- being a strong field ligand causes pairing of electrons thus, $[\text{Ni}(\text{CN})_4]^{2-}$ has zero unpaired electrons with dsp^2 hybridisation, while NH_3 being a weak field ligand, does not cause pairing of electrons thus, $[\text{Ni}(\text{NH}_3)_6]^{2+}$ has two unpaired electrons and 2.83 B.M. magnetic moment.

11. (c) : The size of given metals decreases whereas ionization enthalpy increases from Ti to Fe. Hence, the metallic character of the metals decreases and therefore, basicity of oxides decreases from Ti to Fe.

12. (a) OR (a)

13. (a) : As the size of the lanthanoid ions decreases from La^{3+} to Lu^{3+} , the covalent character of the hydroxides increases and hence the basic strength decreases. Thus $\text{La}(\text{OH})_3$ is more basic whereas $\text{Lu}(\text{OH})_3$ is least basic.

14. (c) : Moles of the complex = $\frac{2.675}{267.5} = 0.01$

Moles of AgCl precipitated = $\frac{4.75}{143.5} = 0.033$

Thus, 1 mole of the complex will precipitate
 $= \frac{0.033}{0.01} = 3$ moles of AgCl

This means that 1 molecule of the complex contains 3 ionisable Cl. Hence, the formula is $[\text{Co}(\text{NH}_3)_6]\text{Cl}_3$.

15. (a)

16. (b)

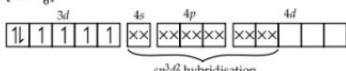
OR

(d) : $[\text{CoF}_6]^{3-}$: $x - 6 = -3 \Rightarrow x = +3$

$\text{Co}^{3+}(3d^6)$: 

F^- ion is a weak field ligand and does not cause pairing of electrons.

$[\text{CoF}_6]^{3-}$:



$[\text{CoF}_6]^{3-}$ ion is highly paramagnetic in nature and magnetic moment corresponds to four unpaired electrons.

17. (a)

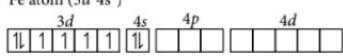
18. (c)

OR

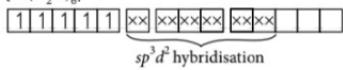


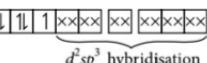
19. (d) : The oxidation number of Pt in Zeise's salt is +2. Zeise's salt is ionic complex with the formula, $\text{K}[\text{PtCl}_3(\text{C}_2\text{H}_4)]$.

20. (c) : Fe atom ($3d^64s^2$)

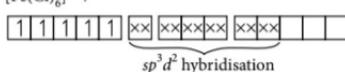


$[\text{Fe}(\text{H}_2\text{O})_6]^{3+}$:



$[\text{Fe}(\text{CN})_6]^{3-}$: 
 d^2sp^3 hybridisation

$[\text{Fe}(\text{Cl})_6]^{3-}$:


 sp^3d^2 hybridisation

OR

(c)

21. (c) : Cr and Mn show the highest oxidation states +6 and +7 respectively.

22. (b)

23. (b) : The electronic configurations of these elements are

V ($Z = 23$) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^3 4s^2$

Cr ($Z = 24$) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^1$

Mn ($Z = 25$) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^5 4s^2$

Fe ($Z = 26$) : $1s^2 2s^2 2p^6 3s^2 3p^6 3d^6 4s^2$

In the case of chromium, the second electron has to be removed from the half-filled d -shell which is more stable.

OR

(a)

24. (c) : The complex is $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$.

$[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl} \rightarrow [\text{Co}(\text{en})_2\text{Cl}_2]^+ + \text{Cl}^-$

Only one Cl^- which is precipitated as AgCl

100 mL of 0.024 M complex = 2.4 millimol = 0.0024 mol

25. (d) : $\text{NiCl}_2 + 4\text{KCN} \rightarrow \underset{\substack{\text{(excess)} \\ \text{potassium tetra cyanonickelate (II)}}}{\text{K}_2[\text{Ni}(\text{CN})_4]} + 2\text{KCl}$

$\text{K}_2[\text{Ni}(\text{CN})_4] + 4\text{HCl} \rightarrow \underset{\substack{\text{(y) potassium tetrachloronickelate (II)}}}{\text{K}_2[\text{Ni}(\text{Cl})_4]} + 4\text{HCN}$

26. (b) : Hybridisation of $X \rightarrow \text{K}_2[\text{Ni}(\text{CN})_4]$ is ds^2p^3 .
 $Y \rightarrow \text{K}_2[\text{NiCl}_4]$ is sp^3 .

27. (i) Transition metals form a large number of interstitial compounds because small atoms of certain non-metallic elements (H, B, C, N, etc.) get trapped in voids or vacant spaces of lattices of the transition metals.

Monthly Test Drive CLASS XI

ANSWER

KEY

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

(ii) As we move along transition metal series from left to right (*i.e.*, Ti to Cu), the atomic radii decrease due to increase in nuclear charge. Hence, the atomic volume decreases. At the same time, atomic mass increases. Hence, the density from titanium to copper increases.

28. (i) For nickel, +2 is the common oxidation state because the sum ($IE_1 + IE_2$) for Ni has lower value than Pt. For platinum, +4 is the common oxidation state as the sum of ($IE_1 + IE_2 + IE_3 + IE_4$) for Pt has lower value than Ni.

(ii) Platinum can form compounds in +4 oxidation state easily as the sum of ($IE_1 + IE_2 + IE_3 + IE_4$) energies is lower for Pt than for Ni.

29. Mn in +2 oxidation state has the electronic configuration $3d^5$. H_2O is a weak ligand. In presence of H_2O molecules, the distribution of electrons is $t_{2g}^3 e_g^2$ *i.e.*, all the electrons are unpaired.

CN^- is a strong ligand. In its presence, the distribution of electrons is $t_{2g}^5 e_g^0$ *i.e.*, one unpaired electron is present.

OR

(i) When a di- or polydentate ligand uses its two or more donor atoms to bind a single metal ion. It is said to be a chelate ligand. Chelating ligands form more stable complexes than monodentate analogs. This is called chelating effect.

(ii) $\dot{N}H_2 - \dot{N}H_2$ have two donor atoms, it can form three membered ring which is very strained, thus it can not act as chelating agent.

30. (i) The most stable oxidation state of lanthanides is +3. Hence, ions in +2 state tend to change to +3 oxidation state by loss of one electron and hence, act as reducing agents.

(ii) La^{3+} has a stable configuration of an inert gas [Xe] $5d^0 6s^0$. To obtain +4 oxidation state, the stable configuration is to be disturbed which is not possible under ordinary conditions and hence, La^{4+} does not exist.

31. (a) Lower wavelength is absorbed in octahedral complex than tetrahedral complex for the same metal and ligand. In tetrahedral coordination entity, formation of the *d*-orbital splitting is inverted and is smaller as compared to the octahedral field splitting. Thus, the energy of tetrahedral complex is smaller as compared to octahedral complex. $\Delta_t = (4/9)\Delta_o$

(b) When white light falls on the complex, some part of it is absorbed. Higher the crystal field splitting, lower will be the wavelength absorbed by the complex. The observed colour of complex is the colour generated from the wavelength left over.

32. (A) $[Cr(H_2O)_6Cl_3]$ (Violet)

(B) $[Cr(H_2O)_5Cl]Cl_2 \cdot H_2O$ (Green)

(C) $[Cr(H_2O)_4Cl_2]Cl \cdot 2H_2O$ (Dark green)

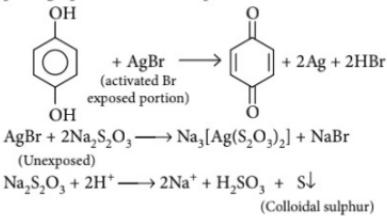
Compound (A) contains six water molecules as coordinated water and thus, does not lose H_2O on treatment with H_2SO_4 . Compound (B) contains five water molecules as coordinated water and one molecule as lattice water which is taken out by H_2SO_4 , showing loss of 18 g out of 266.5 g *i.e.*, 6.75% loss. Similarly, compound (C) contains four coordinated water molecules and two molecules of lattice water which are taken out by H_2SO_4 to show a loss of 13.5%.

33. As $E^\ominus_{Cr^{3+}/Cr^{2+}}$ is negative (-0.4 V), this means Cr^{3+} ions in solution cannot be reduced to Cr^{2+} easily, *i.e.*, Cr^{3+} ions are very stable. As $E^\ominus_{Mn^{3+}/Mn^{2+}}$ is more positive (+1.5 V) as compared to $E^\ominus_{Fe^{3+}/Fe^{2+}}$ (+0.8 V), Mn^{3+} ions can easily be reduced to Mn^{2+} ions in comparison to Fe^{3+} ions. Thus, the relative stability of these ions is : $Mn^{3+} < Fe^{3+} < Cr^{3+}$

(ii) Oxidation potentials for Cr, Mn and Fe will be +0.9 V, +1.2 V and +0.4 V. Thus, the ease of getting oxidised will be in the order, $Mn > Cr > Fe$.

OR

Following reactions occur when a black and white photographic film is developed.



34. (i) Nickel, in +2 oxidation state, has $3d^8$ configuration, mainly forms octahedral complexes. In presence of strong field ligand also it has two unpaired electrons in e_g orbital. Hence, it does not form low spin octahedral complexes.

(ii) The transition metals/ions have empty *d*-orbitals into which the electron pairs can be donated by ligands containing π -electrons.

(iii) CO is stronger ligand than NH_3 because CO has vacant molecular orbitals with which it can form π -bond with metal through back donation.

35. (i) All the lanthanoids predominantly show +3 oxidation state. However, some of the lanthanoids also

CONCEPT MAP

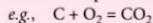
SOME BASIC CONCEPTS OF CHEMISTRY

Law of Conservation of Mass

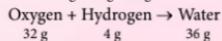
- Proposed by the French Chemist Antoine Lavoisier (1789)
- Mass can neither be created nor destroyed in a chemical reaction.

OR

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



$$12 \text{ g} + 32 \text{ g} = 44 \text{ g}$$



Law of Definite Proportions

- Proposed by Louis Prout (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 molecule 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 $\text{CO}_{1.8}$.

Avogadro's Law

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



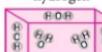
1 volume of hydrogen



1 volume of hydrogen



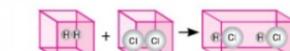
1 volume of oxygen



2 volumes of water vapour

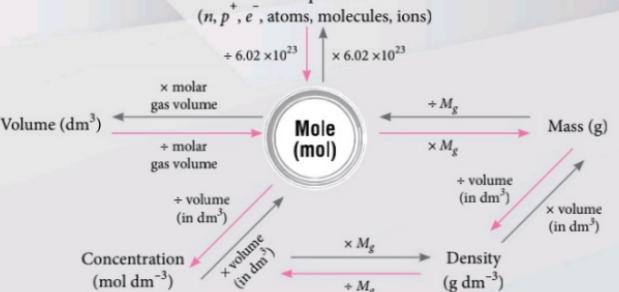
Gay Lussac's Law of Gaseous Volumes

- 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

No. of particles
(n , p^+ , e^- , atoms, molecules, ions)



CONCENTRATION

SOME
COMBINATION

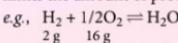
MOLE CONCEPT

Concentration Terms

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



For every 16 g of oxygen, 2 g H₂ is required, if H₂ is present less than 2 g then it will be limiting reagent.

RATION
IS

STOICHIOMETRIC CALCULATIONS

THE BASIC CONCEPTS OF CHEMISTRY

EMPIRICAL FORMULA

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

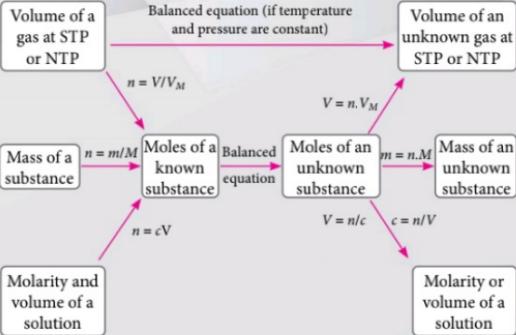
↓ Use molecular mass

Calculate $n = \text{Molecular mass} / \text{Empirical mass}$

↓

Molecular formula = $n \times \text{Empirical formula}$

Mole Calculations



(b) O.N. of Co = $0 + x - 1 - 1 + x + 0 - 4 = 0$

$$\Rightarrow 2x - 6 = 0 \Rightarrow x = +3$$

Name : μ -Amido- μ -nitritobis(tetraamminecobalt(III)) nitrate

(c) O.N. of Pt = $0 - 1 + x - 1 - 1 + x + 0 - 1 = 0$

$$\Rightarrow 2x - 4 = 0 \Rightarrow x = +2$$

Name : *trans*-Di- μ -chloridobis(chloridotriphenylphosphineplatinum(II))

(ii) In $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, water acts as ligand. As a result it causes crystal field splitting. Hence, *d-d* transition is possible in $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and shows colour. In the anhydrous CuSO_4 due to the absence of water (ligand), crystal field splitting is not possible and hence, no *d-d* transition occurs and shows no colour.

37. (i)(a) The ionic species which possesses unpaired electron or electrons in $(n-1)d$ -subshell will show colour. Out of the ions Ag^+ ($4d^{10}$), Co^{2+} ($3d^7$) and Ti^{4+} ($3d^0$), Co^{2+} will be coloured as it contains three unpaired electrons, Ag^+ and Ti^{4+} will be colourless.

(b) When placed in magnetic field, Co^{2+} will be attracted because it is paramagnetic due to unpaired electrons. Ag^+ and Ti^{4+} ions will be repelled by the magnetic field as they are diamagnetic.

(ii) (a) All transition elements except the first and the last member in each series show a large number of variable oxidation states. This is because difference of energy in the $(n-1)d$ and ns orbitals is very little. Hence, electrons from both the energy levels can be used for bond formation.

(b) As transition metals have a large number of unpaired electrons in the *d*-orbitals of their atoms they have strong interatomic attraction or metallic bonds. Hence, they have high enthalpy of atomization.

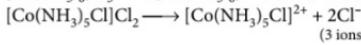
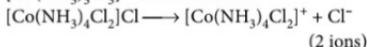
OR

(i) Lanthanoid contraction : The steady decrease in the atomic and ionic radii of lanthanoid elements with increase in atomic number is called lanthanoid contraction. It is caused due to imperfect shielding of nuclear charge by $4f$ -electrons.

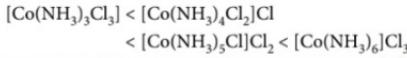
Consequences of lanthanoid contraction :

- The basic strength of oxides and hydroxides of lanthanoids decrease with increasing atomic number.
- Atomic and ionic sizes of $4d$ transition series elements and $5d$ series elements are similar. e.g., atomic radii of zirconium(Zr) is same as that of hafnium Hf.

(ii) These complexes can ionise in solution as :



As the number of ions in solution increases, their conductivity also increases. Therefore, conductivity follows the order :



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MONTHLY TEST DRIVE



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Total Marks : 120

Organic Compounds Containing Nitrogen

Time Taken : 60 Min.

NEET

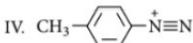
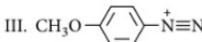
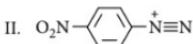
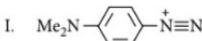
Only One Option Correct Type

- An amine forms salt with BF_3 , if the alkyl group in amine is CH_3^- , the order of basicity towards BF_3 is
 (a) $\text{CH}_3\text{NH}_2 > (\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N}$
 (b) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2$
 (c) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N}$
 (d) $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2$
 - Aniline is treated with NaNO_2/HCl at 0°C to give compound 'X' which on treatment with cuprous cyanide gives another compound 'Y'. When compound 'Y' is treated with H_2/Ni , compound 'Z' is obtained. Compound 'Z' is
 (a) benzyl alcohol (b) benzylamine
 (c) *N*-ethylaniline (d) phenol.
 - Identify the product Z in the given sequence of reactions.



- (a) CH_3CHO (b) CH_3CONH_2
 (c) CH_3COOH (d) $\text{CH}_3\text{CH}_2\text{NHOH}$

- 4.** Consider the following ions:



The reactivity of these ions towards azo coupling reactions under similar conditions is

- (a) I < IV < II < III (b) I < III < IV < II
 (c) III < I < II < IV (d) III < I < IV < II

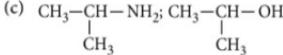
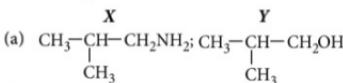
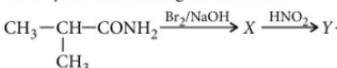
- Butanenitrile may be prepared by heating

 - (a) propyl alcohol with alc. KCN
 - (b) butyl alcohol with alc. KCN
 - (c) butyl chloride with alc. KCN
 - (d) propyl chloride with alc. KCN.

- Which of the following is not a nitro-derivative?

- (a) $\text{CH}_3\text{CH}-\overset{\underset{\text{CH}_3}{\mid}}{\text{N}}=\text{O}$ (b) $\text{CH}_3\text{CH}_2\text{ONO}$
 (c) $\text{C}_6\text{H}_5\text{NO}_2$ (d) $\text{C}_6\text{H}_4(\text{OH})\text{NO}_2$

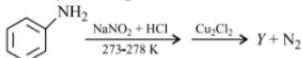
- Identify X and Y in the given reactions.



8. 59 g of an amide obtained from a carboxylic acid, RCOOH , upon heating with alkali liberated 17 g NH_3 . The acid is

- (a) formic acid (b) acetic acid
 (c) propionic acid (d) benzoic acid.

9. Identify the compound 'Y' in the following reaction.



- (a)  (b) 
- (c)  (d) 

10. Aromatic nitriles are not prepared by which of the following reaction?

- (a) $\text{ArX} + \text{KCN}$ (b) $\text{ArN}_2^+ \text{Cl}^- + \text{CuCN}$
 (c) $\text{ArCONH}_2 + \text{P}_2\text{O}_5$ (d) $\text{ArCONH}_2 + \text{SOCl}_2$

11. Aniline is reacted with bromine water and the resulting product is treated with an aqueous solution of sodium nitrite in presence of dilute hydrochloric acid. The compound so formed is converted into a tetrafluoroborate which is subsequently heated dry. The final product is

- (a) *p*-bromoaniline
 (b) *p*-bromofluorobenzene
 (c) 1, 3, 5-tribromobenzene
 (d) 2, 4, 6-tribromofluorobenzene.

12. When aniline reacts with oil of bitter almonds condensation takes place and benzal derivative is formed. This is known as
 (a) iodide of Millon's base
 (b) Hinsberg's reagent
 (c) acetanilide
 (d) Schiff's base.

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 :** In strongly acidic solutions, aniline becomes more reactive towards electrophilic reagents.

Reason : The amino group being completely protonated in strongly acidic solution, the lone pair of electrons on the nitrogen is available for resonance.

14. **Assertion :** Gabriel phthalimide synthesis can be used to convert alkyl chlorides into primary amines.

Reason : With proper choice of reagent, Gabriel synthesis can be used to prepare primary, secondary and tertiary amines.

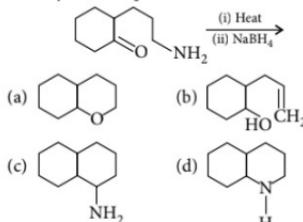
15. **Assertion :** *p*-Methoxyaniline (*p*-anisidine) is a stronger base than *m*-methoxyaniline (*m*-anisidine).

Reason : At *m*-position, methoxy group can exert only *I*-effect but not *R* effect.

JEE MAIN / JEE ADVANCED

Only One Option Correct Type

16. Identify the final product.



17. Which of the following is the strongest acid?

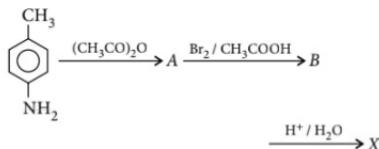
- (a) 4-Nitrobenzoic acid
 (b) 4-Methylbenzoic acid
 (c) 4-Methoxybenzoic acid
 (d) 4-Ethylbenzoic acid

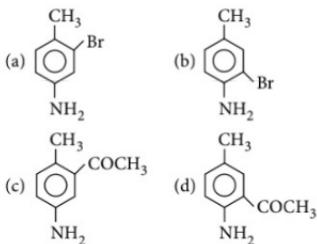
18. A compound 'A' has a molecular formula, $\text{C}_7\text{H}_7\text{NO}$.

On treatment with Br_2 and KOH, 'A' gives an amine 'B' which gives carbylamine test. 'B' upon diazotisation and coupling with phenol gives an azo dye. 'A' can be

- (a) $\text{C}_6\text{H}_5\text{CH} = \text{NOH}$
 (b) $\text{C}_6\text{H}_5\text{CONH}_2$
 (c) $\text{C}_6\text{H}_5\text{CH}_2\text{NO}$
 (d) *o*-, *m*- or *p*- $\text{C}_6\text{H}_4(\text{NH}_2)\text{CHO}$

19. Identify 'X' in the given reactions sequence.



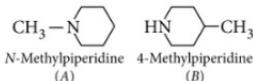


More than One Options Correct Type

20. Select the correct statements.

- (a) Most alkyl amines are more basic than ammonia in aqueous solution.
- (b) pK_a of Me_3NH^+ is higher than that of NH_4^+ .
- (c) Aniline is more stable than anilinium ion.
- (d) pK_b of CH_3NH_2 is higher than that of NH_3 .

21. Which of the following statements are correct?



- (a) A has higher boiling point than B.
- (b) B has higher boiling point than A.
- (c) A and B have same boiling points being isomeric amines.
- (d) B reacts with benzenesulphonyl chloride while A does not.

22. A positive carbonylamine test is given by

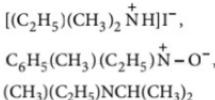
- (a) *N,N*-dimethylaniline
- (b) 2,4-dimethylaniline
- (c) *N*-methyl-*o*-methylaniline
- (d) *p*-methylbenzylamine.

23. The reagents that can be used to convert benzene diazonium chloride to benzene are

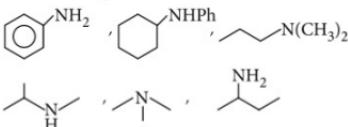
- (a) SnCl_2/HCl
- (b) $\text{CH}_3\text{CH}_2\text{OH}$
- (c) $\text{H}_3\text{PO}_2, \text{H}_2\text{O}$
- (d) HBF_4^-

Numerical Value Type

24. The total number of optically active compounds which can be resolved from the following list is $\text{C}_2\text{H}_5\text{NHCH}_3, \text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{N}(\text{CH}_3)\text{C}_2\text{H}_5, [\text{Ph}(\text{CH}_3)(\text{C}_2\text{H}_5)]\overset{+}{\text{NH}}\text{I}^-,$



25. Number of amines out of the following which will react with CS_2 is

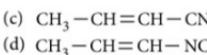
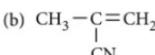
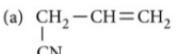


26. $\text{C}_4\text{H}_{11}\text{N}$ on reaction with HNO_2 forms 3° alcohol. Thus, amine is x° . x is _____.

Comprehension Type

A compound 'X' ($\text{C}_4\text{H}_5\text{N}$) exists in two stereoisomeric forms. Compound (X) on reduction with H_2 in the presence of Ni gives a compound (Y). Compound 'Y' ($\text{C}_4\text{H}_{11}\text{N}$) exists in only one form. Compound (X) on treatment with alk. KMnO_4 followed by acidification gives acetic acid and oxalic acid. When compound (X) is reacted with NaOH followed by acidification gives a compound (Z) with molecular formula, $\text{C}_4\text{H}_6\text{O}_2$. Compound (Z) on reaction with alk. KMnO_4 followed by acidification gives again oxalic acid and acetic acid. Compound (Y) on reaction with CHCl_3 and KOH forms a compound 'A' ($\text{C}_5\text{H}_9\text{N}$). Compound (Y) on treatment with HNO_2 followed by reaction with PCC gives a compound (B) which gives positive Tollens' test.

27. The compound (X) must be



28. The compound (Z) must be

- (a) $\text{CH}_2=\text{CH}-\text{COOCH}_3$
- (b) $\text{CH}_3-\text{CH}=\text{CH}-\text{COOH}$
- (c) $\text{CH}_3-\text{CH}=\text{CH}-\text{NC}$
- (d) $\text{OHCCH}_2-\text{CH}=\text{CH}_2$

Matrix Match Type

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

List I (Compounds)	List II (pK_b value)
P. Ammonia	1. 8.92
Q. Methanamine	2. 9.38
R. Benzenamine	3. 3.38
S. <i>N,N</i> -Dimethylaniline	4. 4.75

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

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

List I	List II
P. Benzenesulphonyl chloride	1. Zwitter ion
Q. Sulphanilic acid	2. Hinsberg's reagent
R. Alkyldiazonium salts	3. Dyes
S. Aryldiazonium salts	4. Conversion to alcohols

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

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90-75%	GOOD WORK !	You can score good in the final exam.
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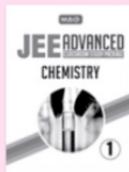
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Unit
4

Equilibrium | Redox Reactions

Equilibrium

Equilibrium state of a system is the state, in which system has no tendency for a change without external stimulation and so there is no net change occurs with time. Equilibrium is attained when the rates of the two opposing processes become equal.

There are two types of equilibrium:

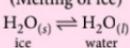
- **Physical equilibrium** : If the opposing processes involve only physical changes, the equilibrium is called physical equilibrium.
 - **Chemical equilibrium** : If the opposing processes involve chemical changes, the equilibrium is called chemical equilibrium.

Physical Equilibrium

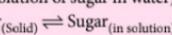
Types of Equilibrium

Chemical Equilibrium

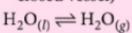
Solid-liquid equilibrium (Melting of ice)



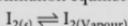
Solid-solution equilibrium Dissolution of sugar in water



Liquid-vapour equilibrium (Evaporation of water in a closed vessel)



Solid-vapour equilibrium (Sublimation equilibrium)



Gas-solution equilibrium (Dissolution of a gas in a liquid under pressure in a closed cell.)



It is governed by Henry's law which states that the mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

A reaction in which not only the reactants react to form the products under certain conditions but also products react to form reactants under the same condition, is called a reversible reaction.

A reaction which cannot take place in the reverse direction, i.e., the products formed do not react to give back the reactants under the same conditions, is called an irreversible reaction.

GENERAL CHARACTERISTICS OF EQUILIBRIA INVOLVING PHYSICAL PROCESSES

Some important characteristics of physical equilibria are as follows :

- At equilibrium, some observable property of the system becomes constant.
- Equilibria involving gases can be attained only in closed vessels. This is because if the vessel is opened, the gas will escape and there will be no equilibrium.
- Equilibrium is dynamic in nature but stable.

- At equilibrium, the concentrations of the reactants and products become constant at constant temperature.



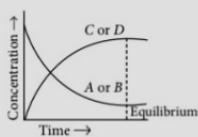
where, K is equilibrium constant.

- The magnitude of the equilibrium constant represents the extent to which the process proceeds before equilibrium is attained. For example, greater value of the K greater will be the dissolution of $\text{CO}_{2(g)}$ in water.

General Characteristics of Chemical Equilibrium

- At equilibrium, the concentration of each of the reactants and the products becomes constant.

This may be represented graphically for a general reversible reaction, $A + B \rightleftharpoons C + D$, as shown in figure.



- Chemical equilibrium can be attained from either direction, i.e., from the direction of the reactants as well as from the direction of the products.

- At equilibrium, the rate of forward reaction becomes equal to the rate of backward reaction and hence, the equilibrium is dynamic in nature.

- A chemical equilibrium can be established only if none of the products is allowed to escape out or separate out as a solid.

Law of Mass Action

The rate at which a substance reacts is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented in the balanced chemical equation.

Laws of Chemical Equilibrium

At a given temperature, the product of concentrations of the products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value which is called equilibrium constant. For a reaction, $aA + bB \rightleftharpoons cC + dD$

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b}$$

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

where, K_p = Equilibrium constant when all the reactants and products are in gaseous state.

Δn_g = Moles of gaseous products – moles of gaseous reactants.

Equilibrium Law

IMPORTANT FEATURES OF EQUILIBRIUM CONSTANT

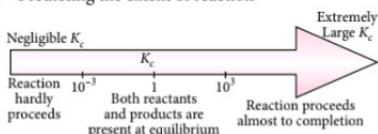
- Expression for equilibrium constant is applicable only when concentrations of the reactants and products have attained constant value at equilibrium state.

- The value of equilibrium constant is independent of initial concentrations of the reactants and products.
- Equilibrium constant is temperature dependent, having one unique value for a particular balanced reaction at a given temperature.

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

APPLICATIONS OF EQUILIBRIUM CONSTANTS

- Predicting the extent of reaction



- Predicting the direction of reaction

$Q < K$	$Q = K$	$Q > K$
Reaction will shift in forward direction.	Reaction in equilibrium	Reaction will shift in backward direction.

- Relation between K_c and standard Gibbs free energy.

$$\Delta_f G^\circ = -RT \ln K_c$$

LE CHATELIER'S PRINCIPLE

- A change in any of the factors that determine the equilibrium conditions of a system will cause the system to change in such a manner so as to reduce or counteract the effect of the change.

Factors Affecting the Equilibrium

- Effect of change of concentration
 - With increase in concentration of any reactant at equilibrium, the equilibrium shifts to forward direction.
- Effect of change of pressure
 - Low pressure favours those reactions which are accompanied by increase in total number of moles.
 - High pressure favours those reactions which are accompanied with decrease in total number of moles.
 - Pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

- Effect of change of temperature
 - K_c for an exothermic reaction decreases as the temperature increases.
 - K_c for an endothermic reaction increases as the temperature increases.

- Effect of adding inert gas on equilibrium
 - At constant volume, when $(n_p = n_r)_{\text{gaseous}}$, there is no effect.
 - At constant pressure, when $(n_p \neq n_r)_{\text{gaseous}}$, effect is observed.
When an inert gas is added, it will increase the volume of the system. Therefore, equilibrium will shift in a direction in which there is increase in number of moles of gases.

- Effect of catalyst
 - Catalyst does not affect equilibrium constant.

Ionic Equilibrium

In weak electrolytes, equilibrium is established between ions and unionised molecules. Such an equilibrium is called ionic equilibrium,
 $AB_{(s)} + aq \rightleftharpoons A_{(aq)}^+ + B_{(aq)}^-$

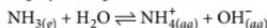
The substances which dissociate almost completely into ions in aqueous solution, are called strong electrolytes. They are very good conductor of electricity, e.g., NaOH, NaCl, HCl, etc.

The substances which dissociate to a small extent in aqueous solution are called weak electrolytes. They conduct electricity to a small extent, e.g., NH₄OH, CH₃COOH, etc.

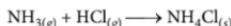
ACIDS, BASES AND SALTS

Arrhenius Concept of Acids and Bases

- Acid is a substance that dissociates in water to give hydrogen ions ($\text{H}^+_{(aq)}$).
- Base is a substance that produces hydroxyl ions ($\text{OH}^-_{(aq)}$) in water.
- Arrhenius concept explained neutralisation, salt hydrolysis, strength of acids and bases, etc.
- It did not explain substances like NH_3 , CaO are known to be basic but do not contain any hydroxyl groups and substances like CO_2 , SO_2 are known to be acidic but do not contain any hydrogen. This limitation is, however overcome if water is supposed to play an important role.

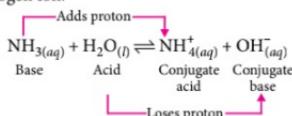


- Inability of explaining the reaction between an acid and base in absence of water.

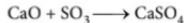


Bronsted-Lowry Concept of Acids and Bases

- Acid is a substance that is capable of donating a hydrogen ion.
- Base is a substance that is capable of accepting a hydrogen ion.



- The acid-base pair that differs only by one proton is called a conjugate acid-base pair.
- A strong Bronsted acid has a weak conjugate base and vice-versa.
- It cannot explain the reactions between acidic oxides like CO_2 , SO_2 etc. and the basic oxides like CaO , BaO , etc. which take place even in the absence of the solvent.



- Substances like BF_3 , AlCl_3 , etc. do not have any hydrogen but are known to behave as acids.

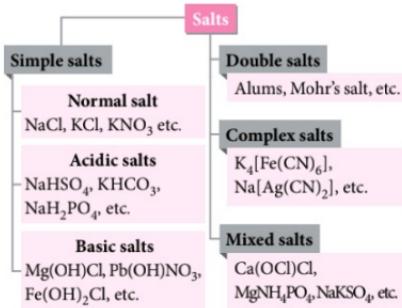
Lewis Concept of Acids and Bases

- An acid is a species which accepts an electron pair.

- A base is a species which donates an electron pair. e.g., $\text{BF}_3 + \text{NH}_3 \longrightarrow \text{BF}_3 : \text{NH}_3$
- Electron deficient species like AlCl_3 , BF_3 , etc. can act as Lewis acids while species like H_2O , NH_3 , OH^- , etc. which can donate a pair of electrons, can act as Lewis bases.

Formation of Salts

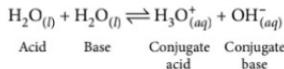
When acids and bases are mixed in right proportion, they react with each other to form salts.



Relative Strength of Acids & Bases

- $\frac{\text{Strength of acid } (\text{HA})_1}{\text{Strength of acid } (\text{HA})_2} = \sqrt{\frac{K_{a_1}}{K_{a_2}}}$
- $\frac{\text{Strength of base } (\text{BOH})_1}{\text{Strength of base } (\text{BOH})_2} = \sqrt{\frac{K_{b_1}}{K_{b_2}}}$
- $K_a = K_{a_1} \times K_{a_2} \times K_{a_3}$ (For tribasic acid)
 $K_{a_1} > K_{a_2} > K_{a_3}$
- Strong acids have very weak conjugate bases.

IONISATION CONSTANT OF WATER AND ITS IONIC PRODUCT



The dissociation constant is given as :

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]}$$

Ionic product of water (K_w)

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

At 298 K, $[OH^-] = [H^+] = 1.0 \times 10^{-7}$ M

$$\therefore K_w = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2$$

$$K_a \times K_b = K_w$$

THE pH SCALE

- pH may be defined as negative logarithm of hydronium ion concentration.
 $pH = -\log [H_3O^+]$
- $pK_w = pH + pOH = 14$
 $pK_w = pK_a + pK_b = 14$
- pH of a solution can be determined with pH paper or more accurately by pH meter.

SALT HYDROLYSIS

The reaction of the cation or anion of the salt with water to produce acidic or basic solution, is called salt hydrolysis.

Degree of hydrolysis : The degree of hydrolysis of a salt is defined as the fraction of the total salt which is hydrolysed.

- Salts of weak acid and strong base

$$K_h = \frac{K_w}{K_a}; h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_a \cdot C}}$$

$$pH = -\frac{1}{2}(\log K_w + \log K_a - \log C)$$

- Salts of strong acid and weak base

$$K_h = \frac{K_w}{K_b}; h = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{K_w}{K_b \cdot C}}$$

$$pH = -\frac{1}{2}(\log K_w - \log K_b + \log C)$$

- Salts of weak acid and weak base

$$K_h = \frac{K_w}{K_a K_b}; h = \sqrt{K_h} = \sqrt{\frac{K_w}{K_a K_b}}$$

$$pH = \frac{1}{2}(pK_w + pK_a - pK_b)$$

BUFFER SOLUTIONS

- A buffer solution is defined as a solution which have any change in its pH value even when small amounts of acid or base are added to it.
- Acidic buffer :** It is the solution of a mixture of a weak acid and its salt with a strong base, e.g., $CH_3COOH + CH_3COONa$.

- Basic buffer :** It is the solution of a mixture of a weak base and its salt with a strong acid, e.g., $NH_4OH + NH_4Cl$.

pH of acidic buffer (Henderson Hasselbalch equation)

$$\begin{aligned} pH &= pK_a + \log \frac{[Salt]}{[Acid]} \\ &= pK_a + \log \frac{[Conjugate\ base]}{[Acid]} \end{aligned}$$

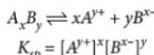
pH of Buffer Mixture

pH of basic buffer (Henderson Hasselbalch equation)

$$\begin{aligned} pOH &= pK_b + \log \frac{[Salt]}{[Base]} \\ pH &= pK_a + \log \frac{[Base]}{[Conjugate\ acid]} \end{aligned}$$

SOLUBILITY EQUILIBRIA AND SOLUBILITY PRODUCT OF SPARINGLY SOLUBLE SALTS

Solubility product of an electrolyte at a specified temperature may be defined as the product of the 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.



COMMON ION EFFECT

If to an ionic equilibrium, $AB \rightleftharpoons A^+ + B^-$, a salt containing a common ion (AC or BD) is added, the equilibrium shifts in the backward direction. This is called common ion effect.

APPLICATIONS OF SOLUBILITY PRODUCT AND COMMON ION EFFECT

- In the precipitation of salts, a salt precipitates if $K_{sp} <$ ionic product.
- In the removal of hardness of water.
- In qualitative analysis.
- In fractional precipitation.

'Chemical equilibrium based model' for describing the strength of sludge !

A new model, based on chemical equilibrium theory, was established to evaluate the strength of sludges in biological wastewater treatment systems. The effectiveness of this model was demonstrated by the experimental results with an anaerobic hydrogen producing sludge. The Gibbs free energy of adhesion (ΔG°) under shear could also be calculated using this model. The equilibrium constant K° and $\Delta G^\circ/RT$ at a shear intensity of 800 per second were estimated to be 6.54 ± 0.12 and 1.88 ± 0.02 , respectively. The two parameters could be used to evaluate the strength of the hydrogen producing sludge.

Redox Reactions

Chemical reactions involve transfer of electrons from one chemical substance to another. These electron-transfer reactions are termed as oxidation-reduction or redox reactions.

OXIDATION AND REDUCTION

Oxidation

Oxidation is a process which involves addition of oxygen, removal of hydrogen, addition of non-metal, removal of metal, increase in +ve charge, loss of electrons and increase in oxidation number, e.g.,

- Addition of oxygen : $2\text{Mg} + \text{O}_2 \rightarrow 2\text{MgO}$
- Removal of hydrogen : $\text{H}_2\text{S} + \text{Cl}_2 \rightarrow 2\text{HCl} + \text{S}$
- Addition of non-metal : $\text{Fe} + \text{S} \rightarrow \text{FeS}$
- Removal of metal : $2\text{K} + \text{H}_2\text{O}_2 \rightarrow 2\text{KOH} + \text{I}_2$
- Increase in +ve charge : $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+} + e^-$
- Loss of electrons (also known as de-electronation) $\text{H}_2^0 \rightarrow 2\text{H}^+ + 2e^-$

Reduction

Reduction is just reverse of oxidation. Reduction is a process which involves removal of oxygen, addition of hydrogen, removal of non-metal, addition of metal, decrease in +ve charge, gain of electrons and decrease in oxidation number, e.g.,

- Removal of oxygen : $\text{CuO} + \text{C} \rightarrow \text{Cu} + \text{CO}$
- Addition of hydrogen : $\text{Cl}_2 + \text{H}_2 \rightarrow 2\text{HCl}$
- Removal of non-metal :

 - $2\text{HgCl}_2 + \text{SnCl}_2 \rightarrow \text{Hg}_2\text{Cl}_2 + \text{SnCl}_4$
 - Addition of metal : $\text{HgCl}_2 + \text{Hg} \rightarrow \text{Hg}_2\text{Cl}_2$
 - Decrease in +ve charge : $\text{Fe}^{3+} \rightarrow \text{Fe}^{2+}$
 - Gain of electrons (also known as electronation) $\text{Zn}_{(aq)}^{2+} + 2e^- \rightarrow \text{Zn}_{(s)}$

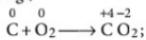
Oxidising and Reducing Agents

An oxidising agent is a substance in which the oxidation number of its element decreases while a reducing agent is a substance in which the oxidation number of its element increases.

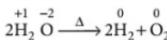
- Oxidation number** : Charge on an atom produced by donating or accepting electrons is called oxidation number or oxidation state, e.g.,
 - For homonuclear species like N_2 , Cl_2 , H_2 , P_4 , S_8 , etc., oxidation state is zero.
 - Oxidation state of H is +1 but -1 when combined with non-metals.
 - Oxidation state of oxygen is -2, but in peroxide it is -1. In OF_2 , it is +2 as oxidation state of fluorine is always -1.

Types of Redox Reactions

- Combination reaction** : The reaction in which two atoms or molecules combine together to form a third molecule, e.g.,



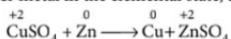
- Decomposition reaction or intramolecular redox reaction** : The reaction in which a molecule breaks down to form two or more components out of which one must be in the elemental state, e.g.,



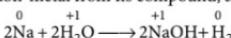
- Displacement reaction or intermolecular redox reaction** : The reaction in which an atom or ion in a compound is replaced by an atom or ion of some other element, e.g.,



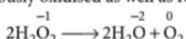
- (a) **Metal displacement reaction** : The reaction in which a metal in the compound is displaced by some other metal in the elemental state, e.g.,



- (b) **Non-metal displacement reaction** : The reaction in which a metal or a non-metal displaces another non-metal from its compound, e.g.,



- **Disproportionation reaction or auto-redox reaction** : The reaction in which the same species is simultaneously oxidised as well as reduced, e.g.,



Applications of Redox Reactions

- In extraction of metals, e.g., $\text{Fe}_2\text{O}_3 + 3\text{C} \longrightarrow 2\text{Fe} + 3\text{CO}$
- In electrochemical cells.
- In photosynthesis.
- In quantitative analysis.

BALANCING OF REDOX REACTIONS

By Oxidation Number Method

- Identify the element whose oxidation number have changed.
- Calculate the increase or decrease in oxidation number per atom and thereby identify oxidising and reducing agents. If more than one atom of the same element is involved, find total increase or decrease in oxidation number by multiplying with the number of atoms involved.
- Multiply the formula of oxidising and reducing agents by suitable integers so that
total increase = total decrease.
- Balance all atoms other than H and O.
- Finally balance H and O atoms by adding H_2O molecules.

- For acidic medium, first balance O- atoms by adding H_2O molecules to the side deficient in O and H^+ ions to the side deficient in hydrogen.
- For basic medium, first balance O- atoms by adding H_2O molecules to the side deficient in O. Then, to balance H add H_2O molecules to the side deficient in H add equal number of OH^- ions to the other side.

By Ion-electron/Half-reaction Method

- Find the atoms whose oxidation numbers undergo a change.
- Split the reaction in two half equations, oxidation half-reaction and reduction half-reaction.
- Balance each half-reaction by balancing all other elements except H and O.
- Balance the oxidation numbers of the half-reactions by adding electrons to the side necessary.
- Balance the charge on the two sides of the half-reaction by adding H^+ ions (if medium is acidic) or adding OH^- ions (if medium is basic).
- Balance H and O by adding H_2O molecules to the side deficient.
- Multiply the two half-reaction by suitable integers so that, on adding, electrons gained in one are cancelled by the electrons lost in the other.

Equivalent Weights of Oxidising and Reducing Agents

Eq. wt. of oxidising agent

$$= \frac{\text{Molecular weight}}{\text{No. of electrons gained by one molecule}} \\ \text{or} \\ \text{Change in O.No. per mole}$$

Eq. wt. of reducing agent

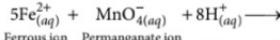
$$= \frac{\text{Molecular weight}}{\text{No. of electrons lost by one molecule}} \\ \text{or} \\ \text{Change in O.No. per mole}$$

REDOX REACTIONS AS THE BASIS FOR TITRATIONS

Redox titrations can be used to determine the exact amount of an oxidising agent (or a reducing agent) in a given solution by titrating it against the standard solution (whose normality or molarity is known) of a suitable reducing agent (or the oxidising agent) in presence of an indicator.

Types of Redox Titrations

- **Potassium permanganate titration** : In this titration, reducing agents like FeSO_4 , Mohr's salt $[(\text{NH}_4)_2\text{SO}_4\text{FeSO}_4\cdot 6\text{H}_2\text{O}]$, H_2O_2 , oxalic acid $(\text{COOH})_2$, sodium oxalate $(\text{COONa})_2$, etc. are directly titrated against KMnO_4 as the oxidising agent in acidic medium, e.g.,



Ferrous ion Permanganate ion



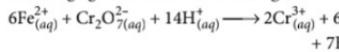
Ferric ion

- **Potassium dichromate titration :** In this titration, reducing agents given in potassium permanganate titration are directly titrated against $K_2Cr_2O_7$ as the oxidising agent in acidic medium. e.g.,

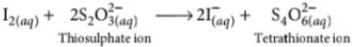
$$6Fe^{2+}_{(aq)} + Cr_2O_7^{2-}_{(aq)} + 14H^+_{(aq)} \longrightarrow 2Cr^{3+}_{(aq)} + 6Fe^{3+}_{(aq)} + 7H_2O_{(l)}$$
 - **Ceric sulphate titration :** In this titration, the reducing agents such as Fe^{2+} salts, Cu^+ salts, nitrates, arsenites, oxalates, etc. are directly titrated against ceric sulphate, $Ce(SO_4)_2$ as the oxidising agent.

$$Fe^{2+}_{(aq)} + Ce^{4+}_{(aq)} \longrightarrow Fe^{3+}_{(aq)} + Ce^{3+}_{(l)}$$

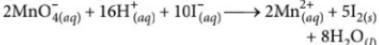
 Ferrous ion Ceric ion Ferric ion Cerous ion
 - **Iodimetric titration :** This titrations involve the direct use of iodine as the oxidising agent (in neutral or slightly acidic medium) using starch as an



indicator. The various reducing agents used in these titrations are thiosulphates, sulphites, arsenites and antimonites.



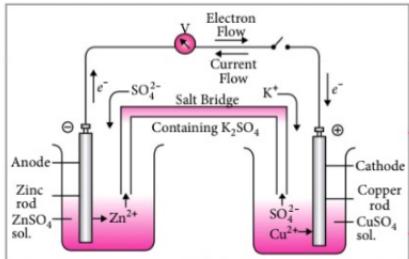
- **Iodometric titration** : This titration is carried out in two steps. In the first step, oxidising agents such as KMnO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CuSO_4 , peroxides, etc. are treated with an excess of KI when I_2 is liberated quickly and quantitatively.



In the second step, the liberated iodine is titrated against a standard solution of sodium thiosulphate using starch as an indicator.

Electrochemical Cell

- It is a device which converts chemical energy produced in an indirect redox reaction into electrical energy.



- Representation of an electrochemical cell
 $\text{Zn} \mid \text{Zn}^{2+} (C_1) \parallel \text{Cu}^{2+} (C_2) \mid \text{Cu}$

- Redox couple is defined as a combination of the oxidised and reduced forms of the same substance taking part in an oxidation or reduction half reaction.

- At anode : $\text{Zn}_{(s)} \longrightarrow \text{Zn}_{(aq)}^{2+} + 2e^-$
 - At cathode : $\text{Cu}_{(aq)}^{2+} + 2e^- \longrightarrow \text{Cu}_{(s)}$

Important generalisation :

- Oxidation occurs at the anode while reduction occurs at the cathode.
 - Anode acts as the negative pole while cathode acts as the positive pole.
 - Electrons flow from anode to cathode in the external circuit while current flows from cathode to anode.
 - Chemical energy of the redox reaction occurring in the galvanic cell is converted into electrical energy.

- By convention, the standard electrode potential (E°) of hydrogen electrode is 0.00 volt.
 - 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.

The electrode potential is termed as oxidation potential if the electrode loses electrons and is called the reduction potential if the electrode gains electrons.

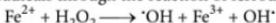
Electromotive series

A list of oxidising agents, arranged in decreasing order of their strength is called the activity or electromotive or electrochemical series.



Chemical oxidation with Fenton's Reagents !

Fenton's reagent generates hydroxyl radicals through the reaction of ferrous ion and hydrogen peroxide :



The hydroxyl radical is a powerful oxidising agent, second only to fluorine. Now, the process is self replicating since the reaction of ferric ion with hydrogen peroxide to generate the perhydroxyl radical also occurs :



The perhydroxyl radical is a weaker oxidizer (between hydrogen peroxide and permanganate). But more importantly the process generates further ferrous ions that in turn stimulate further reaction with hydrogen peroxide to produce more hydroxyl radicals. The hydroxyl radical can react with almost any hydrocarbon to produce carbon dioxide as a final product (as chlorides if a chlorinated hydrocarbon is treated).



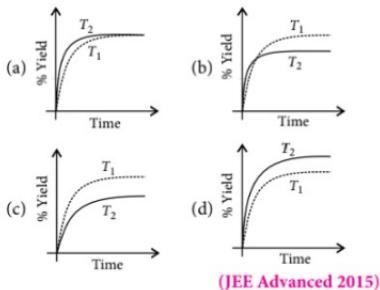
WRAP it up!

1. Calculate the pH of a solution formed by mixing of 0.2 M NH_4Cl and 0.1 M NH_3 . The pK_b of ammonia is 4.75.
(a) 8 (b) 7.67 (c) 8.95 (d) 10.55
2. For a gaseous phase reaction, $\text{A} + 2\text{B} \rightleftharpoons \text{AB}_2$, $K_c = 0.3475$ at 200 °C. When 2 moles of B are mixed with one mole of A, the total pressure required to convert 60% of A to AB_2 is
(a) 190.5 atm (b) 181.5 atm
(c) 101.0 atm (d) 281.5 atm.
3. The change in the oxidation number of S in H_2S and SO_2 in the following industrial reaction :
 $2\text{H}_2\text{S}_{(g)} + \text{SO}_{2(g)} \longrightarrow 3\text{S}_{(s)} + \text{H}_2\text{O}_{(g)}$, will be
(a) -2 to 0, +4 to 0 (b) -2 to 0, +4 to -1
(c) -2 to -1, +4 to 0 (d) -2 to -1, +4 to -2
4. For a sparingly soluble salt A_pB_q , the relationship of its solubility product (K_{sp}) with its solubility (S) is
(a) $K_{sp} = S^{p+q} \cdot p^p \cdot q^q$ (b) $K_{sp} = S^{p+q} \cdot p^l \cdot q^l$
(c) $K_{sp} = S^{pq} \cdot p^q \cdot q^q$ (d) $K_{sp} = S^{pq} \cdot (pq)^{p+q}$
5. A 20 litre container at 400 K contains $\text{CO}_{2(g)}$ at pressure 0.4 atm and an excess of SrO (neglect the volume of solid SrO). The volume of the container is now decreased by moving the movable piston fitted in the container. The maximum volume of the container, when pressure of CO_2 attains its maximum value, will be
(Given that : $\text{SrCO}_{3(s)} \rightleftharpoons \text{SrO}_{(s)} + \text{CO}_{2(g)}$, $K_p = 1.6 \text{ atm}$)
(a) 10 litre (b) 4 litre
(c) 2 litre (d) 5 litre. (NEET 2017)
6. Which of the following is a set of reducing agents?
(a) HNO_3 , Fe^{2+} , F_2 (b) F^- , Cl^- , MnO_4^-
(c) I^- , Na , Fe^{2+} (d) $\text{Cr}_2\text{O}_7^{2-}$, CrO_4^{2-} , Na^+
7. The ionisation constant of benzoic acid is 6.46×10^{-5} and K_{sp} for silver benzoate is 2.5×10^{-13} . How many times is silver benzoate more soluble in a buffer of pH 3.19 as compared to its solubility in pure water?
(a) 2 (b) 3.32 (c) 4 (d) 4.32
8. Which set represents an odd nature with respect to oxidation number per atom of underlined atoms?
(a) $\underline{\text{H}}_2\text{SO}_5$, $\text{H}_2\underline{\text{S}}_2\text{O}_8$, $\text{K}_2\text{Cr}_2\text{O}_7$
(b) $\text{Cr}\underline{\text{O}}_5$, CrO_4^{2-} , SO_4^{2-}
(c) $\text{H}\underline{\text{N}}\text{O}_2$, N_2O_3 , $\underline{\text{N}}\text{F}_3$
(d) $\underline{\text{N}}\text{H}_4^+$, $\underline{\text{N}}_3\text{H}$, $\underline{\text{N}}\text{H}_3$

Applications :

- To compare the relative strength of oxidising and reducing agents.
- Comparison of reactivity of metals.
- To predict whether a metal will liberate hydrogen from the aqueous solution of acids or not.

9. MY and NY_3 , two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3 ?
- The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water.
 - The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities.
 - The molar solubilities of MY and NY_3 in water are identical.
 - The molar solubility of MY in water is less than that of NY_3 . (NEET Phase-I 2016)
10. The degree of dissociation (α) of PCl_5 obeying the equilibrium : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is related to the pressure at equilibrium by
- $\alpha \propto P$
 - $\alpha \propto \frac{1}{\sqrt{P}}$
 - $\alpha \propto \frac{1}{P^2}$
 - $\alpha \propto \frac{1}{P^4}$
11. What will occur if a block of copper metal is dropped into a beaker containing a solution of 1 M $ZnSO_4$?
- The copper metal will dissolve with evolution of oxygen gas.
 - The copper metal will dissolve with evolution of hydrogen gas.
 - No reaction will occur.
 - The copper metal will dissolve and zinc metal will be deposited. (JEE Main Online 2016)
12. The rate of formation of the complex $[Fe(dipy)_3]^{2+}$ at 25 °C in following the reaction
- $$Fe^{2+} + 3dipy \rightleftharpoons [Fe(dipy)]^{2+}$$
- is given as, $1.45 \times 10^{13} [Fe^{2+}] [dipy]^3$
- The rate of disappearance of complex is $1.22 \times 10^{-4} [Fe(dipy)]^{2+}$. The stability constant of complex will be
- 1.19×10^{17}
 - 2.45×10^{17}
 - 1.00×10^{17}
 - 2.30×10^{17}
13. The degree of dissociation of PCl_5 at a certain temperature and under atmospheric pressure is 0.2. Calculate the pressure at which it will be half dissociated at the same temperature.
- 2 atm
 - 0.225 atm
 - 0.123 atm
 - 2.50 atm
14. In which of the following reactions, hydrogen peroxide acts as an oxidizing agent?
- $I_2 + H_2O_2 + 2OH^- \rightarrow 2I^- + 2H_2O + O_2$
 - $PbS + 4H_2O_2 \rightarrow PbSO_4 + 4H_2O$
- (c) $2MnO_4^- + 3H_2O_2 \rightarrow 2MnO_2 + 3O_2 + 2H_2O + 2OH^-$
 (d) $HOCl + H_2O_2 \rightarrow H_3O^+ + Cl^- + O_2$ (JEE Main Online 2017)
15. Maximum oxidation state is present in
- CrO_2Cl_2
 - MnO_2
 - $[Fe(CN)_6]^{3-}$
 - MnO
16. A sparingly soluble salt gets precipitated only when the ionic product becomes greater than its solubility product. If the solubility of $BaSO_4$ in water is 8×10^{-4} mol dm⁻³. Calculate its solubility in 0.01 mol dm⁻³ of H_2SO_4 .
- 6×10^{-5} mol dm⁻³
 - 8×10^{-4} mol dm⁻³
 - 6×10^{-7} mol dm⁻³
 - 8×10^{-6} mol dm⁻³
17. In acidic medium, H_2O_2 changes $Cr_2O_7^{2-}$ to CrO_5 which has two $(-\text{O}-\text{O}-)$ bonds. Oxidation state of Cr in CrO_5 is
- +5
 - +3
 - +6
 - 10
18. Consider the following reactions in which all the reactants and the products are in gaseous state.
- $$2PQ \rightleftharpoons P_2 + Q_2 ; K_1 = 2.5 \times 10^5$$
- $$PQ + \frac{1}{2}R_2 \rightleftharpoons PQR ; K_2 = 5 \times 10^{-3}$$
- The value of K_3 for the equilibrium,
- $$\frac{1}{2}P_2 + \frac{1}{2}Q_2 + \frac{1}{2}R_2 \rightleftharpoons PQR, \text{ is}$$
- 2.5×10^{-3}
 - 2.5×10^3
 - 1.0×10^{-5}
 - 5×10^3
19. 5 g mixture of $FeSO_4 \cdot 7H_2O$ and $Fe_2(SO_4)_3 \cdot 9H_2O$ is completely oxidised by 5.5 mL of 0.1 M $KMnO_4$ in acidic medium. The percentage of $FeSO_4 \cdot 7H_2O$ in mixture is
- 15.29
 - 30.58
 - 20.24
 - 25.29
20. In the disproportionation reaction,
 $3HClO_3 \rightarrow HClO_4 + Cl_2 + 2O_2 + H_2O$, the equivalent mass of the oxidizing agent is (molar mass of $HClO_3 = 84.45$)
- 16.89
 - 32.22
 - 84.45
 - 28.15
21. The % yield of ammonia as a function of time in the reaction,
 $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$ $\Delta H < 0$ at (P, T_1) is given in the graph. If this reaction is conducted at (P, T_2) , with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by
-



(JEE Advanced 2015)

22. In a reversible reaction $A \rightleftharpoons B$, the initial concentration of A and B are a and b in moles per litre and the equilibrium concentration are $(a - x)$ and $(b + x)$ respectively, express x in terms of k_f , k_b , a and b .

$$\begin{array}{ll} (a) \frac{k_f a - k_b b}{k_f + k_b} & (b) \frac{k_f a - k_b b}{k_f - k_b} \\ (c) \frac{k_f a + k_b b}{k_f k_b} & (d) \frac{k_f a + k_b b}{k_f + k_b} \end{array}$$

23. If $E_{M^+/M}^\circ = -1.2$ V, $E_{X_2/X^-}^\circ = 1.1$ V and $E_{O_2/H_2O}^\circ = 1.23$ V then on electrolysis of aqueous solution of salt MX , the products obtained are

- (a) M, X_2 (b) H_2, X_2 (c) H_2, O_2 (d) M, O_2

24. NH_4CN is a salt of weak acid HCN ($K_a = 6.2 \times 10^{-10}$) and a weak base NH_4OH ($K_b = 1.8 \times 10^{-5}$) then molar solution of NH_4CN will be

- (a) neutral (b) strongly acidic
(c) strongly basic (d) weakly basic.

25. Equivalent weight of potassium permanganate in alkaline solution is equal to

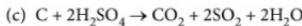
$$\begin{array}{ll} (a) \frac{1}{5} \times \text{Mol.wt.} & (b) \frac{1}{6} \times \text{Mol.wt.} \\ (c) \frac{1}{3} \times \text{Mol.wt.} & (d) \frac{1}{10} \times \text{Mol.wt.} \end{array}$$

26. A weak acid HX has $pK_a = 5$. The per cent degree of hydrolysis of 0.1 M solution of its salt NaX is

- (a) 0.001% (b) 0.01%
(c) 0.1% (d) 0.15%

27. Hot concentrated sulphuric acid is a moderately strong oxidising agent. Which of the following reactions does not show oxidising behaviour?

- (a) $\text{Cu} + 2\text{H}_2\text{SO}_4 \rightarrow \text{CuSO}_4 + \text{SO}_2 + 2\text{H}_2\text{O}$
(b) $\text{S} + 2\text{H}_2\text{SO}_4 \rightarrow 3\text{SO}_2 + 2\text{H}_2\text{O}$



(NEET Phase-II 2016)

28. What is the molecular state of sulphur as reactant in the given reaction:



- (a) S_3^{2-} (b) S_4^{2-} (c) S_8 (d) S_8^-

29. If the salt M_2X, QY_2 and PZ_3 have the same solubilities, their K_{sp} values are related as

(a) $K_{sp}(M_2X) = K_{sp}(QY_2) < K_{sp}(PZ_3)$

(b) $K_{sp}(M_2X) > K_{sp}(QY_2) = K_{sp}(PZ_3)$

(c) $K_{sp}(M_2X) < K_{sp}(QY_2) = K_{sp}(PZ_3)$

(d) $K_{sp}(M_2X) > K_{sp}(QY_2) > K_{sp}(PZ_3)$

30. In which case oxidation number of Cr has been affected?



SOLUTIONS

1. (c) : $\text{pOH} = \text{p}K_b + \log \frac{[\text{Salt}]}{[\text{Base}]}$

$$= 4.75 + \log \frac{0.2}{0.1} = 4.75 + \log 2 \\ = 4.75 + 0.3010 = 5.0510 \approx 5.05$$

Now, $\text{pH} = 14 - \text{pOH} = 14 - 5.05 = 8.95$

2. (b) : $\begin{array}{ccccc} A & + & 2B & \rightleftharpoons & AB_2 \\ \text{Initial mole} & 1 & 2 & 0 & \\ \text{Moles at equilibrium} & (1-x) & (2-2x) & x & \\ \text{Total moles at equilibrium} & = 1-x+2-2x+x & & & \\ & = 3-2x & & & \end{array}$

Let pressure at equilibrium be P ,

Now, $p'_{AB_2} = \left[\frac{x}{3-2x} \right] P ; p'_A = \left[\frac{1-x}{3-2x} \right] P ;$

$$p'_B = \left[\frac{2-2x}{3-2x} \right] P$$

$$K_p = \frac{x \cdot P}{(3-2x) \cdot P \frac{(1-x)}{(3-2x)} \cdot P^2 \frac{(2-2x)^2}{(3-2x)^2}}$$

$$K_p = \frac{x \cdot (3-2x)^2}{P^2 (1-x)(2-2x)^2} \quad \dots(i)$$

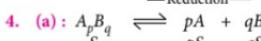
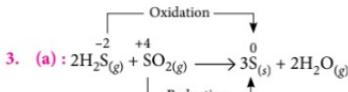
Given that, $x = 0.6$ and $\Delta n = -2$

$$\therefore K_p = K_c (RT)^{\Delta n} \\ = 0.3475 \times (0.0821 \times 473)^{-2} \quad \dots(ii)$$

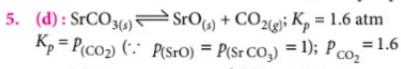
From eqn. (i) and (ii),
 $0.3475 \times (0.0821 \times 473)^{-2}$

$$= \frac{0.6(3-1.2)^2}{P^2(1-0.6)(2-1.2)^2} = \frac{0.6 \times (1.8)^2}{P^2(0.4)(0.8)^2}$$

$$\therefore P = 181.5 \text{ atm}$$



$$\text{Then, } K_{sp} = [A]^p [B]^q = (pS)^p (qS)^q = p^p S^p \cdot q^q S^q = S^{p+q} \cdot p^p \cdot q^q$$



\therefore Maximum pressure of $\text{CO}_2 = 1.6 \text{ atm}$

Let the maximum volume of the container when pressure of CO_2 is 1.6 atm be $V \text{ L}$.

During the process, $PV = \text{constant}$

$$\therefore P_1 V_1 = P_2 V_2 \Rightarrow 0.4 \times 20 = 1.6 \times V$$

$$\Rightarrow V = \frac{0.4 \times 20}{1.6} = 5 \text{ L}$$

6. (c)

7. (b) : For silver benzoate ($\text{C}_6\text{H}_5\text{COOAg}$),

$$K_{sp} = [\text{C}_6\text{H}_5\text{COO}^-][\text{Ag}^+] = 2.5 \times 10^{-13} \quad \dots(\text{i})$$

If S' is the solubility of silver benzoate in pure water, then

$$S' = \sqrt{K_{sp}} = \sqrt{2.5 \times 10^{-13}} = 5 \times 10^{-7} \text{ mol L}^{-1}$$

$$\text{pH} = 3.19 \Rightarrow -\log [\text{H}^+] = 3.19$$

$$\log[\text{H}^+] = -3.19$$

$$[\text{H}^+] = 6.457 \times 10^{-4} \text{ M}$$

For benzoic acid in aqueous solution,



$$K_a = \frac{[\text{C}_6\text{H}_5\text{COO}^-][\text{H}^+]}{[\text{C}_6\text{H}_5\text{COOH}]} \quad \dots(\text{ii})$$

$$\frac{[\text{C}_6\text{H}_5\text{COO}^-]}{[\text{C}_6\text{H}_5\text{COOH}]} = \frac{K_a}{[\text{H}^+]} = \frac{6.46 \times 10^{-5}}{6.457 \times 10^{-4}} = \frac{1}{10}$$

Suppose solubility of silver benzoate in buffer solution is $y \text{ mol L}^{-1}$ then most of the benzoate ions are converted into benzoic acid molecules (which remain almost ionised), we have

$$\begin{aligned} y &= [\text{Ag}^+] = [\text{C}_6\text{H}_5\text{COO}^-] + [\text{C}_6\text{H}_5\text{COOH}] \\ &= [\text{C}_6\text{H}_5\text{COO}^-] + 10[\text{C}_6\text{H}_5\text{COO}^-] \\ &= 11[\text{C}_6\text{H}_5\text{COO}^-] \end{aligned}$$

$$\therefore [\text{C}_6\text{H}_5\text{COO}^-] = \frac{y}{11}$$

$$K_{sp} = [\text{C}_6\text{H}_5\text{COO}^-][\text{Ag}^+]$$

$$\text{i.e., } 2.5 \times 10^{-13} = \frac{y}{11} \times y \Rightarrow y^2 = 2.75 \times 10^{-12}$$

$$y = 1.66 \times 10^{-6}$$

$$\therefore \frac{y(\text{solubility in buffer})}{x(\text{solubility in water})} = \frac{1.66 \times 10^{-6}}{5 \times 10^{-7}} = 3.32$$

8. (d)

9. (d) : For MY : $K_{sp} = S_l^2$

$$\Rightarrow S_l = \sqrt{K_{sp}} = \sqrt{6.2 \times 10^{-13}} = 7.87 \times 10^{-7} \text{ mol L}^{-1}$$

$$\text{For } NY_3: K_{sp} = 27S_2^4$$

$$\Rightarrow S_2 = \sqrt[4]{\frac{6.2 \times 10^{-13}}{27}} = 3.89 \times 10^{-4} \text{ mol L}^{-1}$$

Hence, molar solubility of MY in water is less than that of NY_3 .

10. (b)

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

12. (a) : For the reaction: $\text{Fe}^{2+} + 3\text{dipy} \rightleftharpoons [\text{Fe}(\text{dipy})_3]^{2+}$

$$r_{\text{forward}} = k_f \times [\text{Fe}^{2+}][\text{dipy}]^3 = 1.45 \times 10^{13} [\text{Fe}^{2+}][\text{dipy}]^3$$

$$r_{\text{backward}} = k_b \times [\text{Fe}(\text{dipy})_3]^{2+} = 1.22 \times 10^{-4} [\text{Fe}(\text{dipy})_3]^{2+}$$

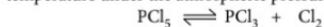
At equilibrium, $r_f = r_b$ and $K_c = \frac{k_f}{k_b} = \frac{[\text{Fe}(\text{dipy})_3]^{2+}}{[\text{Fe}^{2+}][\text{dipy}]^3}$

Also, stability constant of complex = Equilibrium

$$\text{constant of reaction} = \frac{k_f}{k_b}$$

$$= \frac{1.45 \times 10^{13}}{1.22 \times 10^{-4}} = 1.19 \times 10^{17}$$

13. (c) : If α is the degree of dissociation at certain temperature under the atmospheric pressure, then



$$\begin{array}{ccccc} \text{Initial conc.} & 1 & 0 & 0 \\ \text{At equilibrium} & 1 - \alpha & \alpha & \alpha \end{array}$$

$$\text{Now, } K_p = \frac{\alpha^2}{1 - \alpha^2} P$$

$$\text{Putting } P = 1 \text{ atm and } \alpha = 0.2$$

$$K_p = \frac{(0.2)^2}{1 - (0.2)^2} \times 1 = 0.041$$

When $\alpha = \frac{1}{2} = 0.5$, then let pressure is P'

$$K_p = \frac{\alpha^2}{1-\alpha^2} \cdot P' \Rightarrow 0.041 = \frac{(0.5)^2 P'}{1-(0.5)^2}$$

$$P' = \frac{(0.041)[1-(0.5)^2]}{(0.5)^2} = 0.123 \text{ atm}$$

14. (b)

15. (a)



Solubility of $\text{BaSO}_4 = 8 \times 10^{-4} \text{ mol dm}^{-3}$
 $\therefore [\text{Ba}^{2+}] = [\text{SO}_4^{2-}] = 8 \times 10^{-4} \text{ mol dm}^{-3}$

$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = (8 \times 10^{-4})^2 \\ = 64 \times 10^{-8}$$

Now, $\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{H}^+ + \text{SO}_4^{2-}$

$\therefore [\text{SO}_4^{2-}]$ produced from 0.01 mol dm^{-3} of $\text{H}_2\text{SO}_4 = 0.01 \text{ M}$

If x is the solubility of BaSO_4 in H_2SO_4 , then

$$[\text{Ba}^{2+}] = x, [\text{SO}_4^{2-}] = x + 0.01$$

Since K_{sp} is constant for a given salt,

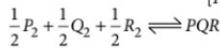
$$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] \\ = x(x + 0.01) = 64 \times 10^{-8}$$

or $x^2 + 0.01x - 64 \times 10^{-8} = 0$
 $\Rightarrow x = 6 \times 10^{-5} \text{ mol dm}^{-3}$

17. (c) : $\text{CrO}_5 : x + 4(-1) + 1(-2) = 0 \Rightarrow x = +6$

$$18. (c) : 2\text{PQ} \rightleftharpoons \text{P}_2 + \text{Q}_2; K_1 = \frac{[\text{P}_2][\text{Q}_2]}{[\text{PQ}]^2} = 2.5 \times 10^5$$

$$\text{PQ} + \frac{1}{2}\text{R}_2 \rightleftharpoons \text{PQR}; K_2 = \frac{[\text{PQR}]}{[\text{PQ}][\text{R}_2]^{1/2}} = 5 \times 10^{-3}$$



$$K_3 = \frac{[\text{PQR}]}{[\text{P}_2]^{1/2}[\text{Q}_2]^{1/2}[\text{R}_2]^{1/2}} \\ = \frac{K_2}{\sqrt{K_1}} = \frac{5 \times 10^{-3}}{\sqrt{2.5 \times 10^5}} = 1 \times 10^{-5}$$

19. (a) : $\text{Mn}^{7+} + 5e^- \longrightarrow \text{Mn}^{2+}$



Meq. of KMnO_4 = Meq. of $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$

$$5.5 \times 0.1 \times 5 = \frac{w}{278} \times 1000$$

$$\therefore w = 0.7645$$

$$\therefore \% \text{ of } \text{FeSO}_4 \cdot 7\text{H}_2\text{O} = \frac{0.7645}{5} \times 100 = 15.29\%$$

20. (a) : $\text{ClO}_3^- \rightarrow \text{Cl}_2^0$

$$x - 6 = -1 \quad x = 0$$

$$x = +5 \quad x = 0 \quad (\text{x} = \text{Oxidation number})$$

$$\text{Equivalent mass} = \frac{\text{Molecular mass}}{\text{Oxidation number}} = \frac{84.45}{5} = 16.89$$



Initially, with increase in temperature ($T_2 > T_1$) % yield increases.

Afterwards, equilibrium is reached and if the temperature is increased, i.e., heat is supplied to the system, then according to Le Chatelier's principle, the equilibrium will shift in the backward direction, where the heat is absorbed. Hence, the % yield decreases.

$$22. (a) : A \rightleftharpoons \frac{k_f}{(a-x)} B, K_c = \frac{k_f}{k_b} = \frac{b+x}{a-x}$$

$$x = \frac{k_f a - k_b b}{k_f + k_b}$$

23. (b)

24. (d) : Since $K_b > K_a$, the solution will be slightly basic.

25. (c)

26. (b) : Hydrolysis reaction is



For a salt of weak acid with strong base,

$$K_h = \frac{K_w}{K_a} = Ch^2 \Rightarrow \frac{10^{-14}}{10^{-5}} = 0.1 \times h^2 \Rightarrow h^2 = 10^{-8}$$

$$\therefore h = 10^{-4}$$

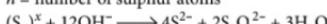
$$\% \text{ hydrolysis} = 10^{-4} \times 100 = 10^{-2} = 0.01\%$$

27. (d)

28. (c) : Let sulphur be as $(\text{S}_n)^x$,

where, x = charge

n = number of sulphur atoms

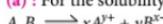


Charge balanced : $x + (-12) = -8 - 4 \therefore x = 0$

Sulphur balanced : $n = 4 + 4 = 8$

Thus, molecular state of sulphur is S_8 .

29. (a) : For the solubility of a salt like A_xB_y



If s is the solubility

$$[A^{y+}] = xs, [B^{x-}] = ys$$

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

For M_2X ($x = 2, y = 1$); $K_{sp} = 4s^3$

QY_2 ($x = 1, y = 2$); $K_{sp} = 4s^3$

PZ_3 ($x = 1, y = 3$); $K_{sp} = 27s^4$

30. (c)





CBSE warm-up!

CLASS-XI

Practice questions for CBSE Exams as per the reduced syllabus, latest pattern and marking scheme issued by CBSE for the academic session 2020-21.

CHAPTERWISE PRACTICE PAPER: Classification of Elements and Periodicity in Properties, Chemical Bonding and Molecular Structure

Time Allowed : 3 hours
Maximum Marks : 70

GENERAL INSTRUCTIONS

Read the following instructions very carefully and strictly follow them :

- (i) Question paper comprises two parts A and B.
 - (ii) Part A : Q. no. 1 to 26 are objective type questions.
 - Q. no. 1 to 19 are objective type questions carrying one mark each.
 - Q. no. 20 to 24 are objective type questions carrying two marks each.
 - Q. no. 25 to 26 are case based objective type questions carrying three marks each.
 - (iii) Part B : Q. no. 27 to 37 are subjective/descriptive type questions.
 - Q. no. 27 to 30 are short answer type-I questions carrying two marks each.
 - Q. no. 31 to 34 are short answer type-II questions carrying three marks each.
 - Q. no. 35 to 37 are long answer type questions carrying five marks each.
 - (iv) There is no overall choice in the question paper. However, internal choices have been provided in both part A and Part B.
 - (v) Use of calculators and log tables is not permitted.

PART - A

4. In which one of the following pairs the radius of the second species is greater than that of the first?

OR

Which of the following represents the correct order of increasing first ionization enthalpy for Ca, Ba, S, Se and Ar?

- (a) Ca < Ba < S < Se < Ar
 (b) Ca < S < Ba < Se < Ar
 (c) S < Se < Ca < Ba < Ar
 (d) Ba < Ca < Se < S < Ar

5. The shape of XeOF_2 on the basis of VSEPR theory is

OR

Five ionization energy values in kJ/mol are listed below:

- $E_1 = 870$, $E_2 = 830$, $E_3 = 1010$, $E_4 = 1290$, $E_5 = 376$.
 These are

 - successive ionization energies for the element with atomic number 5
 - the first I.E. of successive elements in group 15, 16, 17, 18 and 1 respectively
 - the first I.E. of elements with atomic number 1 to 5
 - successive I.E. for transition elements with four electrons in d -subshell.

8. In PO_4^{3-} ion, the formal charge on each oxygen atom and bond order of P–O bond are respectively

 - 0.75, 1.25
 - 0.75, 1.0
 - 0.75, 0.6
 - 3, 1.25

OR

Which one of the following is incorrect?

- (a) An element which has high electronegativity always has high electron gain enthalpy.
 - (b) Electron gain enthalpy is the property of an isolated atom.
 - (c) Electronegativity is the property of a bonded atom.
 - (d) Both electronegativity and electron gain enthalpy are usually directly related to nuclear charge and inversely related to atomic size.

10. The period number in the long form of the periodic table is equal to

 - (a) magnetic quantum number of any element of the period
 - (b) atomic number of any element of the period
 - (c) maximum principal quantum number of any element of the period
 - (d) maximum Azimuthal quantum number of any element of the period.

11. Which transition involves maximum amount of energy?

- (a) $M_{(g)}^- \rightarrow M_{(g)} + e^-$ (b) $M_{(g)}^- \rightarrow M_{(g)}^+ + 2e^-$
 (c) $M_{(g)}^+ \rightarrow M_{(g)}^{2+} + e^-$ (d) $M_{(g)}^{2+} \rightarrow M_{(g)}^{3+} + e^-$

OR

The elements which exhibit both vertical and horizontal similarities are

- (a) noble gas
 - (b) representative elements
 - (c) transition elements
 - (d) rare earth elements

12. Which of the following compounds doesn't have linear structure?

- (a) CO_2 (b) SO_2 (c) BeCl_2 (d) C_2H_2

13. Atomic number of Ag is 47. In the same group, the atomic numbers of elements placed above and below Ag in long form of periodic table will be

14. The hybridisation of atomic orbitals of nitrogen in NO_2^+ , NO_3^- and NH_4^+ are

 - (a) sp , sp^2 and sp^3 respectively
 - (b) sp , sp^3 and sp^2 respectively
 - (c) sp^2 , sp and sp^3 respectively
 - (d) sp^2 , sp^3 and sp respectively.

Question 15 to 19 (Assertion/Reason)

Directions : In the following questions (15-19), a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both Assertion (A) and Reason (R) are correct and Reason (R) is the correct explanation of Assertion (A).
 - (b) If both Assertion (A) and Reason (R) are correct but Reason (R) is not the correct explanation of Assertion (A).
 - (c) If Assertion (A) is correct but Reason (R) is incorrect.
 - (d) If Assertion (A) is incorrect and Reason (R) is correct.

- 15. Assertion :** Helium has the highest value of ionisation energy among all the elements known.

Reason : Helium has the highest value of electron affinity among all the elements known.

OR

Assertion : Lithium having maximum negative E° value is the strongest reducing agent amongst all alkali metals in solution.

Reason : Lithium is the lightest metal in the periodic table.

- 16. Assertion :** The bond order of helium is always zero.

Reason : The number of electrons in bonding molecular orbital and antibonding molecular orbital is equal.

- 17. Assertion :** If the five successive ionization energies of an element are 700, 2145, 3478, 30450 and 38748 kJ mol⁻¹ respectively, the number of valence electrons is three.

Reason : Ionization energy increases abruptly at fourth ionization energy.

- 18. Assertion :** XeF_2 is linear but OH_2 is angular though both are AB_2 -type molecules.

Reason : F is more electronegative than H.

OR

Assertion : Decreasing order of van der Waals' radii is $\text{Cl} > \text{N} > \text{O} > \text{H}$.

Reason : van der Waals' radii increases as the number of energy level increases and decreases as nuclear charge increases.

- 19. Assertion :** Atomic radius in generally decreases along a period.

Reason : In a period, effective nuclear charge decreases.

- 20. Electronic configurations of four elements A, B, C and D are given below :**

(A) $1s^2 2s^2 2p^6$ (B) $1s^2 2s^2 2p^4$

(C) $1s^2 2s^2 2p^6 3s^1$ (D) $1s^2 2s^2 2p^5$

Which of the following is the correct order of increasing tendency to gain electron?

(a) $A < C < B < D$ (b) $A < B < C < D$
(c) $D < B < C < A$ (d) $D < A < B < C$

OR

The correct order in which the first ionisation potential increases is

(a) K, Be, Na (b) Be, Na, K
(c) Na, K, Be (d) K, Na, Be

- 21. Which of the following statements are true (T) or false (F)?**

(I) In SnCl_2 the bonding takes place in ground state and the bond angle Cl—Sn—Cl is slightly less than 120° .

(II) The molecular geometry of XeF_7^+ is pentagonal bipyramidal having two different Xe—F bond lengths.

(III) In SF_4 , the bond angles, instead of being 90° and 120° are 89° and 117° respectively due to the presence of a lone pair.

- (a) T T T (b) F T T (c) T T F (d) T F T

- 22. Which of the following pairs are not isostructural?**

(a) IO_3^- and XeO_3 (b) PF_6^- and SF_6

(c) BH_4^- and NH_4^+ (d) SiF_4 and SF_4

OR

Using the following data, calculate the electronegativity of fluorine.

$$E_{\text{H}-\text{H}} = 104.2 \text{ kcal mol}^{-1}, E_{\text{F}-\text{F}} = 36.6 \text{ kcal mol}^{-1}$$

$$E_{\text{H}-\text{F}} = 134.6 \text{ kcal mol}^{-1}, \chi_{\text{H}} = 2.1.$$

- (a) 3.87 (b) 3.77 (c) 3.67 (d) 4.87

- 23. In which of the following options order of arrangement does not agree with the variation of property indicated against it?**

I. $\text{Al}^{3+} < \text{Mg}^{2+} < \text{Na}^+ < \text{F}^-$ (increasing ionic size)

II. $\text{B} < \text{C} < \text{N} < \text{O}$ (increasing first ionisation enthalpy)

III. $\text{I} < \text{Br} < \text{Cl} < \text{F}$ (increasing electron gain enthalpy)

IV. $\text{Li} < \text{Na} < \text{K} < \text{Rb}$ (increasing metallic radius)

- (a) I and II only (b) II and III only

- (c) III and IV only (d) I and IV only

- 24. Which of the following molecules has the maximum dipole moment?**

- (a) CO_2 (b) CH_4 (c) NH_3 (d) NF_3

Read the following passage and answer the questions 25 and 26.

The shapes of molecules can be predicted by VSEPR theory, hybridisation and dipole moment. Total number of hybrid orbitals (H) on the central atom of a molecule can be calculated by using the following relation : $H = 1/2[\text{Total no. of valence electrons (P)} - 3 \times (\text{no. of atoms surrounding the central atom, excluding hydrogen atoms})]$

One can also calculate total no. of bond pairs (n) around central atom as
 $n = \text{total number of atoms surrounding the central atom}$
Also, total no. of lone pairs (m) = $H - n$

Thus, VSEPR notation of a molecule can be written as AX_nE_m . Where, A denotes central atom of the molecule X denotes bond pair on central atom of the molecule

E denotes lone pairs on central atom of the molecule
In a polar molecule, the net dipole moment of the molecule $\propto m$.

25. VSEPR notation of chlorine trifluoride molecule is
 (a) AX_5 (b) AX_3 (c) AX_2E_3 (d) AX_3E_2

26. For the given molecules: CO_2 (I), SO_2 (II), H_2O (III),
the correct increasing order of their dipole moments is
 (a) I < II < III (b) II < I < III
 (c) III < II < I (d) III < I < II

PART - B

27. Explain why cations are smaller and anions are larger in radii than their parent atoms.
 28. The C = O and C ≡ O bond lengths are generally 121 and 110 pm respectively. The actual C – O bond length in CO_2 is 115 pm. What does this suggest regarding the Lewis structure of CO_2 ?
 29. Apart from tetrahedral geometry, another possible geometry for CH_4 is square planar with the four H-atoms at the corners of the square and the C-atoms at its centre. Explain why CH_4 is not square planar.

OR

Although geometries of NH_3 and H_2O molecules are distorted tetrahedral, bond angle in H_2O is less than that of NH_3 . Discuss.

30. The electron gain enthalpy of bromine is 3.36 eV. How much energy in kcal is released when 8 g of bromine is completely converted to Br^- ions in the gaseous state? (1 eV = 23.06 kcal mol^{-1}).
 31. How many electron pairs available in the valence shell of (i) N in NH_3 (ii) P in PCl_3 (iii) C in CO_2 (iv) N in NH_4^+ (v) P in PCl_5 (vi) S in H_2S

32. (i) Define electronegativity. How does it differ from electron gain enthalpy.
 (ii) State diagonal relationship.
 33. Among the elements B, Al, C and Si:
 (i) Which has the highest first ionization enthalpy?
 (ii) Which has the most negative electron gain enthalpy?
 (iii) Which has the most metallic character?
 Give reasons.

OR

- (i) Explain why Δ_1H_f of Na is lower than that of Mg but Δ_1H_f of Na is higher than that of Mg.
 (ii) The first, second and third ionization enthalpies of an element *E* are 419, 3069 and 4400 kJ mol^{-1} .

To which group of the periodic table does *E* belong?

34. (i) Out of p-orbital and *sp*-hybrid orbital which has greater directional character and why?
 (ii) BH_4^- and NH_4^+ are isostructural. Explain.
 (iii) Why axial bonds of PCl_5 are longer than equatorial bonds?

35. (i) The H—O—H bond angle in the water molecule is 105° . The H—O bond distance is 0.94 Å. The dipole moment of the molecule is 1.85 D. Calculate the charge on oxygen atom.
 (ii) In SF_4 molecule, the lone pair of electrons occupies an equatorial position in the overall trigonal bipyramidal arrangement in preference to an axial position. Why?

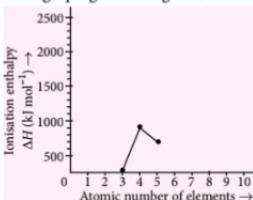
OR

Discuss the shapes of following molecules using VSEPR model : $BeCl_2$, BCl_3 , $SiCl_4$, AsF_5 , H_2S

36. Ionisation enthalpies of elements of second period are given below:

Ionisation enthalpy/kcal mol^{-1} : 520, 801, 899, 1086, 1314, 1402, 1681, 2080.

Match the correct enthalpy with the elements and complete the graph given in figure.



OR

Which elements have the following electronic configuration?

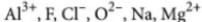
- (i) $1s^2 2s^2 2p^5$ (ii) $[Ar] 4s^2 3d^{10} 4p^1$
 (iii) $[Xe] 6s^2$ (iv) $[Xe] 6s^2 5d^1 4f^7$
 (v) $[Ar] 4s^1 3d^{10}$

37. (i) Explain why the chemical reactivity increases in the order Li < Na < K < Rb < Cs in group 1 but decreases in the order F > Cl > Br > I in group 17.
 (ii) Arrange the given elements in the correct order of their chemical reactivities. F, Cl, O and N?
 (iii) Arrange $HClO_4$, $HClO_2$, $HClO$ and $HClO_3$ in order of acidic nature.

OR

(i) Arrange the elements Na, Mg, K, Cs, Al and B in order of decreasing metallic character. Explain briefly.

(ii) Which of the following atoms / ions are isoelectronic?



Arrange the isoelectronic ions in decreasing order of their sizes.

(iii) Is the second electron gain enthalpy of O expected to be positive, more negative or less negative than the first?

SOLUTIONS

1. (a) : Oxygen does not contain *d*-orbitals in its valence shell and hence cannot extend its coordination number. Hence, oxygen cannot accommodate four fluorine atoms to form OF_4^- .

2. (a) : Na and Mg is not an exception because there is no half-filled or completely filled orbital in them.

3. (d) : Overlapping is better in hybrid orbitals due to same size and equivalent energy than the pure orbitals. Among hybrid orbitals, more is the *s* character greater is the strength of bond.

4. (b) : N^{3-} and O^{2-} both are isoelectronic but differ in the charge possessed by them. As the nuclear charge decreases from O to N, the electrons are held less and less tightly by the nucleus. Hence, the ionic size increases from O^{2-} to N^{3-} .

OR

(d) : Ionization enthalpy increases on moving from left to right across the period as the size decreases and decreases on moving top to bottom in a group as the size increases. Ar has the maximum value of *IE*, since it is a noble gas. So, the correct order of increasing first ionization enthalpy ($\Delta_1\text{H}_1$) is



5. (d) : XeOF_2

π bond = 1

Total number of electron pairs = 6

Number of lone pairs = 2

Shape \rightarrow T-shaped geometry

Hybridization $\rightarrow sp^3d$



6. (c) : In a transition group (from 5th group) ionization energy decreases from first to second element but from second to third element the ionization energy does not decrease due to lanthanide contraction.

7. (c) : In lanthanoids, the electrons are filled in 4*f*-orbitals.

OR

(b) : *I.E.* values are increasing gradually and suddenly decreased in the E_5 value indicating a change from noble gas to alkali metal.

8. (a) : Formal charge on an atom = No. of valence electrons - total no. of electrons of lone pairs - $\frac{1}{2}$ [no. of shared electrons]

Thus, for PO_4^{3-} ions, 3 single bonded oxygen atoms have formal charge = -1 and double bonded oxygen has formal charge = 0.

$$\text{Formal charge on O atoms} = \frac{-3}{4} = -0.75$$

$$\text{P}-\text{O bond order} = \frac{5}{4} = 1.25$$

(5 bonds between 4 oxygen atoms)



9. (d) : $\text{Li}_{(aq)}^+$ ion being smallest in size is heavily hydrated and thus, $\text{Li}_{(aq)}^+$ is largest in size.

OR

(a) : Elements with high electronegativity usually but not always have high negative electron gain enthalpies. e.g., both N and Cl have an electronegativity of 3.0 but the electron gain enthalpy of N is positive while that of chlorine is the highest with negative sign in the periodic table.

10. (c) : The principal quantum number or the value of *n* determines the number of the period in which the element is present.

11. (d) : When an electron is removed from an isolated gaseous atom it forms a cation in which electrons become less but nuclear charge remains same thus, the electrons are more tightly bounded in cations. Hence, energy required to pull out these electrons is higher.

$$IE_3 > IE_2 > IE_1$$

OR

(c) : Transition elements due to same number of valence electrons in outermost shell i.e., ns^2 show both vertical and horizontal similarities.

12. (b) : SO_2 molecule shows sp^2 -hybridisation and has bent structure.



13. (a)

14. (a)

15. (c) : Helium contains fully filled $1s^2$ orbital which has more penetrating effect and is very close to the nucleus and hence, has higher value of ionisation energy.

The electron affinity of He is the lowest of all the noble gases, due to the smallest size of He.

OR

(b)

16. (a)

17. (a) : Ionization energy increases abruptly at fourth ionization energy i.e. $IE_4 \gg IE_3$ and as the 4th electron requires very-very high energy for its removal as this electron is to be knocked out from the noble gas core. Hence, the number of valence electron is three.

18. (b)

OR

(a)

19. (c) : In a period, effective nuclear charge increases.

20. (a) : $A - 1s^2 2s^2 2p^6$ - Noble gas configuration
 $B - 1s^2 2s^2 2p^4$ - 2 electrons short of stable configuration
 $C - 1s^2 2s^2 2p^6 3s^1$ - Requires one electron to complete s-orbital.

$D - 1s^2 2s^2 2p^5$ - Requires one electron to attain noble gas configuration.

Hence, the tendency to gain electron is in the order of $A < C < B < D$.

OR

(d) : The electronic configuration of the elements are :
 $4Be - 1s^2 2s^2$; $11Na - 1s^2 2s^2 2p^6 3s^1$
 $19K - 1s^2 2s^2 2p^6 3s^2 3p^6 4s^1$

The first ionization energy of Be is maximum because electron is to be drawn from stable (fully filled) orbital. The 1st ionization energy of Na is greater than K because size of K is bigger than Na which facilitates easy removal of electron from its outermost shell. So the sequence is $K < Na < Be$.

21. (a)

22. (d) : Molecule/ion Hybridisation Actual shape

IO_3^-	sp^3	pyramidal
XeO_3	sp^3	pyramidal
PF_6^-	$sp^3 d^2$	octahedral
SF_6	$sp^3 d^2$	octahedral
BH_4^-	sp^3	tetrahedral
NH_4^+	sp^3	tetrahedral
SiF_4	sp^3	tetrahedral
SF_4	$sp^3 d$	irregular (see saw)

OR

$$(a) : \chi_F - \chi_H = 0.208 [E_{H-F} - (E_{F-F} \times E_{H-H})^{1/2}]^{1/2}$$

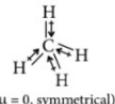
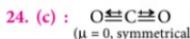
$$\chi_F - 2.1 = 0.208 [134.6 - (36.6 \times 104.2)^{1/2}]^{1/2}$$

$$= 0.208 [134.6 - 61.75]^{1/2} + 2.1$$

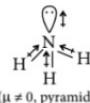
$$= 0.208 \times 8.53 + 2.1 = 1.77 + 2.1 = 3.87$$

23. (b) : Ionisation enthalpy of B < C but N > O due to half filled orbitals in N which have extra stability.

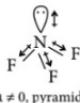
Electron gain enthalpy of Cl > F due to bigger size and lesser electronic repulsion.



$(\mu = 0, \text{symmetrical})$



$(\mu \neq 0, \text{pyramidal})$



$(\mu \neq 0, \text{pyramidal})$

In NH_3 , H is less electronegative than N and hence dipole moment of each N–H bond is towards N and create high net dipole moment whereas in NF_3 , F is more electronegative than N, the dipole moment of each N–F bond is opposite to that of lone pair hence, reducing the net dipole moment.

25. (d) : Number of hybrid orbitals, H in $ClF_3 = \frac{1}{2}$
 $(\text{Valence electrons of Cl} + 3 \times \text{valence electrons of F})$
 $- 3 \times 3 F^- \text{ atoms}) = \frac{1}{2}(7 + 3 \times 7) - 9 = 14 - 9 = 5$

Number of bond pairs (n) = 3

Total number of lone pairs (m) = $H - n = 5 - 3 = 2$
 Hence, VSEPR notation of ClF_3 is AX_3E_2 .

26. (a) : $CO_2 : H = \frac{1}{2}(4 + 2 \times 6) - 3 \times 2 = 2;$

$n = 2; m = H - n = 2 - 2 = 0$

$SO_2 : H = \frac{1}{2}(6 + 2 \times 6) - 3 \times 2 = 3;$

$n = 2; m = 3 - 2 = 1$

$H_2O : H = \frac{1}{2}(2 \times 1 + 6) - 3 \times 0 = 4;$

$n = 2; m = 4 - 2 = 2$

Hence, correct order of dipole moments :
 $CO_2 < SO_2 < H_2O$

27. A cation is smaller than its parent atom because it has fewer electrons while its nuclear charge remains the same. The size of an anion will be larger than that of the parent atom because the addition of one or more

electrons would result in increased repulsion among the electrons and a decrease in effective nuclear charge.

28. The C—O bond length in CO_2 is in between the C = O and C ≡ O lengths. This suggest that the actual structure of CO_2 is a resonance hybrid of the canonical forms containing double and triple bonds between C and O.



29. For tetrahedral geometry, the bond angle is $109^\circ 28'$ but for square planar geometry, the bond angle is 90° . If CH_4 molecule is square planar, bond angle would be 90° and there would be more repulsion between bond pairs, resulting in less stability. Therefore, CH_4 is not square planar.

OR

In NH_3 and H_2O , the central atoms N and O both have four pairs of electrons. In NH_3 , there is only one lone pair but H_2O has two lone pairs of electrons. As $lp-lp$ repulsion is more than $lp-bp$ thereby, decreasing tetrahedral angle to 104.5° in HOH than in case of ammonia where the HNH bond angle is 107° .



Energy released from 80 g gaseous bromine

$$= 3.36 \times 23.06 \text{ kcal}$$

∴ Energy released for conversion of 8 g gaseous bromine into Br^- ions $\frac{3.36 \times 23.06 \times 8}{80} = 7.748 \text{ kcal}$

31. (i) N has 5 electrons in its valence shell and obtains 3 electrons from three H atoms and thus attains a total of 8 electrons, i.e., 4 electron pairs.

(ii) P has 5 electrons in its valence shell and gets 3 from three Cl atoms, thus attaining a total of 8 electrons, i.e., 4 electron pairs.

(iii) C has 4 electrons in its valence shell, gets four from the O atoms so attains total of 8 electrons, i.e., 4 pairs of electrons.

(iv) N has 5 electrons in its valence shell, obtains 4 from the four H atoms and loses 1 due to positive charge, thus attaining $9 - 1 = 8$, i.e., 4 pairs of electrons.

(v) P has 5 electrons in its valence shell and gets 5 from five Cl atoms, thus attaining total of 10 electrons i.e., 5 electron pairs.

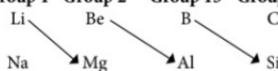
(vi) S has 6 electrons in its valence shell and gets 2 from two H atoms, thus attaining total of 8 electrons i.e., 4 electron pairs.

32. (i) A qualitative measure of the ability of an atom in a chemical compound to attract shared electrons towards itself is called electronegativity.

Electron gain enthalpy	Electronegativity
1. It provides a measure of the ease with which an atom adds an electron to form an anion.	It is a qualitative measure of the ability of an atom in a chemical compound to attract shared electrons to itself.
2. It has an absolute value.	It is not a measurable quantity.
3. Its periodicity is not regular in a period or in a group.	The periodicity is regular in a period but not so regular in a group.
4. Its units are eV/atom or kJ/mole .	It has no units but is merely a number.

(ii) The similarity in properties of elements present diagonally is called diagonal relationship.

Group 1 Group 2 Group 13 Group 14



33. (i) Carbon has highest first ionisation enthalpy.

Ionisation enthalpy increases across a period and decreases down the group.

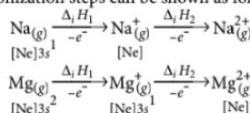
(ii) Carbon has most negative electron gain enthalpy as electron gain enthalpy increases across a period (due to more effective nuclear charge) and decreases down the group (due to larger size).

(iii) Aluminium has the most metallic character.

Metallic character increases down the group and decreases in a period. Hence, the order is : C < Si < B < Al.

OR

(i) The ionization steps can be shown as follows :



It is easier to take out an electron from an incomplete 3s-orbitals of Na than from the filled 3s-orbital of Mg. So, $\Delta_i H_1$ of Na < $\Delta_i H_1$ of Mg.

However, it is more difficult to take out an electron from the noble gas(Ne) configuration of Na^+ than from the incomplete 3s-orbital of Mg^+ .

So, $\Delta_1 H_2$ of Na > $\Delta_1 H_2$ of Mg .

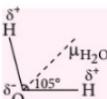
(ii) The large gap between the first and the second ionisation enthalpies suggests that the element has the configuration [noble gas] ns^1 . Thus, element belongs to group 1 of the periodic table.

34. (i) sp -orbital has greater directional character than p -orbital. This is because p -orbital has equal sized lobes with equal electron density in both the lobes whereas sp -hybrid orbital has greater electron density on one side.

(ii) In BH_4^- , B contributes three valence electrons and one each by four H atoms and one negative charge sum up to give 4 valence shell electron pair to give sp^3 hybridisation and tetrahedral structure. In NH_4^+ , N contributes five valence electrons, four electrons by four H atoms minus one electron for positive charge to give four valence shell electron pairs thus, sp^3 hybridisation and tetrahedral shape.

(iii) This is due to greater repulsion on the axial bond pairs by the equatorial bond pairs of electrons.

35. (i) Since H_2O has two vectors of O—H bond acting at 105° , the dipole moment of H_2O , i.e., $\mu_{\text{H}_2\text{O}}$ is as follows:



$$\mu_{\text{H}_2\text{O}} = \sqrt{\mu_{\text{O}-\text{H}}^2 + \mu_{\text{O}-\text{H}}^2 + 2\mu^2 \cos(105^\circ)}$$

$$\therefore 1.85 = \sqrt{2a^2(1 + \cos 105^\circ)}$$

Presuming that dipole moment of O—H bonds is ' a '.

$$\therefore (1.85)^2 = 2a^2(1 - 0.2588)$$

$$a, \text{i.e., } \mu_{\text{H}-\text{O}} = 1.52 \text{ debye} = 1.52 \times 10^{-18} \text{ esu cm}$$

But $\mu_{\text{H}-\text{O}} = \text{Charge}(\delta) \times d$

$$\therefore 1.52 \times 10^{-18} \text{ esu cm} = \delta \times (0.94 \times 10^{-8} \text{ cm})$$

$$\therefore \delta = 1.617 \times 10^{-10} \text{ esu}$$

Since O-atom acquires 2δ charge, one δ charge from each bond, therefore,

$$\text{charge on O-atom} = 2 \times 1.617 \times 10^{-10} = 3.23 \times 10^{-10} \text{ esu cm}$$

(ii)



lp on axial position

(a)



lp on equatorial position

(b)

In figure (a) the lone pair of electrons is on axial position which has $3lp-bp$ repulsions at 90° . In figure (b) the lone pair is on equatorial position and there are only two $lp-bp$ repulsions. Hence in (b) lesser repulsions occur and hence figure (b) has a more stable arrangement than figure (a). Figure (b) results distorted tetrahedron or folded square or see saw structure.

OR

According to VSEPR theory, the shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.

(i) BeCl_2 : The central atom Be has only 2 valence electrons which are bonded to Cl, so there are only 2 bond pairs and no lone pairs. It is of the type AB_2 and hence, the shape is linear.



(ii) BCl_3 : The central atom B has only 3 valence electrons which are bonded with three Cl atoms, so it contains only 3 bond pairs and no lone pair. It is of the type AB_3 and hence, the shape is trigonal planar.



(iii) SiCl_4 : Similarly, the central atom Si has only 4 bond pairs and no lone pair. It is of the type AB_4 and hence, the shape is tetrahedral.



(iv) AsF_5 : The central atom As has only 5 bond pairs and no lone pair. It is of the type AB_5 and hence, the shape is trigonal bipyramidal.



(v) H_2S : The central atom S has 2 bond pairs and 2 lone pairs. It is of the type AB_2L_2 and hence, the shape is bent or V-shaped.

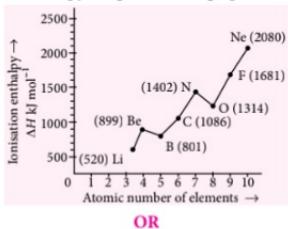


36. We know that as we move from left to right across a period, the ionisation enthalpy keeps on increasing due to increased nuclear charge and simultaneous decrease in atomic radius. However, there are some exceptions also.

(i) In spite of increased nuclear charge, the first ionisation enthalpy of B is lower than that of Be. This is due to the reason that in case of Be, the outermost electron lies in the $2s$ -orbitals but in case of B, it is present in a $2p$ -orbital. Since, the electrons in $2s$ -orbital are more tightly held by the nucleus than those present in $2p$ -orbital, therefore, ionisation enthalpy of B is lower than that of Be.

(ii) The first ionisation enthalphy of N is higher than that of O though the nuclear charge of O is higher than that of N. This is due to reason that in case of N, the electron is to be removed from a more stable exactly

half-filled electronic configuration ($1s^2 2s^2 2p_x^1 2p_y^1 2p_z^1$) but in case of O ($1s^2 2s^2 2p_x^2 2p_y^1 2p_z^1$), it is not so. Therefore, the first ionisation enthalpy of N is higher than that of O. The symbols of elements along with their ionisation enthalpy are given in the graph.



OR

(i) The outer electronic configuration of $1s^2 2s^2 2p^5$ is $2s^2 2p^5$. Therefore, this element is a *p*-block element and belongs to the second period and group 17. Thus, the element is fluorine, F.

(ii) The outer electronic configuration of [Ar] $4s^2 3d^{10} 4p^1$ is $4s^2 4p^1$, therefore, it is a *p*-block element. It belongs to the fourth period and group 13. Therefore, the element is gallium, Ga.

(iii) The outer electronic configuration of [Xe] $6s^2$ is $6s^2$, therefore, it is a *s*-block element. It belongs to the sixth period and group 2 of the periodic table. Therefore, the element is barium, Ba.

(iv) In the electronic configuration [Xe] $6s^2 5d^1 4f^7$ the electrons add to $4f$ -shell, therefore it is a *f*-block element and belongs to the sixth period and third group. Thus, the element is gadolinium, Gd.

(v) The outer electronic configuration of [Ar] $4s^1 3d^{10}$ is $4s^1 3d^{10}$, therefore, it is *d*-block element and belongs to the fourth period and group 11. Thus, the element is copper, Cu.

37. (i) Having the lowest ionisation enthalpies and the lowest electronegativities, the group 1 elements are characterized best as reducing agents and their chemical reactivity will be directly related to their reducing power. As the ionization energy as well as the electronegativity decreases down the group, the reducing power of the elements increases in the same order and so does the chemical reactivity. Thus, in group 1, chemical reactivity follows the order : Li < Na < K < Rb < Cs.

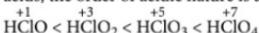
Having the highest negative electron gain enthalpies and the highest electronegativities, the group 17 elements are characterized best as oxidizing agents and their chemical

reactivity will be directly related to their oxidizing power. As the negative electron gain enthalphy as well as the electronegativity decreases down a group, the oxidizing power of an element also decreases in that order and so does the chemical reactivity. Thus, in group 17 chemical reactivity follows the order : F > Cl > Br > I.

(ii) For electronegative elements reactivity is given as oxidizing power and as electronegativity increase left to right hence, chemical reactivity also increases. Between Cl and O, Cl ($3s^2 3p^5$) is a more powerful oxidizing agent than O because it has much higher negative electron gain enthalpy than O ($2s^2 2p^4$), though the electronegativity of Cl (3.0) is lower than that of O (3.5). Therefore, chemical reactivity follows the order :

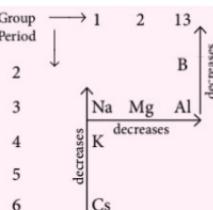
N < O < Cl < F

(iii) On the basis of the oxidation states of Cl in these acids, the order of acidic nature is as follows :



OR

(i) The trend in the metallic character with reference to the position of these elements in the periodic table should be as shown :



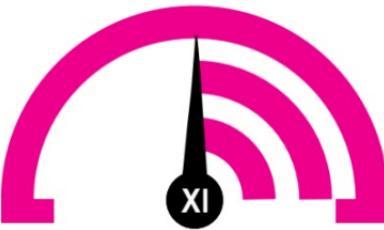
So, the order of decreasing metallic character is Cs > K > Na > Mg > Al > B

(ii) The number of electrons in these atoms or ions are: Ion or atom Al³⁺ F Cl⁻ O²⁻ Na Mg²⁺ No. of electrons 10 9 18 10 11 10 Thus, Al³⁺, O²⁻ and Mg²⁺ are isoelectronic ions because all the three ions have ten electrons. Now nuclear charge in Al³⁺ is +13, in O²⁻ is +8 and in Mg²⁺ is +12. With increase in nuclear charge (electrons remain same), size will decrease. Consequently, the size follows the order: O²⁻ > Mg²⁺ > Al³⁺.

(iii) The second electron gain enthalpy of O is expected to be positive. This is because the nuclear charge remaining the same, electron-electron repulsion in the principal quantum shell 2 increases enormously.



MONTHLY TEST DRIVE



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

Structure of Atom | Classification of Elements and Periodicity in Properties

Time Taken : 60 Min.

Total Marks : 120

NEET

Only One Option Correct Type

- Photoelectric emission is observed from a surface for frequencies ν_1 and ν_2 of the incident radiation ($\nu_1 > \nu_2$). If the maximum kinetic energies of the photoelectrons in the two cases are in the ratio 1 : k , then the threshold frequency ν_0 is given by
 (a) $\frac{\nu_2 - \nu_1}{k-1}$ (b) $\frac{k\nu_1 - \nu_2}{k-1}$
 (c) $\frac{\nu_2 - \nu_1}{k-1}$ (d) $\frac{\nu_2 - \nu_1}{k}$
 - IE_1 and IE_2 of Mg are 178 and 348 kcal mol⁻¹ respectively. The energy required for the reaction,
 $Mg_{(g)} \rightarrow Mg_{(g)}^{2+} + 2e^-$ is
 (a) + 170 kcal mol⁻¹ (b) + 526 kcal mol⁻¹
 (c) - 170 kcal mol⁻¹ (d) - 525 kcal mol⁻¹
 - Two nuclides X and Y are isotonic to each other with mass numbers 70 and 72 respectively. If the atomic number of X is 34, then that of Y would be
 (a) 32 (b) 34
 (c) 36 (d) 38
 - The atomic masses of He and Ne are 4 and 20 amu respectively. The value of the de Broglie wavelength of He gas at -73°C is 'M' times that of the de Broglie wavelength of Ne gas at 727°C. 'M' is
 (a) 2 (b) 3
 (c) 4 (d) 5
 - What is the general electronic configuration for 2nd row transition series?
- (a) $[Ne]3d^{1-10}, 4s^2$ (b) $[Ar]3d^{1-10}, 4s^{1-2}$
 (c) $[Kr]4d^{1-10}, 5s^{1-2}$ (d) $[Xe]5d^{1-10}, 5s^{1-2}$
- In a given shell, the order of screening effect is
 (a) $s > p > d > f$ (b) $f > d > p > s$
 (c) $p < d < s < f$ (d) $d > f > s > p$
 - The potential energy of an electron in the first Bohr orbit in the He^+ ion is
 (a) - 13.6 eV (b) - 27.2 eV
 (c) - 54.4 eV (d) - 108.8 eV
 - The first (Δ_IH_1) and second (Δ_IH_2) ionisation enthalpies (in kJ mol⁻¹) and the electron gain enthalpy ($\Delta_{eg}H$) (in kJ mol⁻¹) of the elements I, II, III, IV and V are given below :
- | Elements | Δ_IH_1 | Δ_IH_2 | $\Delta_{eg}H$ |
|----------|---------------|---------------|----------------|
| I | 520 | 7300 | - 60 |
| II | 419 | 3051 | - 48 |
| III | 1681 | 3374 | - 328 |
| IV | 1008 | 1846 | - 295 |
| V | 2372 | 5251 | + 48 |
- The most reactive and the least reactive element amongst these are respectively
 (a) I and V (b) V and II
 (c) II and V (d) IV and V
- If azimuthal quantum number could have value of n also (in addition to normal value), then electronic configuration of V ($Z = 23$) would have been
 (a) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^3$
 (b) $1s^2, 1p^6, 2s^2, 2p^6, 2d^7$
 (c) $1s^2, 1p^6, 2s^2, 2p^6, 3s^2, 2d^5$
 (d) $1s^2, 1p^6, 2s^2, 2p^6, 3s^1, 2d^6$

10. Which one of the following exhibits the maximum covalent character?

- (a) FeCl_2 (b) AlCl_3
(c) MgCl_2 (d) SnCl_2

11. In which of the following pairs the difference between the covalent radii of the two metals is maximum?

- (a) K, Ca (b) Mn, Fe
(c) Co, Ni (d) Cr, Mn

12. The wavelength of a spectral line in Lyman series, when electron jumping back to 2nd orbit is

- (a) 1162 Å (b) 1216 Å
(c) 1362 Å (d) 1176 Å

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 :** Helium has the highest value of ionisation energy among all the elements known.

Reason : Helium has the highest value of electron affinity among all the elements known.

14. **Assertion :** Energies of two electrons in an atom can be compared by using ' $n + l$ ' rule.

Reason : No two electrons in an atom can have equal energies.

15. **Assertion :** F atom has a less negative electron affinity than Cl atom.

Reason : Additional electrons are repelled more effectively by $3p$ electrons in Cl atom than by $2p$ electrons in F atom.

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Only One Option Correct Type

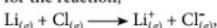
16. Out of the following electronic arrangements, for outer electronic configurations

- (i)
(ii)
(iii)
(iv)

the most stable arrangement is

- (a) (i) (b) (ii)
(c) (iii) (d) (iv)

17. The first ionisation energy for Li is 5.4 eV and electron affinity of Cl is 3.61 eV. The ΔH (in kJ/mol) for the reaction,



if the resulting ions do not combine with each other is

- (a) 70 (b) 100
(c) 170 (d) 270

18. The first orbital of H is represented by :

$$\psi = \frac{1}{\sqrt{x}} \left(\frac{Z}{a_0} \right)^{3/2} e^{-Zr/a_0}, \text{ where } a_0 \text{ is Bohr's radius.}$$

The probability of finding the electron at a distance r , from the nucleus in the region dV is

- (a) $\psi^2 dr$ (b) $\int \psi^2 4\pi r^2 dV$
(c) $\psi^2 4\pi r^2 dr$ (d) $\int \psi dV$

19. Predict the approximate density of Cs from the following data using law of triads.

(Given : Density of K = 0.868 g cm^{-3} ; Rb = 1.532 g cm^{-3})

- (a) 2.196 g cm^{-3}
(b) 4.392 g cm^{-3}
(c) 1.098 g cm^{-3}
(d) None of these

More than One Options Correct Type

20. Which of the following reactions have an endothermic step?

- (a) $\text{S}^-_{(g)} \longrightarrow \text{S}^{\cdot-}_{(g)}$
(b) $\text{Na}^+_{(g)} + \text{Cl}^-_{(g)} \longrightarrow \text{NaCl}_{(s)}$
(c) $\text{N}_{(g)} \longrightarrow \text{N}^\cdot_{(g)}$
(d) $\text{Al}^{2+}_{(g)} \longrightarrow \text{Al}^{3+}_{(g)}$

21. Electron in He^+ ion falls from seventh level and subsequent lower levels to first level, then

- (a) total of six emission lines are obtained
(b) the spectrum belongs to Lyman series
(c) total of five emission lines are obtained
(d) the spectrum belongs to Balmer series.

22. Which of the following statements are correct?

- (a) van der Waals' radius of iodine is more than its covalent radius.
(b) All isoelectronic ions belong to the same period of the periodic table.

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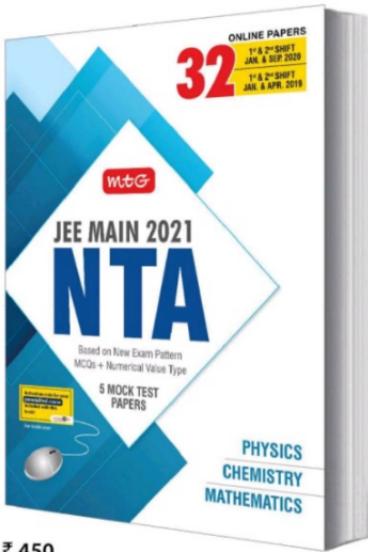
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