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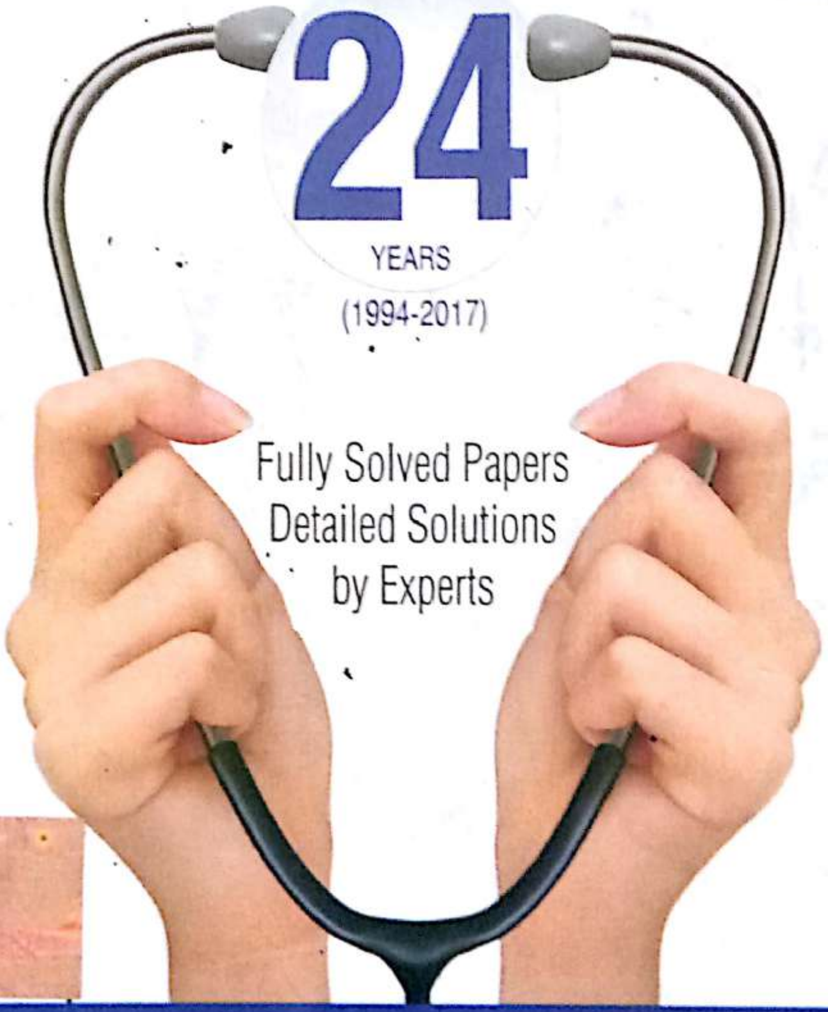

24

YEARS

(1994-2017)

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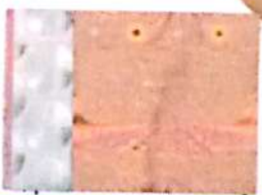

CHEMISTRY

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24

YEARS (1994-2017)

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CHEMISTRY

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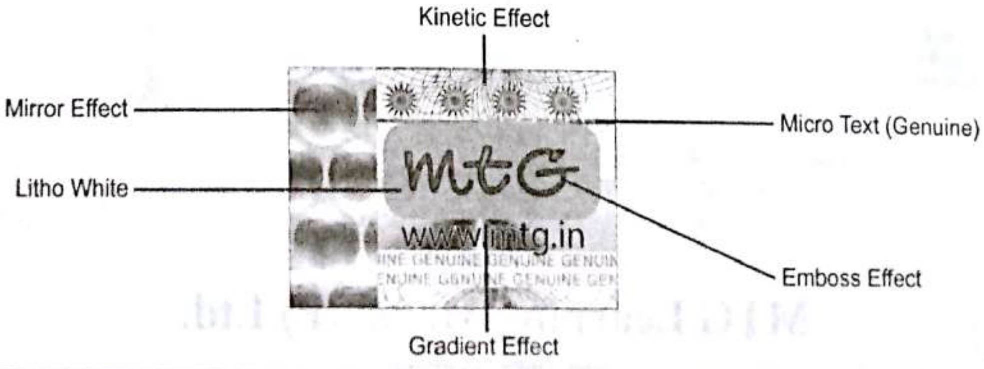

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About*

All India Institute of Medical Sciences (AIIMS)

AIIMS, New Delhi conducts MBBS Entrance Test for admission into AIIMS New Delhi and 6 other AIIMS Institutions in India. All India Institute of Medical Sciences (AIIMS) is an autonomous Institution of national importance that awards its own medical degrees, diplomas and other academic distinctions. The degrees awarded by the Institute are recognised medical qualifications for the purpose of the Indian Medical Council Act and equivalent and treated at par with medical degrees conferred by other Universities.

AIIMS Exam Pattern

The Competitive Entrance Examination will be of 3½ hours duration and will have one paper consisting of 200 objective type (multiple choice and assertion-reason type) questions from Physics, Chemistry, Biology and General Knowledge/ Aptitude. The distribution of questions is as follows:

Subject	Number of Questions
Physics	60
Chemistry	60
Biology (Botany & Zoology)	60
General Knowledge	10
Aptitude & Logical Thinking	10
Total	200

Incorrect responses will be given negative marks.

Each correct response will get a score of 1 mark and each incorrect response will get a score of -1/3 (minus-one-third). No credit will be given for the questions not answered or marked for review.

AIIMS Syllabus

No syllabus for the examination has been prescribed by the Institute for the examination. However, the general standard of the Competitive Entrance Examination will be that of 12th class under the 10+2 Scheme/Intermediate Science.

Directions for Assertion and Reason Type Questions

In this type of questions, a statement of assertion (A) is followed by a statement of reason (R). 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.

These are the general directions for previous years papers of AIIMS. But in 2000 and 2001 option [d] was changed to assertion is false and reason is true.

The questions given in this book are based on memory.

---

* *Subject to change. Please refer to latest prospectu*

CHAPTER

1

1. The weight o
which will g
(a) 0.18 g
(c) 0.24 g

2. A bivalent n
12. The mol
(a) 36
(c) 40

3. The percen
(a) 16%
(c) 40%

4. The numb
180 g of w
(a) 18
(c) 100

5. Avogadro'
(a) 32 g
(c) 56 g

6. The numb
is approxi
(a) 3.5
(c) 2.5

7. How man
diamond
200 mg ar
(a) 5 ×
(c) 7 ×

8. The max
on mixin
corresp
(a) 0.5
(c) 1.5

9. If 0.189
compou
the per
compou
(a) 35
(c) 37

10. The eq
(a) m
(b) m

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CHAPTER

1

SOME BASIC CONCEPTS OF CHEMISTRY

1. The weight of a metal of equivalent weight 12, which will give 0.475 g of its chloride, is
(a) 0.18 g (b) 0.12 g
(c) 0.24 g (d) 0.16 g *(1994)*

2. A bivalent metal has the equivalent weight of 12. The molecular weight of its oxide will be
(a) 36 (b) 24
(c) 40 (d) 32 *(1994)*

3. The percentage of oxygen in NaOH is
(a) 16% (b) 4%
(c) 40% (d) 8% *(1996)*

4. The number of moles of water present in 180 g of water is
(a) 18 (b) 5
(c) 100 (d) 10 *(1996)*

5. Avogadro's number of oxygen atom weighs
(a) 32 g (b) 8 g
(c) 56 g (d) 16 g *(1996)*

6. The number of molecules in 4.25 g of ammonia is approximately
(a) 3.5×10^{23} (b) 0.5×10^{23}
(c) 2.5×10^{23} (d) 1.5×10^{23} *(1996)*

7. How many atoms of carbon are present in a diamond weighing 0.5 carat? (one carat weighs 200 mg and assume diamond to be pure carbon)
(a) 5×10^{21} (b) 6×10^{22}
(c) 7×10^{19} (d) 8×10^{12} *(1997)*

8. The maximum amount of $BaSO_4$ precipitated on mixing $BaCl_2$ (0.5 M) with H_2SO_4 (1 M) will corrrespond to
(a) 0.5 M (b) 1.0 M
(c) 1.5 M (d) 2.0 M *(1997)*

9. If 0.189 g of a chlorine containing organic compound gave 0.287 g of silver chloride, then the percentage of chlorine in the organic compound is
(a) 35.47 (b) 35.57
(c) 37.57 (d) 45.37 *(1997)*

10. The equivalent weight of an acid is equal to
(a) molecular weight/basicity
(b) molecular weight × basicity
(c) molecular weight × acidity
(d) molecular weight/acidity *(1998)*

11. If a compound, on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O = 24.81%, then its empirical formula is
(a) C_2H_2OCl (b) CH_2ClO
(c) $CHClO$ (d) $ClCH_2O$ *(1998)*

12. A compound with empirical formula CH_2O has a vapour density of 30. Its molecular formula is
(a) $C_3H_6O_3$ (b) $C_2H_4O_2$
(c) $C_2H_2O_2$ (d) $C_6H_{12}O_6$ *(1998)*

13. One gram mole of a gas at N.T.P. occupies 22.4 litres. This fact was derived from
(a) Law of gaseous volumes
(b) Dalton's atomic theory
(c) Avogadro's hypothesis
(d) Law of constant proportions. *(1998)*

14. The empirical formula of a compound is CH_2O. Its molecular weight is 180. The molecular formula of the compound is
(a) C_4HO_4 (b) $C_5H_{10}O_5$
(c) $C_3H_6O_3$ (d) $C_6H_{12}O_6$ *(1999)*

15. The equivalent weight of phosphoric acid (H_3PO_4) in the reaction :
$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$ is
(a) 25 (b) 49
(c) 59 (d) 98 *(1999)*

16. Which of the following equations does not obey the law of conservation of mass?
(a) $4H + O_2 \rightarrow 2H_2O$ (b) $H_2 + O \rightarrow 2H_2O$
(c) $2H + O_2 \rightarrow H_2O$ (d) Both (b) and (c) *(1999)*

17. The weight of one molecule of a compound $C_{60}H_{122}$ is
(a) 1.2×10^{-20} g (b) 5.025×10^{23} g
(c) 1.4×10^{-21} g (b) 6.023×10^{23} g *(1999, 2002)*

18. The specific heat of a metal is 0.16. Its approximate atomic weight would be

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(a) 40 (b) 16
(c) 32 (d) 64 *(1999)*

19. 12 g of an alkaline earth metal gives 14.8 g of its nitride. Atomic weight of the metal is
(a) 12 (b) 20
(c) 40 (d) 14.8 *(2000)*

20. Percentage of Se (at. mass = 78.4) in peroxidase anhydrase enzyme is 0.5% by weight, then minimum molecular mass of peroxidase anhydrase enzyme is
(a) 1.576×10^4 (b) 1.576×10^3
(c) 15.76 (d) 2.136×10^4 *(2008)*

21. What is the molarity of H_2SO_4 solution that has a density of 1.84 g/cc at 35°C and contains 98% by weight?
(a) 4.18 M (b) 8.14 M
(c) 18.4 M (d) 18 M *(2009)*

22. 2.5 g of the carbonate of a metal was treated with 100 mL of 1N H_2SO_4. After the completion of the reaction, the solution was boiled off to expel CO_2 and was then titrated against 1N NaOH solution. The volume of alkali that would be consumed, if the equivalent weight of the metal is 20, is
(a) 50 mL (b) 25 mL
(c) 75 mL (d) 100 mL *(2009)*

23. To a 25 mL H_2O_2 solution, excess of acidified solution of KI was added. The iodine liberated required 20 mL of 0.3 N $Na_2S_2O_3$ solution. The volume strength of H_2O_2 solution is
(a) 1.344 g/L (b) 3.244 g/L
(c) 5.4 g/L (d) 4.08 g/L *(2009)*

24. The compound which does not exist as hydrate form
(a) ferrous sulphate (b) copper sulphate
(c) magnesium sulphate
(d) sodium chloride. *(2011)*

25. How much amount of $CuSO_4 \cdot 5H_2O$ is required for liberation of 2.54 g of I_2 when titrated with KI?
(a) 2.5 g (b) 4.99 g
(c) 2.4 g (d) 1.2 g *(2011)*

26. The number of atoms in 52 g of He is
(a) 78.299×10^{24} atoms
(b) 7.820×10^{-24} atoms
(c) 7.829×10^{24} atoms
(d) 78.234×120^{25} atoms *(2014)*

27. The amount of $BaSO_4$ precipitated on mixing $BaCl_2$ (0.5 M) with H_2SO_4 (1 M) will correspond to
(a) 0.5 mol (b) 1.0 mol
(c) 1.5 mol (d) 2.0 mol *(2015)*

28. How many significant figures are present in 0.0000135?
(a) 7 (b) 8
(c) 4 (d) 3 *(2015)*

29. 10 mL of liquid carbon disulphide (specific gravity 2.63) is burnt in oxygen. Find the volume of the resulting gases measured at STP.
(a) 23.25 L (b) 22.26 L
(c) 23.50 L (d) 20.08 L *(2016)*

ASSERTION AND REASON

30. ***Assertion :*** Atoms can neither be created nor destroyed.
Reason : Under similar conditions of temperature and pressure, equal volume of gases does not contain equal number of atoms. *(2002)*

31. ***Assertion :*** S.I. unit of atomic mass and molecular mass is kilograms.
Reason : Atomic mass is equal to the mass of 6.023×10^{24} atoms. *(2010)*

32. ***Assertion :*** One mole of NaCl contains 6.023×10^{23} molecules of sodium chloride.
Reason : 58.5 g of NaCl also contains 6.023×10^{23} molecules of NaCl. *(2015)*

33. ***Assertion :*** Equivalent weight of NH_3 in the reaction, $N_2 \rightarrow NH_3$ is 17/3 while that of N_2 is 28/6.
Reason : Equivalent weight

$$= \frac{\text{Molecular weight}}{\text{Number of } e^- \text{ lost or gained per mole}}$$ *(2017)*

Answer Key

1.	(b)	**2.**	(c)	**3.**	(c)	**4.**	(d)	**5.**	(d)	**6.**	(d)	**7.**	(a)	**8.**	(a)
9.	(c)	**10.**	(a)	**11.**	(c)	**12.**	(b)	**13.**	(c)	**14.**	(d)	**15.**	(d)	**16.**	(d)
17.	(c)	**18.**	(a)	**19.**	(c)	**20.**	(a)	**21.**	(c)	**22.**	(a)	**23.**	(d)	**24.**	(d)
25.	(b)	**26.**	(c)	**27.**	(a)	**28.**	(d)	**29.**	(a)	**30.**	(c)	**31.**	(d)	**32.**	(b)
33.	(a)														

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EXPLANATIONS

1. **(b) :** $\frac{\text{Equivalent weight of metal}}{\text{Equivalent weight of compound}}$

$= \frac{\text{Weight of metal}}{\text{Weight of compound}}$

$\Rightarrow \frac{12}{12+35.5} = \frac{\text{Weight of metal}}{0.475}$

$\Rightarrow$ Weight of metal = 0.12 g

2. **(c) :** Atomic wt. of metal = 2 × 12 = 24

$\therefore$ Mol. wt. of its oxide = 24 + 16 = 40

3. **(c) :** Molecular weight of NaOH is 40.

Atomic weight of oxygen is 16.

$\Rightarrow$ Percentage of oxygen $= \frac{16}{40} \times 100 = 40\%$

4. **(d) :** Molecular weight of water = 18

$\therefore$ No. of moles of water $= \frac{\text{Given Mass}}{\text{Molecular mass}}$

$= \frac{180}{18} = 10$ moles

5. **(d) :** Weight of $6 \cdot 023 \times 10^{23}$ molecules of oxygen (O_2) = 32 g. Since the oxygen is diatomic, therefore weight of Avogadro's number of oxygen atoms $= \frac{32}{2} = 16$ g

6. **(d) :** Given: Weight of ammonia = 4.25 g. 17 g of ammonia (NH_3) contains $6 \cdot 02 \times 10^{23}$ molecules. Therefore, number of molecules in 4.25 g of NH_3

$= \frac{6 \cdot 02 \times 10^{23} \times 4 \cdot 25}{17} = 1 \cdot 50 \times 10^{23}$

7. **(a) :** 1 carat = 200 mg

0.5 carat = 100 mg

1 mole of C-atoms weighs = 12 g

$\Rightarrow$ 12 g of carbon = 6.023×10^{23} C-atoms

$\Rightarrow$ 100 mg of carbon $= \frac{6.023 \times 10^{23} \times 100}{12 \times 1000}$

$= 5.02 \times 10^{21}$ atoms

8. **(a) :** $BaCl_2\ (0.5\ M) + H_2SO_4\ (1M) \rightarrow BaSO_4\downarrow + 2HCl$

As Ba^{2+} ion concentration is only 0.5M, therefore only 0.5M of $BaSO_4$ can be precipitated.

9. **(c) :** Given : Mass of the compound = 0.189 g and mass of AgCl = 0.287 g. Equivalent weight of chlorine is 35.5 and equivalent weight of AgCl is 143.5. Therefore, percentage of chlorine

$= \frac{35.5}{143.5} \times \frac{\text{Mass of AgCl formed}}{\text{Mass of substance taken}} \times 100$

$= \frac{35.5}{143.5} \times \frac{0.2870}{0.1890} \times 100 = 37.57\%$

10. **(a) :** Equivalent mass of an acid is defined as the number of parts by mass of it, which contains 1.008 parts by mass of replaceable hydrogen or it is the quantity of the acid by mass that supplies one mole of H^+ ions.

Eq. mass of acid

$= \frac{\text{Molecular mass of the acid}}{\text{Number of replaceable H atoms}}$

$= \frac{\text{Molecular mass of the acid}}{\text{Basicity of the acid}}$

11. **(c) :**

Element	**%**	**Atomic mass**	**Moles of atoms**	**Relative Simplest ratio of atoms**
C	18.5	12	$\frac{18.5}{12}=1.542$	1
H	1.55	1	$\frac{1.55}{1}=1.5$	1
Cl	55.04	35.5	$\frac{55.04}{35.5}=1.55$	1
O	24.81	16	$\frac{24.16}{16}=1.51$	1

Therefore, empirical formula of the compound is CHClO.

12. **(b) :** Molecular mass = 2 × vapour density

= 2 × 30 = 60

Empirical formula mass = 12 + 2 + 16 = 30

$\Rightarrow n = \frac{60}{30} = 2$

$\Rightarrow$ Molecular formula is $(CH_2O)_2 \equiv C_2H_4O_2$

13. **(c) :** According to Avogadro's hypothesis, equal volumes of different gases, contain same number of molecules under similar conditions of temperature and pressure. Thus, 22.4 litres of any gas at NTP will contain one gram mole or its molecular mass in grams.

14. **(d) :** Empirical formula of compound is CH_2O

Empirical formula mass = 12 + 2 + 16 = 30

Molecular weight of compound = 180

As, $n = \frac{\text{molecular mass}}{\text{empirical mass}} = \frac{180}{30} = 6$

Therefore, molecular formula of compound is $(CH_2O)_6 = C_6H_{12}O_6$

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15. (d) : The given reaction is :

$NaOH + H_3PO_4 \rightarrow NaH_2PO_4 + H_2O$

Molecular mass of H_3PO_4 is 98. As there is only one electron change involved therefore,

Equivalent weight of H_3PO_4 in this reaction is

$$= \frac{98}{1} = 98$$

16. (d) : According to law of conservation of mass, in all chemical changes the total mass of the system remains constant or in a chemical reaction, mass is neither created nor destroyed. This law was proposed by Lavoisier and tested by Landolt. But in (b) and (c), mass of reactants is not equal to the mass of products.

17. (c) : Molecular weight of $C_{60}H_{122}$

$$= 60 \times 12 + 1 \times 122 = 842$$

$\therefore$ Weight of 1 mole of $C_{60}H_{122}$ molecules $= 842$ g

$\Rightarrow$ Weight of 6.023×10^{23} molecules $= 842$ g

$$\Rightarrow \text{Weight of 1 molecule} = \frac{842}{6.023 \times 10^{23}} = 1.4 \times 10^{-21}\text{ g}$$

18. (a) : According to Dulong Petit's law :

Atomic weight × specific heat = 6.4

$$\text{Atomic weight} = \frac{6.4}{0.16} = 40$$

19. (c) Let the alkaline earth metal be A

$\therefore \quad 3A + N_2 \rightarrow A_3N_2$

$$\Rightarrow \frac{\text{Molecular mass of compd.}}{\text{Atomic mass of metal}} = \frac{\text{Wt. of compd.}}{\text{Wt. of metal}}$$

Let atomic mass of metal be x

$\Rightarrow$ Molecular mass of compound $= 3x + 28$

$$\Rightarrow \frac{3x+28}{3x} = \frac{14.8}{12} \Rightarrow x = 40$$

20. (a) : The enzyme must contain at least one atom of Se.

$\because$ 0.5 g of Se is present in 100 g of enzyme

$$\therefore \text{78.4 g of Se will be present in} = \frac{100 \times 78.4}{0.5} = 1.576 \times 10^4 \text{ g of enzyme}$$

21. (c) : Molarity

$$= \frac{\text{wt. of solute}}{\text{mol. wt.}} \times \frac{1000}{\text{vol. of solution (in mL)}}$$

(Volume of solution

$$= \frac{\text{mass}}{\text{density}} = \frac{100}{1.84} = 54.34 \text{ mL})$$

$$\text{Now, molarity} = \frac{98}{98} \times \frac{1000}{54.34} = 18.4 \text{ M}$$

22. (a) : Equivalent weight of metal carbonate $= 20 + 30 = 50$

$$\text{2.5 g of metal carbonate} = \frac{2.5}{50} = 0.05 \text{ eq.}$$

Number of equivalents of H_2SO_4 that would have reacted $= 0.05$

Number of equivalents of H_2SO_4 taken

$$= \frac{100 \times 1}{1000} = 0.1$$

Number of equivalents of H_2SO_4 remains unreacted $= 0.1 - 0.05 = 0.05$ eq.

$\therefore$ Number of equivalent of alkali consumed $= 0.05$ eq.

$\therefore \quad 1.0 \times V = 0.05 \times 1000$

$$V = \frac{0.05 \times 1000}{1.0} = 50 \text{ mL}$$

23. (d) : $2KI + H_2SO_4 + H_2O_2 \rightarrow K_2SO_4 + 2H_2O + I_2$

$2Na_2S_2O_3 + I_2 \rightarrow Na_2S_4O_6 + 2NaI$

millieq. of H_2O_2 in 25 mL = millieq. of I_2 = millieq. of $Na_2S_2O_3$

millieq. of H_2O_2 in 25 mL $= 20 \times 0.3 = 6$

$$\text{millieq. of } H_2O_2 \text{ in 1000 mL} = \frac{6}{25} \times 1000 = 240$$

$$\text{Equivalent per litre} = \frac{240}{1000}$$

$$\text{Gram per litre of } H_2O_2 = \frac{240}{1000} \times 17 = 4.08 \text{ g/L}$$

$$\left(\text{Equivalent weight of } H_2O_2 = \frac{34}{2} = 17\right)$$

24. (d) : Ferrous sulphate → $FeSO_4 \cdot 7H_2O$

Copper sulphate → $CuSO_4 \cdot 5H_2O$

Magnesium sulphate → $MgSO_4 \cdot 7H_2O$

Sodium chloride → $NaCl$

25. (b) : $2CuSO_4 \cdot 5H_2O + 4KI \rightarrow Cu_2I_2 + 2K_2SO_4 + I_2 + 10H_2O$

Molecular weight of $I_2 = 254$ g

Molecular weight of $2CuSO_4 \cdot 5H_2O$

$[2(63.5 + 32 + 64) + 10(18)]$ g $= 499$ g

254 g of I_2 is liberated by 499 g of $CuSO_4 \cdot 5H_2O$

2.54 g of I_2 will be liberated by x g $CuSO_4 \cdot 5H_2O$

$$\therefore \quad x = \frac{499}{254} \times 2.54 = 4.99 \text{ g}$$

26. (c) : $\text{Number of atoms} = \frac{N_A \times \text{mass}}{\text{At. mass}}$

$$= \frac{6.023 \times 10^{23} \times 52}{4} = 7.829 \times 10^{24} \text{ atoms}$$

27. (a) : $[Ba^{2+}] = 0.5 \text{ mol L}^{-1}$

$[SO_4^{2-}] = 1 \text{ mol L}^{-1}$

$Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightleftharpoons$ B

0.5 mol of Ba^{2+} would re

ions to form 0.5 mol of B

28. (d) : Zeros to the le

in a number are not sig

29. (a) : 1 mL of CS_2

10 mL of CS_2 will weig

CS_2 + 3O

12+ (2 × 32)

76 g

$\because$ 76 g of CS_2 yie

and SO_2 at STP.

$\therefore$ 26.3 g of CS_2 wo

30. (c) : Atom

destroyed. This

conservation of

Under similar

pressure, equal

number of atom

As, $PV = nRT$

If, for I case,

for II case, P_2

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$Ba^{2+}_{(aq)} + SO^{2-}_{4(aq)} \rightleftharpoons BaSO_{4(s)}$
0.5 mol of Ba^{2+} would react with 0.5 mol of SO_4^{2-} ions to form 0.5 mol of $BaSO_4$.

28. (d) : Zeros to the left of the first non-zero digit in a number are not significant.

29. (a) : 1 mL of CS_2 weighs 2.63 g.
10 mL of CS_2 will weigh 26.3 g.

$$\underset{\substack{12+(2\times 32)\\ 76\text{ g}}}{CS_2} + 3O_2 \longrightarrow \underbrace{\underset{22.4\text{ L}}{CO_2} + \underset{44.8\text{ L}}{2SO_2}}_{67.2\text{ L}}$$

$\because$ 76 g of CS_2 yields 67.2 L of a mixture of CO_2 and SO_2 at STP.

$\therefore$ 26.3 g of CS_2 would yield $= \frac{67.2}{76} \times 26.3 = 23.25$ L

30. (c) : Atoms can neither be created nor destroyed. This is the statement of law of conservation of mass.
Under similar conditions of temperature and pressure, equal volume of gases contain equal number of atoms.
As, $PV = nRT$ (Ideal gas equation)
If, for I case, $P_1V_1 = n_1RT_1$
for II case, $P_2V_2 = n_2RT_2$

$$\Rightarrow \quad \frac{P_1V_1}{P_2V_2} = \frac{n_1RT_1}{n_2RT_2} \Rightarrow n_1 = n_2$$

31. (d) : Atomic mass and molecular mass have the units u.
Mol. mass

$$= \frac{\text{Wt. of one molecule of the substance}}{1/12 \times \text{wt. of one atom of C}-12}$$

32. (b) : Molar mass or mass of 1 mole of NaCl
$= 23 + 35.5 = 58.5$ g
According to mole concept,
1 mole of molecules = Gram molecular mass
$= 6.023 \times 10^{23}$ molecules
$\therefore$ 58.5 g of NaCl also contains 6.023×10^{23} molecules of NaCl.

33. (a) : $\overset{0}{N_2} + 6e^- \rightarrow 2N^{3-}$

$\therefore$ Equivalent weight of $NH_3 = \frac{14+3}{3} = \frac{17}{3}$
(Mol. wt. of $NH_3 = 17$)

While, equivalent weight of $N_2 = \frac{14\times 2}{6} = \frac{28}{6}$

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CHAPTER 2

STRUCTURE OF ATOM

1. The number of electrons in $[_{19}K^{40}]^{-1}$ is
(a) 28 (b) 19
(c) 40 (d) 20 *(1994)*

2. According to Dalton's atomic theory, the smallest particle in which matter can exist, is called
(a) an electron (b) an atom
(c) a molecule (d) an ion. *(1994)*

3. The number of electrons and neutrons of an element is 18 and 20 respectively. Its mass number is
(a) 37 (b) 17
(c) 38 (d) 22 *(1994)*

4. The position of both an electron and helium atom is known within 1.0 nm. The momentum of the electron is known within 5.0×10^{-26} kg m s^{-1}. The minimum uncertainty in the measurement of the momentum of the helium atom is
(a) 7.0×10^{-26} kg m s^{-1}
(b) 5.0×10^{-26} kg m s^{-1}
(c) 8.0×10^{-26} kg m s^{-1}
(d) 6.0×10^{-26} kg m s^{-1} *(1994)*

5. Which of the following expressions gives the de Broglie relationship?
(a) $\lambda = \frac{h}{mp}$ (b) $\frac{h}{mv} = p$
(c) $\lambda m = \frac{v}{p}$ (d) $\lambda = \frac{h}{mv}$ *(1994)*

6. Rutherford's scattering experiment is related to the size of
(a) electron (b) nucleus
(c) neutron (d) proton. *(1995)*

7. Atom bomb is based on the principle of
(a) nuclear fission
(b) radioactivity
(c) fusion and fission
(d) nuclear fusion. *(1995)*

8. The maximum number of electrons, present in an orbital that is represented by azimuthal quantum number (l) = 3, will be
(a) 8 (b) 2
(c) 14 (d) 6 *(1996)*

9. The maximum energy is possessed by an electron, when it is present
(a) in first excited state
(b) in nucleus
(c) at infinite distance from the nucleus
(d) in ground energy state. *(1996)*

10. A radioactive nuclide decays at such a rate that after 96 min, only 1/8th of the original amount remains. The value of half-life of the nuclide is
(a) 32 min (b) 12 min
(c) 48 min (d) 24 min. *(1996)*

11. Which of the following species is isotonic with $_{37}Rb^{86}$?
(a) $_{38}Sr^{87}$ (b) $_{36}Kr^{84}$
(c) $_{39}Y^{89}$ (d) $_{37}Mg^{85}$ *(1996)*

12. "It is impossible to determine simultaneously the position and velocity of small particles such as electron". It is a statement of
(a) Hund's rule
(b) Aufbau's principle
(c) Pauli's exclusion principle
(d) Heisenberg's uncertainty principle. *(1997)*

13. The total number of orbitals in a shell can be given in the form of n, the principal quantum number is
(a) $2n$ (b) n^2
(c) $2n^2$ (d) $(n + 1)$ *(1997)*

14. Particle nature of the electron was experimentally demonstrated by
(a) de Broglie (b) Schrodinger
(c) Max Born (d) J.J. Thomson. *(1997)*

---

15. Generally, the
(a) 1000 to 3
(b) 4000 to 7
(c) 8000 to 1
(d) 12000 to

16. Which of th
radioactive su
(a) Proton
(c) α-rays

17. Which of the
of filling th
(a) Aufbau
(b) Octet r
(c) Hund's
(d) All of

18. Which of th
discovery c
(a) Neutr
(b) Neutr
(c) Neut
(d) All c

19. Planck's
that of
(a) radi
(b) wor
(c) pov
(d) ang

20. Ratio of
3000 Å
(a) 1
(c) 2

21. Princi
to the
(a)
(b)
(c)
(d)

22. $_{16}S^{3}$
(a)
(c)

23. If r
has
nu
re
(a
(c

15. Generally, the limit of visible spectrum is

(a) 1000 to 3000 Å

(b) 4000 to 7000 Å

(c) 8000 to 10000 Å

(d) 12000 to 15000Å *(1997)*

16. Which of the following is not emitted by radioactive substances?

(a) Proton (b) Positron

(c) α-rays (d) β-rays *(1997)*

17. Which of the following explains the sequence of filling the electrons in different shells?

(a) Aufbau's principle

(b) Octet rule

(c) Hund's rule

(d) All of these *(1998)*

18. Which of the following is the main cause of late discovery of neutron?

(a) Neutron in nucleus moves very fast.

(b) Neutron is highly unstable particle.

(c) Neutron is chargeless particle.

(d) All of these *(1998)*

19. Planck's constant has the same dimensions as that of

(a) radiant energy

(b) work

(c) power

(d) angular momentum. *(1998)*

20. Ratio of the energy of a photon with wavelengths 3000 Å and 6000 Å is

(a) 1 : 3 (b) 1 : 2

(c) 2 : 1 (d) 1 : 6 *(1998)*

21. Principal quantum number of an atom is related to the

(a) orbital angular momentum

(b) spin angular momentum

(c) size of the orbital

(d) orientation of the orbital in space. *(1998)*

22. ${}_{16}S^{32}$ and ${}_{15}Pb^{31}$ are

(a) isotopes (b) isotones

(c) isobars (d) isomers. *(1999)*

23. If magnesium atom having atomic number 12 has an isotope with mass number 26, then the number of protons, neutrons and electrons respectively of the atom are

(a) 12, 14, 12 (b) 12, 12, 14

(c) 14, 12, 12 (d) 12, 12, 12 *(1999)*

24. Principal, azimuthal and magnetic quantum numbers are respectively related to

(a) shape, size and orientation

(b) size, shape and orientation

(c) size, orientation and shape

(d) none of these. *(1999)*

25. Half-life of radium is 1580 years. Its average life will be

(a) 2.275×10^3 years (b) 2.5×10^3 years

(c) 8.825×10^2 years (d) 11.832×10^3 years *(1999)*

26. The following nuclear transformation

$^{23}_{11}\text{Na} + ^{1}_{1}\text{H} \rightarrow ^{23}_{12}\text{Mg} + ^{1}_{0}n$ belongs to

(a) (n, p) type (b) (p, n) type

(c) (e^-, n) type (d) (d, p) type. *(2000)*

27. Which of the following arrangements is possible?

	n	l	m	s
(a)	5	2	2	$+\frac{1}{2}$
(b)	2	2	0	$-\frac{1}{2}$
(c)	3	−2	1	$+\frac{1}{2}$
(d)	0	0	1	$+\frac{1}{2}$

(2001, 2015)

28. Quantum numbers of an atom can be defined on the basis of

(a) Hund's rule

(b) Pauli's exclusion principle

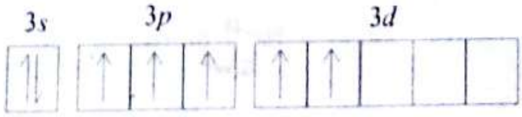
(c) Aufbau's principle

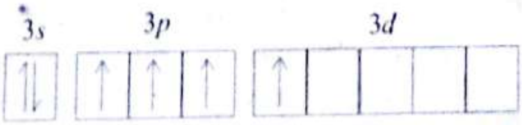
(d) Heisenberg's uncertainty principle. *(2002)*

29. Which of the following has maximum energy?

(a) 

(b) 

(c) 

(d) 

(2002, 2017)

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30. Spectrum of Li^{2+} is similar to that of
(a) H (b) Be
(c) He (d) Ne *(2002)*

31. Azimuthal quantum number defines
(a) e/m ratio of electron
(b) angular momentum of electron
(c) spin of electron
(d) magnetic momentum of electron. *(2002)*

32. The quantum number m of a free gaseous atom is associated with
(a) the effective volume of the orbital
(b) the shape of the orbital
(c) the spatial orientation of the orbital
(d) the energy of the orbital in the absence of a magnetic field. *(2003)*

33. For principal quantum number $n = 4$, the total number of orbitals having $l = 3$ is
(a) 3 (b) 7
(c) 5 (d) 9 *(2004)*

34. The most probable radius (in pm) for finding the electron in He^+ is
(a) 0.0 (b) 52.9
(c) 26.5 (d) 105.8 *(2005)*

35. The isoelectronic pair is
(a) Cl_2O, ICl_2^- (b) ICl_2^-, ClO_2
(c) IF_2^+, I_3^- (d) ClO_2^-, ClF_2^+
(2005)

36. ${}^{238}_{92}U$ emits 8 α-particles and 6 β-particles. The neutron/proton ratio in the product nucleus is
(a) 60/41 (b) 61/40
(c) 62/41 (d) 61/42 *(2005)*

37. α-Particles can be detected using
(a) thin aluminium sheet
(b) barium sulphate
(c) zinc sulphide screen
(d) gold foil. *(2005, 2015)*

38. The de Broglie wavelength associated with a ball of mass 1 kg having kinetic energy 0.5 J is
(a) 6.626×10^{-34} m (b) 13.20×10^{-34} m
(c) 10.38×10^{-21} m (d) 6.626×10^{-34} Å
(2006)

39. X-rays are emitted during
(a) α, n reaction (b) K-capture
(c) n, α reaction (d) β-emission.
(2007)

40. Which of the following radioisotopes is used as anticancerous?
(a) Na-24 (b) C-14
(c) U-235 (d) Co-60 *(2007)*

41. Decay constant of a radioactive substance is 69.3 sec^{-1}, find $t_{1/16}$ of the same substance.
(a) 4×10^{-2} sec (b) 2×10^{-2} sec
(c) 1×10^{-2} sec (d) None of these
(2007)

42. In the ground state of Cu^+, the number of shells occupied, subshells occupied, filled orbitals and unpaired electrons respectively are
(a) 4, 8, 15, 0 (b) 3, 6, 15, 1
(c) 3, 6, 14, 0 (d) 4, 7, 14, 2 *(2010)*

43. Assume that you are travelling at a speed of 90 km/h in a small car with a mass of 1050 kg. If the uncertainty in the velocity of the car is 1% (Δv = 0.9 km/h), what is the uncertainty (in meters) in the position of the car?
(a) $\Delta x \geq 1 \times 10^{-35}$ m (b) $\Delta x \geq 2 \times 10^{-37}$ m
(c) $\Delta x \geq 2 \times 10^{-36}$ m (d) $\Delta x \geq 4 \times 10^{-38}$ m
(2010)

44. Smallest wavelength occurs for
(a) Lyman series (b) Balmer series
(c) Paschen series (d) Brackett series.
(2011)

45. Which of the following is wrong for Bohr model?
(a) It establishes stability of atom.
(b) It is inconsistent with Heisenberg uncertainty principle.
(c) It explains the concept of spectral lines for hydrogen like species.
(d) Electrons behave as particle and wave.
(2011)

46. Threshold frequency of a metal is 5×10^{13} s^{-1} upon which 1×10^{14} s^{-1} frequency light is focused. Then the maximum kinetic energy of emitted electron is
(a) 3.3×10^{-21} J (b) 3.3×10^{-20} J
(c) 6.6×10^{-21} J (d) 6.6×10^{-20} J
(2012)

47. In Bohr's orbit, $\frac{nh}{2\pi}$ indicates
(a) momentum (b) kinetic energy
(c) potential energy
(d) angular momentum. *(2012)*

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48. A particle is moving 3 times faster than the speed of electron. If the ratio of wavelength of particle and electron is 1.8×10^{-4}, then particle is
(a) neutron (b) α-particle
(c) deuteron (d) tritium. *(2013)*

49. Which of the following pairs represents isotones?
(a) $^{77}_{33}As$, $^{78}_{34}Se$ (b) $^{195}_{78}Pt$, $^{190}_{76}Os$
(c) $^{108}_{47}Ag$, $^{112}_{48}Cd$ (d) $^{178}_{72}Hf$, $^{137}_{56}Ba$ *(2014)*

50. In a decay process $^{A}_{Z}X$ changes into $^{A}_{Z-1}Y$. Which of the following processes represents this?
(a) β-decay (b) β^+-decay
(c) α-decay (d) γ-decay *(2015)*

51. According to Bohr's theory, which of the following correctly represents the variation of energy and radius of an electron in n^{th} orbit of H-atom?
(a) $E_n \propto \frac{1}{n^2}, r \propto \frac{1}{n^2}$ (b) $E_n \propto \frac{1}{n^2}, r \propto n^2$
(c) $E_n \propto n^2, r \propto n^2$ (d) $E_n \propto n, r \propto \frac{1}{n}$
(2016)

52. Ionisation potential of hydrogen atom is 13.6 eV. Hydrogen atom in ground state is excited by monochromatic light of energy 12.1 eV. The spectral lines emitted by hydrogen according to Bohr's theory will be
(a) one (b) two
(c) three (d) four. *(2017)*

ASSERTION AND REASON

53. ***Assertion***: A spectral line will be seen for a $2p_x \rightarrow 2p_y$ transition.
Reason: Energy is released in the form of waves of light when the electron drops from $2p_x$ to $2p_y$ orbital. *(1996)*

54. ***Assertion***: Hydrogen has only one electron in its orbit. But it produces several spectral lines.
Reason: There are many excited energy levels available. *(1997)*

55. ***Assertion***: N_2 and NO^+ both are diamagnetic substance.
Reason: NO^+ is isoelectronic with N_2. *(1997)*

56. ***Assertion:*** The energy of an electron is largely determined by its principal quantum number.
Reason: The principal quantum number (n) is a measure of the most probable distance of finding the electrons around the nucleus. *(1998)*

57. ***Assertion:*** The 19th electron in potassium atom enters into the 4*s*-orbital and not into the 3*d*-orbital.
Reason: $(n + l)$ rule is followed for determining the orbitals of the lowest energy state. *(1998)*

58. ***Assertion:*** When an atom in group 1A of the periodic table undergoes radioactive decay by emitting a positron, the resulting element belongs to zero group.
Reason: When an atom emits a positron, its atomic number increases by one unit. *(2000)*

59. ***Assertion :*** Hydrogen nuclei combine to form helium nuclei and energy is released.
Reason : Binding energy/nucleon of He is greater than hydrogen. *(2001)*

60. ***Assertion :*** For Balmer series of hydrogen spectrum, the value $n_1 = 2$ and $n_2 = 3, 4, 5$.
Reason : The value of n for a line in Balmer series of hydrogen spectrum having the highest wavelength is 4 and 6. *(2002)*

61. ***Assertion :*** Absorption spectrum consists of some bright lines separated by dark spaces.
Reason : Emission spectrum consists of dark lines. *(2002)*

62. ***Assertion :*** $^{22}_{11}Na$ emits a positron giving $^{22}_{12}Mg$.
Reason : In β^+ emission, neutron is transformed into proton. *(2003)*

63. ***Assertion :*** The free gaseous Cr atom has six unpaired electrons.
Reason : Half-filled *s* orbital has greater stability. *(2004)*

64. ***Assertion :*** Nuclear binding energy per nucleon is in the order - $^{9}_{4}Be > ^{7}_{3}Li > ^{4}_{2}He$.
Reason : Binding energy per nucleon increases linearly with difference in number of neutrons and protons. *(2004)*

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65. ***Assertion*** **:** The position of an element in periodic table after emission of one α and two β-particles remains unchanged.
Reason **:** Emission of one α and two β-particles give isotope of the element which acquires same position in periodic table. *(2007, 2010)*

66. ***Assertion*** **:** The quantized energy of an electron is largely determined by its principal quantum number.
Reason **:** The principal quantum number, n is a measure of the most probable distance of finding the electron around the nucleus. *(2008)*

67. ***Assertion*** **:** The nuclear isomers are the atoms with the same atomic number and same mass number, but with different radioactive properties.
Reason **:** The nucleus in the excited state will evidently have a different half-life as compared to that in the ground state. *(2010)*

68. ***Assertion*** **:** Bohr model fails in case of multi-electron species.
Reason **:** It does not mention electron-electron interactions. *(2012)*

69. ***Assertion*** **:** The spectrum of He^+ is expected to be similar to that of hydrogen.
Reason **:** He^+ is also one electron system. *(2012)*

70. ***Assertion*** **:** Number of radial and angular nodes for 3p-orbital are 1, 1 respectively.
Reason **:** Number of radial and angular nodes depends only on principal quantum number. *(2013)*

71. ***Assertion*** **:** For Balmer series of hydrogen spectrum, the value $n_1 = 2$ and $n_2 = 3, 4, 5\ldots$.
Reason **:** The value of n_2 for a line in Balmer series of hydrogen spectrum having the highest wavelength is 6. *(2015)*

Answer Key

1.	(d)	**2.**	(b)	**3.**	(c)	**4.**	(b)	**5.**	(d)	**6.**	(b)	**7.**	(a)	**8.**	(b)
9.	(c)	**10.**	(a)	**11.**	(a)	**12.**	(d)	**13.**	(b)	**14.**	(a)	**15.**	(b)	**16.**	(a)
17.	(a)	**18.**	(b)	**19.**	(d)	**20.**	(c)	**21.**	(c)	**22.**	(b)	**23.**	(a)	**24.**	(b)
25.	(a)	**26.**	(b)	**27.**	(a)	**28.**	(b)	**29.**	(c)	**30.**	(a)	**31.**	(b)	**32.**	(c)
33.	(b)	**34.**	(c)	**35.**	(d)	**36.**	(c)	**37.**	(c)	**38.**	(a)	**39.**	(b)	**40.**	(d)
41.	(a)	**42.**	(c)	**43.**	(b)	**44.**	(a)	**45.**	(d)	**46.**	(b)	**47.**	(d)	**48.**	(a)
49.	(a)	**50.**	(b)	**51.**	(b)	**52.**	(c)	**53.**	(d)	**54.**	(a)	**55.**	(b)	**56.**	(a)
57.	(a)	**58.**	(c)	**59.**	(a)	**60.**	(c)	**61.**	(d)	**62.**	(d)	**63.**	(c)	**64.**	(d)
65.	(a)	**66.**	(a)	**67.**	(a)	**68.**	(b)	**69.**	(a)	**70.**	(c)	**71.**	(c)		

---

1. **(d) :** Atomic no
e^- present originally
Total no. of e^-

2. **(b) :** Dalton's a
is the smallest and
materials.

3. **(c) :** Mass no. =
No. of protons = No
$\Rightarrow$ No. of protons
$\Rightarrow$ Mass no. = 20

4. **(b) :** The Heis
$\Delta x \times \Delta p \geq \frac{h}{4\pi}$, wher
Δp = Uncertainty in
As Δx is same for e
constant, therefore
measurement of the
will be same as
5.0×10^{-26} kg m s^-

5. **(d) :** de Brogli
where m = mass,
λ = wavelength.

6. **(b) :** In this ex
was bombarded
α-particles went s
deflections. This le
very small and ver

7. **(a)**

8. **(b) :** $l = 3$ co
seven f-orbitals a
electrons.

9. **(c) :** As the ele
its energy increase

10. **(a) :** $N = \left(\frac{1}{2}\right.$
N_0 = Initial amoun
n = No. of half liv
Given, $\frac{N}{N_0} = \frac{1}{8}$ $\Rightarrow$

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EXPLANATIONS

1. **(d) :** Atomic no. = 19
e^- present originally = 19
Total no. of e^- = 19 + 1 (from –ve charge) = 20

2. **(b) :** Dalton's atomic theory says that an atom is the smallest and indivisible component of all materials.

3. **(c) :** Mass no. = No. of protons + No. of neutrons
No. of protons = No. of electrons
⇒ No. of protons = 18
⇒ Mass no. = 20 + 18 = 38

4. **(b) :** The Heisenberg uncertainty principle, $\Delta x \times \Delta p \geq \frac{h}{4\pi}$, where Δx = Uncertainty in position, Δp = Uncertainty in momentum and $\frac{h}{4\pi}$ = constant.

As Δx is same for electron and helium and $\frac{h}{4\pi}$ is a constant, therefore minimum uncertainty in the measurement of the momentum of the helium atom will be same as that of an electron which is 5.0×10^{-26} kg m s^{-1}.

5. **(d) :** de Broglie relation is $(\lambda) = \frac{h}{mv} = \frac{h}{p}$, where m = mass, v = velocity, p = momentum, λ = wavelength.

6. **(b) :** In this experiment, when a thin foil of gold was bombarded by α-particles, most of the α-particles went straight and very few got large deflections. This led to the conclusion that nucleus is very small and very compact.

7. **(a)**

8. **(b) :** $l = 3$ corresponds to f-orbitals. There are seven f-orbitals and each orbital accomodates 2 electrons.

9. **(c) :** As the electron goes away from the nucleus its energy increases sharply.

10. **(a) :** $N = \left(\frac{1}{2}\right)^n N_0$

N_0 = Initial amount, N = Amount at 't' time
n = No. of half lives

Given, $\frac{N}{N_0} = \frac{1}{8} \Rightarrow \left(\frac{1}{2}\right)^n = \frac{1}{8} = \left(\frac{1}{2}\right)^3 \Rightarrow n = 3$

As by definition, $n = \frac{\text{total time}}{\text{half life time}}$

$\Rightarrow$ half life time $= \frac{96}{3} = 32$ minutes

11. **(a) :** Isotonic species are those which have identical numbers of neutrons.

$_{37}\text{Rb}^{86}$; $n = 86 - 37 = 49$
$_{38}\text{Sr}^{87}$; $n = 87 - 38 = 49$
$_{36}\text{Kr}^{84}$; $n = 84 - 36 = 48$
$_{39}\text{Y}^{89}$; $n = 89 - 39 = 50$
$_{37}\text{Mg}^{85}$; $n = 85 - 37 = 48$

12. **(d) :** According to Heisenberg's uncertainty principle,

$$\Delta x \times \Delta v \geq \frac{h}{4\pi m}$$

Δx = uncertainty in position
Δv = uncertainty in velocity
h = Planck's constant (6.63×10^{-34} J s)
m = Mass of electron

13. **(b) :** If Principal quantum number (n) is 2,
Possible orbitals = $2s$, $2p_x$, $2p_y$, $2p_z$
Total = 4 (*i.e.*, $n^2 = 4$)
If $n = 3$,
Possible orbitals are one s, three p-orbitals and five d-orbitals total = 9 (*i.e.*, $n^2 = 9$)

14. **(a) :** de Broglie proposed the relation :

$\lambda = \frac{h}{mv}$ where, λ = wavelength
mv = momentum of particle

15. **(b) :** Visible spectrum ranges from 4000 Å to 7000 Å.

16. **(a) :** Radioactive substances usually emit α-rays ($^4_2$He nuclei), β-rays (electrons) or γ-rays or sometimes positrons ($^0_1\beta$).

17. **(a) :** According to Aufbau principle, the subshell with minimum energy is filled up first and when this obtains maximum number of electrons, then the next subshell of higher energy starts filling. Sequence comes out to be : $1s$, $2s$, $2p$, $3s$, $3p$, $4s$, $3d$, $4p$, $5s$, $4d$, $5p$, $6s$, $4f$ etc.

18. **(b) :** Neutron in free state immediately decomposes to proton and electron which makes its detection very difficult outside the nucleus.

$$^1_0n \rightarrow {}^1_1p + {}^0_{-1}e$$

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19. **(d) :** Planck's constant, $h = 6.63 \times 10^{-34}$ J s
Also, $E = h\nu$

$$\Rightarrow h = \text{Energy} \times \text{Time} = \text{Force} \times L \times T = MLT^{-2} \times L \times T = ML^2T^{-1}$$

Angular momentum,
$$L = mvr = M \times LT^{-1} \times L = ML^2T^{-1}$$

Therefore, both have same dimensions.

20. **(c) :** Energy of a photon is given by :

$$E = h\nu = \frac{hc}{\lambda}$$

$$\frac{E_1(3000\ \text{Å})}{E_2(6000\ \text{Å})} = \frac{hc/3000}{hc/6000} = \frac{2}{1}$$

21. **(c) :** Principal quantum number (n) represents the name, size and energy of the shell to which the electron belongs. Higher the value of 'n', greater is the distance of the shell from the nucleus.

22. **(b) :** Isotones are the nuclei that have same number of neutrons in them.

$_{16}S^{32}$: number of neutrons = 32 − 16 = 16
$_{15}P^{31}$: number of neutrons = 31 − 15 = 16

23. **(a) :** Isotopes are nuclei that have same atomic number but different mass number.

∴ Atomic number of the isotope = 12
⇒ Number of electrons and protons = 12
Number of neutrons = Mass no. − Atomic no.
= 26 − 12 = 14

24. **(b) :** Principal quantum number (n) represents the name, size and energy of the shell of the electron.
$n = 1, 2, 3, 4$ ....

Azimuthal quantum number (l) describes the spatial distribution of electron cloud and angular momentum.

Magnetic quantum number (m) describes the possible orientations of orbitals.

25. **(a) :** Average life = Half life × 1.44
= 1580 × 1.44
= 2275.2 years
= 2.275×10^3 years

26. **(b) :** $^{23}_{11}\text{Na} + ^{1}_{1}\text{H} \rightarrow ^{23}_{12}\text{Mg} + ^{1}_{0}n$

$^{1}_{1}\text{H}$ represents proton (or p)

$^{1}_{0}n$ represents neutron (or n)

The reaction is of (p, n) type.

27. **(a) :** When $n = 5$, then $l = 0, 1, 2, 3, 4$.
Again when $l = 2$, then $m = -2, -1, 0, +1, +2$.
The 's' value can be ±1/2.
Hence the arrangement, $n = 5, l = 2, m = 2, s = +1/2$ is possible for an electron.

28. **(b) :** Each electron in an atom is designated by a set of four quantum numbers. According to Pauli's exclusion principle, no two electrons in an atom have same values of all the four quantum numbers. Therefore consequently, an orbital accommodates two electrons with opposite spins, these two electrons have the same value of quantum number 'n', 'l' and 'm' but value of 's' will be different.

29. **(c) :** The order of increasing energy of the subatomic orbitals is $s < p < d < f$. The energy in excited state is more than that in the ground state. Since option (c) is in an excited state, therefore it has maximum energy.

30. **(a) :** Number of electrons in Li^{2+} is one, similar to the hydrogen atom. One electron system shows similar kind of spectra. Many electron system spectra is complex due to inter-electronic repulsions.

31. **(b) :** Azimuthal quantum number defines the spatial distribution of electron cloud and angular momentum.

e.g., $l = 0$, s - subshell
$l = 1$, p - subshell
$l = 2$, d - subshell

Orbital angular momentum of an electron is calculated using the expression,

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

32. **(c) :** This quantum number describes the orientation or distribution of electron cloud.

33. **(b) :** $n = 4$
$1s^2\, 2s^2\, 2p^6\, 3s^2\, 3p^6\, 3d^{10}\, 4s^2\, 4p^6\, 4d^{10}\, 4f^{14}$
$l = 3$ only for f orbital.

Thus, the total number of orbitals for $l = 3$ is equal to 7 (because f contains seven orbitals).

34. **(c) :** Most probable radius = a_0/Z
where $a_0 = 52.9$ pm. For helium ion, $Z = 2$

$$r_{mp} = \frac{52.9}{2} = 26.45 \text{ pm}$$

35. **(d) :** Number of electrons in ClO_2^-
$= 17 + 2 \times 8 + 1 = 34$

Number of electrons in $ClF_2^+ = 17 + 2 \times 9 - 1 = 34$

36. **(c) :** $_{92}U^{238} \xrightarrow[-6\beta]{-8\alpha} {_{82}X^{206}}$
Number of protons = 82
Number of neutrons = 124
Neutron/proton ratio in the product

$$= \frac{124}{82} = \frac{62}{41}$$

37. **(c) :** Rutherford first of all use
(ZnS) as phosphor for detection of

38. **(a) :** Kinetic energy $= \frac{1}{2}mv^2$
[m = mas

or, $0.5 = \frac{1}{2} \times 1 \times v^2$ or, $v = 1$ m s

de Broglie wavelength, $\lambda = \frac{h}{mv}$

or, $\lambda = \frac{6.626 \times 10^{-34}\ \text{Js}}{1\ \text{kg} \times 1\ \text{m s}^{-1}} = 6.626 \times$

39. **(b) :** In certain nucleus, the nu
electron from the K-shell (being near
The vacancy created is filled up wit
the higher shells thereby emitting
of K-electron capture, a proton
converted into a neutron ($p + e^-$

40. **(d) :** Radiation (γ-rays) emitte
substances ($_{27}Co^{60}$) destroys the cel
in treatment of cancer in which t
are wiped out.

41. **(a) :** $1 \xrightarrow{t_{1/2}} \frac{1}{2} \xrightarrow{t_{1/2}} \frac{1}{4} \xrightarrow{t_{1/2}} \frac{1}{8}$
So, $t_{1/16} = 4t_{1/2}$

$$= 4 \times \frac{0.693}{\lambda} = 4 \times \frac{0.693}{69.3}$$

42. **(c) :** $Cu^+ = 1s^2\, 2s^2\, 2p^6 3s^2 3$
Shells occupied = 3, sub-s
filled orbitals = 14 and unpaire

43. **(b) :** $\Delta x \geq \frac{h}{(4\pi)(m\Delta v)}$

$$\Delta x \geq \frac{6.626 \times 10^{-34}}{(4 \times 3.14 \times 1050)(0.9)\left(\frac{1}{36\right.}}$$

$\Delta x \geq 2 \times 10^{-37}$ m

The uncertainty in the position o
than the uncertainty in the posi
a hydrogen atom (3×10^{-10} r
value to have any measurable

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36. **(c) :** ${}_{92}U^{238} \xrightarrow[-6\beta]{-8\alpha} {}_{82}X^{206}$

Number of protons = 82

Number of neutrons = 124

Neutron/proton ratio in the product nucleus

$= \frac{124}{82} = \frac{62}{41}$

37. **(c) :** Rutherford first of all used zinc sulphide (ZnS) as phosphor for detection of α-particles.

38. **(a) :** Kinetic energy $= \frac{1}{2}mv^2$

[m = mass, v = velocity]

or, $0.5 = \frac{1}{2} \times 1 \times v^2$ or, $v = 1\ \text{m s}^{-1}$

de Broglie wavelength, $\lambda = \frac{h}{mv}$

or, $\lambda = \frac{6.626 \times 10^{-34}\ \text{Js}}{1\ \text{kg} \times 1\ \text{m s}^{-1}} = 6.626 \times 10^{-34}\ \text{m}$

39. **(b) :** In certain nucleus, the nucleus captures an electron from the K-shell (being nearest to the nucleus). The vacancy created is filled up with the electron from the higher shells thereby emitting X-rays. As a result of K-electron capture, a proton in the nucleus is converted into a neutron ($p + e^- \rightarrow n$).

40. **(d) :** Radiation (γ-rays) emitted by the radioactive substances (${}_{27}Co^{60}$) destroys the cells. Hence, it is used in treatment of cancer in which the malignant cells are wiped out.

41. **(a) :** $1 \xrightarrow{t_{1/2}} \frac{1}{2} \xrightarrow{t_{1/2}} \frac{1}{4} \xrightarrow{t_{1/2}} \frac{1}{8} \xrightarrow{t_{1/2}} \frac{1}{16}$

So, $t_{1/16} = 4t_{1/2}$

$= 4 \times \frac{0.693}{\lambda} = 4 \times \frac{0.693}{69.3} = 4 \times 10^{-2}$ sec

42. **(c) :** $Cu^+ = 1s^2\, 2s^2\, 2p^6 3s^2 3p^6 3d^{10}$

Shells occupied = 3, sub-shells occupied = 6, filled orbitals = 14 and unpaired e^- = 0

43. **(b) :** $\Delta x \geq \frac{h}{(4\pi)(m\Delta v)}$

$$\Delta x \geq \frac{6.626 \times 10^{-34}}{(4 \times 3.14 \times 1050)(0.9)\left(\frac{1}{3600}\right)\left(\frac{1000}{1}\right)}$$

$\Delta x \geq 2 \times 10^{-37}\ \text{m}$

The uncertainty in the position of the car is far smaller than the uncertainty in the position of an electron in a hydrogen atom (3×10^{-10} m) and far too small value to have any measurable consequences.

44. **(a) :** Series → Lyman, Balmer,
Paschen, Brackett, Pfund

$$\xrightarrow[\text{Increasing wavelength}]{\hspace{8cm}}$$

45. **(d) :** (a) It successfully explained the stability of atoms.

(b) It is not in agreement with Heisenberg's uncertainty principle.

(c) It does not explain the spectra of multi-electron atoms.

46. **(b) :** Following the conservation of energy principle,

Kinetic energy $\left(\frac{1}{2}m_e v^2\right) = h(\nu - \nu_0)$

$= (6.626 \times 10^{-34}\ \text{J s})(1 \times 10^{14}\ \text{s}^{-1} - 5 \times 10^{13}\ \text{s}^{-1})$

$= (6.626 \times 10^{-34}\ \text{J s})(5 \times 10^{13}\ \text{s}^{-1})$

$= 3.313 \times 10^{-20}$ J

47. **(d) :** $mvr = \frac{nh}{2\pi}$

48. **(a) :** Given : $\frac{\lambda_{\text{particle}}}{\lambda_{\text{electron}}} = 1.8 \times 10^{-4}$

and $\frac{v_{\text{particle}}}{v_{\text{electron}}} = 3$

According to de-Broglie equation, $\lambda = \frac{h}{mv}$

$$\frac{\lambda_{\text{particle}}}{\lambda_{\text{electron}}} = \frac{h}{m_{\text{particle}} \times v_{\text{particle}}} \times \frac{m_{\text{electron}} \times v_{\text{electron}}}{h}$$

$$= \frac{m_{\text{electron}}}{m_{\text{particle}}} \times \frac{v_{\text{electron}}}{v_{\text{particle}}}$$

$$\Rightarrow 1.8 \times 10^{-4} = \frac{9.1 \times 10^{-31}\ \text{kg}}{m_{\text{particle}}} \times \frac{1}{3}$$

$$m_{\text{particle}} = \frac{9.1 \times 10^{-31}}{1.8 \times 10^{-4} \times 3} = 1.6852 \times 10^{-27}\ \text{kg}$$

Actual mass of neutron is 1.67493×10^{-27} kg. Hence, the particle is neutron.

49. **(a) :** Isotones have the same number of neutrons.

As = 77 – 33 = 44 ; Se = 78 – 34 = 44

50. **(b):** ${}^{A}_{Z}X \rightarrow {}^{A}_{Z-1}Y + {}^{0}_{+1}e$ (or β^+)

51. **(b) :** According to Bohr's theory,

$r = \frac{n^2h^2}{4\pi^2 mZe^2k}$ and $E_n = \frac{-k^2 2\pi^2 mZ^2e^4}{n^2h^2}$

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52. (c) : Since ionisation potential of hydrogen atom is 13.6 eV.

$\therefore \quad E_1 = -13.6$ eV

Now, $E_n - E_1 = \frac{-13.6}{n^2} - (-13.6) = 12.1$

$\frac{-13.6}{n^2} + 13.6 = 12.1$

$\therefore \quad n = 3$

After absorbing 12.1 eV, the electron of H-atom is excited to 3rd shell.

Thus, possible transitions are 3 *i.e.*, $3 \rightarrow 2$, $2 \rightarrow 1$ and $3 \rightarrow 1$.

53. (d) : No transition can take place between $2p_x \rightarrow 2p_y$ as $2p_x$ and $2p_y$ are degenerate orbitals.

54. (a) : Hydrogen (Z = 1); $1s^1$

This single electron can be expected to go in higher energy levels and when de-excited it gives out different spectral lines *e.g.*, Balmer, Paschen, etc.

55. (b) : Due to the absence of unpaired electron in NO^+ and N_2, both are diamagnetic in nature.

Total no. of e^- in $NO^+ = 7 + 8 - 1 = 14$

Total no. of e^- in $N_2 = 7 + 7 = 14$

Therefore, both are isoelectronic.

56. (a) : Principal quantum number (n) represents the name, size and energy of shell to which the electron belongs. Higher the value of 'n', greater is the distance of the shell from the nucleus and hence greater is the energy.

57. (a) : According to Aufbau's principle, the unfilled shell with lowest $(n + l)$ value will be filled first. Therefore, 4*s* orbital is filled first than 3*d* orbital.

For 4*s* - orbital, $(n + l) = 4 + 0 = 4$

For 3*d* - orbital, $(n + l) = 3 + 2 = 5$

58. (c) : Positron emission :

$${}^{b}_{a}X \rightarrow {}^{b}_{a-1}X + \underset{\text{Positron}}{{}^{0}_{1}\beta}$$

Therefore, after positron emission, atomic number of the atom decreases by one and mass number remains unaffected.

59. (a) : A nuclear reaction in which two lighter nuclei are fused together to form a heavier nuclei is called nuclear fusion. In such a process, more stable nuclei come into existence and binding energy per nucleon increases. Fusion reactions are highly exothermic because of loss of mass during fusion.

e.g., ${}^{2}_{1}H + {}^{2}_{1}H \rightarrow {}^{4}_{2}He + 24.9$ MeV

60. (c) : The wavelength of the line can be calculated by the Ritz formula :

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \quad R = \text{Rydberg constant}$$

Therefore, for calculating highest wavelength in Balmer series ($n_1 = 2$), n_2 should be 3.

61. (d) : Absorption spectrum is produced when white light is passed through a substance and transmitted light is analysed by a spectrograph. The dark spaces corresponds to the light radiation absorbed by the substance. And emission spectrum is produced by analysing the radiant energy emitted by an excited substance by a spectrograph. Thus, discontinuous spectra consisting of a series of sharp lines and separated by dark bands are obtained.

62. (d) : ${}_{11}Na^{22} \rightarrow {}_{12}Mg^{22} + {}_{-1}\beta^{0}$

It involves β-particle emission.

While positron emission is due to the conversion of proton into neutron.

$${}^{1}_{1}p \rightarrow {}^{1}_{0}n + {}^{0}_{1}\beta$$

63. (c) : Cr → [Ar] $3d^5\,4s^1$

Fully-filled *s*-orbital has greater stability.

64. (d) : Binding energy per nucleon of ${}_3Li^7$ (5.38 MeV) is lesser than ${}_2He^4$ (7.08 MeV) as helium is found to be more stable than Li. As the number of particles in a nucleus increases, the total binding energy also increases but not with the uniform rate.

65. (a) : The loss of one α-particle will reduce the mass number by four and atomic number by two. Subsequent two β-emissions will increase the atomic number by two without affecting the mass number. Hence, the new element will be only an isotope of the parent nuclide and hence its position in the periodic table remains unchanged.

66. (a) : $E = -\frac{2\pi^2k^2m_e^4}{n^2h^2}$

where n = principal quantum number which has only integral value, it follows that total energy is quantized.

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67. (a) : The nuclear isomerism in
same mass number and same at
arises due to different radioacti
The reason for nuclear isomerism
energy states of two isomeric nucl
in the ground state and other in
The nucleus in the excited state w
half-life.,

68. (b): Bohr model does not ex
multi-electron atoms.

69. (a) : All species like He^+, L
electron are expected to have sim
of hydrogen.

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67. (a) : The nuclear isomerism in the nuclei of same mass number and same atomic number arises due to different radioactive properties. The reason for nuclear isomerism is the different energy states of two isomeric nuclei. One may be in the ground state and other in an excited state. The nucleus in the excited state will have different half-life.,

68. (b): Bohr model does not explain the spectra of multi-electron atoms.

69. (a) : All species like He^+, Li^{2+}, Be^{3+} having one electron are expected to have similar spectrum as that of hydrogen.

70. (c) : For $3p$-orbital, number of radial nodes $= n - l - 1 = 3 - 1 - 1 = 3 - 2 = 1$

Number of angular nodes $= l = 1$

Number of radial and angular nodes depend on both n and l.

71. (c) : The wavelength of the line can be calculated by the Rydberg formula :

$$\frac{1}{\lambda} = R\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right), \quad R = \text{Rydberg constant}$$

Therefore, wavelength will be highest in Balmer series ($n_1 = 2$) when n_2 is 3.

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CHAPTER 3

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES

1. Which of the following elements will have the highest electron affinity?
[✓ (a) Chlorine] (b) Nitrogen
(c) Phosphorus (d) Flourine
(1994, 2015)

2. The long form of periodic table is based on
(a) mass of the atom
(b) atomic number
(c) shape of the atom
(d) electronegativity. *(1994)*

3. Which of the following alkaline earth metals has highest ionic mobility in aqueous solution?
(a) Be^{2+} (b) Ca^{2+}
[✓ (c) Ba^{2+}] (d) Mg^{2+} *(1995)*

4. The element, with atomic number 118, will be
(a) a transition element
(b) an alkali metal
(c) an alkaline earth metal
(d) a noble gas. *(1995)*

5. Which of the following has the maximum electronegativity?
(a) C (b) F
(c) N (d) O *(1995)*

6. In the P^{3-}, S^{2-} and Cl^- ions, the increasing order of size is
(a) $S^{2-} < Cl^- < P^{3-}$ [✓ (b) $Cl^- < S^{2-} < P^{3-}$]
(c) $S^{2-} < P^{3-} < Cl^-$ (d) $P^{3-} < S^{2-} < Cl^-$
(1996)

7. If a neutral atom is converted into a cation, then its
(a) atomic weight increases
(b) size increases
(c) atomic weight decreases
(d) size decreases. *(1996)*

8. The electronic configuration $1s^2\ 2s^2\ 2p^5\ 3s^1$ shows
(a) ground state of fluorine atom
(b) excited state of fluorine atom
[✓ (c) excited state of neon atom]
(d) excited state of ion O_2^- *(1997)*

9. Which of the following is the most electropositive element?
(a) Phosphorus [✓ (b) Magnesium]
(c) Aluminium (d) Sulphur *(1998)*

10. Which of the following has maximum ionisation potential?
(a) Na (b) K
(c) Be (d) Mg *(1999)*

11. Which of the following ions in aqueous solution is the best conductor of electricity?
(a) Li^+ (b) Na^+
(c) Mg^{2+} [✓ (d) Cs^+] *(2000)*

12. Which one of the following is the correct order of the size of iodine species?
(a) $I > I^- > I^+$ (b) $I > I^+ > I^-$
(c) $I^+ > I^- > I$ [✓ (d) $I^- > I > I^+$] *(2000)*

13. Which of the following has highest second ionisation energy?
(a) Ni (b) V
(c) Cr (d) Mn *(2001)*

14. The pair of amphoteric hydroxides is
(a) $Al(OH)_3$, $LiOH$
(b) $Be(OH)_2$, $Mg(OH)_2$
(c) $B(OH)_3$, $Be(OH)_2$
(d) $Be(OH)_2$, $Zn(OH)_2$ *(2005)*

15. Largest difference in radii is found in case of the pair
(a) Li, Na (b) Na, K
(c) K, Rb (d) Rb, Cs.
(2007, 2012)

16. Which of the following statements is correct?
(a) Ionic radius is proportional to atomic number.

(b) Ionic radius is inversely proportional to atomic mass.

(c) Ionic radius is inversely proportional to effective nuclear charge.

(d) All are correct. *(2010)*

17. The phosphate of a metal has the formula $MHPO_4$. The formula of its chloride would be
(a) MCl
(b) MCl_2
(c) MCl_3
(d) M_2Cl_3 *(2010)*

18. Which of the following sequence contains atomic number of only representative elements?
(a) 55,12,48,53
(b) 13,33,54,80
(c) 3,33,53,87
(d) 22,33,55,66 *(2010)*

19. The first ionisation enthalpy of Na, Mg and Si are 496, 737, 776 kJ/mol respectively. What will be the first ionisation enthalpy potential of Al in kJ/mol?
(a) > 766 kJ/mol
(b) > 496 and < 737 kJ
(c) > 737 and < 766 kJ/mol
(d) > 496 kJ/mol *(2013)*

20. Which is correct regarding size of atom?
(a) N < O
(b) B < Ne
(c) V > Ti
(d) Na > K *(2014)*

21. An element (X) belongs to fourth period and fifteenth group of the periodic table. Which one of the following is true regarding the outer electronic configuration of (X)? It has
(a) partially filled d orbitals and completely filled s orbital
(b) completely filled s orbital and completely filled p orbitals
(c) completely filled s orbital and half-filled p orbitals
(d) half-filled d orbitals and completely filled s orbital. *(2016)*

ASSERTION AND REASON

22. ***Assertion***: The first ionisation energy of aluminium is lower than that of magnesium.
Reason: The ionic radius of aluminium is smaller than that of magnesium. *(1994)*

23. ***Assertion***: Electrons are ejected from a certain metal when either blue or violet light strikes the metal surface. However, only violet light causes electron ejection from a second metal.
Reason: The electrons in the first metal require less energy for ejection. *(1996)*

24. ***Assertion***: Ionisation potential of Be (atomic no.4) is less than B (atomic no. 5).
Reason: The first electron released from Be is of p-orbital but that from B is of s-orbital. *(1997)*

25. ***Assertion*** : First ionisation energy for nitrogen is lower than oxygen.
Reason : Across a period effective nuclear charge decreases. *(2005)*

26. ***Assertion*** : E° for Mn^{3+}/Mn^{2+} is more positive than Cr^{3+}/Cr^{2+}.
Reason : The third ionisation energy of Mn is larger than that of Cr. *(2006)*

27. ***Assertion*** : F is more electronegative than Cl.
Reason : F has high electron affinity than Cl. *(2007)*

28. ***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. *(2010)*

29. ***Assertion*** : For hydrogen like species, energy of an electron in a particular orbit increases with increase in value of Z.
Reason : Electronegativity decreases across a period. *(2016)*

Answer Key

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

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EXPLANATIONS

1. **(a) :** In general, electron affinity decreases down the group. But due to inter-electronic repulsions in small sized F-atom, chlorine has larger *E.A.*, than that of F.

2. **(b) :** Modern periodic table (*i.e.* long form of table) is based on the periodic law which says that physical and chemical properties of the elements are periodic function of their atomic numbers.

3. **(c) :** Due to the high heat of hydration of small cations, ionic mobility for the small cations is low. Order of ionic mobility is :

$$Be^{2+} < Mg^{2+} < Ca^{2+} < Ba^{2+}$$

4. **(d) :** Electronic configuration of element with atomic number 118 will be $[Rn]5f^{14}6s^2 6p^6$. Since its electronic configuration in the outermost orbit (ns^2np^6) resembles with inert or noble gases, therefore it will be a noble gas element.

5. **(b) :** Order of electronegativity is :

$$F > O > N > C$$

6. **(b) :** In isoelectronic species, the size of ions increases as negative charge increases. Therefore, $Cl^- < S^{2-} < P^{3-}$.

7. **(d) :** After the removal of electron, to form cation, there is more effective nuclear charge on remaining electrons in the cation. Thus, size decreases.

8. **(c) :** Neon : $1s^2, 2s^2, 2p^6$

Excited state of neon can be represented as :

$$1s^2\ 2s^2, 2p^5, 3s^1$$

9. **(b) :** Sulphur and phosphorus are non-metals, they have very low electropositivity. As aluminium has one extra-nuclear charge than Mg, it has lesser electropositive character than Mg [due to greater pull exerted by nucleus on e^-].

10. **(c) :** Alkali metals have lower ionisation potential than alkaline earth metals due to the extra nuclear charge in alkaline earth metals (which pulls e^- inwards). Also, Mg has lower ionisation potential than Be as electron to be removed from Mg is present in one shell outwards than in Be.

11. **(d) :** As small compact cations are solvated more in the solution which causes their ionic mobility to slow down. Li^+, Mg^{2+} and Na^+ are heavily solvated, so these have lesser ionic mobility.

12. **(d) :** Anions are always larger as compared to the corresponding parent atom as the effective nuclear force of attraction decreases per electron, while on losing an electron (cation formation), size shrinks as effective nuclear charge increases per electron.

13. **(c) :** Electronic configuration for chromium is :

$${}_{24}Cr \rightarrow 1s^2\ 2s^2\ 2p^6\ 3s^2\ 3p^6\ 3d^5\ 4s^1$$

After ionisation of 4*s* electron the next electron which will be ionised is from 3*d* orbital. As 3*d* - orbital is half-filled, therefore it is stable. Hence, the second ionisation of Cr will require much greater ionisation energy than expected.

14. **(d) :** Both $Be(OH)_2$ and $Zn(OH)_2$ are amphoteric in nature.

15. **(b) :** Atomic as well as ionic radii increase from Li to Fr due to increase in one extra shell of electron on going down the group.

	Li	Na	K	Rb	Cs
Metallic radii (pm)	152	186	227	248	265

16. **(c) :** $r_{ionic} \propto \dfrac{1}{Z_{eff}}$

17. **(b) :** Since the phosphate of a metal is $MHPO_4$, therefore, metal *M* must be divalent, *i.e.*, M^{2+}. As a result, the formula of its chloride is MCl_2.

18. **(c) :** Sequence (c) contains only representative elements.

19. **(c) :** Na, Mg, Al and Si are in period 3 and as we move across the period, the atomic size decreases and hence ionisation enthalpy increases. So, the order is Na < Mg < Al < Si

Hence, *IE* of Al is greater than that of Mg (737 kJ/mol) and lower than that of Si (776 kJ/mol).

20. **(b) :** The atomic radii of noble gases are the largest in their respective periods. This is due to the reason that noble gases have only van der Waals radii.

21. **(c) :** The electronic configuration of (*X*) can be written as

$$X = 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^{10} 4p^3$$

So, element (*X*) has completely filled *s* and *d* orbitals and half-filled *p* orbitals.

22. **(b) :** The elements of group III have $ns^2\ np^1$, configuration. Since *p*-electrons are held less tightly

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than *s*-electrons. The first *I*
is low as compared to th
earth metal.

23. **(a)**

24. **(d) :** Be (*Z* = 4): $1s^2$,
B (*Z* = 5): $1s^2$,

Ionisation potential of Be is
first electron released
s-orbital while it is from *p*

25. **(d) :** First ionisatio
greater than oxygen.

	N	O
eV	14.5	13.6

This is due to stable confi
filled 2*p*-orbital).

Due to screening effec
experience less attraction
to this, the valence shell
charge of the nucleus. Th
by the valence shell el
nuclear charge and its ma
when we move from lef

26. **(b) :** It is known t
more negative down t

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than *s*-electrons. The first *IE* of group III element is low as compared to the first *IE* of alkaline earth metal.

23. **(a)**

24. **(d) :** Be (Z = 4); $1s^2, 2s^2$

B (Z = 5); $1s^2, 2s^2, 2p^1$

Ionisation potential of Be is greater than that of B as first electron released from Be is from *s*-orbital while it is from *p*-orbital in B.

25. **(d) :** First ionisation energy for nitrogen is greater than oxygen.

	N	O
eV	14.5	13.6

This is due to stable configuration of nitrogen (half-filled 2*p*-orbital).

Due to screening effect, the valence electrons experience less attraction towards the nucleus. Due to this, the valence shell electrons do not feel the full charge of the nucleus. The actual nuclear charge felt by the valence shell electrons is termed effective nuclear charge and its magnitude increases in a period when we move from left to right.

26. **(b) :** It is known that the value of E° becomes more negative down the series. As chromium is present below in electrochemical series than *Mn*, so Mn has more positive E° value than Cr.

$Mn \rightarrow 3d^5\,4s^2,$

$Mn^{2+} \rightarrow 3d^5\,4s^0,$

$Cr \rightarrow 3d^5\,4s^1,$

$Cr^{2+} \rightarrow 3d^4\,4s^0$

For elimination of one electron from Mn^{2+}, more energy is required due to its stable configuration. Thus, third ionisation energy of *Mn* is larger than Cr.

27. **(c) :** Chlorine has high electron affinity than fluorine. The less negative electron gain enthalpy of fluorine as compared to chlorine is due to very small size of the fluorine atom.

28. **(c) :** He contains fully filled $1s^2$ orbital which has more penetrating effect and is very close to the nucleus and hence has highest value of ionisation energy.

29. **(c) :** For hydrogen like species, energy of an electron in n^{th} orbit is given by

$$E_n = -\frac{2\pi^2 m Z^2 e^4 k^2}{n^2 h^2}$$

i.e., $E_n \propto Z^2$

Electronegativity increases across a period with decrease in size of atoms.

* * *

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CHAPTER
4
CHEMICAL BONDING AND MOLECULAR STRUCTURE

1. The compound containing co-ordinate bond is
   (a) SO_3 (b) O_3
   (c) H_2SO_4 (d) all of these. *(1994)*

2. Maximum covalency of an element of atomic number 7 is
   (a) 4 (b) 2
   (c) 5 (d) 3 *(1995)*

3. Atomic orbitals of carbon in carbon dioxide are
   (a) sp^2-hybridised (b) sp^3d-hybridised
   (c) sp-hybridised (d) sp^3-hybridised. *(1999)*

4. Which among the following has the largest dipole moment?
   (a) HI (b) H_2O
   (c) NH_3 (d) SO_3 *(1999)*

5. Which of the following have non-linear structure?
   (a) $Ag(NH_3)_2^+$ (b) $HgCl_2$
   (c) $SnCl_2$ (d) $BeCl_2$ *(2000)*

6. The boiling point of CCl_4 is higher than that of $CHCl_3$ because
   (a) $CHCl_3$ forms hydrogen bonds
   (b) CCl_4 is highly soluble in water
   (c) CCl_4 has strong van der Waals' forces of attraction than $CHCl_3$
   (d) CCl_4 is more ionic than $CHCl_3$. *(2000)*

7. In which of the following $p\pi - d\pi$ bonding is possible?
   (a) CO_3^{2-} (b) PO_4^{3-}
   (c) NO_3^- (d) NO_2^- *(2001)*

8. Smallest internuclear distance is found in
   (a) O_2 (b) O_2^{2+}
   (c) O_2^- (d) O_2^{2-} *(2001)*

9. Which of the following option w.r.t. increasing bond order is correct?
   (a) $NO < C_2 < O_2^- < He_2^+$
   (b) $C_2 < NO < He_2^+ < O_2^-$
   (c) $He_2^+ < O_2^- < NO < C_2$
   (d) $He_2^+ < O_2^- < C_2 < NO$ *(2001)*

10. The BCl_3 is a planar molecule whereas NCl_3 is pyramidal, because
    (a) B–Cl bond is more polar than N–Cl bond
    (b) N–Cl bond is more covalent than B–Cl bond
    (c) nitrogen atom is smaller than boron atoms
    (d) BCl_3 has no lone pair but NCl_3 has a lone pair of electrons. *(2001)*

11. Which of the following molecule has highest bond energy?
    (a) F – F (b) N – N
    (c) C – C (d) O – O *(2002)*

12. Which of the following compounds possesses the C – H bond with the lowest bond dissociation energy?
    (a) Toluene
    (b) Benzene
    (c) *n*-Pentane
    (d) 2,2-Dimethylpropane *(2003)*

13. Which of the following are arranged in the decreasing order of dipole moment?
    (a) CH_3Cl, CH_3Br, CH_3F
    (b) CH_3Cl, CH_3F, CH_3Br
    (c) CH_3Br, CH_3Cl, CH_3F
    (d) CH_3Br, CH_3F, CH_3Cl *(2003)*

14. The ONO angle is maximum in
    (a) NO_3^- (b) NO_2^-
    (c) NO_2 (d) NO_2^+ *(2004)*

15. Among the following, the species having square planar geometry for central atom are
    (i) XeF_4, (ii) SF_4, (iii) $[NiCl_4]^{2-}$, (iv) $[PdCl_4]^{2-}$

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

16. In $[Ag(CN)_2]^-$, the num
    (a) 2 (
    (c) 4 (

17. Bond length order is
    (a) $O_2 < O_3 < O_2^{2-}$ (
    (c) $O_2^{2-} < O_3 < O_2$

18. Which of the followin coordinate bond?
    (a) H_3O^+
    (c) HF_2^-

19. The correct order of
    (a) $CH_4 < NF_3 < NH$
    (b) $NF_3 < CH_4 < NH$
    (c) $NH_3 < NF_3 < CH$
    (d) $H_2O < NH_3 < N$

20. The molecules havin shape and number are
    (a) SeF_4, XeO_2F_2
    (c) $XeOF_4, TeF_4$

21. Which of the fol correct for resona
    (a) The contribu the same nur
    (b) The contribu similar energ
    (c) The contribu written tha atoms that
    (d) The positiv on the elec negative ch element.

22. CaO and NaCl and approximat the lattice ener lattice energy
    (a) $U/2$
    (c) $2U$

23. Decreasing or
    (a) $BeCl_2 >$
    (b) $BeCl_2 >$

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(a) (i) and (iv)
(b) (i) and (ii)
(c) (ii) and (iii)
(d) (iii) and (iv)
(2006)

16. In $[Ag(CN)_2]^-$, the number of π bonds is
(a) 2
(b) 3
(c) 4
(d) 6
(2006)

17. Bond length order is
(a) $O_2 < O_3 < O_2^{2-}$
(b) $O_2 < O_2^{2-} < O_3$
(c) $O_2^{2-} < O_3 < O_2$
(d) $O_2 = O_2^{2-} > O_3$
(2007)

18. Which of the following does not contain any coordinate bond?
(a) H_3O^+
(b) BF_4^-
[✓ (c) HF_2^-]
(d) NH_4^+
(2007)

19. The correct order of dipole moment is
(a) $CH_4 < NF_3 < NH_3 < H_2O$
(b) $NF_3 < CH_4 < NH_3 < H_2O$
(c) $NH_3 < NF_3 < CH_4 < H_2O$
(d) $H_2O < NH_3 < NF_3 < CH_4$
(2008)

20. The molecules having the same hybridisation, shape and number of lone pairs of electrons are
(a) SeF_4, XeO_2F_2
(b) SF_4, XeF_2
(c) $XeOF_4$, TeF_4
(d) $SeCl_4$, XeF_4
(2009)

21. Which of the following conditions is not correct for resonating structures?
(a) The contributing structures must have the same number of unpaired electrons.
(b) The contributing structures should have similar energies.
(c) The contributing structures should be so written that unlike charges reside on atoms that are far apart.
(d) The positive charge should be present on the electropositive element and the negative charge on the electronegative element.
(2010)

22. CaO and NaCl have the same crystal structure and approximately the same ionic radii. If *U* is the lattice energy of NaCl, the approximate lattice energy of CaO is
(a) *U*/2
(b) *U*
(c) 2*U*
(d) 4*U*
(2010)

23. Decreasing order of bond angle is
(a) $BeCl_2 > NO_2 > SO_2$
(b) $BeCl_2 > SO_2 > NO_2$
(c) $SO_2 > BeCl_2 > NO_2$
(d) $SO_2 > NO_2 > BeCl_2$
(2011)

24. The dipole moment is minimum in
(a) NH_3
(b) NF_3
(c) SO_2
(d) BF_3
(2012)

25. Total number of antibonding electrons present in O_2 will be
(a) 6
(b) 8
(c) 4
(d) 2
(2013)

26. In BF_3, the B—F bond length is 1.30 Å, when BF_3 is allowed to be treated with Me_3N, it forms an adduct, $Me_3N \rightarrow BF_3$, the bond length of B—F in the adduct is
(a) greater than 1.30 Å
(b) smaller than 1.30 Å
(c) equal to 1.30 Å
(d) none of these.
(2013)

27. In O_3 molecule, the formal charge on the central O-atom is
(a) 0
(b) −1
(c) −2
(d) +1
(2014)

28. Which of the following represents the correct bond order?
(a) $O_2^+ < O_2^- > O_2^{2-}$
(b) $O_2^- > O_2^{2-} > O_2^+$
(c) $O_2^{2-} > O_2^+ > O_2^-$
(d) $O_2^+ > O_2^- > O_2^{2-}$
(2014)

29. Which of the following molecules has more than one lone pair?
(a) SO_2
(b) XeF_2
(c) SiF_4
(d) CH_4
(2016)

30. Four diatomic species are listed below in different sequences. Which of these represents the correct order of their increasing bond order?
(a) $C_2^{2-} < He_2^+ < NO < O_2^-$
(b) $He_2^+ < O_2^- < NO < C_2^{2-}$
(c) $O_2^- < NO < C_2^{2-} < He_2^+$
(d) $NO < C_2^{2-} < O_2^- < He_2^+$
(2016)

31. H_2O is polar, whereas BeF_2 is not because
(a) electronegativity of F is greater than that of O
(b) H_2O involves H-bonding, whereas BeF_2 is a discrete molecule
(c) H_2O is angular and BeF_2 is linear
(d) H_2O is linear and BeF_2 is angular. *(2017)*

32. The AsF_5 molecule is trigonal bipyramidal. The hybrid orbitals used by the As atoms for bonding are

(a) $d_{x^2-y^2}, d_{z^2}, s, p_x, p_y$
(b) d_{xy}, s, p_x, p_y, p_z
(c) $d_{x^2-y^2}, s, p_x, p_y$
(d) $s, p_x, p_y, p_z, d_{z^2}$ *(2017)*

ASSERTION AND REASON

33. ***Assertion***: Ionic compounds tend to be non-volatile.
Reason: The intermolecular forces in these compounds are electrostatic forces of attraction. *(1994)*

34. ***Assertion:*** Bond order in a molecule, can assume any value positive or negative, integral or fractional including zero.
Reason: Bond order depends on the number of electrons in the bonding and antibonding orbitals. *(1994, 1998, 2000)*

35. ***Assertion***: The atoms in a covalent molecule are said to share electrons, yet some covalent molecules are polar.
Reason: In a polar covalent molecule, the shared electrons spend more time than the average near one of the atoms. *(1996)*

36. ***Assertion:*** Bond order can assume any value number including zero.
Reason: Higher the bond order, shorter is the bond length and greater is the bond energy. *(1999)*

37. ***Assertion:*** The dipole moment helps to predict whether a molecule is polar or non-polar.
Reason: The dipole moment helps to predict geometry of molecules. *(1999)*

38. ***Assertion :*** $CHCl_3$ and CH_3OH are miscible.
Reason : One of them is polar. *(2001)*

39. ***Assertion :*** B_2H_6, Si_2H_6 are said to have similar structure.
Reason : B_2H_6 has two 2 electron and 3 centre bonds. *(2001)*

40. ***Assertion*** : Sigma (σ) is a strong bond, while pi (π) is a weak bond.
Reason : Atoms rotate freely about pi (π) bond. *(2002)*

41. ***Assertion :*** All F – S – F angle in SF_4 is greater than 90° but less than 180°.
Reason : The lone pair-bond pair repulsion is weaker than bond pair-bond pair repulsion. *(2004)*

42. ***Assertion*** : B_2 molecule is diamagnetic.
Reason : The highest occupied molecular orbital is of σ type. *(2005)*

43. ***Assertion :*** Molecular nitrogen is less reactive than molecular oxygen.
Reason : The bond length of N_2 is shorter than that of oxygen. *(2006, 2015)*

44. ***Assertion*** : $SeCl_4$ does not have a tetrahedral structure.
Reason : Se in $SeCl_4$ has two lone pairs. (2008)

45. ***Assertion :*** Bond energy and bond dissociation energy have identical value for diatomic molecules.
Reason : Greater the bond dissociation energy, less reactive is the bond. *(2010)*

46. ***Assertion*** : ClF_3 has T-shape structure.
Reason : It has two lone pairs arranged at 180° angle. *(2012)*

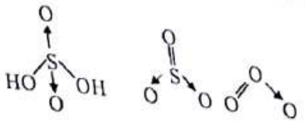
47. ***Assertion*** : O_2 is paramagnetic.
Reason : It has one unpaired electron. *(2012)*

48. ***Assertion :*** Both $\pi(2p_x)$ and $\pi^*(2p_x)$ MO's have one nodal plane each.
Reason : All MO's formed by side way overlapping of $2p$-orbitals have one nodal plane. *(2017)*

Answer Key

1.	(d)	2.	(a)	3.	(c)	4.	(b)	5.	(c)	6.	(c)	7.	(b)	8.	(b)
9.	(d)	10.	(d)	11.	(c)	12.	(a)	13.	(b)	14.	(d)	15.	(a)	16.	(c)
17.	(a)	18.	(c)	19.	(a)	20.	(a)	21.	(c)	22.	(d)	23.	(a)	24.	(d)
25	(a)	26.	(a)	27.	(d)	28.	(d)	29.	(b)	30.	(b)	31.	(c)	32.	(d)
33.	(a)	34.	(a)	35.	(a)	36.	(b)	37.	(a)	38.	(c)	39.	(d)	40.	(c)
41.	(c)	42.	(d)	43.	(a)	44.	(c)	.45.	(b)	46.	(c)	47.	(c)	48.	(d)

EXPLAN

1. **(d) :** 

All of these, therefore contain co-ordinate bonding.

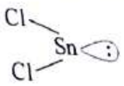
2. **(a) :** The electronic configuration of an element of atomic number 7, is $1s^2 2s^2 2p_x^1, 2p_y^1 2p_z^1$. Thus, the valence shell is second principal shell which has only four orbitals. Therefore, the element car form maximum of four covalent bonds. Thus, th covalency is 4.

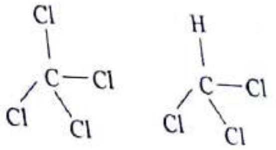
3. **(c) :** $C_{\text{excited state}} = 2s^1 2p_x^1 2p_y^1 2p_z^1$
$O_{\text{ground state}} = 2s^2 2p_x^2 2p_y^1 2p_z^1$
In the formation of CO_2 molecule, hybridisation orbitals of carbon occurs only to a limited ext involving only one s and one p orbital and g rise to sp hybridisation.

4. **(b) :** Dipole moment in the molecule dep upon the charge and the distance betweer charges.

As oxygen is more electronegative than nit iodine or sulphur, H_2O will have greater moment.

5. **(c) :** $SnCl_2$ is non-linear due to the pre lone pair of electrons on the central tin a



6. **(c) :** 

There is a stronger van der Waal attraction between the molecules in CC than in $CHCl_3$.

7. **(b) :** Carbon, oxygen and ni do not have any d-orbital available CO_3^{2-}, NO_2^- and NO_3^-, there is nc $p\pi$–$d\pi$ type of bonding.

In PO_4^{3-}, phosphorus atom has available which is used to form $p\pi$– p-orbital of oxygen atom.

8. **(b) :** In O_2, the bond order =
In O_2^{2+}, the bond order = 3
In O_2^-, the bond order = 1.5

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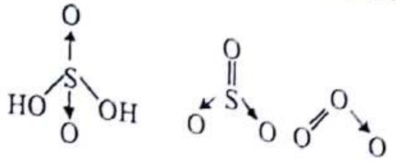
EXPLANATIONS

1. **(d) :** 

All of these, therefore contain co-ordinate bonding.

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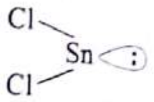
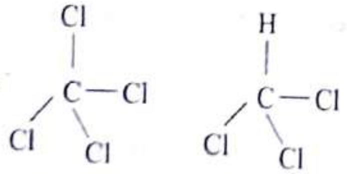
$O_{\text{ground state}} = 2s^2\ 2p_x^2\ 2p_y^1\ 2p_z^1$
In the formation of CO_2 molecule, hybridisation of orbitals of carbon occurs only to a limited extent involving only one *s* and one *p* orbital and gives rise to *sp* hybridisation.

4. **(b) :** Dipole moment in the molecule depends upon the charge and the distance between the charges.
As oxygen is more electronegative than nitrogen, iodine or sulphur, H_2O will have greater dipole moment.

5. **(c) :** $SnCl_2$ is non-linear due to the presence of lone pair of electrons on the central tin atom.



6. **(c) :** 

There is a stronger van der Waals' forces of attraction between the molecules in CCl_4 compound than in $CHCl_3$.

7. **(b) :** Carbon, oxygen and nitrogen atoms do not have any *d*-orbital available. Therefore, in CO_3^{2-}, NO_2^- and NO_3^-, there is no possibility of $p\pi-d\pi$ type of bonding.
In PO_4^{3-}, phosphorus atom has vacant *d*-orbital available which is used to form $p\pi-d\pi$ bonding with *p*-orbital of oxygen atom.

8. **(b) :** In O_2, the bond order = 2
In O_2^{2+}, the bond order = 3
In O_2^-, the bond order = 1.5
In O_2^{2-}, the bond order = 1
As the bond order in O_2^{2+} is highest, so its internuclear distance is smallest.

9. **(d) :** Bond order of the molecules :

O_2^- : $KK(\sigma 2s)^2\,(\sigma^*2s)^2\,(\sigma 2p_z)^2\,(\pi 2p_x)^2(\pi 2p_y)^2\,(\pi^*2p_x)^2\,(\pi^*2p_y)^1$

Bond order of $O_2^- = \frac{1}{2}(8-5) = 1.5$

$He_2^+ : (\sigma 1s)^2\,(\sigma^*1s)^1$

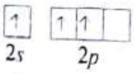
Bond order of $He_2^+ = \frac{1}{2}(2-1) = 0.5$

$C_2 : KK(\sigma 2s)^2\,(\sigma^*2s)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2$

Bond order $= \frac{1}{2}(6-2) = 2.0$

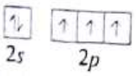
$NO : KK(\sigma 2s)^2\,(\sigma^*2s)^2(\sigma 2p_z)^2\,(\pi 2p_x)^2\,(\pi 2p_y)^2\,(\pi^*2p_x)^1$

Bond order $= \frac{1}{2}(8-3) = 2.5$

10. **(d) :** BCl_3 : 

(Central Boron atom)

No lone pair of electrons is available in BCl_3.

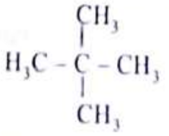
NCl_3 : 

(Central N-atom)

One lone pair of electrons is available on N-atom. Therefore, NCl_3 is pyramidal in shape.

11. **(c) :** The bond energies of F – F, C – C, N – N and O – O bonds are 33, 80, 39 and 34.2 kJ/mole respectively. Therefore, molecule of C – C has the highest bond energy.

12. **(a) :** Bond dissociation energy for C – H bond are given below in the given molecules:

$C_6H_5CH_3$	- 85 kcal/mol
C_6H_6	- 110 kcal/mol
$CH_3CH_2CH_2CH_2CH_3$	- 98 kcal/mol
 $H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH_3$	- 92 kcal/mol

13. **(b) :** The values of dipole moments of methyl halides :

CH_3F - 1.51 D ; CH_3Cl - 1.56 D;
CH_3Br - 1.4 D ; CH_3I - 1.29 D

$\therefore$ $CH_3Cl > CH_3F > CH_3Br > CH_3I$

14. **(d) :** The actual geometry of the NO_3^- ion is trigonal planar with bond angle of 120°. Hybridisation is sp^2.

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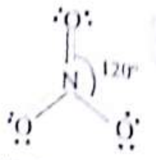
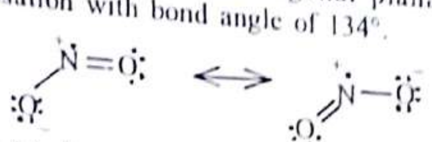
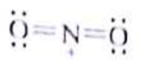


NO_2^- : Ideal geometry is trigonal planar, sp^2 hybridisation with bond angle of 116°.

NO_2 : Ideal geometry is trigonal planar; sp^2 hybridisation with bond angle of 134°.



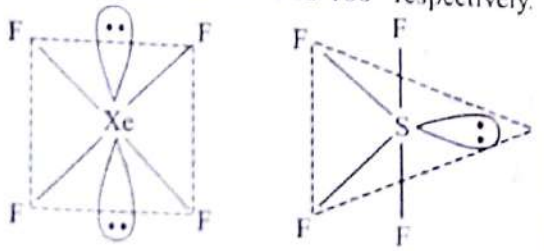
NO_2^+ : Ideal geometry is linear; sp hybridisation with bond angle of 180°.



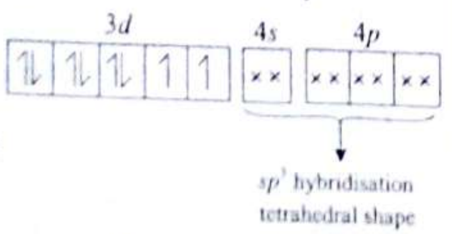
$$\ddot{\underset{\cdot\cdot}{O}}=\overset{+}{N}=\ddot{\underset{\cdot\cdot}{O}}$$

15. **(a) :** XeF_4 : It has sp^3d^2 hybridisation, shape is square planar instead of octahedral due to presence of two lone pairs of electrons on Xe atom.

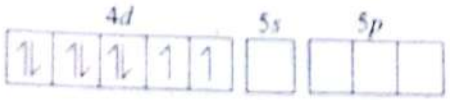
SF_4 : SF_4 molecule shows sp^3d hybridisation but its expected trigonal bipyramidal geometry gets distorted due to presence of a lone pair of electrons and it becomes distorted tetrahedral or see-saw with the bond angles equal to 89° and 177° instead of the expected angles of 90° and 180° respectively.



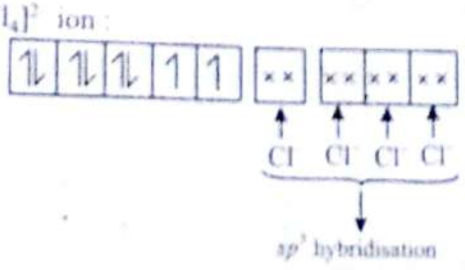
$[NiCl_4]^{2-}$ ion :



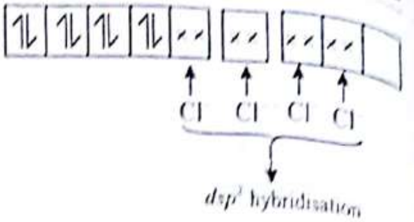
Pd^{2+} ion
$(4d^8\ 5s^0\ 5p^0)$



$[PdCl_4]^{2-}$ ion :



$[PdCl_4]^{2-}$ ion :



Experiments have, however, shown that 4-coordinated complexes of Pd(II) are diamagnetic ($n = 0$). Thus it is dsp^2 hybridisation which is involved in the formation of $[PdCl_4]^{2-}$ ion *i.e.*, 4-coordinated complexes of Pd(II) have square planar geometry with $n = 0$ (diamagnetic).

16. **(c) :** The dicyanides $[M(CN)_2]^-$ (M = Cu, Ag, Au) are linear in geometry.

$-\overset{1\sigma}{\underset{2\pi}{C\equiv N}}-$ Thus, two cyanide ions have 4π-bonds.

17. **(a) :** Ozone molecule is V-shaped with O – O bond length 1.278 Å.

The bond length is intermediate between that for a single bond (1.48 Å as in H_2O_2) and for a double bond (1.21 Å as in O_2).

Also, bond order $\propto \dfrac{1}{\text{bond length}}$

Hence, $O_2 < O_3 < O_2^{2-}$.

18. **(c) :** Only HF_2^- has H-bonding $[F\text{–}H.....F]^-$ rest all the molecules have coordinate bonds.

19. **(a) :** In H_2O, electronegativity difference is highest. So, dipole moment is highest in H_2O. CH_4 is a symmetrical tetrahedral structure and its dipole moment is zero.

20. **(a) :** SeF_4 and XeO_2F_2, both are sp^3d hybridised, trigonal bipyramidal and see-saw shaped with one lone pair of electrons each.
SF_4 has one lone pair, XeF_2 has 3 lone pairs. $XeOF_4$ is square pyramidal with 1 lone pair, TeF_4 is see-saw shaped with 1 lone pair, $SeCl_4$ has see-saw shape with 1 lone pair, XeF_4 has square planar shape with 2 lone pairs.

21. **(c) :** There is no restriction that resonating structures should have +ve and –ve charges on atoms that are far apart.

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22. **(d) :** Lattice energy $= -\frac{q_1 q_2}{r^2}$

where q_1 and q_2 are charges on ions and r is the distance between them. Since interionic distances in CaO and NaCl are similar, (larger cation has smaller anion and vice versa) therefore, r is almost the same. Therefore, lattice energy depends only on charge. Since the magnitude of charge on Na^+ and Cl^- ions is unity and that on Ca^{2+} and O^{2-} ions is 2 each, therefore, the lattice energy of CaO is four times the lattice energy of NaCl, *i.e.*, 4*U*.

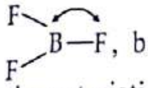
23. **(a) :** Compound : $BeCl_2 > NO_2 > SO_2$
Angle : $180° > 132° > 119.5°$

24. **(d) :** BF_3 has zero dipole moment.

25. **(a) :** $O_2 : (\sigma 1s)^2(\sigma^* 1s)^2(\sigma 2s)^2(\sigma^* 2s)^2(\sigma 2p_z)^2(\pi 2p_x^2 = \pi 2p_y^2)$
$(\pi^* 2p_x^{\ 1} = \pi^* 2p_y^1)$

Thus, there are total 6 electrons in antibonding orbitals.

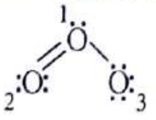
26. **(a) :** In BF_3, there is back bonding in between fluorine and boron due to presence of p-orbital in boron.



, back bonding imparts double bond characteristics.

As BF_3 forms adduct the back bonding is no longer present and thus double bond characteristic disappears. Hence, bond becomes a bit longer than earlier (1.30 Å).

27. **(d) :** Lewis gave the structure of O_3 molecule as



Using the relation,

Formal charge = [Total no. of valence electrons in the free atom] − [Total no. of non-bonding (lone pair) electrons] − $\frac{1}{2}$ [Total no. of bonding (shared) electrons]

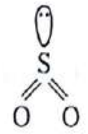
The formal charge on central O – atom *i.e.*, no. 1 = + 1

28. **(d) :**

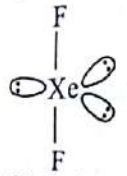
Ion	Total no. of electrons	MO configuration	B.O.
O_2^+	15	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^{\ 2}$ $\pi 2p_x^2 = \pi 2p_y^{\ 2}\ \pi^* 2p_x^{\ 1}$ $= \pi^* 2p_y^{\ 0}$	2.5
O_2^-	17	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^{\ 2}$ $\pi 2p_x^{\ 2} = \pi 2p_y^{\ 2}\ \pi^* 2p_x^{\ 2}$ $= \pi^* 2p_y^{\ 1}$	1.5
O_2^{2-}	18	$KK\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^{\ 2}$ $\pi 2p_x^2 = \pi 2p_y^{\ 2}\ \pi^* 2p_x^{\ 2}$ $= \pi^* 2p_y^{\ 2}$	1.0

Hence, the correct B.O. is $O_2^+ > O_2^- > O_2^{2-}$.

29. **(b) :**

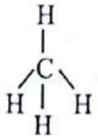


SO_2 (One lone pair)



XeF_2 (Three lone pairs)

SiF_4 (No lone pair)



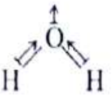
CH_4 (No lone pair)

30. **(b) :** According to molecular orbital theory, the energy level of the given molecules are

$C_2^{2-} \rightarrow \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \pi 2p_x^{\ 2}\ \pi 2p_y^{\ 2}\ \sigma 2p_z^{\ 2}$
B.O. = 1/2[10 − 4] = 3
$He_2^+ \rightarrow \sigma 1s^2\ \sigma^* 1s^1$
B.O. = 1/2[2 − 1] = 1/2 = 0.5
$NO \rightarrow \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^{\ 2}\ \pi 2p_x^{\ 2}\ \pi 2p_y^{\ 2}\ \pi^* 2p_x^1$
B.O. = 1/2[10 − 5] = 2.5
$O_2^- \rightarrow \sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^{\ 2}\ \pi 2p_x^{\ 2}\ \pi 2p_y^{\ 2}\ \pi^* 2p_x^{\ 2}\ \pi^* 2p_y^1$
B.O. = 1/2[10 − 7] = 1.5

So, the correct order of their increasing bond order is $He_2^+ < O_2^- < NO < C_2^{2-}$

31. **(c) :** Because of linear shape, dipole moments cancel each other in BeF_2 $(F \leftrightarrows Be \rightleftarrows F)$ and thus, it is non-polar, whereas H_2O is V-shaped and hence, it is polar.



32. **(d) :** AsF_5 has sp^3d hybridisation. In sp^3d hybridisation, the d_{z^2} orbital is used along with the 's' and three 'p' orbitals to form three equatorial bonds and two equally strong axial bonds for a trigonal bipyramid.

33. **(a)**

34. **(a) :** Bond order is the half of the difference between bonding and antibonding electrons. Bond order

$$= \frac{1}{2}\left[\left(\begin{array}{c}\text{no. of } e^- \text{ in} \\ \text{bonding M.O.}\end{array}\right) - \left(\begin{array}{c}\text{no. of } e^- \text{ in} \\ \text{antibonding M.O.}\end{array}\right)\right]$$

Higher the value of bond order, stronger is the bond.

35. (a)

36. (b) : Bond order

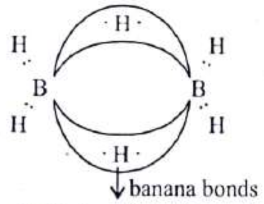
$$= \frac{1}{2}\left[\begin{matrix}\text{No. of bonding}\\ \text{orbital electrons}\end{matrix} - \begin{matrix}\text{No. of antibonding}\\ \text{orbital electrons}\end{matrix}\right].$$

The bond order zero indicates that the bond does not exist.

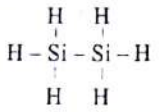
37. (b) : The linear triatomic molecules of the type *B–A–B e.g.*, CO_2 have no dipole moment, not because the individual C=O bonds are non-polar but because the two bond moments (polarity) cancel each other. Therefore, geometry of molecules can be predicted by the value of dipole moment.

38. (c) : $CHCl_3$ and CH_3OH are miscible due to intermolecular van der Waals' forces of attraction. Both are polar molecules.

39. (d) : B_2H_6 is an electron deficient compound. B_2H_6 contain some unusual bonds which are called as 2-electron, 3-centre bonds.



Si_2H_6 is called disilane.

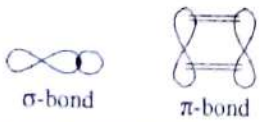


$$\begin{array}{ccccc} & H & & H & \\ H- & Si & - & Si & -H \\ & H & & H & \end{array}$$

40. (c) : Sigma bonding involves end to end overlapping of the two atomic orbitals *e.g.*, between *s* and *s*, *s* and *p* and *p* and *p* orbitals.

Pi bonding (π) involves sidewise overlapping of the two atomic orbitals *e.g.*, between *p* and *p* orbitals.

Overlapping of orbitals is more effective in σ-bonding than in π-bonding. Due to the geometry of the overlapping orbitals, rotation of an atom is not possible around π-bond.



41. (c) : Due to greater lone pair - bond pair repulsions than bond pair - bond pair repulsions, the F – S – F bond angle decreases from 180°.

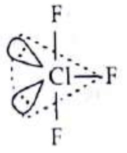
42. (d) : In B_2, total number of electrons = 10
$B_2 \rightarrow \sigma(1s)^2\ \sigma^*(1s^2)\ \sigma(2s)^2\ \sigma^*(2s)^2\ \pi(2p_x)^1\ \pi(2p_y)^1$
Presence of unpaired electron shows the paramagnetic nature.
The highest occupied molecular orbital is of π-type.

43. (a) : Bond order of N_2 = 3, bond order of O_2 = 2.
Higher the bond order, higher is the bond dissociation energy. *i.e.*, higher stability or less reactivity. Thus, N_2 is less reactive than O_2.
Higher the bond order, shorter is the bond length. Shorter bond length of N_2 shows its higher bond order.

44. (c) : $SeCl_4$ possesses see-saw geometry, which can be regarded as a distorted trigonal bipyramidal structure, having one lone pair of electrons in the basal position of the trigonal bipyramid. See-saw geometry of $SeCl_4$ molecules arises due to the sp^3d hybridisation of the central atom. The distortion in shape is due to the presence of one lone pair of electrons.

45. (b) : Bond dissociation energy is the energy required to break a particular bond in one mole of a gaseous molecule. Bond energy is the average value of dissociation energies of the same type of bond present in the molecule. Thus, bond energy and bond dissociation energy have same values for diatomic molecules. Bond energy of C–H bond in methane is 99.2 kcal/mol. Thus, for polyatomic molecules, average bond energy is taken as the dissociation bond energy.

46. (c) :



ClF_3 (T-shape)

The lone pairs are at equatorial position (120° angle).

47. (c) : Oxygen has two unpaired electrons. So it is paramagnetic.

48. (d) : $\pi(2p_x)$ has one nodal plane whereas $\pi^*(2p_x)$ has two nodal planes.

CHAPTER 5

ST
(GAS

1. If the density ratio of O_2 and H_2 is
ratio of their v_{rms} will be
(a) 1 : 1 (b) 1 : 4
(c) 16 : 1 (d) 1 : 16

2. Which of the following gases
highest rate of diffusion?
(a) CO_2 (b) N_2
(c) NH_3 (d) O_2

3. A mixture of 40 g of oxygen and
has a total pressure of 0.9 at
pressure of oxygen is
(a) 0.5 atm (b) 0.1
(c) 0.9 atm (d) 0.

4. Two different gases enclosed i
A and *B* at same temperature a
found to contain same number
ratio of volumes of the flasks
(a) 1 : 3 (b)
(c) 1 : 4 (d)

5. The temperature, at which
1 atm, is the same as that
(a) 273°C (b)
(c) 546°C (d)

6. A certain gas diffuses fou
oxygen. The molecular w
(a) 2 (b
(c) 16 (d

7. Which of the following
equal total kinetic ene
kinetic energy?
(a) O_2
(c) CH_4

8. If a gas occupies a vo
and 620 mm pressure
gas at 47°C and 640

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CHAPTER 5

STATES OF MATTER (GASEOUS AND LIQUIDS)

1. If the density ratio of O_2 and H_2 is 16:1, then ratio of their v_{rms} will be
(a) 1 : 1
(b) 1 : 4
(c) 16 : 1
(d) 1 : 16 *(1994)*

2. Which of the following gases will have the highest rate of diffusion?
(a) CO_2
(b) N_2
(c) NH_3
(d) O_2 *(1994)*

3. A mixture of 40 g of oxygen and 40 g of helium has a total pressure of 0.9 atm. The partial pressure of oxygen is
(a) 0.5 atm
(b) 0.1 atm
(c) 0.9 atm
(d) 0.2 atm. *(1994)*

4. Two different gases enclosed in different flasks *A* and *B* at same temperature and pressure were found to contain same number of molecules. The ratio of volumes of the flasks *A* and *B* must be
(a) 1 : 3
(b) 1 : 1
(c) 1 : 4
(d) 1 : 2 *(1995)*

5. The temperature, at which the density of O_2 at 1 atm, is the same as that of CH_4 at S.T.P., is
(a) 273°C
(b) 100°C
(c) 546°C
(d) 150°C *(1995)*

6. A certain gas diffuses four times as quickly as oxygen. The molecular weight of the gas is
(a) 2
(b) 1
(c) 16
(d) 1.5 *(1995)*

7. Which of the following gas molecules have equal total kinetic energy and translational kinetic energy?
(a) O_2
(b) He
(c) CH_4
(d) N_2 *(1996)*

8. If a gas occupies a volume of 300 cc at 27°C and 620 mm pressure, then the volume of the gas at 47°C and 640 mm pressure, is
(a) 310 cc
(b) 410 cc
(c) 500 cc
(d) 600 cc *(1997)*

9. The compressibility factor of an ideal gas is
(a) 1
(b) 2
(c) 4
(d) 6 *(1997)*

10. In the gas equation: $PV = nRT$
(a) V is the volume of one mole of the gas
(b) n no. of moles of the gas have volume V
(c) n is the number of molecules of the gas
(d) P is the pressure of one mole of the gas. *(1998)*

11. At what pressure, will a quantity of gas, which occupies 100 mL at a pressure of 720 mm, occupy a volume of 84 mL
(a) 820.20 mm
(b) 784.15 mm
(c) 736.18 mm
(d) 857.14 mm. *(1998)*

12. If 300 mL of a gas at 27°C is cooled to 7°C at constant pressure, its final volume will be
(a) 350 mL
(b) 540 mL
(c) 135 mL
(d) 280 mL. *(1999)*

13. Pressure in a mixture of 4 g of O_2 and 2 g of H_2 confined in a bulb of 1 litre at 0°C is
(a) 45.215 atm
(b) 31.205 atm
(c) 25.215 atm
(d) 15.210 atm. *(1999)*

14. Helium atom is two times heavier than a hydrogen molecule. At 298 K, the average kinetic energy of the helium atom is
(a) two times that of a hydrogen molecule
(b) same as that of a hydrogen molecule
(c) four times that of a hydrogen molecule
(d) half that of a hydrogen molecule. *(2000)*

15. If the *r.m.s.* speed of a gas molecule at 27°C is $100\sqrt{2}$ m s^{-1}, the *r.m.s.* speed at 327°C would be

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(a) 100 m s^{-1} (b) 200 m s^{-1}
(c) 300 m s^{-1} (d) 400 m s^{-1} *(2000)*

16. If P is pressure and ρ is density of a gas, then P and ρ are related as
(a) $P \propto \rho$ (b) $P \propto (1/\rho)$
(c) $P \propto \rho^2$ (d) $P \propto (1/\rho^2)$ *(2002)*

17. Dominance of strong repulsive forces among the molecules of the gas (Z = compressibility factor)
(a) depends on Z and indicated by $Z = 1$
[✓ (b)] depends on Z and indicated by $Z > 1$
(c) depends on Z and indicated by $Z < 1$
(d) is independent of Z. *(2006)*

18. In P versus V graph, the horizontal line is found in which _____ exists.
(a) gas
(b) liquid
(c) equilibrium between gas and liquid
(d) super critical temperature *(2006)*

19. Critical temperatures for A, B, C and D gases are 25°C, 10°C, –80°C and 15°C respectively. Which gas will be liquefied more easily?
(a) A (b) B
(c) C (d) D *(2006)*

20. The root mean square speed of the molecules of diatomic gas is u. When the temperature is doubled, the molecules dissociate into two atoms. The new *rms* speed of the atom is
(a) $\sqrt{2}u$ (b) u
[✓ (c)] $2u$ (d) $4u$ *(2008)*

21. Equal weights of CO and CH_4 are mixed together in an empty container at 300 K. The fraction of total pressure exerted by CH_4 is
(a) $\frac{16}{17}$ [✓ (b)] $\frac{7}{11}$
(c) $\frac{8}{9}$ (d) $\frac{5}{16}$ *(2010)*

22. Two flasks X and Y have capacity 1 L and 2 L respectively and each of them contains 1 mole of a gas. The temperatures of the flasks are so adjusted that average speed of molecules in X is twice as those in Y. The pressure in flask X would be
(a) same as that in Y
(b) half of that in Y
(c) twice of that in Y
(d) 8 times of that in Y. *(2010)*

23. In the van der Waals' equation, 'a' signifies
(a) intermolecular attraction
(b) intramolecular attraction
(c) attraction between molecules and walls of container
(d) volume of molecules. *(2011)*

24. Arrange the following gases in order of their critical temperature.
NH_3, H_2O, CO_2, O_2
(a) $NH_3 > H_2O > CO_2 > O_2$
(b) $O_2 > CO_2 > H_2O > NH_3$
(c) $H_2O > NH_3 > CO_2 > O_2$
(d) $CO_2 > O_2 > H_2O > NH_3$ *(2012)*

25. The density of a gas A is thrice that of a gas B at the same temperature. The molecular weight of gas B is twice that of A. What will be the ratio of the pressures acting on B and A?
(a) $\frac{1}{4}$ (b) $\frac{7}{8}$
(c) $\frac{2}{5}$ (d) $\frac{1}{6}$ *(2017)*

ASSERTION AND REASON

26. ***Assertion:*** For an ideal gas, at constant temperature, the product of the pressure and volume is constant.
Reason: The mean square velocity of the molecules is inversely proportional to mass. *(1998)*

27. ***Assertion :*** Effusion rate of oxygen is smaller than nitrogen.
Reason : Molecular size of nitrogen is smaller than oxygen. *(2004)*

28. ***Assertion :*** Compressibility factor for hydrogen varies with pressure with positive slope at all pressures.
Reason : Even at low pressures, repulsive forces dominate for hydrogen gas. *(2005, 2009)*

29. ***Assertion :*** If H_2 and Cl_2 enclosed separately in the same vessel exert pressure of 100 and 200

---

mm respectively, their mixture in th
at the same temperature will exert
300 mm.
Reason : Dalton's law of par
states that total pressure is the
pressures.

30. ***Assertion :*** At critical point,
substance in gaseous and l
same.

1.	(b)	**2.**
9.	(a)	**10.**
17.	(b)	**18.**
25.	(d)	**26.**

mm respectively, their mixture in the same vessel at the same temperature will exert a pressure of 300 mm.

Reason : Dalton's law of partial pressures states that total pressure is the sum of partial pressures. *(2008)*

30. ***Assertion :*** At critical point, the densities of substance in gaseous and liquid states are same.

Reason : Critical temperature is the temperature at which the real gas exhibit ideal behaviour for considerable range of pressure. *(2013)*

31. **Assertion :** Critical temperature of CO_2 is 304 K, it cannot be liquified above 304 K.

Reason : At a certain temperature,

$$\text{volume} \propto \frac{1}{\text{pressure}}$$ *(2016)*

Answer Key

1.	(b)	**2.**	(c)	**3.**	(b)	**4.**	(b)	**5.**	(a)	**6.**	(a)	**7.**	(b)	**8.**	(a)
9.	(a)	**10.**	(b)	**11.**	(d)	**12.**	(d)	**13.**	(c)	**14.**	(b)	**15.**	(b)	**16.**	(a)
17.	(b)	**18.**	(c)	**19.**	(a)	**20.**	(c)	**21.**	(b)	**22.**	(d)	**23.**	(a)	**24.**	(c)
25.	(d)	**26.**	(b)	**27.**	(c)	**28.**	(a)	**29.**	(d)	**30.**	(c)	**31.**	(b)		

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EXPLANATIONS

1. **(b) :** $\frac{\rho(O_2)}{\rho(H_2)}=\frac{16}{1}\Rightarrow\frac{M(O_2)}{M(H_2)}=\frac{16}{1}$

$v_{rms}\propto\left(\frac{1}{M}\right)^{1/2}$

$\Rightarrow\frac{v_{rms}(O_2)}{v_{rms}(H_2)}=\left(\frac{M(H_2)}{M(O_2)}\right)^{1/2}=\left(\frac{1}{16}\right)^{1/2}=\frac{1}{4}$

2. **(c)** Rate of diffusion $\propto (1/M)$

M = molecular mass

$M(CO_2)=44,\quad M(N_2)=28$

$M(NH_3)=17,\quad M(O_2)=32$

Therefore, rate of NH_3 diffusion is greater than others.

3. **(b) :** No. of moles of $O_2=\frac{\text{Given mass}}{\text{Mol. mass}}=\frac{40}{32}$

$=1.25$ mol

No. of moles of He $=\frac{40}{4}=10$ mol

Mole fraction of $O_2=\frac{1.25}{1.25+10}=\frac{1.25}{11.25}=\frac{1}{9}$

Partial pressure of oxygen $=\frac{1}{9}\times 0.9$ atm

$=0.1$ atm

4. **(b) :** The Avogadro's law states that same volume of all gases at the same temperature and pressure, contain equal number of molecules. Hence, ratio of volumes must be 1 : 1.

5. **(a) :** The density of O_2 at S.T.P.

$(d_1)=\frac{32}{22\cdot 4}$ g/litres and that of CH_4 at S.T.P.

$(d_2)=\frac{16}{22\cdot 4}$ g/litres

We know that $d_1T_1=d_2T_2$ or $T_2=\frac{d_1T_1}{d_2}$

$=\frac{32}{22\cdot 4}\times\frac{273}{1}\times\frac{22\cdot 4}{16}=546\text{ K}=273^\circ\text{C}$

(where T_1 at STP is 273 K.)

6. **(a) :** Rate of diffusion $\propto\frac{1}{\sqrt{M}}$

M = Molecular mass

Let r_x = Rate of diffusion of x (gas)

$\Rightarrow\quad\frac{r_x}{r_{O_2}}=4=\sqrt{\frac{M_{O_2}}{M_x}}$

M_x = Molecular mass of x

$\Rightarrow\quad\frac{r_x}{r_{O_2}}=4=\sqrt{\frac{M_{O_2}}{M_x}}\Rightarrow 16=\frac{32}{M_x}\quad\Rightarrow\quad M_x=2$

7. **(b) :** The total kinetic energy of a molecule is the sum of its translational, vibrational and rotational kinetic energies. The monatomic molecules do not possess vibrational and rotational kinetic energies. Hence, noble gases (like He, Ar etc.) fulfill the criteria.

8. **(a) :** According to Charles' and Boyle's law,

$\frac{P_1V_1}{T_1}=\frac{P_2V_2}{T_2}\Rightarrow\frac{620\times 300}{300}=\frac{640\times V_2}{320}$

$\Rightarrow\quad V_2=310$ cc

9. **(a) :** Compressibility factor is defined as:

$Z=\frac{PV}{(PV)_{ideal}}=\frac{PV}{nRT}$

For non ideal gases, $Z\neq 1$

For ideal gases, $Z=1$

10. **(b) :** Ideal gas equation is :

$PV=nRT$

P = pressure of the gas;

V = volume of gas

n = no. of moles of the gas;

R = gas constant

T = temperature

11. **(d) :** According to Boyle's law,

$P_1V_1=P_2V_2$

Putting values here, we get;

$100\times 720=P_2\times 84$

$\Rightarrow\quad P_2=857.14$ mm

12. **(d) :** According to Charles' law,

$\frac{V_1}{T_1}=\frac{V_2}{T_2}$

$\Rightarrow$ Putting the given values :

$\frac{300\text{ mL}}{300\text{ K}}=\frac{V_2}{280}\Rightarrow V_2=280$ mL

13. **(c) :** Moles of oxygen, $n_{O_2}=\frac{4}{32}=0.125$ mol

Moles of hydrogen, $n_{H_2}=\frac{2}{2}=1.00$ mol

Temperature = 273 K, Volume = 1 litre

$\Rightarrow$ Total pressure $=\frac{(n_{O_2}+n_{H_2})\times RT}{V}$

$=\frac{1.125\times 0.0821\times 273}{1}$

$=25.215$ atm

---

14. **(b) :** Average kinetic energy pe
depend on the nature of the gas *i.e.*,
of the gas depends only on tempera

Average kinetic energy per molecul

k = Boltzmann constant, T = Tempe

15. **(b) :** Root mean square veloci

$v_{rms}=\sqrt{\frac{3RT}{M}}\Rightarrow v_{rms}\propto\sqrt{T}$

$\Rightarrow\quad\frac{v_{rms}(\text{at }27^\circ\text{ C})}{v_{rms}(\text{at }327^\circ\text{ C})}=\sqrt{\frac{(27+273)}{(327+273}}$

$=\sqrt{\frac{300}{600}}=\frac{1}{\sqrt{2}}$

$\therefore\quad v_{rms}(\text{at }327^\circ\text{C})=100\sqrt{2}\times\surd$

16. **(a) :** Ideal gas equation is giv

$PV=nRT$

P = Pressure of gas, V = Vol

n = Moles of gas, R = Gas co

T = Temperature

$\Rightarrow\quad PV=\frac{w}{M}RT,\ w$ = Mass of ga

M = Molecular mass of gas

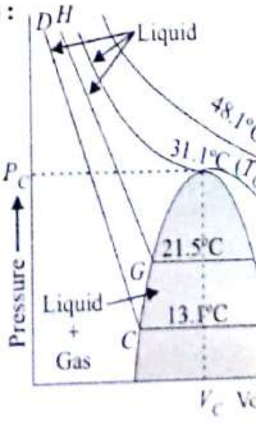
$P=\left(\frac{w}{V}\right)\frac{RT}{M}\Rightarrow P=\rho\frac{RT}{M}$

$\left(\text{As }\rho=\frac{w}{V}\right)$

$\Rightarrow\quad P\propto\rho$

17. **(b) :** When the value of Z
attractive forces between molecules
when $Z>1$, it is due to repulsi
electron clouds of the molecules

18. **(c) :**



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14. (b) : Average kinetic energy per mole does not depend on the nature of the gas *i.e.*, molecular mass of the gas depends only on temperatrue.

Average kinetic energy per molecule $= \frac{3}{2}kT$

k = Boltzmann constant, T = Temperature.

15. (b) : Root mean square velocity is given by :

$$v_{rms} = \sqrt{\frac{3RT}{M}} \Rightarrow v_{rms} \propto \sqrt{T}$$

$$\Rightarrow \frac{v_{rms}(\text{at } 27°\text{ C})}{v_{rms}(\text{at } 327°\text{ C})} = \sqrt{\frac{(27+273)\text{K}}{(327+273)\text{K}}}$$

$$= \sqrt{\frac{300}{600}} = \frac{1}{\sqrt{2}}$$

$\therefore$ v_{rms} (at 327°C) $= 100\sqrt{2} \times \sqrt{2} = 200$ m s^{-1}

16. (a) : Ideal gas equation is given as :

$PV = nRT$

P = Pressure of gas, V = Volume of gas

n = Moles of gas, R = Gas constant

T = Temperature

$\Rightarrow$ $PV = \frac{w}{M}RT$, w = Mass of gas

M = Molecular mass of gas

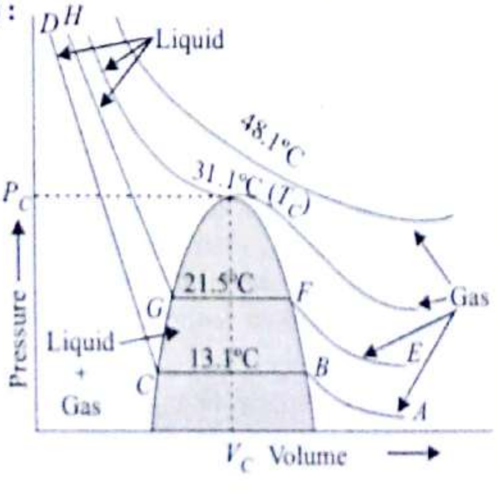
$$P = \left(\frac{w}{V}\right)\frac{RT}{M} \Rightarrow P = \rho\frac{RT}{M}$$

$$\left(\text{As } \rho = \frac{w}{V}\right)$$

$\Rightarrow$ $P \propto \rho$

17. (b) : When the value of $Z < 1$, it is due to attractive forces between molecules. At high pressure, when $Z > 1$, it is due to repulsive forces between electron clouds of the molecules of gases.

18. (c) :



From the graph, at point A, CO_2 exists as a gas, As pressure is increased, the volume of the gas decreases along the curve AB. At B liquefaction of the gas starts. Hence, volume decreases rapidly along BC because liquid has much less volume than the gas. At point C, liquefaction is complete.

Amount of gas decreased = Amount of liquid formed or increased.

Because along horizontal line, gas converts into liquid.

19. (a) : Critical temperature of gas may be defined as that temperature above which it cannot be liquefied howsoever high pressure may be applied on the gas.

As we know, $T_C = \frac{8a}{27Rb}$

where a = van der Waals' constant which is a measure of intermolecular forces of attraction. Greater the value of a more easily the gas can be liquefied and hence larger T_C mean larger the value of a.

20. (c) : $u = \sqrt{\frac{3RT}{M}}$

If $T = 2T$ and $M = M/2$, then $u_1 = \sqrt{\frac{3R \times 2T}{M/2}}$

$\therefore$ $\frac{u_1}{u} = \sqrt{4} = 2$

21. (b) : Let the weight of CO = weight of CH_4 = a g

Moles of CO $= \frac{a}{28}$

Moles of CH_4 $= \frac{a}{16}$

Total moles $= \frac{a}{28} + \frac{a}{16}$

$$x_{CH_4} = \frac{\frac{a}{16}}{\frac{a}{28}+\frac{a}{16}} = \frac{a}{16} \times \frac{28 \times 16}{44a} = \frac{14}{22} = \frac{7}{11}$$

$\therefore$ Fraction of pressure exerted by CH_4 = 7/11

22. (d) : $P = \frac{1}{3}\frac{mnu^2}{V}$

$$\frac{P_X}{P_Y} = \frac{n_X u_X V_Y}{n_Y u_Y V_X} = \frac{(N_0/1000)}{(N_0/2000)} \times 2 \times \frac{2}{1} = 8$$

23. (a) : In van der Waals' equation, a signifies the intermolecular force of attraction.

24. (c) : Greater are the intermolecular forces of attraction, higher is the critical temperature.

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25. (d) : $\frac{d}{p} = \frac{M}{RT}$

Let density of gas B be d.

∴ Density of gas $A = 3d$

and let molecular weight of A be M.

∴ Molecular weight of $B = 2M$

Since, R is gas constant and T is same for both gases, so

$$p_A = \frac{d_A RT}{M_A} \text{ and } p_B = \frac{d_B RT}{M_B}$$

$$\frac{p_B}{p_A} = \frac{d_B}{d_A} \times \frac{M_A}{M_B} = \frac{d}{3d} \times \frac{M}{2M} = \frac{1}{6}.$$

26. (b) : The ideal gas equation is

$PV = nRT$; where P = pressure, V = volume; T = temperature; R = universal gas constant, n = no. of moles

Now, if T = constant, then PV = constant.

27. (c) : Effusion rate of oxygen is smaler than nitrogen as molecular mass of oxygen is greater than nitrogen, as effusion rate $\propto \frac{1}{\sqrt{M}}$.

Molecular size of oxygen is smaller than nitrogen.

28. (a) : In case of H_2, compressibility factor increases with the pressure. At 273 K, $Z > 1$ which shows that it is difficult to compress the gas as compared to ideal gas. In this case, repulsive forces dominate.

29. (d) : H_2 and Cl_2 react chemically. Hence Dalton's law is not applicable. Dalton's law states that "at a given temperature, the total pressure exerted by two or more non-reacting gases occupying a definite volume is equal to the sum of the partial pressures of the component gases."

30. (c) : Temperature at which the real gas exhibits ideal behaviour for considerable range of pressure is known as Boyle's temperature. $T_b = \frac{a}{bR}$ where a and b are van der Waals' constant. Critical temperature is the temperature above which the gas cannot be liquefied, how so ever high pressure may be applied : $T_c = \frac{8a}{27Rb}$.

31. (b) : Critical temperature of a gas may be defined as that temperature above which it cannot be liqufied however high pressure may be applied on the gas. Hence, CO_2 cannot be liquified above its critical temperature.

According to Boyle's law

$$P \propto \frac{1}{V} \text{ or } V \propto \frac{1}{P} \text{ (at constant } T \text{ and } n)$$

CHAPTER

6

T

1. The heat liberated when 1.89 g
is burnt in a bomb calorimeter
increases the temperature of 18
by 0.632 °C. If the specific heat
is 0.998 cal/g-deg, the value
combustion of benzoic acid is
(a) 881.1 kcal (b) 7
(c) 981.1 kcal (d) 8
(19

2. Which of the following stat
entropy is correct?
(a) At absolute zero tempe
of all crystalline subst
zero.
(b) At 0°C, the entropy
substances is taken t
(c) At absolute zero tem
perfect crystalline su
zero.
(d) At 0°C, the entropy
substance is taken

3. The property, which ca
intensive property, is
(a) volume
(c) heat capacity

4. For the reaction, $H_{2(g)}$ +
in enthalpy (ΔH) will
(a) $= \Delta E$
(c) $< \Delta E$

5. The enthalpy chang
depend upon
(a) state of reacta
(b) nature of react
(c) different inter
(d) initial and f
reaction.

6. In the reaction :
and $SO_2 + 1/2O$
formation of SO

CHAPTER
6
THERMODYNAMICS

1. The heat liberated when 1.89 g of benzoic acid is burnt in a bomb calorimeter at 25 °C and it increases the temperature of 18.94 kg of water by 0.632 °C. If the specific heat of water at 25 °C is 0.998 cal/g-deg, the value of the heat of combustion of benzoic acid is
   (a) 881.1 kcal [✓ (b) 771.124 kcal]
   (c) 981.1 kcal (d) 871.2 kcal
   (1994, 2016, 2017)

2. Which of the following statements regarding entropy is correct?
   [✓ (a) At absolute zero temperature, the entropy of all crystalline substances is taken to be zero.]
   (b) At 0°C, the entropy of all crystalline substances is taken to be zero.
   (c) At absolute zero temperature, entropy of a perfect crystalline substance is taken to be zero.
   (d) At 0°C, the entropy of a perfect crystalline substance is taken to be zero. *(1994)*

3. The property, which can be classified as an intensive property, is
   (a) volume (b) mass
   (c) heat capacity [✓ (d) temperature.]
   (1995)

4. For the reaction, $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$, the change in enthalpy (ΔH) will be
   [✓ (a) $= \Delta E$] (b) $> \Delta E$
   (c) $< \Delta E$ (d) either (b) or (c)
   (1997)

5. The enthalpy change of a reaction does not depend upon
   (a) state of reactants and products
   (b) nature of reactants and products
   [✓ (c) different intermediate reaction]
   (d) initial and final enthalpy change of a reaction. *(1997)*

6. In the reaction : $S + 3/2O_2 \longrightarrow SO_3 + 2x\,\text{kcal}$ and $SO_2 + 1/2O_2 \longrightarrow SO_3 + y\,\text{kcal}$, heat of formation of SO_2 is
   (a) $(x + y)$ (b) $(x - y)$
   (c) $(2x + y)$ [✓ (d) $(2x - y)$] *(1997)*

7. Hess's law is applicable for the determination of heat of
   (a) transition (b) formation
   (c) reaction [✓ (d) all of these.]
   (1998)

8. If enthalpies of formation for $C_2H_{4(g)}$, $CO_{2(g)}$ and $H_2O_{(l)}$ at 25 °C and 1 atm pressure are 52, −394 and −286 kJ/mol respectively, then enthalpy of combustion of $C_2H_{4(g)}$ will be
   (a) −141.2 kJ/mol (b) +14.2 kJ/mol
   (c) +141.2 kJ/mol [✓ (d) −1412 kJ/mol]
   (1998)

9. In an endothermic reaction, the value of change in enthalpy (ΔH) is
   (a) zero (b) negative
   (c) positive (d) either (b) or (c).
   (1998)

10. Internal energy does not include
   (a) rotational energy
   (b) vibrational energy
   (c) nuclear energy
   [✓ (d) gravitational pull.] *(1999)*

11. The enthalpy change for the following reaction $NaOH_{(aq)} + HCl_{(aq)} \rightarrow NaCl_{(aq)} + H_2O_{(l)}$ is −57 kJ. Predict the value of the enthalpy change in the following reaction.
   $Ba(OH)_{2(aq)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + 2H_2O_{(l)}$
   (a) −57 kJ (b) −76 kJ
   (c) −114 kJ (d) −228 kJ *(2000)*

12. The combustion enthalpies of carbon, hydrogen and methane are −395.5 kJ mol^{-1}, −284.8 kJ mol^{-1} and −890.4 kJ mol^{-1} respectively at 25 °C. The value of standard formation enthalpies of methane at that temperature is
   (a) 890.4 kJ mol^{-1} (b) −298.8 kJ mol^{-1}
   [✓ (c) −74.7 kJ mol^{-1}] (d) −107.7 kJ mol^{-1}
   (2000)

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13. Which of the following is always feasible?
(a) $\Delta H = T\Delta S$
(b) ΔH (+ve), $T\Delta S$ (–ve) and $\Delta H > T\Delta S$
(c) ΔH (–ve), $T\Delta S$ (+ve) and $\Delta H > T\Delta S$
(d) ΔH (–ve), $T\Delta S$ (–ve) and $\Delta H > T\Delta S$ *(2001)*

14. Given that $C + O_2 \rightarrow CO_2$; $\Delta H° = -a$ kJ
$2CO + O_2 \rightarrow 2CO_2$; $\Delta H° = -b$ kJ
The heat of formation of CO is
(a) $b - 2a$
(b) $\frac{2a-b}{2}$
(c) $\frac{b-2a}{2}$
(d) $2a - b$ *(2001)*

15. The heat of neutralization of a strong base and a strong acid is 57 kJ/mol. The heat released when 0.5 mole of HNO_3 solution is added to 0.20 moles of NaOH solution, is
(a) 11.4 kJ
(b) 34.7 kJ
(c) 23.5 kJ
(d) 58.8 kJ *(2002)*

16. One gram sample of NH_4NO_3 is decomposed in a bomb calorimeter. The temperature of the calorimeter increases by 6.12 K. The heat capacity of the system is 1.23 kJ/g/deg. What is the molar heat of decomposition for NH_4NO_3?
(a) – 7.53 kJ/mol
(b) – 398.1 kJ/mol
(c) – 16.1 kJ/mol
(d) 602 kJ/mol *(2003)*

17. Which one of the following has $\Delta S°$ greater than zero?
(a) $CaO_{(s)} + CO_{2\,(g)} \rightleftharpoons CaCO_{3\,(s)}$
(b) $NaCl_{(aq)} \rightleftharpoons NaCl_{(s)}$
(c) $NaNO_{3\,(s)} \rightleftharpoons Na^+_{(aq)} + NO^-_{3(aq)}$
(d) $N_{2\,(g)} + 3H_{2\,(g)} \rightleftharpoons 2NH_{3\,(g)}$ *(2003)*

18. How much energy is released when 6 moles of octane is burnt in air? Given; $\Delta H_f°$ for $CO_{2(g)}$, $H_2O_{(g)}$ and $C_8H_{18(l)}$ respectively are – 490, –240 and +160 kJ/mol.
(a) – 6.22 kJ
(b) 37440 kJ/mol
(c) – 35502 kJ
(d) – 20.0 kJ *(2004)*

19. $\Delta H_f°$ (298 K) of methanol is given by the chemical equation
(a) $CH_{4(g)} + \frac{1}{2}O_{2(g)} \rightarrow CH_3OH_{(g)}$
(b) $C_{(graphite)} + \frac{1}{2}O_{2(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$
(c) $C_{(diamond)} + \frac{1}{2}O_{2(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$
(d) $CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$ *(2005)*

20. For the reaction of one mole of zinc dust with one mole of sulphuric acid in a bomb calorimeter, ΔU and w correspond to
(a) $\Delta U < 0, w = 0$
(b) $\Delta U < 0, w < 0$
(c) $\Delta U > 0, w = 0$
(d) $\Delta U > 0, w > 0$ *(2005, 2015)*

21. For a spontaneous process, the correct statement is
(a) entropy of the system always increases
(b) free energy of the system always increases
(c) total entropy change is always negative
(d) total entropy change is always positive. *(2006)*

22. For a phase change,
$$H_2O_{(l)} \xrightleftharpoons{0°C,\ 1\ bar} H_2O_{(s)}$$
(a) $\Delta G° = 0$
(b) $\Delta S° = 0$
(c) $\Delta H°_f = 0$
(d) $\Delta U° = 0$ *(2006)*

23. The enthalpy change (ΔH) for the reaction,
$$N_{2(g)} + 3H_{2(g)} \rightarrow 2NH_{3(g)}$$
is –92.38 kJ at 298 K. The internal energy change (ΔU) at 298 K is
(a) –92.38 kJ
(b) –87.42 kJ
(c) –97.34 kJ
(d) –89.9 kJ *(2006)*

24. Calculate change in internal energy if $\Delta H = -92.2$ kJ, $P = 40$ atm and $\Delta V = -1$ L.
(a) –42 kJ
(b) –88 kJ
(c) +88 kJ
(d) +42 kJ *(2007)*

25. ΔH_{fusion} of a substance is 'x' and ΔH_{vap} is 'y', then $\Delta H_{sublimation}$ will be
(a) $x + y$
(b) $x - y$
(c) x/y
(d) y/x *(2007)*

26. ΔS_{surr} for an exothermic reaction is
(a) always positive
(b) always negative
(c) zero
(d) may be positive or negative. *(2007)*

27. In an isobaric process, when temperature changes from T_1 to T_2, ΔS is equal to
(a) $2.303\ C_P \log (T_2/T_1)$
(b) $2.303\ C_P \ln (T_2/T_1)$
(c) $C_P \ln (T_1/T_2)$
(d) $C_V \ln (T_2/T_1)$ *(2009)*

28. The variation of volume V, with temperature T, keeping pressure constant is called the coefficient of thermal expansion (α) of a gas. *i.e.*, $\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P$. For an ideal gas α is equal to
(a) T
(b) $1/T$
(c) P
(d) $1/P$ *(2009)*

---

29. Match List I with List
answer using the code
List I
A. $\left(\frac{\partial G}{\partial P}\right)_T$
B. $\left(\frac{\partial G}{\partial T}\right)_P$
C. $\left(\frac{\partial H}{\partial S}\right)_P$
D. $\left(\frac{\partial T}{\partial P}\right)_H$

	A	B
(a)	5	1
(b)	5	3
(c)	3	5
(d)	5	3

30. The enthalpy o
$N_2O_{(g)}$ and N_2O
10 kJ/mol respe
$N_2O_{4(g)} + 3CO_{(g)}$
is
(a) –212
(c) +48

31. For adiabatic
(a) $\Delta T = 0$
(c) $q = 0$

32. Which of the
function?
(a) Interna
(c) Enthal

33. Which of th
(a) Enthal
(c) Speci

34. Bond disso
and C_2H_6 i
energy of
(a) 170
(c) 80 k

35. Which th
function
(a) q a
(b) q a
(c) W
(d) W

36. A diat
adiaba
final p

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

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

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

(2010)

30. The enthalpy of formation of $CO_{(g)}$, $CO_{2(g)}$, $N_2O_{(g)}$ and $N_2O_{4(g)}$ is −110, −393, +811 and 10 kJ/mol respectively. For the reaction,

$N_2O_{4(g)} + 3CO_{(g)} \rightarrow N_2O_{(g)} + 3CO_{2(g)}$ ΔH_r (kJ/mol) is

(a) −212 (b) +212
(c) +48 (d) − 48 *(2011)*

31. For adiabatic process, which is correct?

(a) $\Delta T = 0$ (b) $\Delta S = 0$
(c) $q = 0$ (d) $q_p = 0$ *(2011)*

32. Which of the following is not a thermodynamic function?

(a) Internal energy (b) Work done
(c) Enthalpy (d) Entropy *(2011)*

33. Which of the following is intensive property?

(a) Enthalpy (b) Entropy
(c) Specific heat (d) Volume *(2011)*

34. Bond dissociation energy of CH_4 is 360 kJ/mol and C_2H_6 is 620 kJ/mol. Then bond dissociation energy of C – C bond is

(a) 170 kJ/mol (b) 50 kJ/mol
(c) 80 kJ/mol (d) 220 kJ/mol *(2012)*

35. Which thermodynamic parameter is not a state function?

(a) q at constant pressure
(b) q at constant volume
(c) W at adiabatic
(d) W at isothermal *(2013)*

36. A diatomic gas at pressure P, compressed adiabatically to half of its volume, what is the final pressure?

(a) $(2)^{1.4}P$ (b) $P/(2)^{1.4}$
(c) $(2)^{5/3}P$ (d) $P/(2)^{5/3}$ *(2014)*

ASSERTION AND REASON

37. ***Assertion*:** Enthalpy of graphite is lower than that of diamond.

***Reason*:** Entropy of graphite is greater than that of diamond. *(1995)*

38. ***Assertion*:** The enthalpy of formation of gaseous oxygen molecules at 298 K under a pressure of one atm is zero.

***Reason*:** The entropy of formation of gaseous oxygen molecules under the same conditions is zero. *(1996)*

39. ***Assertion*:** Decrease in free energy causes spontaneous reaction.

***Reason*:** Spontaneous reactions are invariably exothermic reactions. *(1997)*

40. ***Assertion:*** The temperature of a gas does not change, when it undergoes an adiabatic expansion.

Reason: During an adiabatic process, the container should be a perfect conductor. *(1998)*

41. ***Assertion:*** Heat energy is completely transformed into work during the isothermal expansion of a gas.

Reason: During an isothermal process, the change in internal energy of a gas due to decrease in pressure is nullified by the change due to increase in volume. *(1998)*

42. ***Assertion :*** During an adiabatic process, heat energy is not exchanged between system and its surroundings.

Reason : The temperature of a gas increases when it undergoes an adiabatic expansion. *(2002)*

43. ***Assertion :*** Mass and volume are extensive properties.

Reason : Mass/volume is also an extensive property. *(2002)*

44. ***Assertion :*** Absolute values of internal energy of substances cannot be determined.

Reason : It is impossible to determine exact values of constituent energies of the substances. *(2002)*

45. ***Assertion :*** The increase in internal energy (ΔE) for the vaporization of one mole of water at 1 atm and 373 K is zero.

Reason : For all isothermal processes, $\Delta E = 0$. *(2003)*

46. ***Assertion :*** ΔH and ΔE are almost the same for the reaction, $N_{2\,(g)} + O_{2\,(g)} \rightleftharpoons 2NO_{(g)}$.
Reason : All reactants and products are gases. *(2003)*

47. ***Assertion :*** Molar entropy of vaporisation of water is different from ethanol.
Reason : Water is more polar than ethanol. *(2004)*

48. ***Assertion :*** Water in liquid state is more stable than ice at room temperature.
Reason : Water in liquid form has higher entropy than ice. *(2006)*

49. ***Assertion :*** Salt such as NaCl dissolves, the Na^+ and Cl^- ions leaving the crystal lattice acquire far greater freedom.
Reason : In thermodyanamic terms, the formation of solution occurs with a favourable change in free energy, *i.e.*, ΔH has a high positive value and $T\Delta S$ a low negative value. *(2007)*

50. ***Assertion :*** Many endothermic reactions that are not spontaneous at room temperature become spontaneous at high temperature.
Reason : Entropy of the system increases with increase in temperature. *(2008)*

51. ***Assertion :*** Heat of neutralisation of nitric acid with NaOH is same as that of HCl and NaOH.
Reason : In both cases strong acid and strong bases are neutralised.

$$H^+ + OH^- \rightarrow H_2O \quad (2009)$$

52. ***Assertion :*** A reaction which is spontaneous and accompanied by decrease of randomness must be exothermic.
Reason : All exothermic reactions are accompanied by decrease in randomness. *(2009, 2016)*

53. ***Assertion :*** Entropy is always constant for a closed system.
Reason : Closed system is always reversible. *(2011)*

54. ***Assertion :*** For an isolated system, q is zero.
Reason : In an isolated system, change in U and V is zero. *(2013)*

55. ***Assertion :*** Entropy of system increases for a spontaneous reaction.
Reason : Enthalpy of reaction always decreases for spontaneous reaction. *(2013)*

56. ***Assertion :*** A process is called adiabatic if the system does not exchange heat with the surroundings.
Reason : It does not involve increase or decrease in temperature of the system. *(2013)*

57. ***Assertion :*** Heat of neutralisation for both H_2SO_4 and HCl with NaOH is 53.7 kJ mol^{-1}.
Reason : Both HCl and H_2SO_4 are strong acids. *(2016)*

58. ***Assertion :*** Spontaneous process is an irreversible process and may be reversed by some external agency.
Reason : Decrease in enthalpy is a contributory factor for spontaneity. *(2017)*

Answer Key

1.	(b)	**2.**	(c)	**3.**	(d)	**4.**	(a)	**5.**	(c)	**6.**	(d)	**7.**	(d)	**8.**	(d)
9.	(c)	**10.**	(d)	**11.**	(c)	**12.**	(c)	**13.**	(c)	**14.**	(c)	**15.**	(a)	**16.**	(d)
17.	(c)	**18.**	(b)	**19.**	(b)	**20.**	(a)	**21.**	(d)	**22.**	(a)	**23.**	(b)	**24.**	(b)
25.	(a)	**26.**	(d)	**27.**	(a)	**28.**	(b)	**29.**	(d)	**30.**	(d)	**31.**	(c)	**32.**	(b)
33.	(c)	**34.**	(c)	**35.**	(d)	**36.**	(a)	**37.**	(b)	**38.**	(c)	**39.**	(b)	**40.**	(d)
41.	(a)	**42.**	(c)	**43.**	(c)	**44.**	(a)	**45.**	(a)	**46.**	(b)	**47.**	(b)	**48.**	(a)
49.	(c)	**50.**	(b)	**51.**	(a)	**52.**	(c)	**53.**	(d)	**54.**	(b)	**55.**	(a)	**56.**	(c)
57.	(a)	**58.**	(b)												

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EXPLANATIONS

1. **(b) :** Given: Weight of benzoic acid = 1.89 g; Temperature of bomb calorimeter = 25 °C = 298 K; Mass of water (m) = 18.94 kg = 18940 g; Increase in temperature (ΔT) = 0.632 °C and specific heat of water (s) = 0.998 cal/g-deg.
We know that, heat gained by water or heat liberated by benzoic acid (Q) = $m\,s\Delta T$

$$= 18940 \times 0.998 \times 0.632 = 11946.14 \text{ cal}$$

Since 1.89 g of acid liberates 11946.14 cal of heat, therefore heat liberated by 122 g of acid

$$= \frac{11946.14 \times 122}{1.89}$$

$$= 771126.5 \text{ cal} = 771.12 \text{ kcal}$$

(where 122 g is the molecular weight of benzoic acid)

2. **(c) :** This is the statement of third law of thermodynamics. In a perfect crystal, at absolute zero temperature, each constituent of lattice must have the lowest energy, so it leads to perfect order, therefore zero entropy.

3. **(d) :** Intensive property is that which is independent of the amount of the substance present in the system *e.g.*, density, temperature, concentration etc.
Extensive property depends upon the amount of the substance present in the system. *e.g.*, volume, mass etc.

4. **(a) :** $H_{2(g)} + I_{2(g)} \rightarrow 2HI_{(g)}$
Δn = No. of gaseous product – no. of gaseous reactant
$= 2 - (1 + 1) = 0$
As $\Delta H = \Delta E + \Delta nRT$
$\Rightarrow \Delta H = \Delta E + 0 \times RT \Rightarrow \Delta H = \Delta E$

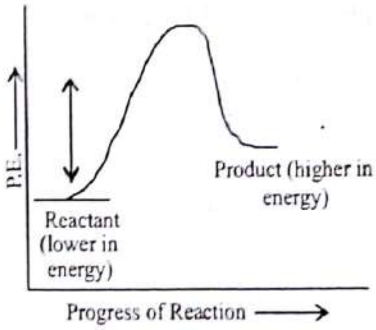
5. **(c) :** Enthalpy change (ΔH) is a state function so it does not depend on the path taken by the reaction, It depends only on the difference of final and initial values of enthalpy change.

6. **(d) :** $S + 3/2\,O_2 \rightarrow SO_3 + 2x$ kcal ... (i)
$SO_2 + 1/2\,O_2 \rightarrow SO_3 + y$ kcal ... (ii)
Now, subtract eq. (ii) from (i), we get
$S + O_2 \rightarrow SO_2 + 2x - y$ kcal
$\therefore$ Heat of formation of SO_2 is equal to $2x - y$ kcal.

7. **(d) :** According to this law, the total enthalpy change is independent of intermediate steps involved in the change. It depends only on initial and final values of enthalpy change. So it can be used for the calculation of heat of formation, reaction or transition.

8. **(d) :** $2C_{(s)} + 2H_2 \rightarrow C_2H_{4(g)}$; $\Delta H_1 = 52$ kJ/mole ....(i)
$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}, \Delta H_2 = -394$ kJ/mole ....(ii)
$H_{2(g)} + ½O_{2(g)} \rightarrow H_2O_{(l)}, \Delta H_3 = -286$ kJ/mole ....(iii)
The combustion of C_2H_4 can be derived as follows :
$C_2H_{4(g)} \rightarrow 2C_{(s)} + 2H_2, \Delta H_1 = -52$ KJ/mole
$2C_{(s)} + 2O_{2(g)} \rightarrow 2CO_{2(g)}, \Delta H_2 = -2 \times 394$
$2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}, \Delta H_3 = -2 \times 286$
$\Rightarrow \Delta H = -52 - 2 \times 394 - 2 \times 286$
$= -1412$ kJ/mole

9. **(c) :** In an endothermic reaction, enthalpy for the product is higher than that of reactants.
$\therefore \Delta H = \Delta H_{(\text{products})} - \Delta H_{(\text{reactant})} = +\text{ve}$



10. **(d) :** Every substance is associated with a definite amount of energy which depends upon its chemical nature as well as on temperature, pressure and volume. This energy is called as internal energy and it includes translational, rotational and vibrational energy of the molecule.

11. **(c) :** $Ba(OH)_{2(aq)} + H_2SO_{4(aq)} \rightarrow BaSO_{4(s)} + 2H_2O_{(l)}$
In this reaction, the neutralisation of dibasic acid takes place by diacidic base. Neutralisation reactions involves two protons. Hence, in this case enthalpy change is –114 kJ.

12. **(c) :** Combustion reaction of carbon is
$C_{(s)} + O_{2(s)} \rightarrow CO_{2(g)}, \Delta H_1 = -395.5$ kJ/mol
Combustion reaction of hydrogen is

$$H_{2(g)} + \frac{1}{2}O_{2(s)} \rightarrow H_2O_{(g)}, \Delta H_2 = -284.8 \text{ kJ/mol}$$

Combustion of methane ;
$CH_{4(g)} + 2O_{2(g)} \rightarrow CO_{2(g)} + 2H_2O_{(g)},$
$\Delta H_3 = -890.4$ kJ/mol
Reaction for the formation of methane is
$C_{(s)} + 2H_{2(g)} \rightarrow CH_{4(g)}; \Delta H = ?$

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From the above equations, we get
$\Delta H = \Delta H_1 + 2\Delta H_2 - \Delta H_3$
$= -395.5 - 2 \times 284.8 + 890.4 = -74.7$ kJ/mole

13. **(c) :** Feasibility of reaction is determined by free energy change (ΔG) value.
ΔG is given by Gibbs – Helmholtz equation :
$\Delta G = \Delta H - T\Delta S$
Reaction is feasible if ΔG value is negative. Therefore, if ΔH is negative and $T\Delta S$ is positive then the ΔG will always be negative.

14. **(c) :** $C + O_2 \rightarrow CO_2$; $\Delta H° = -a$ kJ ... (i)
$2CO + O_2 \rightarrow 2CO_2$; $\Delta H° = -b$ kJ ... (ii)
Formation of CO can be written as :

$$C + \frac{1}{2}O_2 \rightarrow CO\ ;\ \Delta H° = ?$$

Dividing equation (ii) by 2 and reversing, we get

$$CO_2 \rightarrow CO + \frac{1}{2}O_2,\ \Delta H° = b/2\text{kJ} \quad \text{... (iii)}$$

On adding equations (i) and (iii), we get

$$\Delta H°_f(CO) = \frac{b}{2} - a = \frac{b-2a}{2}$$

15. **(a) :** Heat of neutralization (ΔH) = 57 kJ/mol, moles of HNO_3 = 0.5 mole and moles of NaOH = 0.2 mole. When HNO_3 solution is added to NaOH solution, then 0.2 mole of HNO_3 solution will combine with 0.2 mole of NaOH solution.
∴ Heat released = $\Delta H \times 0.2 = 57 \times 0.2 = 11.4$ kJ

16. **(d) :** Heat of decomposition, $\Delta E = m \cdot s \cdot \Delta T$
$= 1 \times 1.23 \times 6.12 = 7.5276$ kJ
Molar heat of decomposition for NH_4NO_3
$= 7.5276 \times 80 = 602.2$ kJ/mol

17. **(c) :** Here, the number of product species is greater than the number of reactant species. So entropy change is positive.

18. **(b) :** $[C + O_2 \rightarrow CO_2] \times 8$
$\Delta H_f° = -490$ kJ/mol × 8 ... (i)
$[H_2 + \frac{1}{2}O_2 \rightarrow H_2O] \times 9$
$\Delta H_f° = -240$ kJ/mol × 9 ... (ii)
$8C + 18H \rightarrow C_8H_{18}$,
$\Delta H_f° = +160$ kJ/mol ... (iii)
Adding equations (i) and (ii) and subtracting (iii), we get

$$8C + 8O_2 + 9H_2 + \frac{9}{2}O_2 - 8C - 18H \rightarrow 8CO_2 + 9H_2O - C_8H_{18}$$

$C_8H_{18} + \frac{25}{2}O_2 \rightarrow 8CO_2 + 9H_2O$;
$\Delta H_f° = -3920 - 2160 - 160 = 6240$ kJ/mol
$\Delta H°$ for 6 moles of octane = 6240 × 6 = 37440 kJ/mol

19. **(b) :** Methanol can be prepared synthetically by heating carbon monoxide and hydrogen gas under pressure in the presence of a catalyst.
$C_{(graphite)} + 1/2\ O_{2(g)} \rightarrow CO_{(g)}$
$CO_{(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$ ...(i)
$C_{(graphite)} + 1/2\ O_{2(g)} + 2H_{2(g)} \rightarrow CH_3OH_{(l)}$ ...(ii)

20. **(a) :** Bomb calorimeter is commonly used to find the heat of combustion of organic substances which consists of a sealed combustion chamber, called a bomb. If a process is run in a sealed container then no expansion or compression is allowed, so $w = 0$ and $\Delta U = q$.
$\Delta U < 0,\ w = 0$.

21. **(d) :** $\Delta S_{total} = \Delta S_{system} + \Delta S_{surroundings}$
For a spontaneous process, ΔS_{total} must be positive. *i.e.*, $\Delta S_{total} > 0$.

22. **(a) :** $\Delta G° = -RT\ln K$ [$\Delta G°$ = standard free energy change, K = equilibrium constant]
If a substance is in equilibrium between two phases at constant temperature and pressure, its chemical potential must have the same value in both the phases.
∴ $\Delta G° = 0$.

23. **(b) :** $\Delta H = \Delta U + \Delta nRT$
[where, Δn = no. of mole of products – no. of mole of reactants]
or, $-92.38 \times 1000 = \Delta U - 2 \times 8.314 \times 298$
or, $\Delta U = -87424$ J $= -87.424$ kJ

24. **(b) :** $\Delta H = \Delta E + P\Delta V$
$\Delta E = \Delta H - P\Delta V = -92.2 - 40 \times (-1) \times 101 \times 10^{-3}$
$= -92.2 + 4.04 = -88.16$ kJ ≈ −88 kJ

25. **(a) :** Solid $\xrightarrow{\text{fusion}}$ Liquid $\Delta H_{fusion} = x$
Liquid $\xrightarrow{\text{vaporisation}}$ Gas $\Delta H_{vap} = y$
Solid $\xrightarrow{\text{sublimation}}$ Gas $\Delta H_{sub} = ?$
So, $\Delta H_{sub} = \Delta H_{fusion} + \Delta H_{vap}$, $\Delta H_{sub} = x + y$

26. **(d)**

27. **(a) :** The entropy change for a process, when T and P are the variables is given by

$$\Delta S = C_p \ln\frac{T_2}{T_1} - R\ln\frac{P_2}{P_1}$$

For an isobaric process $P_1 = P_2$. Hence the above equation reduces to

$$C_p \ln\frac{T_2}{T_1} = \Delta S \quad \text{or} \quad \Delta S = 2.303C_p \log\frac{T_2}{T_1}$$

---

28. **(b) :** For n moles of an ideal gas $PV = nRT$
or $V = n\frac{RT}{P}$
Differentiating with respect to T at constant P, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} = \frac{V}{T}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \times \frac{V}{T} = \frac{1}{T}$$

29. **(d) :** From thermodynamics, $dG = VdP - SdT$
At constant T, $dT = 0$ so that $\left(\frac{\partial G}{\partial P}\right)_T = V$
At constant P, $dP = 0$ so that $\left(\frac{\partial G}{\partial T}\right)_P = -S$
Also, $\mu_{JT} = \left(\frac{\partial T}{\partial P}\right)_H$

30. **(d) :** $N_2O_{4(g)} + 3CO_{(g)} \longrightarrow N_2O_{(g)} + 3CO_{2(g)}$
$\Delta H_{reaction} = \Sigma_{\text{Heat of formation of products}} - \Sigma_{\text{Heat of formation of reactants}}$
$\Delta H_{reaction} = [\Delta H_f(N_2O) + 3 \times \Delta H_f(CO_2)] - [\Delta H_f(N_2O_4) + 3 \times \Delta H_f(CO)$
$\Delta H_r = [+811 + 3(-393)] - [10 + 3(-110)]$
$= [811 - 1179] - [-320] = -368 + 320$
$= -48$ kJ/mol

31. **(c) :** For adiabatic process, no exchange of heat takes place between the system and surroundings. *i.e.*, $q = 0$.

32. **(b) :** Thermodynamic functions are : Internal energy, enthalpy, entropy, pressure, volume, temperature, free energy, number of moles.

33. **(c) :** Intensive property : Specific heat
Extensive property : Enthalpy, entropy, volume.

34. **(c) :** Dissociation energy of methane
$= 360$ kJ mol^{-1}
∴ Bond energy of C—H bond $= \frac{360}{4} = 90$ kJ
Bond energy of ethane.
1 B.E. (C—C) + 6 B.E. (C—H) = 620 kJ/mol
B.E. (C—C) + 6 × 90 = 620
B.E. (C—C) + 540 = 620
B.E. (C—C) = 620 − 540
B.E. (C—C) = 80 kJ mol^{-1}
Bond dissociation of C—C bond = 80 kJ mol^{-1}

35. **(d) :** H and U are state functions but W and
are not state functions.
From the equation, $\Delta H = \Delta U + \Delta PV$
At constant pressure, $\Delta H = \Delta U + P\Delta V$
At constant volume, $\Delta H = \Delta U + V\Delta P$

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At constant v
so, it is a sta
Work done in
$\Delta U = q - W$
$\Delta U = -W$
Work done
function.
$W = -q$ (
36. **(a) :** F
$P_1V_1^{\gamma} = P_2$
$P_2 = P_1$
$P_2 = P_1$
$P_2 = P$
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28. **(b) :** For n moles of an ideal gas $PV = nRT$

or $V = n\dfrac{RT}{P}$

Differentiating with respect to T at constant P, we have

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{nR}{P} = \frac{V}{T}$$

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{V} \times \frac{V}{T} = \frac{1}{T}$$

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Also, $\mu_{JT} = \left(\dfrac{\partial T}{\partial P}\right)_H$

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$\Delta H_{\text{reaction}} = \Sigma_{\text{Heat of formation of products}}$
$\qquad - \Sigma_{\text{Heat of formation of reactants}}$

$\Delta H_{\text{reaction}} = [\Delta H_f(N_2O) + 3 \times \Delta H_f(CO_2)] -$
$\qquad [\Delta H_f(N_2O_4) + 3 \times \Delta H_f(CO)$

$\Delta H_r = [+811 + 3(-393)] - [10 + 3(-110)]$
$\quad = [811 - 1179] - [-320] = -368 + 320$
$\quad = -48$ kJ/mol

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$= 360$ kJ mol^{-1}

$\therefore$ Bond energy of C—H bond $= \dfrac{360}{4} = 90$ kJ

Bond energy of ethane,

1 B.E. (C—C) + 6 B.E. (C—H) = 620 kJ/mol
B.E. (C—C) + 6 × 90 = 620
B.E. (C—C) + 540 = 620
B.E. (C—C) = 620 − 540
B.E. (C—C) = 80 kJ mol^{-1}

Bond dissociation of C—C bond = 80 kJ mol^{-1}

35. **(d) :** H and U are state functions but W and q are not state functions.

From the equation, $\Delta H = \Delta U + \Delta PV$
At constant pressure, $\Delta H = \Delta U + P\Delta V$
At constant volume, $\Delta H = \Delta U + V\Delta P$
At constant pressure, $\Delta P = 0$, $\Delta H = q_p$
so, it is a state function.
At constant volume, $\Delta V = 0$, $\Delta U = q_v$
so, it is a state function.
Work done in any adiabatic process is state function.
$\Delta U = q - W \qquad (\because q = 0)$
$\Delta U = -W$
Work done in isothermal process is not a state function.
$W = -q \ (\because \Delta T = 0, q \neq 0)$

36. **(a) :** For adiabatic conditions, PV^{γ} = Constant

$P_1V_1^{\gamma} = P_2V_2^{\gamma}$; $V_2 = \dfrac{1}{2}V_1$

$P_2 = P_1\left(\dfrac{V_1}{V_2}\right)^{\gamma}$ [For diatomic gas, $\gamma = 1.4$]

$$P_2 = P_1\left(\frac{V_1 \times 2}{V_1}\right)^{1.4}$$

$P_2 = P_1\,(2)^{1.4} = (2)^{1.4}\,P$

37. **(b) :** Greater entropy of graphite is related to its structure as graphite is less compact and rigid than diamond. ΔH_f° for graphite is zero, but the ΔH°_f for diamond is 2 kJ/mol. That is because graphite is the standard state of carbon, not diamond.

38. **(c) :** The heat of formation of all the elements in their standard states are arbitrarily assumed to be zero.

39. **(b) :** Gibbs free energy (ΔG) is given by :
$\Delta G = \Delta H - T\Delta S$

In chemical systems, the reaction moves in a direction in which there is decrease in free energy *i.e.*, $\Delta G = -$ve.

Also, decrease in free energy is a measure of the maximum useful work that can be obtained from a reaction. But the reaction can be exothermic or endothermic *e.g.*, water evaporation is endothermic but it is a spontaneous process (*i.e.*, $\Delta G = -$ve)

40. **(d) :** A process is called adiabatic if no heat enters or leaves the system during any step of the reaction. So temperature does not remain same.

41. **(a) :** In an isothermal expansion, temperature is maintained constant so internal energy change is zero. ($\Delta E = 0$).

According to the first law of thermodynamics,
$\Delta E = q + w$
q = heat, w = work done $\Rightarrow q = -w$
This shows that work is done by the system at the expense of heat absorbed.

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42. (c) : In adiabatic process, no heat enters or leaves the system. The system is completely insulated from its surroundings. From first law of thermodynamics, change in internal energy,
$\Delta E = q - W = 0 - W = -W$.
Since the work is done at the expense of internal energy, therefore internal energy of the system decreases and hence temperature of the gas falls.

43. (c) : Extensive properties are dependent upon the amount of the substance. *e.g.*, mass, volume, etc. Intensive properties are independent of the amount of the substance. *e.g.* temperature, density.

44. (a) : Internal energy is given by :

$$E = E_{\text{translational}} + E_{\text{rotational}} + E_{\text{vibrational}} + E_{\text{bonding}} + E_{\text{electronic}}$$

Accurate measurement of some forms of energy which contribute to the absolute value of internal energy for a given substance in a given state is impossible. So difference of the initial state and final state is calculated and is denoted by

$$\Delta E = E_f - E_i$$

45. (a) : At 373 K or 100°C, the water starts boiling and at this temperature the vaporization of water is an isothermal process.
The internal energy change (ΔE), depends only on temperature and at constant temperature, the internal energy of the gas remains constant, *i.e.*, ΔE is zero.

46. (b) : $\Delta H = \Delta E + \Delta nRT$
Δn = change in number of moles of products and reactant species.
$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$
$\Delta n = 2 - 2 = 0$
$\Delta H = \Delta E + 0 \times RT$ or, $\Delta H = \Delta E$

47. (b) : Molar entropy of vaporization of water is more than ethanol, as water has greater forces of attraction than ethanol.

48. (a) : Fusion of ice is a spontaneous process, because the process proceeds in the direction of more random state, *i.e.*, liquid state is more random (higher entropy) in comparison to solid state. *i.e.*, ice.

49. (c) : In thermodynamic terms, formation of solution occurs with a favourable change in free energy

$$\Delta G = \Delta H - T\Delta S$$

where ΔH has a small positive value and $T\Delta S$ a large positive value; thus, ΔG is negative.

50. (b) : The factor $T\Delta S$ increases with increase in temperature.

51. (a)

52. (c) : $\Delta G = \Delta H - T\Delta S$
$-\text{ve} = \Delta H - [T(-\text{ve})]$ (as spontaneous)
Exothermic reactions may be accompanied by increase or decrease in randomness.

53. (d) : For a closed system, the entropy can increase, decrease or remain constant.
Closed system can be reversible or irreversible.

54. (b) : For an isolated system,
$W = q = 0$
$\Delta U = q + W$
Hence, $\Delta U = 0$
$W = P\Delta V$
as $W = 0$ so, $\Delta V = 0$

55. (a) : ΔS is +ve and ΔH is –ve for a spontaneous reaction at all temperatures.

56. (c) : It may involve increase or decrease in temperature of the system. Systems in which such process occur, are thermally insulated from the surroundings.

57. (a) **58. (b)**

* * *

CHAPTER
7

1. Which of the fc
(a) Br⁻
(c) S⁻

2. The law of equ
(a) Boyle
(c) Waage

3. A buffer solut
and 0.1 M of
pH? (pK_a of
(a) 5.00
(c) 5.25

4. In N_2 + 3H
increase in p
(a) reversi
(b) forwar
(c) irrever
(d) backw

5. If pH valu
water, it be
by
(a) 500 t
(c) 1000

6. Ostwald's
(a) stror
(b) solu
(c) wea
(d) solv

7. The pH
is 10%
(a) 3
(c) 4

8. Which
(a) H
(c) H

9. The pl
(a) 4
(c) 7

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CHAPTER 7

EQUILIBRIUM

1. Which of the following is a Lewis acid?
(a) Br^- (b) Cl^-
(c) S^- (d) Ag^+ *(1994)*

2. The law of equilibrium was first given by
(a) Boyle (b) Guldberg
(c) Waage (d) both (b) and (c). *(1994)*

3. A buffer solution contains 0.1 M of acetic acid and 0.1 M of sodium acetate. What will be its pH? (pK_a of acetic acid is 4.75)
(a) 5.00 (b) 4.00
(c) 5.25 (d) 4.75 *(1995)*

4. In $N_2 + 3H_2 \rightarrow 2NH_3$ reversible reaction, increase in pressure will favour
(a) reversible reaction
(b) forward direction
(c) irreversible reaction
(d) backward direction. *(1995)*

5. If pH value of a solution is 3 and by adding water, it becomes 6, then the dilution is increased by
(a) 500 times (b) 10 times
(c) 1000 times (d) 100 times. *(1995)*

6. Ostwald's dilution law is applicable only to
(a) strong electrolytes
(b) solute
(c) weak electrolytes
(d) solvent. *(1996)*

7. The pH of 0.001 N acetic acid solution, which is 10% dissociated, is
(a) 3 (b) 1
(c) 4 (d) 2 *(1996)*

8. Which of the following is the strongest base?
(a) H_2^+ (b) H
(c) HCO_3^- (d) H^- *(1996)*

9. The pH value of human blood is about
(a) 4.5 to 5.6 (b) 2.3 to 3.4
(c) 7.3 to 7.5 (d) 3.5 to 4.3 *(1996)*

10. Which of the following indicators is known as metal indicator?
(a) Phenolphthalein
(b) Phenol red
(c) Eriochrome Black T
(d) Methyl orange *(1996)*

11. The aqueous solution of which of the following salts will have the lowest pH?
(a) $NaClO_3$ (b) NaClO
(c) $NaClO_4$ (d) $NaClO_2$ *(1996, 2001)*

12. A solution with pH = 2 is more acidic than one with a pH = 6, by a factor
(a) 4000 (b) 5000
(c) 8000 (d) 10000 *(1997)*

13. A base, as defined by Bronsted theory, is a substance which can
(a) accept protons
(b) donate protons
(c) lose a pair of electrons
(d) gain a pair of electrons. *(1997)*

14. In the reaction : $I_2 + I^- \rightarrow I_3^-$, the Lewis base is
(a) I^- (b) I_2
(c) I_3^- (d) none of these. *(1997)*

15. In the gas phase reaction, $C_2H_4 + H_2 \rightleftharpoons C_2H_6$, the equilibrium constant can be expressed in
(a) mole $litre^{-1}$ (b) mole $litre^{-2}$
(c) $mole^{-1}$ $litre^{-1}$ (d) litre $mole^{-1}$. *(1997)*

16. Which of the following information can be obtained on the basis of Le Chatelier's principle?
(a) Equilibrium constant of a chemical reaction
(b) Dissociation constant of a weak acid
(c) Entropy change in a reaction
(d) Shift in equilibrium position on changing value of a constant *(1998)*

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17. The ionic product of water at 25°C is 10^{-14}. Its ionic product at 90°C will be
(a) 1×10^{-14}
(b) 1×10^{-12}
(c) 1×10^{-20}
(d) 1×10^{-16} *(1998)*

18. The solubility of $BaSO_4$, in water, is 2.33×10^{-3} gram/litre. Its solubility product will be (molecular weight of $BaSO_4 = 233$)
(a) 1×10^{-15}
(b) 1×10^{-10}
(c) 1×10^{-5}
(d) 1×10^{-20} *(1998)*

19. An equilibrium mixture of the reaction $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$, had 0.5 mole H_2S, 0.10 mole H_2 and 0.4 mole S_2 in one litre vessel. The value of equilibrium constant (K) in mole $litre^{-1}$ is
(a) 0.016
(b) 0.008
(c) 0.004
(d) 0.160 *(1998)*

20. The unit in which the solubility product of barium phosphate is expressed is
(a) $mol^2\ dm^{-6}$
(b) $mol^3\ dm^{-9}$
(c) $mol^4\ dm^{-12}$
(d) $mol^5\ dm^{-15}$. *(2000)*

21. A vessel of one litre capacity containing 1 mole of SO_3 is heated till a state of equilibrium is attained.

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

At equilibrium, 0.6 moles of SO_2 had formed. The value of equilibrium constant is
(a) 0.18
(b) 0.36
(c) 0.45
(d) 0.68
(2000, 2009, 2015)

22. The pH value of 0.1 M NaOH solution is (when there is a given reaction $[H^+][OH^-] = 10^{-14}$)
(a) 13
(b) 12
(c) 11
(d) 2 *(2000)*

23. The pH value of decinormal solution of NH_4OH which is 20% ionised is
(a) 12.95
(b) 12.30
(c) 14.70
(d) 13.30 *(2001)*

24. When the temperature of reaction increases then the effect on pH value will
(a) increase
(b) decrease
(c) first increase then decrease
(d) remains same. *(1995, 2007)*

25. The pH of aqueous solution of ammonium formate is
(pK_a of HCOOH = 3.8 and pK_b of NH_3 = 4.8)
(a) 7
(b) 6.0
(c) 6.5
(d) 8.9 *(2001)*

26. In which of the following reaction $K_p > K_c$?
(a) $PCl_3 + Cl_2 \rightarrow PCl_5$
(b) $H_2 + I_2 \rightarrow 2HI$
(c) $2SO_3 \rightarrow O_2 + 2SO_2$
(d) $N_2 + 3H_2 \rightarrow 2NH_3$ *(1995, 2001)*

27. Which of the following is a characteristic of a reversible reaction?
(a) It never proceeds to completion.
(b) It can be influenced by a catalyst.
(c) It proceeds only in forward direction.
(d) Number of moles of reactants and products are equal. *(1996, 2001)*

28. The equilibrium constant of a reaction is 300. If the volume of a reaction flask is tripled, the equilibrium constant will be
(a) 300
(b) 100
(c) 600
(d) 150 *(1996, 2001)*

29. At 80°C, distilled water has concentration equal to 1×10^{-6} mole/litre. The value of K_w at this temperature will be
(a) 1×10^{-6}
(b) 1×10^{-12}
(c) 1×10^{-9}
(d) 1×10^{-15} *(2002)*

30. The pH of solution containing 0.10 M sodium acetate and 0.03 M acetic acid is
(pK_a for CH_3COOH = 4.57)
(a) 4.09
(b) 6.09
(c) 5.09
(d) 7.09 *(2002)*

31. The solubility of CuBr is 2×10^{-4} mol/L at 25°C. The K_{sp} value for CuBr is
(a) $4 \times 10^{-8}\ mol^2\ L^{-2}$
(b) $4 \times 10^{-4}\ mol^2\ L^{-2}$
(c) $4 \times 10^{-11}\ mol^2\ L^{-2}$
(d) $4 \times 10^{-15}\ mol^2\ L^{-2}$ *(2002)*

32. Which one of the following is not a buffer solution?
(a) 0.8 M H_2S + 0.8 M KHS
(b) 2 M $C_6H_5NH_2$ + 2 M $C_6H_5NH_3^+Br^-$
(c) 3 M H_2CO_3 + 3 M $KHCO_3$
(d) 0.05 M $KClO_4$ + 0.05 M $HClO_4$ *(2003)*

33. In which of the following acid-base titration, pH is greater than 8 at equivalence point?
(a) Acetic acid versus ammonia
(b) Acetic acid versus sodium hydroxide
(c) Hydrochloric acid versus ammonia
(d) Hydrochloric acid versus sodium hydroxide *(2003)*

34. Dimethyl glyoxime gives a red precipitat
Ni^{2+}, which is used for its detection. To g
precipitate readily the best pH range is
(a) < 1
(b) 2 - 3
(c) 3 - 4
(d) 5 - 9

35. The compound insoluble in water is
(a) mercurous nitrate
(b) mercuric nitrate
(c) mercurous chloride
(d) mercurous perchlorate.

36. For the equilibrium $H_2O_{(l)} \rightleftharpoons H_2O$
and 298 K,
(a) standard free energy change is
($\Delta G° = 0$)
(b) free energy change is les
($\Delta G < 0$)
(c) standard free energy chang
zero ($\Delta G° < 0$)
(d) standard free energy chang
zero ($\Delta G° > 0$).

37. What is the pH of 0.01 M glyc
glycine, $K_{a_1} = 4.5 \times 10^{-3}$ and
at 298 K?
(a) 3.0
(b)
(c) 7.06
(d)

38. Of the following which ch
reaction towards the prod
$I_{2(g)} \rightleftharpoons 2I_{(g)}$, $\Delta H_r°$ (298
(a) Increase in concentr
(b) Decrease in concen
(c) Increase in temper
(d) Increase in total p

39. When 10 mL of 0.1 M
is titrated against 10
solution (pK_b = 5.0)
occurs at pH
(a) 5.0
(c) 7.0

40. For reaction, 2NOC
at 427°C is 3×10
nearly
(a) 7.5×10^{-5}
(c) 2.5×10^{-4}

41. 40 mL of 0.1 M a
20 mL of 0.1 M
mixture? (pK_b o

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34. Dimethyl glyoxime gives a red precipitate with Ni^{2+}, which is used for its detection. To get this precipitate readily the best pH range is
(a) < 1 (b) 2 - 3
(c) 3 - 4 (d) 5 - 9 *(2004)*

35. The compound insoluble in water is
(a) mercurous nitrate
(b) mercuric nitrate
(c) mercurous chloride
(d) mercurous perchlorate. *(2004)*

36. For the equilibrium $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$ at 1 atm and 298 K,
(a) standard free energy change is equal to zero ($\Delta G^\circ = 0$)
(b) free energy change is less than zero ($\Delta G < 0$)
(c) standard free energy change is less than zero ($\Delta G^\circ < 0$)
(d) standard free energy change is greater than zero ($\Delta G^\circ > 0$). *(2004)*

37. What is the pH of 0.01 M glycine solution? For glycine, $K_{a_1} = 4.5 \times 10^{-3}$ and $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K?
(a) 3.0 (b) 10.0
(c) 7.06 (d) 7.2 *(2004, 2010)*

38. Of the following which change will shift the reaction towards the product?
$I_{2(g)} \rightleftharpoons 2I_{(g)}$, ΔH_r° (298 K) = +150 kJ
(a) Increase in concentration of I
(b) Decrease in concentration of I_2
(c) Increase in temperature
(d) Increase in total pressure *(2004)*

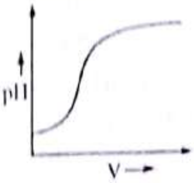
39. When 10 mL of 0.1 M acetic acid ($pK_a = 5.0$) is titrated against 10 mL of 0.1 M ammonia solution ($pK_b = 5.0$), the equivalence point occurs at pH
(a) 5.0 (b) 6.0
(c) 7.0 (d) 9.0 *(2005)*

40. For reaction, $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$, K_c at 427°C is 3×10^{-6} L mol^{-1}. The value of K_p is nearly
(a) 7.5×10^{-5} (b) 2.5×10^{-5}
(c) 2.5×10^{-4} (d) 1.75×10^{-4} *(2005)*

41. 40 mL of 0.1 M ammonia solution is mixed with 20 mL of 0.1 M HCl. What is the pH of the mixture? (pK_b of ammonia solution is 4.74)
(a) 4.74 (b) 2.26
(c) 9.26 (d) 5.00 *(2006)*

42. The pH of the solution obtained on neutralisation of 40 mL 0.1 M NaOH with 40 mL 0.1 M CH_3COOH is
(a) 7 (b) 8
(c) 6 (d) 3 *(2007)*

43. During titration of acetic acid with aq. NaOH solution, the neutralisation graph has a vertical line. This line indicates



(a) alkaline nature of equivalence
(b) acidic nature of equivalence
(c) neutral nature of equivalence
(d) depends on experimental proceeding. *(2007)*

44. The dissociation equilibrium of a gas AB_2 can be represented as

$$2AB_{2\,(g)} \rightleftharpoons 2AB_{(g)} + B_{2\,(g)}$$

The degree of dissociation is x and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure p is
(a) $(2K_p/p)^{1/2}$ (b) K_p/p
(c) $2K_p/p$ (d) $(2K_p/p)^{1/3}$ *(2008)*

45. The correct order of increasing $[H_3O^+]$ in the following aqueous solutions is
(a) 0.01 M H_2S < 0.01 M H_2SO_4 < 0.01 M NaCl < 0.01 M $NaNO_2$
(b) 0.01 M NaCl < 0.01 M $NaNO_2$ < 0.01 M H_2S < 0.01 M H_2SO_4
(c) 0.01 M $NaNO_2$ < 0.01 M NaCl < 0.01 M H_2S < 0.01 M H_2SO_4
(d) 0.01 M H_2S < 0.01 M $NaNO_2$ < 0.01 M NaCl < 0.01 M H_2SO_4 *(2008)*

46. pH of a 0.01 M solution ($K_a = 6.6 \times 10^{-4}$)
(a) 7.6 (b) 8
(c) 2.6 (d) 5 *(2009)*

47. The equilibrium constant for mutarotation α-*D* Glucose ⇌ β-*D* Glucose is 1.8. What percentage of α form remains at equilibrium?
(a) 35.7 (b) 64.3
(c) 55.6 (d) 44.4 *(2009)*

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48. K_{sp} of $CaSO_4 \cdot 5H_2O$ is 9×10^{-6}, find the volume for 1 g of $CaSO_4$ (M.wt. = 136).
(a) 2.45 litre (b) 5.1 litre
(c) 4.52 litre (d) 3.2 litre *(2011)*

49. Which of the following is not a characteristic of equilibrium?
(a) Rate is equal in both directions.
(b) Measurable quantities are constant at equilibrium.
(c) Equilibrium occurs in reversible condition.
(d) Equilibrium occurs only in open vessel at constant temperature. *(2011)*

50. 25 mL, 0.2 M $Ca(OH)_2$ is neutralised by 10 mL of 1 M HCl. Then pH of resulting solution is
(a) 1.37 (b) 9
(c) 12 (d) 7 *(2011)*

51. At equilibrium which is correct?
(a) $\Delta G = 0$ (b) $\Delta S = 0$
(c) $\Delta H = 0$ (d) $\Delta G^\circ = 0$ *(2012)*

52. Which has the highest pH?
(a) CH_3COOK (b) Na_2CO_3
(c) NH_4Cl (d) $NaNO_3$ *(2012)*

53. $\frac{K_p}{K_c}$ for following reaction will be

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}$$

(a) RT (b) $\frac{1}{RT}$
(c) $\frac{1}{\sqrt{RT}}$ (d) $\frac{RT}{2}$ *(2012)*

54. At 60° and 1 atm, N_2O_4 is 50% dissociated into NO_2 then K_p is
(a) 1.33 atm (b) 2 atm
(c) 2.67 atm (d) 3 atm. *(2012)*

55. What will be the solubility product of AX_3?
(a) $27S^4$ (b) $4S^3$
(c) $36S^4$ (d) $9S^3$ *(2013)*

56. The equilibrium constant for the reaction,

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)} \text{ is } K_c$$

Equilibrium constant for the reaction,
$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$ will be
(a) $1/K_c$ (b) $1/(K_c)^2$
(c) $2/K_c$ (d) $2/(K_c)^2$ *(2014)*

57. K_p for the reaction $A \rightleftharpoons B$ is 4. If initially only A is present then what will be the partial pressure of B after equilibrium?
(a) 1.2 (b) 0.8
(c) 0.6 (d) 1 *(2016)*

58. For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$, $K = 47.6$. If the initial number of moles of each reactant and product is 1 mole then at equilibrium
(a) $[I_2] = [H_2]$, $[I_2] > [HI]$
(b) $[I_2] = [H_2]$, $[I_2] < [HI]$
(c) $[I_2] < [H_2]$, $[I_2] = [HI]$
(d) $[I_2] > [H_2]$, $[I_2] = [HI]$ *(2017)*

59. Which of the following pairs of substances cannot exist together in solution?
(a) $Na_2CO_3 + NaOH$
(b) $NaHCO_3 + Na_2CO_3$
(c) $NaHCO_3 + NaOH$
(d) $NaOH + NaCl$ *(2017)*

60. K_a for HCN is 5×10^{-10} at 25 °C. For maintaining a constant pH = 9, the volume of 5 M KCN solution required to be added to 10 mL of 2 M HCN solution is
(a) 4 mL (b) 2.5 mL
(c) 2 mL (d) 6.4 mL *(2017)*

ASSERTION AND REASON

61. ***Assertion*** : Relative strength of acids can be known by knowing the value of dissociation constant.
Reason : It gives the value of H^+ dissolved in solution. *(2001)*

62. ***Assertion*** : Addition of silver ions to a mixture of aqueous sodium chloride and sodium bromide solution will first precipitate AgBr rather than AgCl.
Reason : K_{sp} of AgCl < K_{sp} of AgBr *(2004)*

63. ***Assertion :*** Sb_2S_3 is not soluble in yellow ammonium sulphide.
Reason : The common ion effect due to S^{2-} ions reduces the solubility of Sb_2S_3. *(2006)*

64. ***Assertion*** : Mixture of CH_3COOH and CH_3COONH_4 is an example of acidic buffer.
Reason : Acidic buffer contains equimolar mixture of weak acid and its salt with weak base. *(2007, 2014)*

Equilibrium

65. ***Asser***
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1. (d)
9. (c)
17. (a)
25. (c)
33. (b
41. (c)
49. (d
57. (b
65. (c)

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65. ***Assertion*** **:** The equilibrium constant is fixed and a characteristic for any given chemical reaction at a specified temperature.
Reason **:** The composition of the final equilibrium mixture at a particular temperature depends upon the starting amount of reactants. *(2007, 2010)*

66. ***Assertion*** **:** According to Le-Chatelier's principle addition of heat to an equilibrium solid $\rightleftharpoons$ liquid results in decrease in the amount of solid.
Reason **:** Reaction is endothermic, so on heating forward reaction is favoured. *(2008)*

67. ***Assertion*** **:** Ice $\rightleftharpoons$ Water, if pressure is applied water will evaporate.
Reason **:** Increase of pressure pushes the equilibrium towards the side in which number of gaseous molecule increases. *(2009)*

68. ***Assertion*** **:** In an acid-base titration involving strong base and a weak acid, methyl orange can be used as an indicator.
Reason **:** Methyl orange changes its colour in pH range of 7 to 9. *(2009)*

69. ***Assertion*** **:** Aqueous solution of $CoCl_2$ is pink in colour. It turns blue in presence of conc. HCl.
Reason **:** It is due to the formation of $[CoCl_4]^{2-}$. *(2013)*

70. ***Assertion*** **:** The second dissociation constant of fumaric acid is greater than maleic acid.
Reason **:** Higher the dissociation constant of acid, more is the acidic character. *(2017)*

Answer Key

1.	(d)	**2.**	(d)	**3.**	(d)	**4.**	(b)	**5.**	(c)	**6.**	(c)	**7.**	(c)	**8.**	(d)
9.	(c)	**10.**	(c)	**11.**	(c)	**12.**	(d)	**13.**	(a)	**14.**	(a)	**15.**	(d)	**16.**	(a)
17.	(a)	**18.**	(b)	**19.**	(a)	**20.**	(d)	**21.**	(d)	**22.**	(a)	**23.**	(b)	**24.**	(b)
25.	(c)	**26.**	(c)	**27.**	(b)	**28.**	(a)	**29.**	(b)	**30.**	(c)	**31.**	(a)	**32.**	(d)
33.	(b)	**34.**	(d)	**35.**	(c)	**36.**	(c)	**37.**	(c)	**38.**	(c)	**39.**	(c)	**40.**	(d)
41.	(c)	**42.**	(b)	**43.**	(a)	**44.**	(d)	**45.**	(c)	**46.**	(c)	**47.**	(a)	**48.**	(a)
49.	(d)	**50.**	(d)	**51.**	(a)	**52.**	(b)	**53.**	(c)	**54.**	(b)	**55.**	(a)	**56.**	(b)
57.	(b)	**58.**	(b)	**59.**	(c)	**60.**	(c)	**61.**	(a)	**62.**	(c)	**63.**	(d)	**64.**	(d)
65.	(c)	**66.**	(a)	**67.**	(d)	**68.**	(d)	**69.**	(a)	**70.**	(b)				

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EXPLANATIONS

1. **(d) :** Ag^+ can accept electron pair so it acts as Lewis acid.

2. **(d) :** According to Guldberg and Waage, the rate at which substance reacts is directly proportional to its active mass (*i.e.* molar concentration);

$$aA + bB \rightleftharpoons xX + yY$$

$$K_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b},\ K_c = \text{equilibrium constant}$$

3. **(d) :** Applying the equation :

$$\text{pH} = \log\frac{[\text{Salt}]}{[\text{Acid}]} + \text{p}K_a$$

$$\Rightarrow \quad \text{pH} = \text{p}K_a + \log 1$$

$$\therefore \quad \text{pH} = 4.75$$

4. **(b) :** According to Le-Chatelier's principle, increase in pressure will favour the direction where there are lesser no. of species.

5. **(c) :** Given: Initial pH = 3 and final pH = 6. We know that pH ∝ Dilution. Therefore, initially $[H^+] = 10^{-3}$ and after dilution $[H^+] = 10^{-6}$. Thus increase in dilution

$$= \frac{\text{Original H}^+ \text{ concentration}}{\text{Concentration of H}^+ \text{ after dilution}} = \frac{10^{-3}}{10^{-6}} = 10^3$$

= 1000 times

6. **(c) :** According to Ostwald's dilution law, the degree of dissociation of a weak electrolyte is proportional to the square root of dilution.

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

α = degree of dissociation, C = concentration

K = equilibrium constant (dissociation)

7. **(c) :** Concentration of acetic acid = 0.001N for 10% dissociation, the effective concentration of H^+ is one-tenth of total concentration.

$$\text{Therefore, effective concentration} = \frac{1}{10} \times 0.001 \text{ N}$$

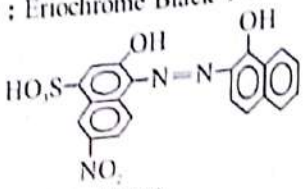
$$= 0.0001 \text{ N}$$

$$\Rightarrow \quad \text{pH} = -\log[H^+] = 4$$

8. **(d) :** Hydride ion is a strong base, stronger than OH^-, OMe^-, etc.

9. **(c) :** Human blood is slightly alkaline *i.e.* pH of 7.3 to 7.5 (pH = 7 is neutral).

10. **(c) :** Eriochrome Black T :



(unionised form)

11. **(c) :**

$$NaClO_4 \rightarrow Na^+ + ClO_4^-$$

$$NaClO_3 \rightarrow Na^+ + ClO_3^-$$

$$NaClO_2 \rightarrow Na^+ + ClO_2^-$$

$$NaClO \rightarrow Na^+ + ClO^-$$

In aqueous solution, these compounds decompose into ions. ClO_4^- will most easily abstract proton from water molecules. So it will be most acidic.

12. **(d) :** pH = −log [H⁺]

$$\Rightarrow \quad 2 = -\log[H^+]_1, \text{ and } 6 = -\log[H^+]_2$$

$$\Rightarrow \quad \frac{\log[H^+]_1}{\log[H^+]_2} = \frac{10^{-2}}{10^{-6}} = 10^4 = 10{,}000$$

Therefore, acidity is more in pH = 2 than pH = 6 by an order of 10,000.

13. **(a) :** According to Bronsted theory, acid is a substance that can release protons while base are those that accept protons.

14. **(a) :** I^- ion can act as Lewis base *i.e.*, it can donate electron pair to some species *e.g.*, I_2. The electron donor species are termed as Lewis base.

$$I^- + I_2 \rightarrow I_3^-$$

15. **(d) :** Equilibrium constant

$$\frac{[C_2H_6]}{[C_2H_4][H_2]} = \frac{\text{mole.litre}^{-1}}{(\text{mole.litre}^{-1}).(\text{mole.litre}^{-1})}$$

$$= \frac{1}{\text{mole.litre}^{-1}} = \frac{\text{litre}}{\text{mole}}$$

16. **(a) :** According to Le-Chatelier principle, if a system at equilibrium is subjected to change in concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect. So the equilibrium constant of a reaction can be calculated.

17. **(a) :** The product of H^+ and OH^- ions in water at a particular temperature is known as ionic product of water. It is denoted as K_w.

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

The value of K_w increase with the increase of temperature *i.e.* concentration of H^+ and OH^- ions increase with increase of temperature, but it still exists in the range of 10^{-14}

e.g. 25°C 1.00×10^{-14}
100°C 7.50×10^{-14}

18. **(b) :** Solubility of $BaSO_4$ in g $L^{-1} = 2.33 \times 10^{-3}$
Solubility of $BaSO_4$ in mol L^{-1}

$$= \frac{2.33}{233} \times 10^{-3} = 10^{-5}$$

Now, $BaSO_4 \rightleftharpoons Ba^{2+} + SO_4^{2-}$
Solubility s s

$\therefore$ Solubility Product $= [Ba^{2+}][SO_4^{2-}] = s^2$
$= (10^{-5})^2 = 10^{-10}$

19. **(a) :** $2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$
Equilibrium constant is,

$$K = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{[0.1]^2[0.4]}{[0.5]^2} = 0.016 \text{ mol L}^{-1}$$

20. **(d) :** Barium phosphate when dissolved in water:
$Ba_3(PO_4)_2 \rightarrow 3Ba^{2+} + 2PO_4^{3-}$
Let the solubility of $Ba_3(PO_4)_2$ be s mol dm^{-3}
$\Rightarrow$ Solubility product $= (Ba^{2+})^3 (PO_4^{3-})^2$
$= s^5 \text{ mol}^5 \text{ dm}^{-15}$

21. **(d) :** $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

Inital conc.	1.0 mole	0.0 mole	0.0 mole
Equilibrium	0.4 mole	0.6 mole	0.3 mole

$\Rightarrow$ Equilibrium constant is given by :

$$K = \frac{[SO_2]^2[O_2]}{[SO_3]^2} = \frac{(0.6)^2(0.3)}{(0.4)^2} = 0.675 \approx 0.68$$

22. **(a) :** $[H^+][OH^-] = 10^{-14}$
Concentration of OH^- *i.e.* $[OH^-]$ in 0.1 M NaOH solution, $[OH^-] = 10^{-1}$ M

$$\Rightarrow [H^+] = \frac{10^{-14}}{10^{-1}} = 10^{-13}$$

$$\Rightarrow pH = -\log[H^+] = 13$$

23. **(b) :** Concentration of NH_4OH solution = 0.1 N
Concentration of OH^- ions in solution,

$$[OH^-] = 20\% \text{ of } 0.1 \text{ N} = \frac{20}{100} \times 0.1 = 0.02 \text{ N}$$

$$\Rightarrow pOH = -\log[OH^-] = -\log(0.02)$$
$$= 2 - 0.301$$

$$\Rightarrow pH = 14 - pOH = 12.30$$

24. **(b) :** As the temperature increases, the dissociation of water in solution increases. Hence, the H^+ ion conc. increases and pH of the solution decreases with increase in temperature.

25. **(c) :** For a salt of weak acid and weak base, its

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b$$

$$= 7 + \frac{1}{2} \times 3.8 - \frac{1}{2} \times 4.8 = 6.5$$

26. **(c) :** $K_p = K_c (RT)^{\Delta n}$
Δn = change in number of moles
If Δn = positive then K_p will be greater than K_c.
$PCl_3 + Cl_2 \rightarrow PCl_5$, $\Delta n = 1 - 2 = -1$, $K_p < K_c$
$H_2 + I_2 \rightarrow 2HI$, $\Delta n = 0$, $K_p = K_c$
$2SO_3 \rightarrow O_2 + 2SO_2$, $\Delta n = 1$, $K_p > K_c$
$N_2 + 3H_2 \rightarrow 2NH_3$; $\Delta n = -2$, $K_p < K_c$

27. **(b) :** Reversible reactions are those reaction in which there is equilibrium established at every infinitesimal step. But the rate of forward and rate of backward reaction can be influenced (or speed up) by the use of catalyst.

28. **(a) :** The equilibrium constant is not affected by changing the volume of the whole reaction flask.

29. **(b) :** $[H_3O^+] = 1 \times 10^{-6}$ mol L^{-1}
or $[H^+] = 1 \times 10^{-6}$ mol L^{-1}
As for distilled water $[H^+] = [OH^-]$
$[H^+] = [OH^-] = 1 \times 10^{-6}$ mol L^{-1}
$K_w = [H^+][OH^-] = 10^{-12}$ mol^2 L^{-2}

30. **(c) :** According to Henderson's equation,

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

$CH_3COOH + NaOH \rightarrow CH_3COONa + H_2O$
Putting the values, we get :

$$pH = 4.57 + \log\frac{0.10}{0.03} \Rightarrow pH = 5.09$$

31. **(a) :** $CuBr \rightarrow Cu^+ + Br^-$
Solubility of CuBr is 2×10^{-4} mol L^{-1}
Therefore, solubility of $Cu^+ = 2 \times 10^{-4}$ mol L^{-1}
$\Rightarrow$ Solubility product $= 2 \times 10^{-4} \times 2 \times 10^{-4}$
$= 4 \times 10^{-8}$ mol^2L^{-2}

32. **(d) :** Buffer solutions can be obtained by mixing a weak acid with its salt formed with a strong base or by mixing a weak base with its salt formed with a strong acid.
As $HClO_4$ is a strong acid, therefore equimolar mixture of $HClO_4$ and its salt $KClO_4$ is not a buffer solution.

33. **(b) :** Acetic acid is a weak acid while sodium hydroxide is a strong base. Therefore at the equivalent point, there will be enough hydroxide ions left.

34. **(d) :** Nickel(II) forms a precipitate with the organic compound dimethylglyoxime, $C_4H_6(NOH)_2$. The formation of the red chelate occurs quantitatively in a solution in which the pH is buffered in the range of 5 to 9.

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35. (c) : According to "solubility rule" following compounds are soluble in water:

(i) All common group IA and NH_4^+ compounds.

(ii) All common NO_3^- (nitrate), CH_3COO^- (acetate), ClO_4^- (perchlorate) compounds

(iii) All common Cl^-, Br^-, I^- compounds, except those of Ag^+, Pb^{2+}, Cu^+ and Hg_2^{2+} (mercurous)

(iv) All common SO_4^{2-} (sulphate) compounds, except those of Ca^{2+}, Sr^{2+}, Ba^{2+} and Pb^{2+}.

36. (c) : $H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$

This is a spontaneous process at standard conditions thus, the standard free energy change must be less then zero, *i.e.* $\Delta G° < 0$.

37. (c) : $K_a = K_{a_1} \times K_{a_2} = 4.5 \times 10^{-3} \times 1.7 \times 10^{-10}$

$$= 7.65 \times 10^{-13}$$

$$[H^+] = \sqrt{K_aC} = \sqrt{7.65 \times 10^{-13} \times 0.01}$$

$$= \sqrt{7.65 \times 10^{-15}} = 0.87 \times 10^{-7}$$

$pH = -\log(0.87 \times 10^{-7}) = 7 - (-0.06) = 7.06$

38. (c) : The given reaction is endothermic, so on increasing the temperature, it will shift in forward direction.

39. (c) : $pK_a = -\log K_a$, $pK_b = -\log K_b$

$$pH = -\frac{1}{2}[\log K_a + \log K_w - \log K_b]$$

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

$$= -\frac{1}{2}[-5 - 14 + 5] = -\frac{1}{2}(-14) = 7$$

40. (d) : $2NOCl_{(g)} \rightleftharpoons 2NO_{(g)} + Cl_{2(g)}$

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

$K_p = 3 \times 10^{-6}(0.0821 \times 700) = 172.41 \times 10^{-6}$

$$= 1.72 \times 10^{-4}$$

41. (c) : 40 mL of 0.1 M ammonia solution

= 40 × 0.1

= 4 milli-equivalent ammonia solution

20 mL of 0.1 M HCl = 20 × 0.1

= 2 milli-equivalent of HCl

	NH_4OH +	$HCl \rightarrow$	$NH_4Cl + H_2O$
Initial milli-eq.	4	2	0
Milli-eq. after reaction	4 − 2 = 2	0	2

$$\therefore \quad pOH = pK_b + \log\frac{[NH_4Cl]}{[NH_4OH]} = 4.74 + \log\frac{2}{2}$$

$$= 4.74 + \log 1 = 4.74$$

$\therefore \quad pH = 14 - 4.74 = 9.26$

42. (b) : $NaOH + CH_3COOH$ forms CH_3COONa which gives basic solution with pH > 7.

43. (a) : In any type of acid-base titration, there is a sudden change in the pH value at the end point. During the titration of a weak acid with a strong base, beyond the equivalent point, the solution will contain the salt and excess of free base.

$$CH_3COOH + NaOH \longrightarrow \underset{\text{Sodium acetate}}{CH_3COONa} + H_2O$$

Due to the presence of free base, solution becomes alkaline in nature.

44. (d) :

	$2AB_{2(g)}$	$\rightleftharpoons 2AB_{(g)}$ +	$B_{2(g)}$
Initial	2	0	0
Equilibrium	2(1 − x)	2x	x

Moles at equilibrium $= 2(1 - x) + 2x + x$

$$= 2 - 2x + 2x + x = x + 2$$

$$K_p = \frac{[P_{AB}]^2[P_{B_2}]}{[P_{AB_2}]^2} = \frac{\left(\frac{2x}{x+2} \times p\right)^2\left(\frac{x}{x+2} \times p\right)}{\left[\frac{2(1-x)}{x+2} \times p\right]^2}$$

$$= \frac{\frac{4x^3}{x+2} \times p}{4(1-x)^2} = \frac{4x^2 \times p}{2} \times \frac{1}{4}$$

$$x = \left(\frac{2K_p}{p}\right)^{1/3} \qquad (\text{as } 1 - x \approx 1,\ 2 + x \approx 2)$$

45. (c) : H_2SO_4 is strong acid having pH < 7. $NaNO_2$ on hydrolysis gives alkaline solution of pH > 7. NaCl is neutral and H_2S is weak acid.

46. (c) : $\alpha = \sqrt{\frac{K_a}{C}} = \sqrt{\frac{6.6 \times 10^{-4}}{0.01}} = \sqrt{6.6 \times 10^{-2}}$

$$= 0.257$$

$[H^+] = C\alpha = 0.01 \times 0.257 = 2.57 \times 10^{-3}$

$pH = 3 - \log 2.5 = 2.6$

47. (a) :

	α-*D* glucose $\rightleftharpoons$	β-*D* glucose
Initial	1	0
At equilibrium	1 − α	α

$$K = \frac{\alpha}{1-\alpha} = 1.8$$

Solving $\alpha = 0.642$

$1 - \alpha = 0.358$

Percent of α-*D* glucose remaining at equilibrium

$$= 35.8\%.$$

48. (a) : $CaSO_{4(s)} \rightleftharpoons \underset{S}{Ca^{2+}_{(aq)}} + \underset{S}{SO_4^{2-}{}_{(aq)}}$

$K_{sp} = S^2 = 9 \times 10^{-6}$

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

Solubility in g $litre^{-1}$ = molecul

$= 136 \times 3 \times 10^{-3}$

408×10^{-3} g of $CaSO_4$ present

1 g of $CaSO_4$ present is $\frac{1}{408 \times}$

49. (d) : Equilibrium state c a reversible reaction is carried

50. (d) : Number of mill $Ca(OH)_2) = N_1V_1 = 2 \times M_1 \times$

Number of millimoles of ac

As, no. of millimoles of ac

∴ Acid is complete forming a neutral solution

∴ pH of the resulting

51. (a)

52. (b) : NH_4Cl solution solution is neutral, its pH solutions are basic their p more basic, its pH > pH

53. (c) : $\Delta n_g = n_p - n$

$\Delta n_g = \frac{-1}{2}$. Hence K_p

$\frac{K_p}{K_c} = \frac{1}{(RT)^{1/2}} = \frac{1}{\sqrt{R}}$

54. (b) : N_2O_4

Initially 1

At equilibrium 1 − α

N_2O_4 is 50% dissoc

$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} =$

55. (a) : AX_3

$K_{sp} = [A^{3+}][X^-]$

56. (b) : The

$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_2$

Hence, $K_c =$

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Solubility in g litre^{-1} = molecular mass × S

$= 136 \times 3 \times 10^{-3} = 408 \times 10^{-3}$ g L^{-1}

408×10^{-3} g of $CaSO_4$ present in 1 litre

1 g of $CaSO_4$ present is $\frac{1}{408 \times 10^{-3}} = 2.45$ litre

49. (d) : Equilibrium state can only be achieved if a reversible reaction is carried out in a closed space.

50. (d) : Number of millimoles of base (*i.e.*, $Ca(OH)_2$) = $N_1V_1 = 2 \times M_1 \times V_1 = 2 \times 0.2 \times 25 = 10$

Number of millimoles of acid (*i.e.*, HCl) = N_2V_2

$= 10 \times 1 = 10$

As, no. of millimoles of acid = no. of millimoles of base

∴ Acid is completely neutralised by base forming a neutral solution.

∴ pH of the resulting solution = 7

51. (a)

52. (b) : NH_4Cl solution is acidic, its pH < 7. $NaNO_3$ solution is neutral, its pH = 7. CH_3COOK and Na_2CO_3 solutions are basic their pH > 7. But Na_2CO_3 solution is more basic, its pH > pH of CH_3COOK solution.

53. (c) : $\Delta n_g = n_p - n_r = 1 - \frac{3}{2}$

$\Delta n_g = \frac{-1}{2}$. Hence $K_p = K_c(RT)^{-1/2}$

$$\frac{K_p}{K_c} = \frac{1}{(RT)^{1/2}} = \frac{1}{\sqrt{RT}}$$

54. (b) :

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initially	1		0
At equilibrium	$1 - \alpha$		2α

N_2O_4 is 50% dissociated, so $\alpha = \frac{1}{2}$

$$K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{\left(2 \times \frac{1}{2}\right)^2}{\left(1 - \frac{1}{2}\right)} = 2 \text{ atm}$$

55. (a) : $AX_3 \rightleftharpoons \underset{S}{A^{3+}} + \underset{3S}{3X^-}$

$K_{sp} = [A^{3+}]\,[X^-]^3 = (S)\cdot(3S)^3 = 27S^4$

56. (b) : The given reaction is,

$$\frac{1}{2}H_{2(g)} + \frac{1}{2}I_{2(g)} \rightleftharpoons HI_{(g)} \quad \text{...(i)}$$

$$\text{Hence, } K_c = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} \quad \text{...(ii)}$$

Now, reverse the eqn. (i) and multiply by 2, we get

$2HI \rightleftharpoons H_{2(g)} + I_{2(g)}$

$$\text{Hence, } K_c' = \frac{[H_2][I_2]}{[HI]^2} \quad \text{...(iii)}$$

Equating equations (ii) and (iii), we get

$$K_c' = \frac{1}{(K_c)^2}$$

57. (b) : Assuming that reaction is started with 1 mol of A and at equilibrium x moles of A have reacted,

	A	$\rightarrow$	B
Initially	1 mol		0
At equilibrium	$1 - x$ mol		x mol

$$K_p = \frac{p_B}{p_A} = 4 \Rightarrow \frac{x}{1-x} = 4 \Rightarrow x = 0.8$$

58. (b) : For the given reaction, $K = \frac{[HI]^2}{[H_2][I_2]}$

As 1 mole of H_2 reacts with 1 mole of I_2, even at equilibrium, $[H_2] = [I_2]$

Hence, $K = \frac{[HI]^2}{[I_2]^2}$ or $\sqrt{K} = \frac{[HI]}{[I_2]} = \sqrt{47.6}$

i.e., $[HI] > [I_2]$

59. (c) : $NaHCO_3$ is a sodium salt of weak acid, while NaOH is a strong base so, they react and cannot exist together in solution.

$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$

60. (c) : $pH = pK_a + \log\frac{[Salt]}{[Acid]}$

$$= pK_a + \log\frac{[KCN]}{[HCN]} \quad \text{...(i)}$$

Let the volume of KCN solution required be V mL

∴ $[KCN] = \frac{5 \times V}{V+10}$ and $[HCN] = \frac{10 \times 2}{V+10}$

Now from eqn. (i),

$$pH = -\log(5 \times 10^{-10}) + \log\left[\frac{5 \times V}{V+10} \Big/ \frac{10 \times 2}{V+10}\right]$$

$$9 = -\log(5 \times 10^{-10}) + \log\frac{V}{4}$$

On solving, $V = 1.99 \approx 2$ mL

61. (a) : $HA \rightleftharpoons H^+ + A^-$

Dissociation consant for this reaction can be given as :

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

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Therefore, we can say that dissociation constant is a measure of its ability to furnish protons in the solution.

62. **(c) :** K_{sp} of AgCl > K_{sp} of AgBr
For the precipitation to occur, its ionic product should exceed solubility product.

63. **(d) :** Sb_2S_3 is soluble in yellow ammonium sulphide.

$$Sb_2S_3 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_3$$

The stability of sulphides increases with increase in atomic number of the element.

64. **(d) :** CH_3COOH/CH_3COONH_4 is not an example of acidic buffer. Acidic buffer contains equimolar mixture of weak acid and its salt with strong base. *e.g.*, CH_3COOH/CH_3COONa.

65. **(c) :** The equilibrium constant is always fixed and is a characteristic of a reaction at specified temperature. It defines the composition of the final equilibrium mixture of that reaction, regardless of the starting amount of reactants and products.

66. **(a) :** Solid + heat $\rightleftharpoons$ Liquid. So on heating forward reaction is favoured and amount of solid will decrease.

67. **(d) :** Increase in pressure favours melting of ice into water because at higher pressure melting point of ice is lowered.
According to Le-Chatelier's principle, if pressure is increased the equilibrium will shift in direction which produces smaller number of moles.

68. **(d) :** In a titration of strong base and weak acid phenolphthalein is used as indicator.
Methyl orange changes its colour in pH of range 3 to 5.

69. **(a) :**

$$\underset{\text{Pink}}{[Co(H_2O)_6]^{2+}} + 4Cl^- \rightleftharpoons \underset{\text{Blue}}{[CoCl_4]^{2-}} + 6H_2O$$

According to Le Chatelier's principle, on adding conc. HCl, the equilibrium shifts in forward direction giving blue colour. And when this blue colour is diluted, equilibrium shifts in backward direction leading to pink colour.

70. **(b) :** Both fumaric and maleic acids have two ionisable H^+ ions *i.e.*, protons. The maleate monoanion shows intramolecular H-bonding, whereas fumarate monoanion shows intermolecular H-bonding. Thus, fumarate monoanion requires more energy to give fumarate dianion. Hence, second dissociation of fumaric acid is more than that of maleic acid.

CHAPTER 8

REDO

1. Which of the following is a strong reducing agent?
   (a) Cr (b) Cl
   [✓ (c) Na] (d) Ca (1994

2. Which is an oxidising substance amongst th following?
   (a) SO_2 (b) CO_2
   [✓ (c) SO_3] (d) NO_2 (199

3. If an atom is reduced, its oxidation number
   (a) does not change
   (b) increases
   (c) decreases
   (d) may increase of decrease. (1

4. The oxidation number of oxygen atom i ion is
   (a) − 3 (b) − 1
   (c) − 5 (d) − 2

5. Which of the following metals does not H₂ from dilute H_2SO_4?
   (a) Zn (b) Al
   [✓ (c) Cu] (d) Mg

6. In the reaction: $2P_2O_5 + 2HNO_3 \rightarrow P_4O_{10}$ the term x is
   (a) N_2O_4 (b) NO
   [✓ (c) N_2O_5] (d) NO_2

7. The oxidation state of chromium in dichromate is
   (a) + 2 (b) − 2
   (c) − 5 (d) + 6

8. The oxidation numbers of hydr MgH_2 and NaH are respectively
   (a) + 2, + 1 and − 2 (b) + 1, +
   [✓ (c) − 1, − 1 and − 1] (d) − 2,

9. What is the oxidation number $Na_2S_4O_6$?
   (a) $\frac{3}{5}$ (b) $\frac{3}{2}$
   (c) $\frac{2}{5}$ (d) $\frac{5}{2}$

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CHAPTER
8
REDOX REACTIONS

1. Which of the following is a strong reducing agent?
   (a) Cr (b) Cl
   [✓ (c)] Na (d) Ca *(1994)*

2. Which is an oxidising substance amongst the following?
   (a) SO_2 (b) CO_2
   [✓ (c)] SO_3 (d) NO_2 *(1994)*

3. If an atom is reduced, its oxidation number
   (a) does not change
   (b) increases
   (c) decreases
   (d) may increase of decrease. *(1995)*

4. The oxidation number of oxygen atom in O_2^{2-} ion is
   (a) – 3 (b) – 1
   (c) – 5 (d) – 2 *(1995)*

5. Which of the following metals does not liberate H_2 from dilute H_2SO_4?
   (a) Zn (b) Al
   [✓ (c)] Cu (d) Mg *(1996)*

6. In the reaction: $2P_2O_5 + 2HNO_3 \rightarrow P_4O_{10} + H_2O + x$, the term x is
   (a) N_2O_4 (b) NO
   [✓ (c)] N_2O_5 (d) NO_2 *(1996)*

7. The oxidation state of chromium in potassium dichromate is
   (a) + 2 (b) – 2
   (c) – 5 (d) + 6 *(1997)*

8. The oxidation numbers of hydrogen in KH, MgH_2 and NaH are respectively
   (a) + 2, + 1 and – 2 (b) + 1, + 1 and + 1
   [✓ (c)] – 1, – 1 and – 1 (d) – 2, – 3 and – 1 *(1998)*

9. What is the oxidation number of sulphur in $Na_2S_4O_6$?
   (a) $\frac{3}{5}$ (b) $\frac{3}{2}$
   (c) $\frac{2}{5}$ (d) $\frac{5}{2}$ *(1998)*

10. In the reaction : $4Fe + 6O_2 \rightleftharpoons 4Fe^{3+} + 6O_2^{2-}$ which of the following statements is incorrect?
    (a) Metallic iron is a reducing agent.
    (b) Fe^{3+} is an oxidising agent.
    (c) It is a redox reaction.
    [✓ (d)] Metallic iron is reduced to Fe^{3+}. *(1998)*

11. Oxidation state of osmium (Os) in OsO_4 is
    (a) +4 (b) +6
    (c) +7 [✓ (d)] +8 *(1999)*

12. Oxidation state of sulphur in S_8, H_2S and S_2F_2 is
    (a) 0, –2, –1 (b) 0, +2, –1
    (c) 1, –2, +1 (d) 0, –2, +1 *(2000)*

13. A gas z is bubbled through a solution containing x^- and y^-. If the reduction potential are in the order $x > y > z$, then
    [✓ (a)] y will oxidise z and not x
    (b) y will oxidise x and not z
    (c) y will oxidise both x and z
    (d) y will reduce both x and z. *(2000)*

14. Oxidation state of Fe in Fe_3O_4 is
    (a) 3/2 (b) 5/4
    (c) 4/5 [✓ (d)] 8/3 *(2002)*

15. MnO_4^{2-} (1 mole) in neutral aqueous medium is disproportionated to
    (a) 2/3 mole of MnO_4^- and 1/3 mole of MnO_2
    (b) 1/3 mole of MnO_4^- and 2/3 mole of MnO_2
    (c) 1/3 mole of Mn_2O_7 and 1/3 mole of MnO_2
    (d) 2/3 mole of Mn_2O_7 and 1/3 mole of MnO_2 *(2003)*

16. For decolourization of 1 mole of $KMnO_4$, the moles of H_2O_2 required is
    (a) 1/2 (b) 3/2
    (c) 5/2 (d) 7/2 *(2004)*

17. In the balanced chemical reaction :
    $$IO_3^- + aI^- + bH^+ \rightarrow cH_2O + dI_2$$
    a, b, c and d respectively correspond to
    (a) 5, 6, 3, 3 (b) 5, 3, 6, 3
    (c) 3, 5, 3, 6 (d) 5, 6, 5, 5 *(2005)*

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18. When $KMnO_4$ reacts with KBr in alkaline medium and gives bromate ion, then oxidation state of Mn changes from +7 to
(a) +6 (b) +4
(c) +3 (d) +2 *(2011)*

19. Oxidation state of iron in haemoglobin is
(a) 0 (b) +2
(c) −2 (d) +3 *(2013)*

20. $K_2Cr_2O_7$ in acidic medium converts into
(a) Cr^{2+} (b) Cr^{3+}
(c) Cr^{4+} (d) Cr^{5+} *(2013)*

21. What is the oxidation number of Br in $KBrO_4$?
(a) + 6 (b) + 7
(c) + 5 (d) + 8 *(2014)*

22. Substances that are oxidised and reduced in the following reaction are respectively
$N_2H_{4(l)} + 2H_2O_{2(l)} \longrightarrow N_{2(g)} + 4H_2O_{(l)}$
(a) N_2H_4, H_2O (b) N_2H_4, H_2O_2
(c) N_2, H_2O_2 (d) H_2O, N_2 *(2016)*

23. On the basis of standard electrode potential of redox couples given below, find out which of the following is the strongest oxidising agent.
(E° values : $Fe^{3+} | Fe^{2+} = +0.77$ V ;
$I_{2(s)} | I^- = +0.54$ V; $Cu^{2+} | Cu = +0.34$ V ;
$Ag^+ | Ag = +0.80$ V)
(a) Fe^{3+} (b) $I_{2(s)}$
(c) Cu^{2+} (d) Ag^+ *(2017)*

ASSERTION AND REASON

24. ***Assertion*:** Copper liberates hydrogen from a solution of dilute hydrochloric acid.
***Reason*:** Hydrogen is below copper in the electrochemical series. *(1995)*

25. ***Assertion*:** Amongst the halogens, fluorine can oxidise the elements to the highest oxidation state.
***Reason*:** Due to small size of fluoride ion, it is difficult to ozidise fluoride ion to fluorine. Hence reverse reaction takes place more easily. *(1996)*

26. ***Assertion :*** In some cases oxygen shows positive oxidation number though it is an electronegative element.
Reason : Fluorine is more electronegative than oxygen. *(2001)*

27. ***Assertion :*** Stannous chloride gives grey precipitate with mercuric chloride, but stannic chloride does not do so.
Reason : Stannous chloride is a powerful oxidising agent which oxidises mercuric chloride to metallic mercury. *(2002)*

28. ***Assertion :*** Reaction of SO_2 and H_2S in the presence of Fe_2O_3 catalyst gives elemental sulphur.
Reason : SO_2 is a reducing agent. *(2005)*

29. ***Assertion :*** The formal oxidation number of sulphur in $Na_2S_4O_6$ is 2.5.
Reason : Two S-atoms are not directly linked with O-atoms. *(2011)*

30. ***Assertion :*** Fluorine is a stronger oxidizing agent than iodine.
Reason : Fluorine has greater electronegativity than iodine. *(2012)*

31. ***Assertion :*** Cl_2 gas bleaches the articles permanently.
Reason : Cl_2 is a strong reducing agent. *(2012)*

32. ***Assertion :*** Cu is stronger reducing agent than H_2.
Reason : E° of Cu^{2+}/Cu is negative. *(2013)*

Answer Key

1.	(c)	**2.**	(c)	**3.**	(c)	**4.**	(b)	**5.**	(c)	**6.**	(c)	**7.**	(d)	**8.**	(c)
9.	(d)	**10.**	(d)	**11.**	(d)	**12.**	(d)	**13.**	(a)	**14.**	(d)	**15.**	(a)	**16.**	(c)
17.	(a)	**18.**	(b)	**19**	(b)	**20.**	(b)	**21.**	(b)	**22.**	(b)	**23.**	(d)	**24.**	(d)
25.	(b)	**26.**	(a)	**27.**	(c)	**28.**	(b)	**29.**	(a)	**30.**	(b)	**31.**	(c)	**32.**	(d)

EX

1. **(c) :** Ionisation energy of Na is very
compared to alkaline earth metals or tr
elements. So, it acts as a good reducing ag

2. **(c) :** SO_3 acts as a strong oxidising ag
$2SO_3 + S \xrightarrow{100°C} 3SO_2$
$5SO_3 + 2P \longrightarrow 5SO_2 + P_2O_5$
$SO_3 + 2HBr \longrightarrow SO_2 + Br_2 + H_2O$

3. **(c)**

4. **(b)**

5. **(c) :** Cu is below hydrogen in the electro
series, so it cannot liberate H_2 from dilute
$E^\circ(Cu^{2+}/Cu) = +0.34$ V

6. **(c) :** $2P_2O_5 + 2HNO_3 \rightarrow P_4O_{10} + N_2$

7. **(d) :** Potassium dichromate : K_2Cr_2O
Let the oxidation state of Cr be x.
$\Rightarrow 2 \times (+1) + 2x + 7 \times (-2) = 0$
$\Rightarrow x = +6$

8. **(c) :** Hydrogen is present as hydride io
molecules *i.e.*, oxidation state is − 1.

9. **(d) :** Let oxidation state of S be x.
$\therefore 2 \times (+1) + 4x + 6 \times (-2) = 0$
$\Rightarrow 2 + 4x - 12 = 0 \Rightarrow x = \frac{+5}{2}$

10. **(d) :** $4Fe + 6O_2 \rightleftharpoons 4Fe^{3+} + 6O_2^{2-}$

In this redox reaction, iron is acting as a
agent (as it is giving out electrons).
i.e., $Fe \rightarrow Fe^{3+} + 3e^-$
As Fe is readily converted to Fe^{3+} ther
oxidised.

11. **(d) :** Let oxidation state of Os be x.
$x + 4 \times (-2) = 0 \Rightarrow x = +8$

12. **(d) :** Oxidation state of S in $S_8 = 0$
Oxidation state of S in $H_2S \Rightarrow +2 + x$
$\Rightarrow x = -2$
Oxidation state of S in $S_2F_2 \Rightarrow 2x + 2$
$\Rightarrow x = +1$

13. **(a) :** More the value of reduction pote
is the tendency to get reduced. As gas z
reduction potential, therefore, z will be oxid

14. **(d) :** Let the oxidation state of Fe b
$\Rightarrow 3x + 4(-2) = 0 \Rightarrow x = +\frac{8}{3}$

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EXPLANATIONS

1. **(c) :** Ionisation energy of Na is very low as compared to alkaline earth metals or transition elements. So, it acts as a good reducing agent.

2. **(c) :** SO_3 acts as a strong oxidising agent. *e.g.*,

$$2SO_3 + S \xrightarrow{100\,^\circ C} 3SO_2$$
$$5SO_3 + 2P \longrightarrow 5SO_2 + P_2O_5$$
$$SO_3 + 2HBr \longrightarrow SO_2 + Br_2 + H_2O$$

3. **(c)**

4. **(b)**

5. **(c) :** Cu is below hydrogen in the electrochemical series, so it cannot liberate H_2 from dilute H_2SO_4.

$E^\circ(Cu^{2+}/Cu) = +0.34$ V

6. **(c) :** $2P_2O_5 + 2HNO_3 \rightarrow P_4O_{10} + N_2O_5 + H_2O$

7. **(d) :** Potassium dichromate : $K_2Cr_2O_7$

Let the oxidation state of Cr be x.

$\Rightarrow\ 2 \times (+1) + 2x + 7 \times (-2) = 0$

$\Rightarrow\ x = +6$

8. **(c) :** Hydrogen is present as hydride ion in these molecules *i.e.*, oxidation state is -1.

9. **(d) :** Let oxidation state of S be x.

$\therefore\ 2 \times (+1) + 4x + 6 \times (-2) = 0$

$\Rightarrow\ 2 + 4x - 12 = 0 \ \Rightarrow x = \dfrac{+5}{2}$

10. **(d) :** $4Fe + 6O_2 \rightleftharpoons 4Fe^{3+} + 6O_2^{2-}$

In this redox reaction, iron is acting as a reducing agent (as it is giving out electrons).

i.e., $Fe \rightarrow Fe^{3+} + 3e^-$

As Fe is readily converted to Fe^{3+} therefore it is oxidised.

11. **(d) :** Let oxidation state of Os be x.

$x + 4 \times (-2) = 0 \Rightarrow x = +8$

12. **(d) :** Oxidation state of S in $S_8 = 0$

Oxidation state of S in H_2S $\Rightarrow\ +2 + x = 0$

$\Rightarrow\ x = -2$

Oxidation state of S in S_2F_2 $\Rightarrow\ 2x + 2(-1) = 0$

$\Rightarrow\ x = +1$

13. **(a) :** More the value of reduction potential, more is the tendency to get reduced. As gas z has lowest reduction potential, therefore, z will be oxidised easily.

14. **(d) :** Let the oxidation state of Fe be x.

$\Rightarrow\ 3x + 4(-2) = 0 \ \Rightarrow\ x = +\dfrac{8}{3}$

15. **(a) :** $3MnO_4^{2-} + 2H_2O \rightarrow MnO_{2\,(s)} + 2MnO_4^- + 4OH^-$

For one mole

$$MnO_4^{2-} + \frac{2}{3}H_2O \rightarrow \frac{1}{3}MnO_{2\,(s)} + \frac{2}{3}MnO_4^- + \frac{4}{3}OH^-$$

16. **(c) :** Acidified $KMnO_4$ is decolourised by H_2O_2 in following way :

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$

$5H_2O_2 + 5O \rightarrow 5H_2O + 5O_2$

$2KMnO_4 + 3H_2SO_4 + 5H_2O_2 \rightarrow K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$

Thus,

2 moles of $KMnO_4$, requires 5 moles of H_2O_2

$\therefore$ 1 mole of $KMnO_4$ will require 5/2 moles of H_2O_2

17. **(a) :** $IO_3^- + aI^- + bH^+ \rightarrow cH_2O + dI_2$

Step 1 : $I^- \rightarrow I_2$ (oxidation)

$IO_3^- \rightarrow I_2$ (reduction)

Step 2 : $2IO_3^- + 12H^+ \rightarrow I_2 + 6H_2O$

Step 3 : $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

$2I^- \rightarrow I_2 + 2e^-$

Step 4 : $2IO_3^- + 12H^+ + 10e^- \rightarrow I_2 + 6H_2O$

$[2I^- \rightarrow I_2 + 2e^-]5$

Step 5 : $2IO_3^- + 10I^- + 12H^+ \rightarrow 6I_2 + 6H_2O$

$IO_3^- + 5I^- + 6H^+ \rightarrow 3I_2 + 3H_2O$

On comparing, $a = 5$, $b = 6$, $c = 3$, $d = 3$

18. **(b) :** $2MnO_4^- + Br^- + H_2O \rightarrow 2\overset{+4}{Mn}O_2 + BrO_3^- + 2OH^-$

19. **(b) :** Oxidation state of iron in haemoglobin is +2.

20. **(b) :** $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$

21. **(b) :** Let the oxidation no. of Br be x.

$+1 + x + 4(-2) = 0,\ -7 + x = 0,\ x = +7$

22. **(b) :**

Decrease in O.N. (Reduction)

$$\overset{-2}{N_2}H_4 + 2H_2\overset{-1}{O_2} \longrightarrow \overset{0}{N_2} + 4H_2\overset{-2}{O}$$

Increase in O.N. (Oxidation)

23. **(d) :** Higher the electrode potential, better is the oxidising agent. Since, the electrode potential decreases in the order :

$Ag^+ | Ag\ (+0.80\ V) > Fe^{3+} | Fe^{2+}\ (+0.77\ V) >$

$I_{2(s)} | I^-\ (+0.54\ V) > Cu^{2+} | Cu\ (+0.34\ V)$

Hence, Ag^+ is the strongest oxidising agent.

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24. (d) : Cu cannot liberate H_2 from a solution of dilute HCl as hydrogen is above copper in the electrochemical series.

$$E^\circ_{H^+/\frac{1}{2}H_2} = 0.00\ V;$$

$$E^\circ_{Cu^{2+}/Cu} = +0.34\ V$$

25. (b) : Due to high electronegativity and high heat of dissociation, fluorine oxidises the elements to their highest oxidation state.

26. (a) : Oxygen is the most electronegative element after fluorine. Therefore, in the compounds between oxygen and fluorine, oxygen is found to show positive oxidation state.

e.g., OF_2 : Oxygen difluoride.

Oxidation state of oxygen here is +2.

27. (c) : $SnCl_2$ (stannous chloride) on reaction with mercuric chloride ($HgCl_2$), oxidises to $SnCl_4$ (stannic chloride)

$$SnCl_2 + 2HgCl_2 \rightarrow SnCl_4 + \underset{\text{(Greyish)}}{Hg_2Cl_2}$$

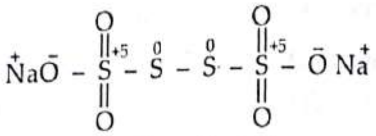
So in this reaction, stannous chloride is acting as reducing agent that reduces Hg (II) to Hg (I) and then to Hg (0)

$$SnCl_2 + Hg_2Cl_2 \rightarrow 2Hg + SnCl_4$$

28. (b) : SO_2 shows both oxidising as well as reducing nature.

The reaction given in assertion is due to oxidising nature of SO_2.

$$2H_2S + SO_2 \rightarrow 2H_2O + 3S$$

29. (a) : 

$$\overset{+}{Na}\bar{O}-\overset{+5}{S}(=O)_2-\overset{0}{S}-\overset{0}{S}-\overset{+5}{S}(=O)_2-\bar{O}\overset{+}{Na}$$

Formal oxidation number of sulphur

$$= \frac{2\times5+2\times0}{4} = 2.5$$

30. (b): Fluorine has higher standard electrode potential (reduction potential) than iodine.

31. (c) : Cl_2 is an oxidising agent. It bleaches the articles permanently by oxidation in presence of moisture.

32. (d) : E° of Cu^{2+}/Cu is + 0.34 V and positive E° means that the redox couple is a weaker reducing agent than the H^+/H_2 couple.

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CHAPTER 9

HYDROGEN

1. Permanent hardness of water can be removed by adding
(a) Na_2CO_3 (b) K
(c) Ca(OCl)Cl (d) Cl_2 *(1994)*

2. Which of the following metals reacts with water?
(a) Copper (b) Nickel
(c) Sodium (d) Silver *(1994)*

3. The volume of 3.0 N H_2O_2 strength is
(a) 16.8 litres (b) 4.2 litres
(c) 33.6 litres (d) 8.4 litres *(1996)*

4. Which of the following is the best scientific method to test presence of water in a liquid?
(a) Use of litmus paper
(b) Taste
(c) Smell
(d) Use of anhydrous copper sulphate *(1999)*

5. The reagent commonly used to determine hardness of water titrimetrically is
(a) oxalic acid
[✓ (b)] disodium salt of EDTA
(c) sodium citrate
(d) sodium thiosulphate. *(2003)*

6. 100 cm^3 of a given sample of H_2O_2 gives 1000 cm^3 of O_2 at S.T.P. The given sample is
(a) 10% H_2O_2
(b) 90% H_2O_2
[✓ (c)] 10 volume H_2O_2
(d) 100 volume H_2O_2 *(2010)*

7. In ice, oxygen atom is surrounded
[✓ (a)] tetrahedrally by 4 hydrogen atoms
(b) octahedrally by 2 oxygen and 4 hydrogen atoms
(c) tetrahedrally by 2 hydrogen and 2 oxygen atoms
(d) octahedrally by 6 hydrogen atoms. *(2011)*

8. Predict the product of reaction of I_2 with H_2O_2 in basic medium.
(a) I^- (b) I_2O_3
(c) IO_3^- (d) I_3^- *(2011)*

9. Strength of H_2O_2 is 15.18 g L^{-1}, then it is equal to
(a) 1 volume (b) 10 volume
(c) 5 volume (d) 7 volume *(2013)*

10. Which of the following reactions increases the production of dihydrogen from synthesis gas?

(a) $CH_{4(g)} + H_2O_{(g)} \xrightarrow[Ni]{1270\text{ K}} CO_{(g)} + H_{2(g)}$

(b) $C_{(s)} + H_2O_{(g)} \xrightarrow{1270\text{ K}} CO_{(g)} + H_{2(g)}$

(c) $CO_{(g)} + H_2O_{(g)} \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_{2(g)} + H_{2(g)}$

(d) $C_2H_6 + 2H_2O \xrightarrow[Ni]{1270\text{ K}} 2CO + 5H_2$

(2014)

11. Which of the following reactions produces hydrogen?
(a) $Mg + H_2O$ (b) $H_2S_2O_8 + H_2O$
(c) $BaO_2 + HCl$ (d) $Na_2O_2 + 2HCl$
(2015)

12. H_2O_2 can be obtained when following reacts with H_2SO_4 except with
(a) BaO_2 (b) PbO_2
(c) Na_2O_2 (d) SrO_2 *(2017)*

ASSERTION AND REASON

13. ***Assertion :*** The O – O bond length in H_2O_2 is shorter than that of O_2F_2.
Reason : H_2O_2 is an ionic compound.
(2003)

14. ***Assertion :*** Sulphur is oxidised by H_2O_2 in presence of Fe (III).
Reason : Fe (III) oxidises sulphur to sulphate. *(2011)*

15. ***Assertion :*** Permanent hardness of water is removed by treatment with washing soda.
Reason : Washing soda reacts with soluble calcium and magnesium chlorides and sulphates in hard water to form insoluble carbonates.

16. ***Assertion :*** H_2O_2 has higher boiling point than water.
Reason : H_2O_2 has stronger dipole-dipole interactions than that shown by water. *(2015)*

Answer Key

1.	(a)	**2.**	(c)	**3.**	(a)	**4.**	(d)	**5.**	(b)	**6.**	(c)	**7.**	(a)	**8.**	(a)
9.	(c)	**10.**	(c)	**11.**	(a)	**12.**	(b)	**13.**	(d)	**14.**	(a)	**15.**	(a)	**16.**	(c)

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EXPLANATIONS

1. **(a) :** When hard water is treated with a certain amount of washing powder (Na_2CO_3) the chlorides and sulphates of calcium and magnesium are converted into their respective carbonates, which get precipitated. As a result of this, the hardness of water is removed.

$$CaSO_4 + Na_2CO_3 \longrightarrow CaCO_3\downarrow + Na_2SO_4$$

2. **(c) :** Sodium reacts with water, yielding NaOH and H_2 gas.

$$2H_2O + 2Na \rightarrow 2NaOH + H_2$$

3. **(a)**

4. **(d) :** $\underset{\text{Blue}}{CuSO_4\cdot 5H_2O} \rightleftharpoons \underset{\text{Pale blue}}{CuSO_4\cdot 3H_2O} \rightleftharpoons$

$$\underset{\text{Bluish white}}{CuSO_4\cdot H_2O} \rightleftharpoons \underset{\text{White}}{CuSO_4}$$

Reaction of water with copper sulphate will produce blue colour so, water can be detected.

5. **(b) :** Disodium salt of ethylenediaminetetraacetic acid has been used for the estimation of M^{2+} metal ions like Mg^{2+}, Ca^{2+}, etc. by complexometric titrations.

In this titration, indicator ions (D^{3-} ions) form red-metal indicator complex, $[MD^-]$ with M^{2+} ions.

$$\text{(i)}\quad \underset{\substack{\text{Metal ion}\\(Mg^{2+}\text{ or }Ca^{2+})}}{M^{2+}} + \underset{\substack{\text{Indicator}\\\text{ion (blue)}}}{D^{3-}} \xrightleftharpoons{pH=10} \underset{\substack{\text{Metal indicator}\\\text{complex (red)}}}{[M^{2+}D]^-}$$

$$\text{(ii)}\quad \underset{\text{(red)}}{[M^{2+}D]^-} + \underset{\text{EDTA ion}}{EDTA^{4-}} \rightleftharpoons \underset{\substack{\text{Metal-EDTA}\\\text{complex}}}{[M^{2+}(EDTA)]^{2-}} + \underset{\text{(blue)}}{D^{3-}}$$

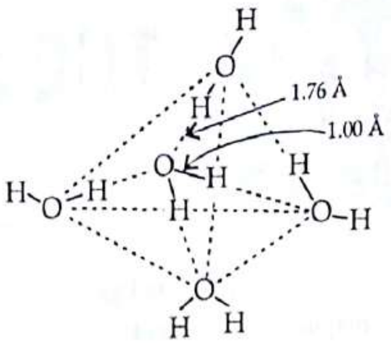
The release of the free indicator ion is marked by a change from red (colour of $[M^{2+}D]^-$ complex) to blue (colour of D^{3-} ion) colour.

6. **(c) :** $\underset{100\text{ mL}}{2H_2O_2} \longrightarrow 2H_2O + \underset{1000\text{ mL}}{O_2}$

or 1 mL of H_2O_2 will give 10 mL of O_2 at STP

Thus, its volume strength is 10 volume.

7. **(a) :** X-ray studies have shown that in ice, four hydrogen atoms tetrahedrally surround each oxygen atom.



Tetrahedral arrangement of water

8. **(a) :** $I_{2(s)} + H_2O_{2(aq)} + 2OH^-_{(aq)} \longrightarrow 2I^-_{(aq)} + 2H_2O_{(l)} + O_{2(g)}$

9. **(c) :** $\text{Volume strength} = \dfrac{5.6 \times \text{Strength in g L}^{-1}}{\text{Eq. wt. of } H_2O_2}$

$$= \frac{5.6 \times 15.18}{17} = 5 \text{ volumes}$$

10. **(c) :** The production of dihydrogen can be increased by reacting carbon monoxide of syngas with steam in the presence of iron chromate as catalyst.

$$CO_{(g)} + H_2O_{(g)} \xrightarrow[\text{Catalyst}]{673\text{ K}} CO_{2(g)} + H_{2(g)}$$

This is called water-gas shift reaction.

11. **(a) :** Alkali and alkaline earth metals react with water to produce hydrogen gas and metal hydroxides. This is due to their high electropositive character.

$$Mg + 2H_2O \longrightarrow Mg(OH)_2 + H_2$$

12. **(b) :** H_2O_2 is prepared by the reaction of peroxide with H_2SO_4. PbO_2 is a dioxide. Hence, it does not give H_2O_2 with dilute H_2SO_4.

13. **(d) :** O_2F_2 has the similar structure as that of H_2O_2 but the O – O bond length is shorter in O_2F_2 than in H_2O_2. This is due to the high electronegativity of attached F-atoms. H_2O_2 is a covalent compound.

14. **(a) :** H_2O_2 oxidises sulphur to sulphate in presence of Fe^{3+} ions.

15. **(a) :** $MCl_2 + Na_2CO_3 \rightarrow MCO_3\downarrow + 2NaCl$

$MSO_4 + Na_2CO_3 \rightarrow MCO_3\downarrow + Na_2SO_4$

(where, M = Mg, Ca)

16. **(c) :** H_2O_2 is more extensively associated by hydrogen bonding than water.

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CHAPTER

10

THE s-BLOCK ELEMENTS

1. $MgCl_2 \cdot 6H_2O$ when heated gives
   (a) magnesium dichloride
   (b) magnesium oxide
   (c) magnesium oxychloride
   (d) magnesium chloride. *(1994)*

2. Which of the following substances is used, in the laboratory, for fast drying of neutral gases?
   (a) Sodium sulphate
   (b) Phosphorus pentoxide
   (c) Sodium phosphate
   (d) Anhydrous calcium chloride *(1998)*

3. The solubility in water of sulphates down the Be group is Be > Mg > Ca > Sr > Ba. This is due to
   (a) decreasing hydration energy
   (b) high ionisation energy
   (c) increase in melting point
   (d) all of these. *(1999)*

4. Which of the following will not undergo hydrolysis in water?
   (a) Ammonium sulphate
   (b) Sodium sulphate
   (c) Calcium sulphate
   (d) All the salts will hydrolyse. *(1999)*

5. The correct order of the increasing ionic character is
   (a) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$
   (b) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$
   (c) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$
   (d) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$ *(1999)*

6. The formula of microcosmic salt and the product obtained by heating it is
   (a) $Na(NH_4)PO_4$, $NaPO_3$
   (b) $Na(NH_4)_2HPO_4$; $NaPO_3$
   (c) $Na(NH_4)HPO_4$, $NaPO_4$
   (d) $Na(NH_4)HPO_4$, $NaPO_3$ *(2000)*

7. Portland cement contains the following amount of CaO
   (a) 5-15% (b) 20-35%
   (c) 61-67% (d) 70-80% *(2000)*

8. Baking soda or baking powder is
   (a) washing soda
   (b) caustic soda
   (c) soda ash
   (d) sodium bicarbonate. *(2000)*

9. NaOH is prepared by the electrolysis of
   (a) aqueous solution of sodium chloride with platinum electrode
   (b) sodium chloride solution with graphite anode and mercury cathode
   (c) sodium carbonate with platinum electrodes
   (d) sodium carbonate with nickel electrodes. *(2000)*

10. The process associated with sodium carbonate manufacture is known as _____ process.
   (a) Chamber (b) Haber
   (c) Le-Blanc (d) Castner *(2000)*

11. Identify the correct statement:
   (a) Elemental sodium can be prepared and isolated by electrolysing an aqueous solution of sodium chloride.
   (b) Elemental sodium is a strong oxidising agent.
   (c) Elemental sodium is insoluble in ammonia.
   (d) Elemental sodium is easily oxidised. *(2000)*

12. Which has lowest thermal stability?
   (a) Li_2CO_3 (b) Na_2CO_3
   (c) K_2CO_3 (d) Rb_2CO_3 *(2000)*

13. Which of the following is soluble in water?
   (a) Be (b) Sr
   (c) Mg (d) Ba *(2001)*

14. The electronic configuration of $1s^2\,2s^2\,2p^5\,3s^1$ shows
   (a) ground state of fluorine atom
   (b) excited state of fluorine atom
   (c) excited state of neon atom
   (d) excited state of O_2^- ion. *(2001)*

15. Which of the following has highest hydration energy?
   (a) $MgCl_2$ (b) $CaCl_2$
   (c) $BaCl_2$ (d) $SrCl_2$ *(2001,2015)*

16. Which of the following reactions produces hydrogen?
   (a) $Mg + H_2O$ (b) $H_2S_4O_8 + H_2O$
   (c) $BaO_2 + HCl$ (d) $Na_2O_2 + 2HCl$

17. The pair whose both species are used in a acid medicinal preparation is (20
   (a) $NaHCO_3$ and $Mg(OH)_2$
   (b) Na_2CO_3 and $Ca(HCO_3)_2$
   (c) $Ca(HCO_3)_2$ and $Mg(OH)_2$
   (d) $Ca(OH)_2$ and $NaHCO_3$

18. Among the following components o which is present in highest amount?
   (a) Ca_2SiO_4 (b) Ca_3SiO
   (c) Al_2O_3 (d) Ca_3Al

19. Formula of microcosmic salt is
   (a) Na_2HPO_4 (b) Na(N
   (c) K_2HPO_4 (d) Na_2

20. The correct order of stability of is
   (a) $KO_2 > RbO_2 > CsO_2$
   (b) $KO_2 > CsO_2 > RbO_2$
   (c) $CsO_2 > RbO_2 > KO_2$
   (d) $RbO_2 > CsO_2 > KO_2$

21. Which of the following th melting point?
   (a) BaF_2 (
   (c) CaF_2

22. Which of the following to give the reaction,
   $M^+_{(g)} \xrightarrow[\text{medium}]{\text{aqueous}} M^+$
   (a) Na
   (c) K

23.

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14. The electronic configuration of $1s^2\ 2s^2\ 2p^5\ 3s^1$ shows
(a) ground state of fluorine atom
(b) excited state of fluorine atom
(c) excited state of neon atom
(d) excited state of O_2^- ion. *(2001)*

15. Which of the following has highest hydration energy?
(a) $MgCl_2$ (b) $CaCl_2$
(c) $BaCl_2$ (d) $SrCl_2$ *(2001, 2015)*

16. Which of the following reactions produces hydrogen?
[✓ (a) $Mg + H_2O$] (b) $H_2S_4O_8 + H_2O$
(c) $BaO_2 + HCl$ (d) $Na_2O_2 + 2HCl$
(2002)

17. The pair whose both species are used in anti-acid medicinal preparation is
(a) $NaHCO_3$ and $Mg(OH)_2$
(b) Na_2CO_3 and $Ca(HCO_3)_2$
(c) $Ca(HCO_3)_2$ and $Mg(OH)_2$
(d) $Ca(OH)_2$ and $NaHCO_3$ *(2006)*

18. Among the following components of cement which is present in highest amount?
(a) Ca_2SiO_4 (b) Ca_3SiO_5
(c) Al_2O_3 (d) $Ca_3Al_2O_6$ *(2007)*

19. Formula of microcosmic salt is
(a) Na_2HPO_4 [✓ (b) $Na(NH_4)HPO_4$]
(c) K_2HPO_4 (d) $Na_2PO_4{\cdot}K_2PO_4$
(2009)

20. The correct order of stability of the superoxides is
(a) $KO_2 > RbO_2 > CsO_2$
(b) $KO_2 > CsO_2 > RbO_2$
[✓ (c) $CsO_2 > RbO_2 > KO_2$]
(d) $RbO_2 > CsO_2 > KO_2$ *(2009)*

21. Which of the following fluorides has the lowest melting point?
(a) BaF_2 (b) SrF_2
(c) CaF_2 (d) BeF_2 *(2009)*

22. Which of the following has the highest tendency to give the reaction,
$M^+_{(g)} \xrightarrow[\text{medium}]{\text{aqueous}} M^+_{(aq)}$?
(a) Na [✓ (b) Li]
(c) K (d) Rb *(2009)*

23. Beryllium and aluminium exhibit many properties which are similar. But the two elements differ in
(a) maximum covalency in compounds
(b) exhibiting amphoteric nature in their oxides
(c) forming covalent halides
(d) forming polymeric hydrides. *(2010)*

24. Which of the following acids will not evolve H_2 gas on reaction with alkali metals?
(a) Hydrazoic acid (b) Perxenic acid
(c) Boric acid (d) None of these
(2010)

25. Which of the following is not hygroscopic?
(a) CsCl (b) $MgCl_2$
(c) $CaCl_2$ (d) LiCl *(2011)*

26. Which is correct order of solubility in water?
(a) $Ba(OH)_2 < Mg(OH)_2$
(b) $BaCO_3 > CaCO_3$
[✓ (c) $CaSO_4 < MgSO_4$]
(d) $Ca(OH)_2 = Mg(OH)_2$ *(2012, 2017)*

27. Bleaching powder does not contain
(a) $CaCl_2$ (b) $Ca(OH)_2$
(c) $Ca(OCl)_2$ (d) $Ca(ClO_3)_2$ *(2013)*

28. Which of the following statements is incorrect?
[✓ (a) Li^+ has minimum degree of hydration.]
(b) The oxidation state of K in KO_2 is +1.
(c) Na is used to make a Na/Pb alloy.
(d) $MgSO_4$ is readily soluble in water.
(2014)

ASSERTION AND REASON

29. ***Assertion***: Helium and beryllium having similar outer electronic configuration of type ns^2.
Reason: Both are chemically inert. *(1994)*

30. ***Assertion***: Na_2SO_4 is soluble in water while $BaSO_4$ is not.
Reason: Lattice energy of $BaSO_4$ exceeds its hydration energy. *(1997)*

31. ***Assertion:*** Alkali metals impart colour to the flame.
Reason: Their ionisation energies are low.
(1995, 1998)

32. ***Assertion :*** Potassium and caesium are used in photoelectric cells.
Reason : Potassium and caesium emit electrons on exposure to light. *(2002)*

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33. ***Assertion :*** Barium is not required for normal biological function in human.
Reason : Barium does not show variable oxidation state. *(2003)*

34. ***Assertion :*** Mg is not present in enamel of human teeth.
Reason : Mg is an essential element for biological functions of human. *(2004)*

35. ***Assertion :*** Addition of NH_4OH to an aqueous solution of $BaCl_2$ in the presence of NH_4Cl (excess) precipitates $Ba(OH)_2$.
Reason : $Ba(OH)_2$ is insoluble in water. *(2005)*

36. ***Assertion :*** In fused state, calcium chloride cannot be used to dry alcohol or NH_3.
Reason : $CaCl_2$ is not a good dessicant. *(2009)*

37. ***Assertion :*** Magnesium is extracted by the electrolysis of fused mixture of $MgCl_2$, NaCl and $CaCl_2$.
Reason : Calcium chloride acts as a reducing agent. *(2010)*

38. ***Assertion :*** $BeSO_4$ is soluble in water while $BaSO_4$ is not.
Reason : Hydration energy decreases down the group from Be to Ba and lattice energy remains almost constant. *(2015)*

39. ***Assertion :*** Generally alkali and alkaline earth metals form superoxides.
Reason : There is a single bond between O and O in superoxides. *(2016)*

40. ***Assertion :*** The carbonate of lithium decomposes easily on heating to form lithium oxide and CO_2.
Reason : Lithium being very small in size polarises large carbonate ion leading to the formation of more stable Li_2O and CO_2. *(2017)*

Answer Key

1.	(b)	**2.**	(a)	**3.**	(a)	**4.**	(d)	**5.**	(b)	**6.**	(d)	**7.**	(c)	**8.**	(d)
9.	(b)	**10.**	(c)	**11.**	(d)	**12.**	(a)	**13.**	(d)	**14.**	(c)	**15.**	(a)	**16.**	(a)
17.	(a)	**18.**	(d)	**19.**	(b)	**20.**	(c)	**21.**	(d)	**22.**	(b)	**23.**	(a)	**24.**	(d)
25.	(a)	**26.**	(c)	**27.**	(d)	**28.**	(a)	**29.**	(c)	**30.**	(a)	**31.**	(a)	**32.**	(a)
33.	(b)	**34.**	(b)	**35.**	(d)	**36.**	(c)	**37.**	(c)	**38.**	(a)	**39.**	(d)	**40.**	(a)

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as a reducing
(2010)
ı water while

ases down the
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alkaline earth

etween O and
(2016)
of lithium
form lithium

mall in size
ading to the
d CO_2.
(2017)

8.	(d)
16.	(a)
24.	(d)
32.	(a)
40.	(a)

EXPLANATIONS

1. **(b) :** $MgCl_2 \cdot 6H_2O \xrightarrow{\text{Heat}} MgCl_2 \cdot 2H_2O \xrightarrow{\Delta} \underset{\text{Magnesium oxychloride}}{MgOCl} + HCl \xrightarrow{\text{Heat}} MgO$

2. **(a) :** Anhydrous sodium sulphate absorbs moisture very efficiently.

3. **(a) :** In the alkaline earth metal group, the small sized metals have high heat of hydration than the larger ones due to the fact that heat of hydration is higher for small sized highly charged cations. So solubility of sulphate of these metals decreases down the group.

4. **(d) :** Ammonium sulphate and sodium sulphate readily hydrolysed in water. Calcium sulphate is sparingly soluble.

5. **(b) :** In the alkaline earth metals group, down the group as the size increases, the ability to lose electrons *i.e.*, ionic character increases. The smaller metal requires more ionisation potential for cation formation.

6. **(d) :** Microcosmic salt is $Na(NH_4)HPO_4$.

$$Na(NH_4)HPO_4 \xrightarrow{\Delta} NaPO_3 + H_2O + NH_3$$

It is prepared by

$$NH_4Cl + Na_2HPO_4 + 4H_2O \rightarrow Na(NH_4)HPO_4.4H_2O + NaCl$$

7. **(c) :** Composition of portland cement is as follows:

Calcium oxide	CaO	61.5%
Silica	SiO_2	22.5%
Alumina	Al_2O_3	7.5%
Magnesium oxide	MgO	2.5%
Ferric oxide	Fe_2O_3	2.0%
Potassium oxide	K_2O	1.5%
Sulphur trioxide	SO_3	1.0%
Sodium oxide	NaO_2	1.5%

8. **(d)**　　9. **(b)**

10. **(c) :** Le-Blanc process : It involves the following steps :

$$NaCl + H_2SO_4 \rightarrow NaHSO_4 + HCl$$
$$NaHSO_4 + NaCl \rightarrow Na_2SO_4 + HCl$$
$$Na_2SO_4 + CaCO_3 + 4C \rightarrow Na_2CO_3 + CaS + 4CO$$

Na_2CO_3 is separated from CaS by dissolving it in water.

11. **(d) :** Elemental sodium can lose electrons very easily so, it acts as strong reducing agent.

$$Na_{(s)} \rightarrow Na^+ + e^-$$

It dissolves in liquid ammonia giving out a conducting and reducing solution. It cannot be prepared by electrolysing sodium chloride solution in water as sodium reacts violently with water.

12. **(a) :** Since the alkali metals are highly electropositive, their carbonates are highly stable towards heat. As the electropositivity increases down the group, the stability is in order of :

$$Cs_2CO_3 > Rb_2CO_3 > K_2CO_3 > Na_2CO_3 > Li_2CO_3$$

Lithium carbonate decomposes on heating.

13. **(d) :** 'Ba' reacts with water giving soluble hydroxide (Baryata) solution. While Mg and Sr forms insoluble hydroxides and Be does not react even with boiling water.

14. **(c) :** The ground state electronic configuration of neon atom (Z = 10) is

$$1s^2, 2s^2, 2p^6$$

Therefore, first excited state of neon will be

$$1s^2, 2s^2, 2p^5, 3s^1$$

15. **(a) :** Smaller sized and highly charged metal ions have higher hydration energy. In the alkaline earth metals, the hydration energy for the compact and charged ions is greater than the large sized charged ions. Therefore, order of hydration energy in this group is

$$Be^{2+} > Mg^{2+} > Ca^{2+} > Sr^{2+} > Ba^{2+}.$$

16. **(a) :** Alkali and alkaline earth metals react with water to produce hydrogen gas and metal hydroxide. This is due to their high electropositive character.

$$2Na + 2H_2O \rightarrow 2NaOH + H_2$$
$$Mg + 2H_2O \rightarrow Mg(OH)_2 + H_2$$

17. **(a)**

18. **(d) :** Tricalcium aluminate $3CaO.Al_2O_3$ - Calcium aluminate cements are hydraulic cements made primarily from limestone and bauxite. They are well adapted for use in refractory (high temperature resistant) concretes *e.g.*, furnace linings.

19. **(b)**

20. **(c) :** Stability of superoxides increases with increase in size and electropositivity of the metal. Hence, the order is $CsO_2 > RbO_2 > KO_2$.

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21. (d) : Being covalent, BeF_2 has the lowest melting point (800°C) while other fluorides melt at around 1300°C.

22. (b) : Because of its smallest size, Li^+ has highest hydration energy and hence, the highest stability of hydrated Li^+ ion.

23. (a) : Be exhibits maximum covalency of four whereas Al shows maximum covalency of six.

24. (d) : None of these acids evolve H_2 gas with alkali metals.

25. (a) : CsCl is not hygroscopic in nature while $MgCl_2$, $CaCl_2$ and LiCl are hygroscopic in nature.

26. (c) : $MgSO_4$ is readily soluble in water. The solubility of the sulphates of alkaline earth metals decreases with increase in size of the central metal ion. The greater hydration enthalpies of Mg^{2+} ions overcome the lattice enthalpy factor and therefore, $MgSO_4$ is more soluble in water.

27. (d) : Bleaching powder is a mixture of calcium hypochlorite, $Ca(OCl)_2$ and the basic chloride $CaCl_2$, H_2O with some slaked lime, $Ca(OH)_2$.

28. (a) : The hydration enthalpies of alkali metal ions decreases with increase in ionic sizes Hence, the order is $Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$.
Therefore, Li^+ has maximum degree of hydration.

29. (c) : Helium : $Z = 2$; $1s^2$
Beryllium : $Z = 4$; $1s^2$, $2s^2$
Helium is an inert gas while beryllium is reactive due to unfilled $2p$ valence shells.

30. (a) : Solubility decreases down the group:
$BeSO_4 > MgSO_4 > CaSO_4 > SrSO_4 > BaSO_4$
As hydration energy decreases due to increase in size of the cation while the lattice energy remains the same.

31. (a) : Alkali metals have very low value of ionisation energy as compared to other metals. So, valence electrons easily get excited and impart colour to flame.

32. (a) : The valence shell electron in the alkali metals is so loosely held that even the low energy photons (light) can eject this electron from the metal surface. This phenomenon is called photoelectric effect. K and Cs are used in photoelectric cells which are sensitive to blue light.

33. (b) : Ba - [Xe] $6s^2$
It shows oxidation state of +II only.

34. (b) : Enamel, the hardest substance of the body is composed of fluorine not magnesium. Magnesium is an essential element as it acts as a co-factor of many enzymes of glycolysis and a number of other metabolic reactions.

35. (d) : $Ba(OH)_2$ is soluble in water.

36. (c) : $CaCl_2$ forms addition products with alcohol and ammonia. ($CaCl_2.4NH_3$ or $CaCl_2.\ 4C_2H_5OH$).

37. (c) : NaCl and $CaCl_2$ are added to provide conductivity to the electrolyte and also to lower the fusion temperature of anhydrous $MgCl_2$.

38. (a)

39. (d) : Only K, Rb and Cs from alkali metals form superoxides and superoxides possess three electron bond $(:\ddot{O}-\ddot{O}:)^{-}$.

40. (a)

CHAPTER 11

The *p*-Block Elements (Group 13 and 14)

1. Which of the following bonds is shown in silicone?
(a) Si–C–Si–C–Si (b) Si–Si–Si–Si
(c) –Si–O–Si–O–Si– (d) Si–C–Si–O–Si
(1994, 2009)

2. Which of the following is an alum?
(a) $FeSO_4 \cdot (NH_4)_2SO_4 \cdot 6H_2O$
(b) $NaAlO_2$
(c) $Na_2SO_4 \cdot Al_2(SO_4)_3 \cdot 24H_2O$
(d) $KCl \cdot MgCl_2 \cdot 6H_2O$ *(1994)*

3. Which of the following glasses is the most heat resistant?
(a) Bottle glass (b) Flint glass
(c) Water glass (d) Pyrex glass
(1994)

4. Which of the following is the least stable and its existence is doubtful?
(a) SnI_4 (b) CI_4
(c) PbI_4 (d) GeI_4 *(1995)*

5. The number of unpaired electrons in $1s^2 2s^2 2p^2$ is
(a) 3 (b) 1
(c) 5 (d) 2 *(1995)*

6. Hydrolysis of beryllium carbide produces
(a) acetylene (b) methane
(c) ethene (d) none of these.
(1996)

7. Silicon is an important constituent of
(a) alloys (b) rocks
(c) vegetables (d) animals. *(1996)*

8. Which of the following is an alloy of aluminium?
(a) Magnalium (b) Duralumin
(c) Brass (d) both (a) and (b)
(1997)

9. The BCl_3 is a planar molecule whereas NCl_3 is pyramidal, because
(a) B–Cl bond is more polar than N–Cl bond
(b) N–Cl bond is more covalent than B–Cl bond
(c) nitrogen atom is smaller than boron atoms
(d) BCl_3 has no lone pair but NCl_3 has a lone pair of electrons. *(1997)*

10. Potash alum is used as
(a) catalyst (b) disinfectant
(c) mordant (d) coolant. *(1997)*

11. Which of the following does not show electrical conduction?
(a) Diamond (b) Graphite
(c) Sodium (d) Potassium
(1999)

12. Which of the following does not act as a Lewis acid?
(a) BF_3 (b) $SnCl_4$
(c) CCl_4 (d) SF_3 *(2000)*

13. Hardest compound of boron is
(a) magnesium boride
(b) aluminium boride
(c) boron nitride
(d) boron carbide. *(2001)*

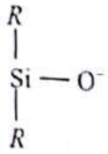
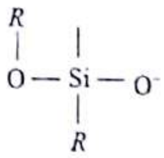
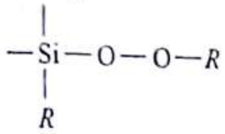
14. Which of the following is stable (inert) to fire?
(a) CCl_4 (b) C_2H_5OH
(c) CH_4 (d) C_4H_{10} *(2001)*

15. Which of the following is only acidic in nature?
(a) $Be(OH)_2$ (b) $Mg(OH)_2$
(c) $B(OH)_3$ (d) $Al(OH)_3$ *(2004)*

16. Which of the following imparts green colour to the burner flame?
(a) $B(OMe)_3$ (b) $Na(OMe)$
(c) $Al(OPr)_3$ (d) $Sn(OH)_2$ *(2004)*

17. In diborane, the two H – B – H angles are nearly
(a) 60°, 120° (b) 95°, 120°
(c) 95°, 150° (d) 120°, 180°
(2005)

18. Borax is used as a cleansing agent because on dissolving in water it gives
(a) alkaline solution
(b) acidic solution
(c) bleaching solution
(d) basic solution. *(2006)*

19. The repeating unit in silicone is
(a) SiO_2
(b)

$R_2Si{-}O^-$
(c)

$O{-}SiR_2{-}O^-$
(d)

$-SiR{-}O{-}O{-}R$ *(2007)*

20. Which of the following is an example of chain silicates?
(a) Kaolinite (b) Zircon
(c) Benitoite (d) Diopside *(2009)*

21. Which of the element shows +4 oxidation state?
(a) Sn (b) Ra
(c) Fr (d) Sc *(2009)*

22. Incorrect statement about Ge is
(a) GeO_2 is weakly acidic
(b) $Ge(OH)_2$ is amphoteric
(c) $GeCl_2$ is more stable than $GeCl_4$
(d) Ge–Ge bond energy is lesser than that of Si – Si. *(2009)*

23. Which material is used as a neutron moderator?
(a) Graphite (b) Cadmium
(c) Boron (d) Uranium *(2011)*

24. Iodine oxidises sodium borohydride to give
(a) B_2H_6 (b) sodium hydride
(c) HI (d) I_3 *(2011)*

25. The wrong statement about fullerene is
(a) it has 5-membered carbon ring
(b) it has 6-membered carbon ring
(c) it has sp^2 hybridization
(d) it has 5-membered rings more than 6-membered rings. *(2011)*

26. For silicon which is not correct?
(a) It is a type of silicate.
(b) It is thermally unstable.
(c) It is hydrophilic.
(d) Repeating unit is R_2SiO. *(2012)*

27. Which of the following is not sp^2 hybridised?
(a) Graphite (b) Graphene
(c) Fullerene (d) Dry ice *(2014)*

28. The pair of amphoteric hydroxides is
(a) $Be(OH)_2$, $Al(OH)_3$
(b) $Al(OH)_3$, LiOH
(c) $B(OH)_3$, $Be(OH)_2$
(d) $Be(OH)_2$, $Mg(OH)_2$ *(2015)*

29. Which of the following reactions does not take place?
$BF_3 + F^- \longrightarrow BF_4^-$ ...(I)
$BF_3 + 3F^- \longrightarrow BF_6^{3-}$ ...(II)
$AlF_3 + 3F^- \longrightarrow AlF_6^{3-}$ ...(III)
(a) Only (I) (b) Only (II)
(c) Only (III) (d) Only (I) and (III) *(2016)*

30. Hydride of boron occurs as B_2H_6 but B_2Cl_6 does not exist. This is because
(a) $p\pi$–$d\pi$ back bonding is possible in B_2H_6 but not in B_2Cl_6
(b) boron and hydrogen have almost equal values of electronegativity
(c) boron and chlorine have almost equal atomic sizes
(d) small hydrogen atoms can easily fit in between boron atoms but large chlorine atoms do not. *(2017)*

31. Among the following substituted silanes, the one which will give rise to cross-linked silicone polymer on hydrolysis is
(a) R_3SiCl (b) R_4Si
(c) $RSiCl_3$ (d) R_2SiCl_2 *(2017)*

32. Select the correct options from the following :
(a) Graphene is an atomic layer of graphite.
(b) Graphene is an atomic layer composed of sp^2-hybridised carbon.
(c) Chemical bonds in graphite are similar in strength to that of diamond.
(d) All of these. *(2017)*

ASSERTION AND REASON

33. ***Assertion***: The first ionization energy of aluminium is lower than that of magnesium.
Reason: The ionic radius of aluminium is smaller than that of magnesium. *(1994)*

34. ***Assertion :*** Pb^{4+} can be reduced easily to Pb^{2+}.
Reason: Pb^{2+} is paramagnetic. *(2000)*

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35. *Assertion*
Reason :

36. *Assertion*
Reason :
state.

37. *Assertion*
Reason :
pair of el
Si strong

38. *Assertio*
for Al(III
Reason

39. *Asserti*
nature.
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1. (c
9. (c
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41. (

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35. ***Assertion :*** Diamond is a bad conductor.
Reason : Graphite is a good conductor. *(2002)*

36. ***Assertion :*** PbI_4 is a stable compound.
Reason : Iodide stabilizes higher oxidation state. *(2003)*

37. ***Assertion :*** SiF_6^{2-} is known but $SiCl_6^{2-}$ is not.
Reason : Size of fluorine is small and its lone pair of electrons interacts with *d*-orbitals of Si strongly. *(2005)*

38. ***Assertion :*** Borax bead test is not suitable for Al(III).
Reason : Al_2O_3 is insoluble in water. *(2005)*

39. ***Assertion :*** Silicones are hydrophobic in nature.
Reason : Si – O – Si linkages are moisture sensitive. *(2006)*

40. ***Assertion :*** SnI_4 is an orange solid.
Reason : The colour arises due to charge transfer. *(2007)*

41. ***Assertion :*** Al forms $[AlF_6]^{3-}$ but B does not form $[BF_6]^{3-}$.
Reason : B does not react with fluorine. *(2009)*

42. ***Assertion :*** Diamond and graphite do not have the same crystal structure.
Reason : Diamond is crystalline while graphite is amorphous. *(2012)*

43. ***Assertion :*** Al becomes passive in conc. HNO_3.
Reason : Conc. HNO_3 has no action on aluminium metal. *(2014)*

44. ***Assertion :*** H_3BO_3 is a weak acid.
Reason : Water extracts the proton of H_3BO_3. *(2016)*

Answer Key

1.	(c)	**2.**	(c)	**3.**	(d)	**4.**	(c)	**5.**	(d)	**6.**	(b)	**7.**	(b)	**8.**	(d)
9.	(d)	**10.**	(b)	**11.**	(a)	**12.**	(c)	**13.**	(d)	**14.**	(a)	**15.**	(c)	**16.**	(a)
17.	(b)	**18.**	(a)	**19.**	(b)	**20.**	(d)	**21.**	(a)	**22.**	(c)	**23.**	(a)	**24.**	(a)
25.	(d)	**26.**	(c)	**27.**	(d)	**28.**	(a)	**29.**	(b)	**30.**	(d)	**31.**	(c)	**32.**	(d)
33.	(a)	**34.**	(b)	**35.**	(b)	**36.**	(d)	**37.**	(a)	**38.**	(b)	**39.**	(c)	**40.**	(a)
41.	(c)	**42.**	(c)	**43.**	(c)	**44.**	(c)								

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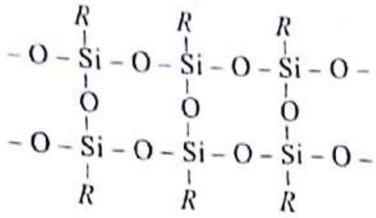
EXPLANATIONS

1. **(c) :** Silicones are organic silicon polymers containing Si–O–Si linkages.



(cross linked silicon)

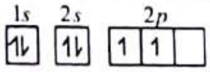
2. **(c) :** The term alum is used for all the double sulphates having the composition, $M_2SO_4.M'_2(SO_4)_3.24H_2O$, where M stands for monovalent basic radicals such Na^+, K^+, etc. and M' for trivalent basic radicals such as Al^{3+}, Cr^{3+}, etc.

3. **(d) :** Boron sesquioxide, B_2O_3 is used in making borosilicates, heat resistant pyrex glass. Pyrex glass contains 14% B_2O_3.

4. **(c) :** Non-existence of PbI_4 can be explained on the basis of strong oxidising nature of Pb^{4+}. The I^- ions are reducing agents, *i.e.*, in presence of this ion, Pb^{4+} ion is reduced to Pb^{2+} ion.

$$Pb^{4+} + 2I^- \rightarrow Pb^{2+} + I_2$$

5. **(d) :** There are two unpaired electrons.



6. **(b) :** Beryllium carbide (Be_2C), on hydrolysis evolves methane.

$$Be_2C + 4H_2O \rightarrow 2Be(OH)_2 + CH_4$$

7. **(b) :** Silicon is present in soil, rocks, etc. in the form of silica (SiO_2) or silicates or aluminosilicates.

8. **(d) :** Magnalium : 95% Al, 5% Mg. It is used in the construction of airships, weighing balance and pistons of motor engine.

Duralumin : 95% Al, 4% Cu, 0.5% Mg, 0.5% Mn. It is used in aeroplanes and automobile parts.

9. **(d) :** As there is no lone pair on boron in BCl_3, therefore, no repulsion takes place. But there is a lone pair on nitrogen in NCl_3 therefore, repulsion takes place. Thus, BCl_3 is planar molecule but NCl_3 is pyramidal molecule.

10. **(b) :** Potash alum is $K_2SO_4.Al_2(SO_4)_3.24H_2O$. It is used for disinfectant purposes.

11. **(a) :** Potassium and sodium are metals so have mobile electrons. In graphite, each of the C-atom is covalently bonded to three other C-atoms so one valence electron is available for electrical and thermal conduction but there is no mobile electron present in diamond as each C-atom is bonded to four other C-atoms by covalent bonds.

12. **(c) :** Lewis acids are those molecules which can accept electron pair and those who can donate electron pairs are called Lewis base.

CCl_4 molecule does not have vacant d-orbital where it can accept pair of electrons so CCl_4 cannot act as Lewis acid.

13. **(d) :** Boron carbide is written as B_4C. It is produced by reducing B_2O_3 with C at 1600° C. Fibres of B_4C have an enormous tensile strength and are used to make bullet-proof clothing.

14. **(a) :** CCl_4 is non-inflammable due to strong C—Cl bonds in it. Therefore, it is inert to fire and used as a fire-extinguisher under the name of pyrene.

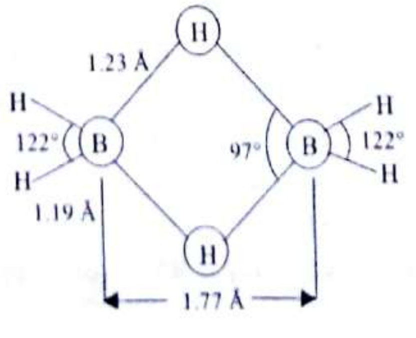
15. **(c) :** The solution of $B(OH)_3$ in water acts as a weak acid. Thus, it reacts with NaOH solution to produce the sodium salt.

$$\begin{aligned} B(OH)_3 + NaOH &\rightleftharpoons Na^+[B(OH)_4]^- \\ &\rightleftharpoons \underset{\text{sodium metaborate}}{Na^+\,BO_2^- + 2H_2O} \end{aligned}$$

16. **(a) :** The vapours of trialkyl borates $B(OR)_3$ or R_3BO_3 burn with green edged flame. This is a qualitative test for borates.

$$2BO_3^- + 3H_2SO_4 \rightarrow 3SO_4^{2-} + 2H_3BO_3$$
$$H_3BO_3 + 3ROH \rightarrow R_3BO_3 + 3H_2O$$

17. **(b) :** Dilthey in 1921 proposed a bridge structure for diborane. Four hydrogen atoms, two on the left and two on the right, known as terminal hydrogens and two boron atoms lie in the same plane. Two hydrogen atoms forming bridges, one above and other below, lie in a plane perpendicular to the rest of molecule.



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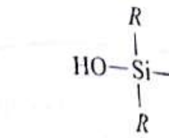
18. **(a) :** Borax diss
solutions.

$Na_2B_4O_7 + 7H_2$

Borax is therefore
cleansing agent.

19. **(b) :** R_2SiO— i



20. **(d) :** Diopside

21. **(a)**

22. **(c) :** $GeCl_4$ is
greater tendency

23. **(a) :** Neutron
of neutrons by
neutrons. *e.g.*, w

24. **(a) :** The ox
iodine in diglym

$2NaBH_4 +$

25. **(d) :** Fuller
rings and 20 s
membered ring

26. **(c) :** Silic

27. **(d) :** Solid
undergoes *sp*-

28. **(a) :** Al a
their diagonal

29. **(b) :** BF_3
$[BF_4^-]$ in whi
its C.N. beyo
orbitals in its
hybridisation
can extend i
of d-orbitals

30. **(d)**

33. **(a) :** T
configuratio
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as compare

34. **(b) :**
not partic
effect. Si
the group

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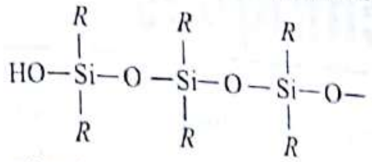
18. (a) : Borax dissolves in water to give alkaline solutions.

$$Na_2B_4O_7 + 7H_2O \rightarrow \underset{\text{strong base}}{2NaOH} + \underset{\text{weak acid}}{4H_3BO_3}$$

Borax is therefore used as a water softener and cleansing agent.

19. (b) : R_2SiO— is the repeating unit in silicone.



20. (d) : Diopside → $CaMg[(SiO_3)_2]$

21. (a)

22. (c) : $GeCl_4$ is more stable than $GeCl_2$. Ge has greater tendency to form +4 state than +2 state.

23. (a) : Neutron moderators slow down the speed of neutrons by collisions. They do not absorb neutrons. *e.g.*, water and graphite.

24. (a) : The oxidation of sodium borohydride with iodine in diglyme gives diborane.

$$2NaBH_4 + I_2 \xrightarrow{\text{Diglyme}} B_2H_6 + 2NaI + H_2$$

25. (d) : Fullerene consists of 12 five-membered rings and 20 six-membered rings. So it has five membered rings less than six membered rings.

26. (c) : Silicon is hydrophobic.

27. (d) : Solid CO_2 is dry ice in which carbon atom undergoes *sp*-hybridisation.

28. (a) : Al and Be show similar properties due to their diagonal relationship.

29. (b) : BF_3 forms complex halides of the type $[BF_4^-]$ in which B atom has C.N. 4, it cannot extend its C.N. beyond 4 due to the non-availability of *d*-orbitals in its configuration. Hence, BF_6^{3-} ion (sp^3d^2 hybridisation) is not formed. On the other hand, Al can extend its C.N. beyond 4 due to the availability of *d*-orbitals in its configuration.

30. (d) **31. (c)** **32. (d)**

33. (a) : The elements of group III have $ns^2\ np^1$, configuration. Since *p*-electrons are held less tightly than *s*-electrons. The first IE of each element is low as compared to the first IE of alkaline earth metal.

34. (b) : When ns^2 electrons of outermost shell do not participate in bonding, it is called inert pair effect. Since the inert pair effect increases down the group, therefore Pb^{2+} compounds are more stable than Pb^{4+} compounds. Pb^{4+} compounds thus, act as oxidizing agent.

35. (b) : In diamond, each carbon atom is in sp^3 hybridised state and linked to four other carbon atoms tetrahedrally by covalent bonds. Since there is no mobile electron present, diamond is bad conductor of heat and electricity.

In graphite each carbon atom is in sp^2 hybridised state and is linked to three other carbon atoms in a hexagonal planar structure. The π-electrons are free to move throughout the entire layers, therefore graphite is good conductor of heat and electricity.

36. (d) : Due to screening effect, down the group, lower oxidation states become more stable. *e.g.*, Pb(II) is more stable than Pb(IV). But small, highly electronegative elements like F-atoms can somewhat stabilise its higher oxidation state.

37. (a)

38. (b) : Borax bead test is not suitable for Al(III) because its oxidising as well as reducing flame is colourless in both hot as well as cold.

Alumina is insoluble in water as they exist in hydrated form like $Al_2O_3{\cdot}2H_2O$, $Al_2O_3{\cdot}H_2O$ etc.

39. (c) : Silicones are strongly water repellent.

40. (a) : The orange colour of SnI_4 is caused by the absorption of blue light, the reflected light thus containing a higher proportion of red and orange. The energy absorbed in this way causes the transfer of an electron from I to Sn. Since transferring an electron to another atom is transferring a charge, such spectra are called charge transfer spectra.

41. (c) : B does not have vacant *d*-orbitals (sub-shell) in its valence shell.

42. (c) : In diamond, C-atoms are sp^3 hybridized while in graphite, they are sp^2 hybridized. Diamond and graphite both are crystalline forms of carbon.

43. (c) : Al metal is rendered passive when treated with conc. HNO_3 because concentrated HNO_3 is oxidising agent and produces a protective layer of oxide on the surface of aluminium metal.

44. (c) : H_3BO_3 is a very weak monobasic acid ($K_a = 5.6 \times 10^{-10}$) but it does not act as a proton donor. It behaves as a Lewis acid *i.e.*, it accepts a pair of electrons from OH^- ion of H_2O.

$$H-OH + B(OH)_3 \longrightarrow [B(OH)_4]^- + H^+$$

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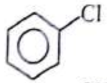
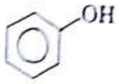
CHAPTER

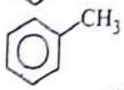
12

Organic Chemistry - Some Basic Principles and Techniques

1. The molecular mass of a volatile substance may be measured by
   (a) Liebig's method
   (b) Hofmann's method
   (c) Victor Meyer's method
   (d) Both (b) and (c). *(1994)*

2. Which of the following compounds will be most easily attacked by an electrophile?
   (a) 
   (b) 

   (c) 

   (d) 

   (1994)

3. Heterolytic fission of an organic covalent bond gives only
   (a) anion (b) free radicals
   (c) cation (d) both (a) and (c). *(1994)*

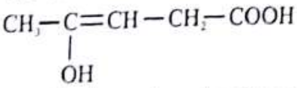
4. The fractional distillation is used in
   (a) petroleum (b) crude oil
   (c) coal tar (d) all of these. *(1995)*

5. The most suitable method for the separation of a 1 : 1 mixture of *ortho* - and *para* - nitrophenols is
   (a) filtration (b) sublimation
   (c) crystallisation (d) steam distillation. *(1997)*

6. The isomers, which can be converted into another form by rotation of the molecules around single bond, are
   (a) conformers
   (b) enantiomers
   (c) diastereomers
   (d) geometrical isomers. *(1997)*

7. If 1, 3-dibromopropane reacts with zinc and NaI, the product obtained is
   (a) propene (b) propane
   (c) cyclopropane (d) hexane. *(1997)*

8. When the hybridisation state of carbon atom changes from sp^3, sp^2 and sp, the angle between the hybridized orbitals
   (a) decreases considerably
   (b) increases progressively
   (c) may increase or decrease
   (d) remains constant. *(1998)*

9. The IUPAC name of the compound
   
   $CH_3-\underset{OH}{\underset{|}{C}}=CH-CH_2-COOH$
   (a) 4-hydroxy-4-pentenoic acid
   (b) 4-hydroxy-3-pentenoic acid
   (c) hydroxy pentenoic acid
   (d) 4-hydroxy-4-methyl-3-ene-pentanoic acid. *(1998)*

10. Beilstein test is used for the detection of
    (a) Cl^- (b) Na
    (c) N_2 (d) CO_2 *(1999)*

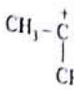
11. Gasoline is a mixture of hydrocarbons containing
    (a) C_3 to C_5 carbon atoms
    (b) C_7 to C_9 carbon atoms
    (c) C_{12} to C_{16} carbon atoms
    (d) C_{14} to C_{18} carbon atoms. *(1999)*

12. The percentage of CH_4 in coal gas is
    (a) 10-15% (b) 25-35%
    (c) 2-5% (d) 35-50% *(2000)*

13. The IUPAC name of $CH\equiv C-CH=CH-CH_3$ is
    (a) pent-1-yn-3ene (b) pent-3-en-1-yne
    (c) pent-2-en-4 yne (d) 3-en-pent-1 yne. *(2000)*

14. If 0.189 g of a chlorine containing organic compound gives 0.287 g of silver chloride, then the percentage of chlorine in the organic compound is
    (a) 35.47 (b) 35.57
    (c) 37.57 (d) 45.37 *(2001)*

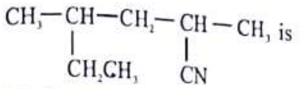
---

15. Which of the following is mos carbocation?
    (a) CH_3^+
    (b) CH_3CH_2
    (c) $CH_3\overset{+}{C}HCH_3$
    (d) 
    $CH_3-\overset{+}{\underset{Cl}{\underset{|}{C}}}$
    (199

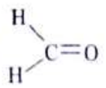
16. Hybridisation in $\dot{C}H_3$, $\dot{C}H_3$ and respectively
    (a) sp^2, sp^2, sp^3 (b) $sp^2, sp^3,$
    (c) sp^3, sp^3, sp^2 (d) $sp^3, sp^2,$

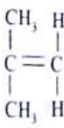
17. The IUPAC name of the compound h formula CCl_3CH_2CHO is
    (a) 2, 2, 2-trichloropropanal
    (b) 1, 1, 1-trichloropropanal
    (c) 3, 3, 3-trichloropropanal
    (d) 1, 2, 1-trichloromethanal. *(199*

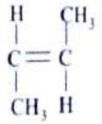
18. Which of the following alkanes is active?
    (a) 3-Methylhexane
    (b) Propane
    (c) 2, 3, 4-Trimethylpentane
    (d) 2-Methylbutane *(199*

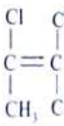
19. IUPAC name of
    
    $CH_3-\underset{CH_2CH_3}{\underset{|}{CH}}-CH_2-\underset{CN}{\underset{|}{CH}}-CH_3$ is
    (a) 2-cyano-4-methylhexane
    (b) 2-dimethyl-4-cyanopentane
    (c) 3-methyl-5-cyanohexane
    (d) 2-cyano-3-methylhexane.

20. Which of the following is a chiral co
    (a) Hexane
    (b) *n*-Butane
    (c) Methane
    (d) 2,3,4-Trimethylhexane

21. Which of the following has the high moment?
    (a) 

    (b) 

    (c) 

    (d) 

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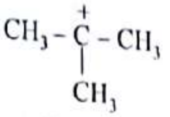
15. Which of the following is most stable carbocation?

(a) CH_3^+ (b) $CH_3CH_2\overset{+}{C}H_2$

(c) $CH_3\overset{+}{C}HCH_3$ (d)



$CH_3-\overset{+}{\underset{CH_3}{C}}-CH_3$

(1996, 2001)

16. Hybridisation in $\dot{C}H_3$, $\overset{+}{C}H_3$ and $\overset{-}{C}H_3$ are respectively

(a) sp^2, sp^2, sp^3 (b) sp^2, sp^3, sp^3

(c) sp^3, sp^3, sp^2 (d) sp^3, sp^2, sp^2

(2001)

17. The IUPAC name of the compound having the formula CCl_3CH_2CHO is

(a) 2, 2, 2-trichloropropanal

(b) 1, 1, 1-trichloropropanal

(c) 3, 3, 3-trichloropropanal

(d) 1, 2, 1-trichloromethanal. *(1995, 2001)*

18. Which of the following alkanes is optically active?

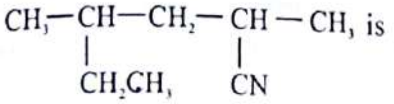
(a) 3-Methylhexane

(b) Propane

(c) 2, 3, 4-Trimethylpentane

(d) 2-Methylbutane *(1996, 2001)*

19. IUPAC name of



$CH_3-\underset{CH_2CH_3}{CH}-CH_2-\underset{CN}{CH}-CH_3$ is

(a) 2-cyano-4-methylhexane

(b) 2-dimethyl-4-cyanopentane

(c) 3-methyl-5-cyanohexane

(d) 2-cyano-3-methylhexane. *(2002)*

20. Which of the following is a chiral compound?

(a) Hexane

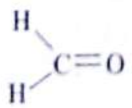
(b) *n*-Butane

(c) Methane

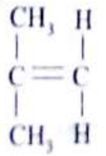
(d) 2,3,4-Trimethylhexane *(2002)*

21. Which of the following has the highest dipole moment?

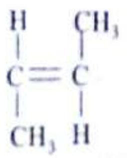
(a)



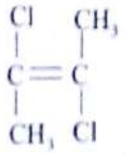
(b)



(c)



(d)



(2002)

22. The number of σ- and π-bonds present in pent-4-ene-1-yne is

(a) 10, 3 (b) 4, 9

(c) 3, 10 (d) 9, 4 *(2002)*

23. The compound used for gravimetric estimation of copper(II) is

(a) $Cu_2(SCN)_2$ (b) Cu_2O

(c) Cu_2I_2 (d) Cu_2CO_3 *(2003)*

24. Among the following, the achiral amino acid is

(a) 2-ethylalanine

(b) 2-methylglycine

(c) 2-hydroxymethylserine

(d) tryptophan. *(2003, 2016)*

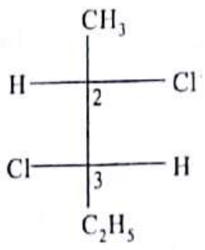
25. The most reactive nucleophile among the following is

(a) CH_3O^- (b) $C_6H_5O^-$

(c) $(CH_3)_2CHO^-$ (d) $(CH_3)_3CO^-$

(2003)

26. The absolute configuration of the following compound is



(a) 2 *S*, 3 *R* (b) 2 *S*, 3 *S*

(c) 2 *R*, 3 *S* (d) 2 *R*, 3 *R* *(2003)*

27. The dipole moment is the highest for

(a) *trans*-2-butene

(b) 1,3-dimethylbenzene

(c) acetophenone

(d) ethanol. *(2004)*

28. Among the following the strongest nucleophile is

(a) C_2H_5SH (b) CH_3COO^-

(c) CH_3NH_2 (d) $NCCH_2^-$ *(2005)*

29. Among the following the most stable compound is

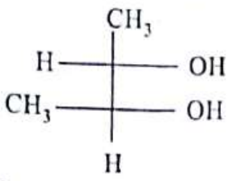
(a) *cis*-1,2-cyclohexanediol

(b) *trans*-1,2-cyclohexanediol

(c) *cis*-1,3-cyclohexenediol

(d) *trans*-1,3-cyclohexanediol. *(2005)*

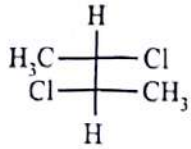
30. Correct configuration of the following is

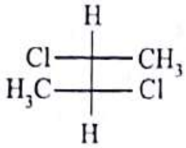


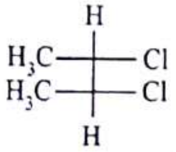
(a) 1*S*, 2*S* (b) 1*S*, 2*R*
(c) 1*R*, 2*S* (d) 1*R*, 2*R* *(2005)*

31. Among the following which one can have a *meso* form?
(a) $CH_3CH(OH)CH(Cl)C_2H_5$
(b) $CH_3CH(OH)CH(OH)CH_3$
(c) $C_2H_5CH(OH)CH(OH)CH_3$
(d) $HOCH_2CH(Cl)CH_3$ *(2006)*

32. Which of the following is optically inactive?

(a)


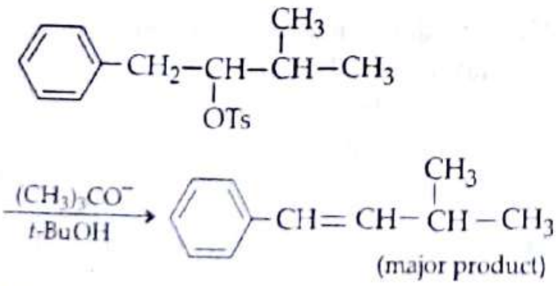
(b)


(c)


(d) none of these. *(2007)*

33. Decreasing order of stability of ions is
(i) $CH_3-\overset{+}{C}H-CH_3$
(ii) $CH_3-\overset{+}{C}H-OCH_3$
(iii) $CH_3-\overset{+}{C}H-COCH_3$
(a) (i) > (ii) > (iii) (b) (ii) > (i) > (iii)
(c) (ii) > (iii) > (i) (d) (iii) > (i) > (ii) *(2009)*

34. Consider the reaction,



The correct explanation is
(a) the product is formed due to nucleophilic substitution
(b) the product is formed according to Saytzeff's rule
(c) conjugated double bond product is formed due to higher stability because of resonance stabilisation
(d) $(CH_3)_3CO$ is a better leaving group. *(2009)*

35. In solvents like DMSO, acetonitrile, F^- ion of dissolved NaF is more reactive than in methyl alcohol because
(a) CH_3OH is more polar than DMSO and CH_3CN
(b) CH_3OH is less polar than DMSO and CH_3CN
(c) unsolvated F^- ion in DMSO or CH_3CN acts more efficiently as nucleophile
(d) –OH group is a better leaving group than F^- ion. *(2009)*

36. How many geometrical isomers are possible in the following two alkenes?
(i) $CH_3-CH=CH-CH=CH-CH_3$
(ii) $CH_3-CH=CH-CH=CH-Cl$
(a) 4 and 4 (b) 4 and 3
(c) 3 and 3 (d) 3 and 4 *(2009)*

37. 2-Phenylethylbromide when heated with NaOEt, elimination takes place. No deuterium exchange takes place when the reaction is carried out in C_2H_5OD solvent. The mechanism will be
(a) E1 elimination (b) E_2 elimination
(c) E1cB elimination (d) E_2 or E1cB. *(2009)*

38. The strained tetracyclic alkane is isomerized thermally to the cyclic alkene. The reaction involves
(a) free radical (b) carbocation
(c) carbanion (d) carbene. *(2010)*

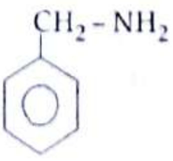
39. Decreasing order of nucleophilicity is
(a) $OH^- > NH_2^- > CH_3O^- > R\dot{N}H_2$
(b) $NH_2^- > OH^- > CH_3O^- > RNH_2$
(c) $NH_2^- > CH_3O^- > OH^- > RNH_2$
(d) $CH_3O^- > NH_2^- > OH^- > RNH_2$ *(2011)*

40. Find the number of stereoisomers of 1, 2-dihydroxycyclopentane.
(a) 1 (b) 2
(c) 3 (d) 4 *(2011)*

41.

(I)

(II)



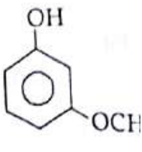
(III)

(IV)

Organic Chemistry-Some

The correct d
(a) I > II > II
(c) II > III >

42. The correct d



(I)

(a) II > IV
(c) III > II

43. S_N2 reactic
(a) CH_3C
(b) CH_3-
(c) CH_2=
(d) Ph –

44. Number
(a) 2
(c) 4

45. pK_a in
substitu
then "x"
(a) –C
(c) –C

46. The p
determ
(a) ch
(b) cr
(c) m
(d) bo

47. The II
(CH$_3$)
(a) 2
(b) 1
(c) 2
(d) 3

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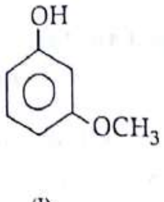
The correct decreasing order of pK_b is

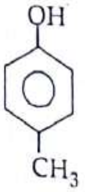
(a) I > II > III > IV (b) III > IV > II > I

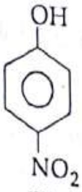
(c) II > III > IV > I (d) IV > II > I > III

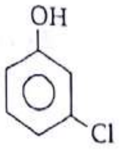
(2011)

42. The correct decreasing order of pK_a is


(I)


(II)


(III)


(IV)

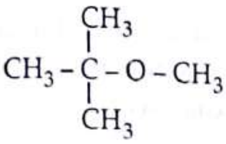
(a) II > IV > I > III (b) IV > II > III > I

(c) III > II > IV > I (d) IV > I > II > III

(2011)

43. S_N2 reaction readily occurs in

(a) $CH_3CH_2-O-CH_3$

(b) 
$CH_3-C(CH_3)_2-O-CH_3$

(c) $CH_2=CH-CH_2-O-CH_3$

(d) $Ph-CH_2-O-CH_2-CH_3$ *(2011)*

44. Number of isomers of C_5H_6

(a) 2 (b) 3

(c) 4 (d) 5 *(2012)*

45. pK_a increases in benzoic acid when substituent "x" is bonded at *para*-position, then "x" is

(a) $-COOH$ (b) $-NO_2$

(c) $-CN$ (d) $-OCH_3$ *(2012)*

46. The purity of an organic compound is determined by

(a) chromatography

(b) crystallisation

(c) melting or boiling point

(d) both (a) and (c). *(2014)*

47. The IUPAC name of the given compound is $(CH_3)_3CCH_2C(CH_3)_3$

(a) 2, 3, 4, 4-tetramethylpentane

(b) 1, 2, 2, 4-tetramethylpentene

(c) 2, 2, 4, 4-tetramethylpentane

(d) 3, 3-dimethylpentane. *(2014)*

48. Lassaigne's test for the detection of nitrogen fails in

(a) $H_2N-CO-NHNH_2\cdot HCl$

(b) $NH_2-NH_2\cdot HCl$

(c) $C_6H_5-NH-NH_2\cdot HCl$

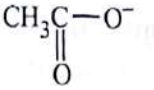
(d) $C_6H_5CONH_2$ *(2015)*

49. Which of the following is an electrophile?

(a) CCl_2 (b) CH_3^-

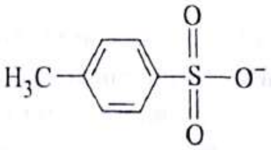
(c) H_2O (d) NH_3 *(2017)*

50. Arrange the following nucleophiles in the decreasing order of nucleophilicity :

(*A*) 
$CH_3C(=O)-O^-$

(*B*) CH_3O^-

(*C*) CN^-

(*D*) 

(a) *C*, *B*, *A*, *D* (b) *A*, *B*, *C*, *D*

(c) *D*, *C*, *B*, *A* (d) *B*, *C*, *A*, *D*

(2017)

ASSERTION AND REASON

51. ***Assertion :*** The Duma's method is more applicable to nitrogen containing organic compounds than the Kjeldahl's method.

Reason : The Kjeldahl's method does not give satisfactory results for compounds in which nitrogen is directly linked to oxygen. *(1995, 2016)*

52. ***Assertion :*** Cyclobutane is less stable than cyclopentane.

Reason : Presence of 'bent bonds' causes "loss of orbital overlap". *(1995)*

53. ***Assertion :*** The term tautomerism was introduced by Maxwell in order to explain the chemical reactivity of a substance according to two possible structures.

Reason : Metamers can also be chain isomers or position isomers. *(1999)*

54. ***Assertion :*** Maleic acid shows geometrical isomerism.

Reason : It has different group attached to $-C=C-$ bond. *(2000)*

55. ***Assertion :*** *Cis*-1,3-dihydroxycyclohexane exists in boat conformation.

Reason : In the chair form, there will be no hydrogen bonding between the two hydroxyl groups. *(2003)*

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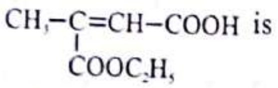
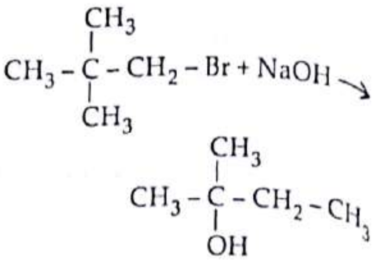
56. ***Assertion :*** Diastereomers have different physical properties.
Reason : They are non-superimposable mirror images. *(2006)*

57. ***Assertion :*** The lactic acid shows the geometrical isomerism.
Reason : Lactic acid has carbon-carbon double bond. *(2007)*

58. ***Assertion :*** Tertiary carbonium ions are generally formed more easily than primary carbonium ions.
Reason : Hyperconjugation as well as inductive effect due to additional alkyl groups stabilize tertiary carbonium ions. *(2008)*

59. ***Assertion :*** Electromeric effect is brought into play only at the requirement of the reagent.
Reason : It is a temporary effect in which bond pair is shifted to one of the constituent atoms. *(2009)*

60. ***Assertion :*** 
$CH_3-\underset{COOC_2H_5}{C}=CH-COOH$ is 3-carbethoxy- 2-butenoic acid.
Reason : Principal functional group gets lowest number followed by double bond or triple bond. *(2010)*

61. ***Assertion :*** 
$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-CH_2-Br + NaOH \rightarrow CH_3-\underset{OH}{\overset{CH_3}{C}}-CH_2-CH_3$
Reason : It follows with the formation of more stable carbocation. *(2011)*

62. ***Assertion :*** *Ortho* and *para*-nitrophenol can be separated by steam distillation.
Reason : *Para*-nitrophenol is steam volatile due to intramolecular hydrogen bonding. *(2014)*

63. **Assertion :** CN^- ion is an ambident nucleophile.
Reason : Nucleophiles are electron rich species. *(2015)*

64. **Assertion :** Thiophene present in commercial benzene as an impurity can be removed by shaking the mixture with cold concentrated H_2SO_4.
Reason : Thiophene is a heterocyclic aromatic compound. *(2017)*

Answer Key

1.	(d)	**2.**	(c)	**3.**	(d)	**4.**	(d)	**5.**	(d)	**6.**	(a)	**7.**	(c)	**8.**	(b)
9.	(b)	**10.**	(a)	**11.**	(b)	**12.**	(b)	**13.**	(b)	**14.**	(c)	**15.**	(d)	**16.**	(a)
17.	(c)	**18.**	(a)	**19.**	(a)	**20.**	(d)	**21.**	(a)	**22.**	(a)	**23.**	(a)	**24.**	(c)
25.	(d)	**26.**	(b)	**27.**	(c)	**28.**	(a)	**29.**	(d)	**30.**	(a)	**31.**	(b)	**32.**	(c)
33.	(b)	**34.**	(c)	**35.**	(c)	**36.**	(d)	**37.**	(b)	**38.**	(a)	**39.**	(c)	**40.**	(c)
41.	(d)	**42.**	(a)	**43.**	(a)	**44.**	(b)	**45.**	(d)	**46.**	(d)	**47.**	(c)	**48.**	(b)
49.	(a)	**50.**	(d)	**51.**	(b)	**52.**	(a)	**53.**	(c)	**54.**	(a)	**55.**	(d)	**56.**	(c)
57.	(d)	**58.**	(a)	**59.**	(a)	**60.**	(a)	**61.**	(a)	**62.**	(c)	**63.**	(b)	**64.**	(b)

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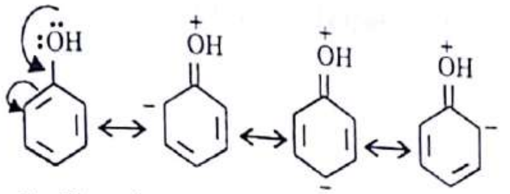
EXPLANATIONS

1. **(d) :** According to Avogadro's hypothesis, the mass of 22.4 L of the vapour of any volatile substance at NTP is equal to the molecular mass of the substance.

2. **(c) :** –OH group in phenol can release electrons to the ring better than $-CH_3$ group in toluene. Cl atom has electron withdrawing effect which inhibits electrophilic attack.



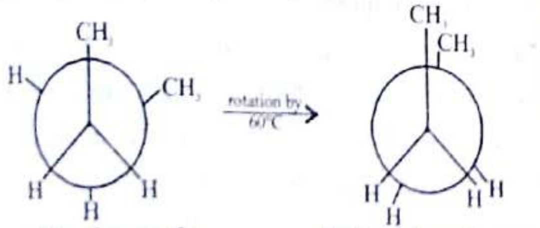
3. **(d) :** Heterolytic fission : Unequal distribution of bonded pair of electrons after cleavage.

$$A-B \longrightarrow \underset{\text{Anion}}{\overset{-}{A}} + \underset{\text{Cation}}{B^+}$$

4. **(d) :** Fractional distillation : In this process, the distillate is collected in fractions under different temperature, *e.g.*, it is used these days for distillation of coal tar, petroleum, and crude oil, etc.

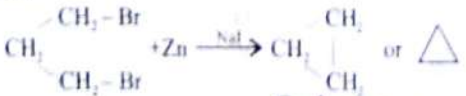
5. **(d) :** Steam distillation is employed as there is a large difference between boiling points of *ortho* and *para*-nitrophenols. This is due to the presence of intramolecular H-bonding in the case of *o*-nitrophenol (so low b.pt.) and intermolecular H-bonding in *p*-nitrophenol (so high b.pt.).

6. **(a) :** Conformers are obtained by rotating molecules around σ-bonds between C-atoms.
e.g., $CH_3-CH_2-CH_2-CH_3$



Gauche conformer Eclipsed conformer

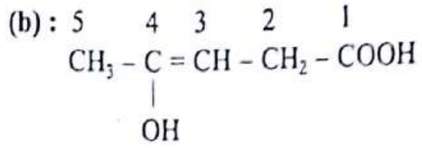
7. **(c) :** α, γ-Dihalides when treated with sodium or zinc form cycloalkanes. Reaction is called Freund reaction.



Cyclopropane

8. **(b) :** In sp^3 hybridisation, bond angle = 109°
In sp^2 hybridisation, bond angle = 120°
In sp hybridisation, bond angle = 180°

9. **(b) :**



$$\overset{5}{C}H_3-\underset{\underset{OH}{|}}{\overset{4}{C}}=\overset{3}{C}H-\overset{2}{C}H_2-\overset{1}{C}OOH$$

Therefore, IUPAC name is
4-hydroxy-3-penten-1-oic acid.

10. **(a) :** Beilstein's test : A small quantity of organic compound is taken on the flattened end of Cu wire and introduced in the flame. A green or blue colour indicates halogens.

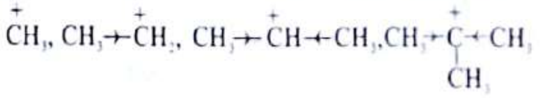
11. **(b)**

12. **(b) :** In coal gas, methane composition ranges from 25 to 35%.

13. **(b) :** $\overset{1}{C}H\equiv\overset{2}{C}-\overset{3}{C}H=\overset{4}{C}H-\overset{5}{C}H_3$
IUPAC name : Pent-3-ene-1-yne.

14. **(c) :** Percentage of chlorine in AgCl
$= \frac{35.5}{143.35}\times 100 = 24.74\%$
Weight of chlorine in 0.287 g AgCl
$= \frac{24.74}{100}\times 0.287 = 0.0710$ g
Percentage of chlorine in 0.189 g organic compound
$= \frac{0.0710}{0.189}\times 100 = 37.568\% \approx 37.57\%$

15. **(d) :** Carbocation is more stable if it is bonded to electron releasing group which somewhat stabilises the carbocation. So more the number of electron releasing groups, more is the stability.



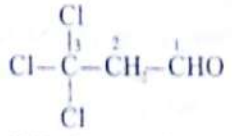
$$\overset{+}{C}H_3,\ CH_3\rightarrow\overset{+}{C}H_2,\ CH_3\rightarrow\overset{+}{C}H\leftarrow CH_3,\ CH_3\rightarrow\underset{\underset{CH_3}{|}}{\overset{+}{C}}\leftarrow CH_3$$

(least stable) (most stable)

16. **(a) :** $\dot{C}H_3$ (methyl free radical) has planar structure with sp^2 hybridisation of 'C' atom. The odd electron is present in unhybridised $2p_z$ orbital.
$\overset{+}{C}H_3$ (methyl carbonium ion) also has trigonal planar structure (sp^2).

$\overset{-}{C}H_3$ (methyl carbanion) has tetrahedral structure (sp^3) and one of the hybrid orbitals contains the lone pair of electrons.

17. **(c) :**



$$Cl-\underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{\overset{3}{C}}}-\overset{2}{C}H_2-\overset{1}{C}HO$$

Therefore, IUPAC name is 3,3,3-trichloropropanal.

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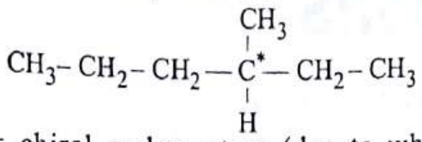
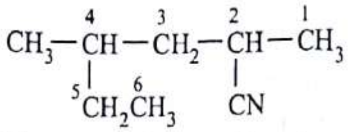
18. **(a)** : 3-Methylhexane is



$CH_3-CH_2-CH_2-\overset{CH_3}{\underset{H}{C^*}}-CH_2-CH_3$

C* = chiral carbon atom (due to which the compound is optically active).

19. **(a)** :



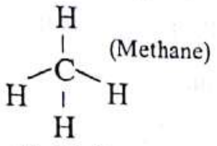
$\overset{4}{C}H_3-\overset{}{C}H(\overset{5}{C}H_2\overset{6}{C}H_3)-\overset{3}{C}H_2-\overset{2}{C}H(CN)-\overset{1}{C}H_3$

∴ IUPAC name is 2-cyano-4-methylhexane.

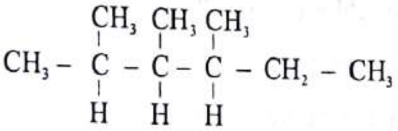
20. **(d)** : Chiral compound contains one or more 'chiral' carbon atoms. Chiral carbon atoms usually are bonded to four different atoms or group of atoms.

$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ (Hexane)
(Achiral)

$CH_3-CH_2-CH_2-CH_3$ (*n*-Butane)
(Achiral)



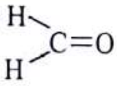
(Methane)
(Achiral)



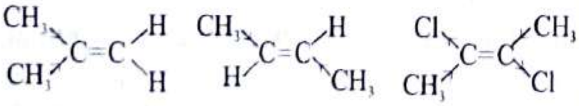
$CH_3-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-\overset{CH_3}{\underset{H}{C}}-CH_2-CH_3$

(Chiral)
(2, 3, 4-Trimethylhexane)

21. **(a)** :



The electronegative oxygen atom is a strong electron withdrawing group. So there is polarity in the carbonyl compounds. This polarity is even greater than in the asymmetric alkene.



(Some polarity) (Polarity is compensated) (Polarity cancels out)

22. **(a)** : Pent-4-ene-1-yne

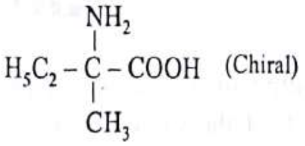
$\overset{1}{C}H\equiv\overset{2}{C}-\overset{3}{C}H_2-\overset{4}{C}H=\overset{5}{C}H_2$

No. of (σ)-bonds = 4 (C–C) + 6(C–H) = 10
No. of π-bonds = 1 (C=C) + 2(C≡C) = 3

23. **(a)** : Copper thiocyanate, $Cu_2(SCN)_2$ is used to estimate copper gravimetrically.

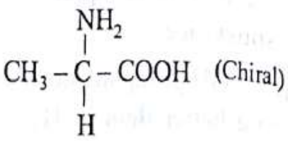
$$2Cu^{2+} + SO_3^{2-} + 2SCN^- + H_2O \rightarrow 2CuSCN + H_2SO_4$$

24. **(c)** : 2-Ethylalanine ;



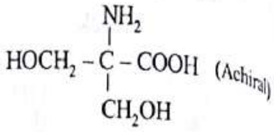
$H_5C_2-\overset{NH_2}{\underset{CH_3}{C}}-COOH$ (Chiral)

2-Methylglycine;



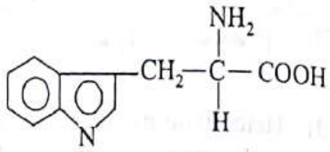
$CH_3-\overset{NH_2}{\underset{H}{C}}-COOH$ (Chiral)

2-Hydroxymethylserine;



$HOCH_2-\overset{NH_2}{\underset{CH_2OH}{C}}-COOH$ (Achiral)

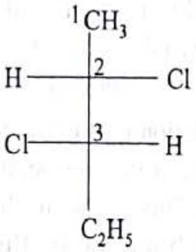
Tryptophan ;



(Chiral)

25. **(d)** : More the number of attached methyl groups, better is the nucleophilicity due to +*I*-effect.

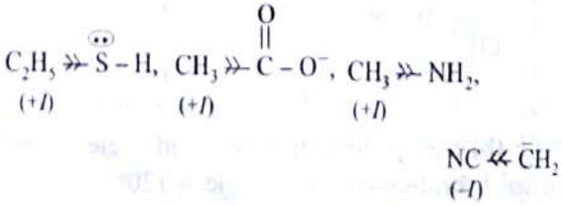
26. **(b)** :



Nomenclature is according to Cahn-Ingold-Prelog method *i.e.*, priority rule.

27. **(c)** : The value of dipole moment of acetophenone is 3 debye, which is maximum among the given compounds.

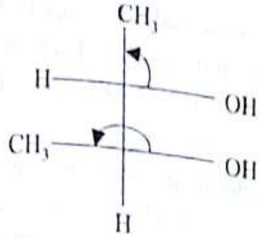
28. **(a)** : Nucleophiles are those substances which can donate a pair of electrons. These can be neutral or negative. The nucleophilic power depends on the tendency of species to donate electrons. This is more, when an electron releasing group (+*I* group) is present. Among the alkyl groups, those have higher number of C-atoms will release more electrons, hence ethyl > methyl.



$C_2H_5 \gg \ddot{S}-H$, $CH_3 \gg \overset{O}{\overset{\|}{C}}-O^-$, $CH_3 \gg NH_2$, $NC \ll CH_2$
(+*I*) (+*I*) (+*I*) (–*I*)

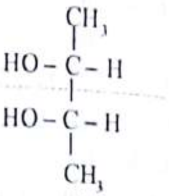
29. **(d)**

30. **(a) :**



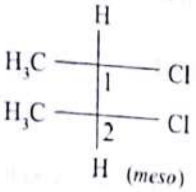
Following the procedure outlined under 'Golden Rule' the absolute configuration is 1*S*, 2*S*.

31. **(b) :**



meso form

32. **(c) :** Due to internal compensation, this compound is optically inactive.



(*meso*)

33. **(b) :** The dispersal of positive charge stabilizes the carbocation. More the number of electron donating groups, greater is the dispersal of positive charge and therefore, more is the stability of carbocation.

So, the order is

$$\mathrm{CH_3-\dot{C}H-OCH_3 > CH_3-\dot{C}H-CH_3 > CH_3-\dot{C}H-COCH_3}$$

34. **(c) :** $\mathrm{(CH_3)_3CO^-}$ is a better base than a nucleophile. Hence, elimination occurs. The product formed is resonance stabilised.

35. **(c) :** In methyl alcohol, F^- ion is solvated but in DMSO or $\mathrm{CH_3CN}$ (aprotic solvent) F^- ion is not solvated. Unsolvated F^- ion acts more efficiently as a nucleophile.

36. **(d) :** When the ends of alkene containing *n* double bonds are different, the number of geometrical isomers is 2^n. Thus for

$$\mathrm{CH_3-CH=CH-CH=CH-Cl}$$

Number of geometrical isomers $= 2^2 = 4$

When the ends of alkene containing *n* double bonds are same, then the number of geometrical isomers $= 2^{n-1} + 2^{p-1}$

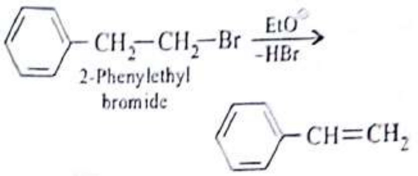
where, $p = \frac{n}{2}$ for even *n* and $\frac{n+1}{2}$ for odd *n*, thus

For, $\mathrm{CH_3-CH=CH-CH=CH-CH_3}$

Number of geometrical isomers

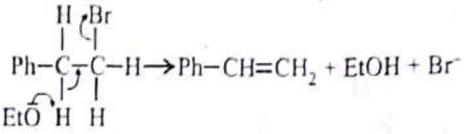
$$= 2^{2-1} + 2^{\frac{2}{2}-1} = 2^1 + 2^0 = 2 + 1 = 3$$

37. **(b):**

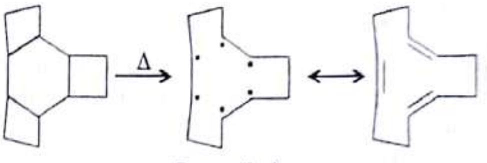


It is a primary bromide. So it will undergo elimination either by E2 or E1cB. Since there is no deuterium exchange in $\mathrm{C_2H_5OD}$ solvent,

C − H bond is not broken to form carbanion. Hence, the actual mechanism is E2 only.



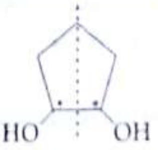
38. **(a) :**



Free radical

39. **(c) :** If the nucleophilic atoms are in the same row of the periodic table, nucleophilicity is approximately in order of basicity. So, the order is $\mathrm{NH_2^- > CH_3O^- > OH^- > RNH_2}$.

40. **(c) :** Symmetrical molecule



Number of chiral carbon atoms = 2 (even)

Number of stereoisomers $= 2^{n-1} + 2^{\frac{n}{2}-1}$

$$= 2^{2-1} + 2^{\frac{2}{2}-1} = 2^1 + 2^0 = 2 + 1 = 3$$

41. **(d) :** Substituent with strong +*R* effect, +*I* effect and weaker −*I* effect increases the basicity. Hence pK_b decreases. Also, alkylamines are stronger bases than arylamines.

42. **(a) :** Weaker acids have higher pK_a. $-\mathrm{OCH_3}$ at *meta*-position exerts only −*I* effect, hence increases the acidity.

−*I* effect order : $-\mathrm{NO_2} > -\mathrm{OCH_3} > -\mathrm{Cl}$.

$-\mathrm{CH_3}$ has +*I* effect.

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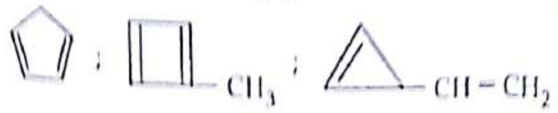
43. **(a)**

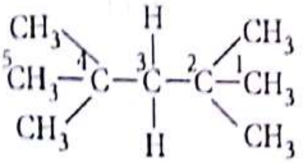
44. **(b)** : Isomers of C_5H_6 :



45. **(d)** : Larger the value of pK_a, smaller will be its acidity. Out of the four groups, $-COOH$, $-NO_2$ and $-CN$ are e^- withdrawing which makes benzoic acid more acidic whereas $-OCH_3$ is e^- donating which reduces the acidity (makes H^+ less easily available). pK_a value increases if $-OCH_3$ is present at *para*-position of benzoic acid.

46. **(d)** : Most of the pure compounds have sharp melting and boiling points. Chromatographic and spectroscopic techniques are the new methods of checking the purity.

47. **(c)** :

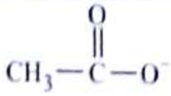


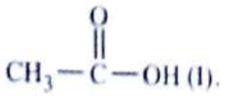
2,2,4,4- Tetramethylpentane

48. **(b)** : Lassaigne's test is given by those nitrogenous compounds in which carbon is also present along with nitrogen.
In $NH_2-NH_2{\cdot}HCl$, carbon is absent, so it does not give Lassaigne's test.

49. **(a)** : Electron deficient species or electron acceptors are called electrophiles. Hence, out of the given species, CCl_2, has only $6e^-$ with carbon so, it is an electrophile.

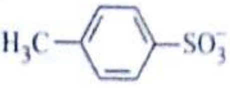
50. **(d)** : Conjugate base (nucleophile) is strong if acid is weak and *vice-versa*.

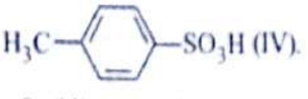
(A)  $CH_3-\overset{\overset{O}{||}}{C}-O^-$ is a conjugate base of

 $CH_3-\overset{\overset{O}{||}}{C}-OH$ (I).

(B) CH_3O^- is a conjugate base of CH_3OH (II).

(C) CN^- is a conjugate base of HCN (III).

(D)  is a conjugate base of

 (IV).

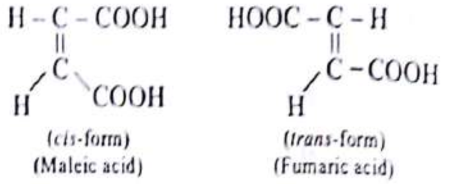
Order of acidic nature is IV > I > III > II.
Hence, the decreasing order of nucleophilicity is B > C > A > D.

51. **(b)** : Duma's method can be applied in case of all nitrogenous compounds. But Kjeldahl's method cannot be used in case of nitro, azo and azoxy compounds.

52. **(a)** : In cyclobutane, there is angle strain as bond angle (C–C–C) is close to 90°. Due to this kind of angle, overlapping of orbitals gets affected.

53. **(c)** : Metamers differ in nature of alkyl groups attached to the same functional group.
e.g., $CH_3-O-C_3H_7$ Methyl propyl ether $C_2H_5-O-C_2H_5$ Diethyl ether

54. **(a)** : Geometrical isomerism is possible when different groups are attached to the double bonded carbon atoms. *e.g.*, maleic acid and fumaric acid are geometrical isomers.

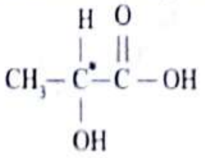


(*cis*-form) (Maleic acid) (*trans*-form) (Fumaric acid)

55. **(d)** : *Cis*-1,3-dihydroxycyclohexane exists in chair form as intramolecular H-bonding is possible only in chair form.

56. **(c)** : Stereoisomers which are not mirror images of each other are called diastereomers.
Diastereomers have different physical properties.

57. **(d)** : 2-Hydroxy propanoic acid is known as lactic acid. It has the following structure:



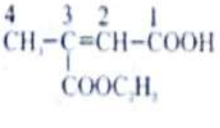
$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C^*}}-\overset{\overset{O}{||}}{C}-OH$$

It has no carbon-carbon double bond and hence cannot show geometrical isomerism. However, it shows optical isomerism due to the presence of a chiral carbon atom.

58. **(a)**

59. **(a)**

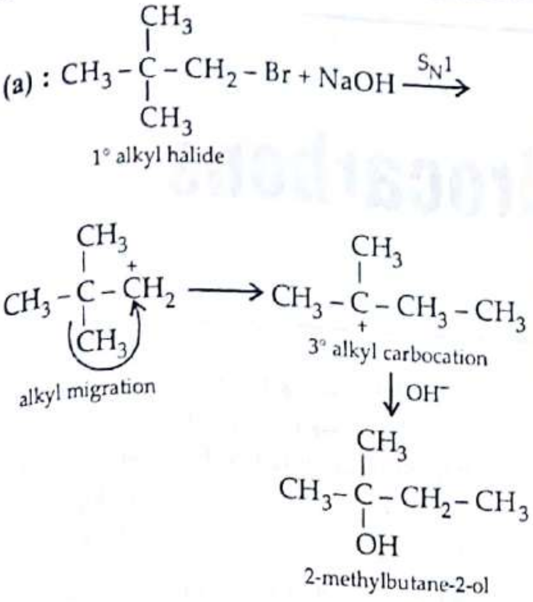
60. **(a)** :



$$\overset{4}{C}H_3-\underset{\underset{COOC_2H_5}{|}}{\overset{3}{C}}=\overset{2}{C}H-\overset{1}{C}OOH$$

Here since $-COOH$ is the principal functional group, it gets the lowest number than the secondary functional group (3-carbethoxy). So it is 3-carbethoxy-2-butenoic acid.

61. **(a) :**



62. **(c) :** *o*-Nitrophenol is steam volatile due to intramolecular hydrogen bonding while *p*-nitrophenol is less volatile due to intermolecular hydrogen bonding.

63. **(b) :** Nucleophilic species which have more than one site of reaction are called ambident nucleophiles.

$$:\overset{-}{C}\equiv N: \longleftrightarrow :C=\ddot{N}:^{-}$$

64. **(b) :** On shaking with concentrated H_2SO_4 thiophene being more reactive undergoes sulphonation and the thiophene-2-sulphonic acid thus formed dissolves in concentrated H_2SO_4.

CHAPTER

13

Hydrocarbons

1. When propyne is treated with aqueous H_2SO_4, in the presence of $HgSO_4$, the product formed is
   (a) acetone (b) ether
   (c) aldehyde (d) propanal. *(1994)*

2. The type of isomerism not exhibited by alkenes is
   (a) chain isomerism (b) metamerism
   (c) position isomerism
   (d) stereoisomerism. *(1994)*

3. The formation of 2-butene as a major product by dehydration of 2-butanol is in accordance with
   (a) Blanc rule (b) Huckel rule
   (c) Markownikoff's rule
   (d) Saytzeff's rule. *(1994)*

4. The incomplete combustion of CH_4 gives
   (a) $CO + H_2O$ (b) $CO + H_2$
   (c) $CO + N_2O$ (d) $CO + N_2$ *(1995)*

5. In the presence of mercuric ion and conc. sulphuric acid, the reaction of acetylene with water produces
   (a) $CH_3-CO-CH_3$ (b) CH_3-CHO
   (c) CH_3-CH_2-OH (d) CH_3-COOH
   (1995)

6. Ozonolysis of acetylene gives
   (a) HCHO (b) CH_3CHO
   (c) CHO–CHO (d) none of these.
   (1996)

7. In which of the following methane is formed?
   (a) $CH_3COOH \xrightarrow{[H]}$
   (b) $CH_3COOH \xrightarrow{NaOH/CaO}$
   (c) $CH_3COOH \xrightarrow{[O]}$
   (d) $CH_3CH_2COOH \xrightarrow{NaOH/CaO}$ *(1997)*

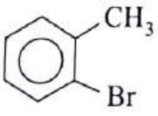
8. Formation of polyethylene, from calcium carbide, takes place as follows:
   $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$;
   $C_2H_2 + H_2 \longrightarrow C_2H_4$;
   $n(C_2H_4) \longrightarrow (-CH_2-CH_2-)_n$. The amount of polyethylene obtained from 64.1 kg of CaC_2 is
   (a) 7 kg (b) 14 kg
   (c) 21 kg (d) 28 kg *(1997)*

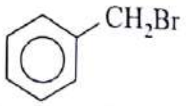
9. Which of the following is not an aromatic compound?
   (a) Benzene (b) Cyclohexane
   (c) *Ortho* xylene (d) Picric acid *(1997)*

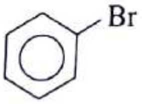
10. Baeyer's reagent is used in the laboratory for
    (a) detection of glucose
    (b) reduction process
    (c) oxidation process
    (d) detection of double bond. *(1998)*

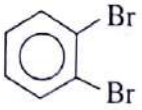
11. The reaction:
    benzene + methyl halide $\xrightarrow{\text{Anhy. AlCl}_3}$ toluene, is known as
    (a) Perkin's reaction
    (b) Wurtz reaction
    (c) Kolbe's reaction
    (d) Friedel-Crafts reaction. *(1998)*

12. Which of the following compounds is 2-bromotoluene?

(a) 

(b) 

(c) 

(d) 

(1998)

13. The most reactive compound for the electrophilic nitration, is
    (a) benzoic acid (b) nitrobenzene
    (c) benzene (d) toluene. *(1998)*

14. Which of the following is the most stable alkene?
    (a) $CH_2=CHR$ (b) $RCH=CHR$
    (c) $R_2C=CR_2$ (d) $CH_2=CH_2$
    (1998)

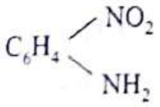
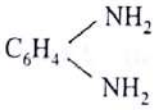
15. The propene reacts with HBr to form
(a) hexane (b) bromopropane
(c) propane (d) ethane. *(1999)*

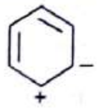
16. $C_6H_6 \xrightarrow[H_2SO_4]{HNO_3} X \xrightarrow[FeCl_3]{Cl_2} Y$. In the above sequence Y can be
(a) 3-nitrochlorobenzene
(b) 1-nitrochlorobenzene
(c) 4-nitrochlorobenzene
(d) none of these. *(1999, 2008)*

17. Toluene can be oxidised to benzoic acid by
(a) H_2SO_4 (b) $KMnO_4$
(c) $K_2Cr_2O_7$ (d) both (b) and (c). *(1999)*

18. If benzene reacts with Cl_2 in presence of ultraviolet light then which of the following is formed?
(a) CCl_4 (b) C_6Cl_6
(c) C_6H_5Cl (d) $C_6H_6Cl_6$ *(1999)*

19. The meta-directing group in the following is
(a) $-OH$ (b) $-NH_2$
(c) $-CH_3$ (d) $-NO_2$ *(1999)*

20. Identify the product in the reaction.
$C_6H_6 \xrightarrow[Reflux]{HNO_3/H_2SO_4}$ intermediate compound $\xrightarrow{Sn/HCl}$ product.
(a) $C_2H_5NO_2$ (b) $C_6H_4(NO_2)_2$
(c) 
$C_6H_4(NO_2)(NH_2)$
(d) 
$C_6H_4(NH_2)_2$ *(2000)*

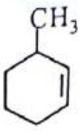
21. Which of the following is aromatic?
(a) 
(b) 
(c) 
(d) 
(2001,2008)

22. Rate determining step in nitration of benzene is
(a) formation of NO_2^+
(b) formation of carbocation
(c) replacement of H atom
(d) none of these. *(2001)*

23. Action of acetylene on dilute H_2SO_4 gives
(a) acetic acid (b) acetaldehyde
(c) acetone (d) acetoacetic ester. *(2002)*

24. Which of the following is most stable?
(a) 1-Butene (b) 1-Pentene
(c) 2-Butene (d) 2-Pentene *(2002)*

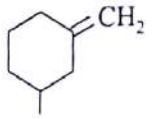
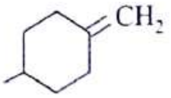
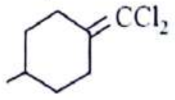
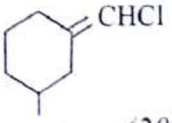
25. The length of C – C bond in benzene is
(a) 1.22 Å (b) 1.54 Å
(c) 1.39 Å (d) 1.56 Å *(2002)*

26. IUPAC name of  is
(a) 3-methylcyclohexene
(b) 1-methylcyclohex-2-ene
(c) 6-methylcyclohexene
(d) 1-methylcyclohex-5-ene. *(2003)*

27. The *ortho/para* directing group among the following is
(a) COOH (b) CN
(c) $COCH_3$ (d) $NHCOCH_3$ *(2003)*

28. The treatment of benzene with *iso*-butene in the presence of sulphuric acid gives
(a) *iso*-butylbenzene
(b) *tert*-butylbenzene
(c) *n*-butylbenzene (d) no reaction. *(2003)*

29. The compound having only primary hydrogen atoms is
(a) isobutene
(b) 2,3-dimethylbutene
(c) cyclohexane
(d) all of these. *(2004)*

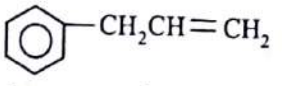
30. The geometrical isomerism is shown by
(a) 
(b) 
(c) 
(d) 
(2004)

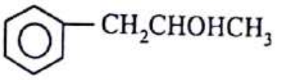
31. Among the following the aromatic compound is
(a) 
(b) 
(c) 
(d) 
(2004)

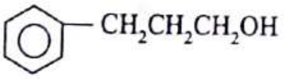
32. Which of the following gives propyne on hydrolysis?
(a) Al_4C_3 (b) Mg_2C_3
(c) B_4C (d) La_4C_3 *(2005)*

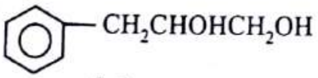
33. Which of the following sequence of reagents can be used for the conversion of $C_6H_5CH_2CH_3$ into $C_6H_5CH=CH_2$?
(a) $SOCl_2$; H_2O (b) SO_2Cl_2; alc.KOH
(c) $Cl_2/h\upsilon$; H_2O (d) $SOCl_2$; alc.KOH
(2006)

34. Propene on hydroboration and oxidation produces
(a) $CH_3CH_2CH_2OH$ (b) $CH_3CHOHCH_3$
(c) $CH_3CHOHCH_2OH$ (d) CH_3CH_2CHO
(2007)

35.  on mercuration and demercuration produces

(a) 

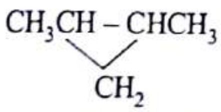
(b) 

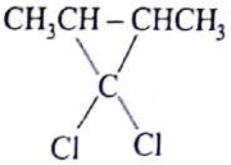
(c) 

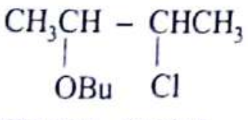
(d) none of these. *(2007)*

36. Which of the following species participate in sulphonation of benzene ring ?
(a) H_2SO_4 (b) SO_3
(c) HSO_3^- (d) SO_2^- *(2007)*

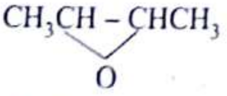
37. $CH_3CH=CHCH_3 + CHCl_3 + t\text{-BuOK} \rightarrow A$. A is

(a) 

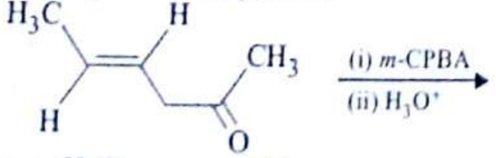
(b) 

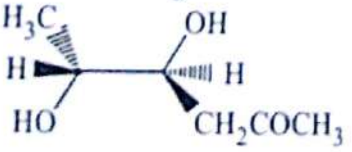
(c) 

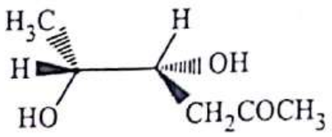
$CH_3\underset{|}{\underset{OBu}{CH}} - \underset{|}{\underset{Cl}{CHCH_3}}$

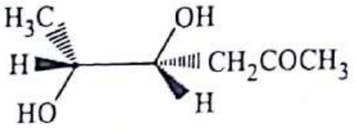
(d)  *(2008)*

38. Identify the final product.



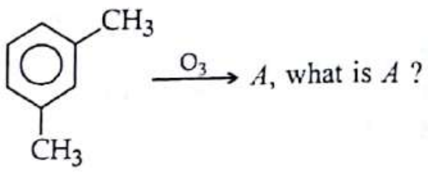
(a) 

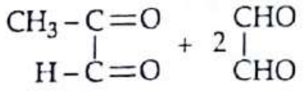
(b) 

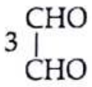
(c) 

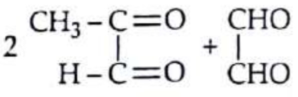
(d) none of these. *(2008)*

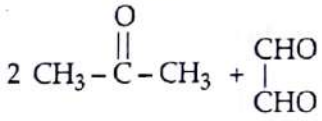
39. The function of $AlCl_3$ in Friedel-Craft's reaction is to
(a) absorb HCl
(b) absorb water
(c) produce nucleophile
(d) produce electrophile. *(2008)*

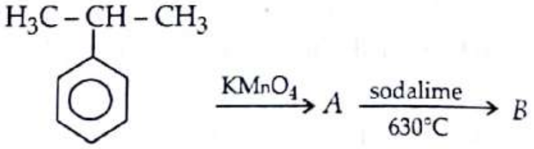
40.  A, what is A ?

(a) 

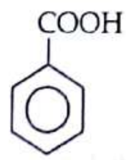
(b) 

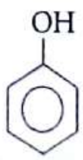
(c) 

(d)  *(2009)*

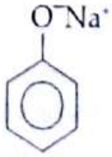
41. 

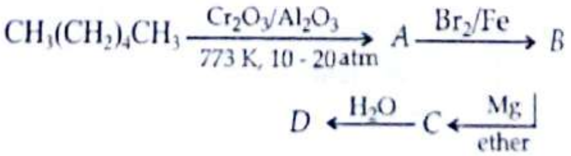
What is B ?

(a) 

(b) 

(c) 

(d)  *(2009)*

42. 

$$\begin{tikzcd} CH_3(CH_2)_4CH_3 \arrow[r, "Cr_2O_3/Al_2O_3"', "773\ K,\ 10-20\ atm"] & A \arrow[r, "Br_2/Fe"] & B \arrow[d] \\ D & C \arrow[l, "H_2O"'] & \arrow[l, "Mg", "ether"'] \end{tikzcd}$$

Scanned by CamScanner

What is D?

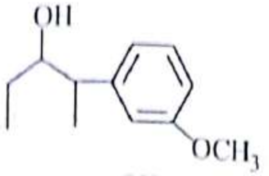
(a) 

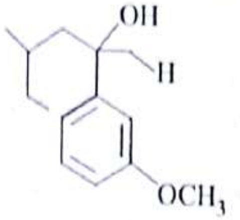
(b) 

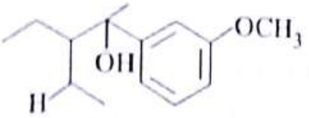
(c) 

(d)  *(2009)*

43.  $\xrightarrow[HgSO_4]{H_2SO_4, H_2O}$ P. The product P is

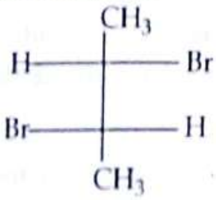
(a) 

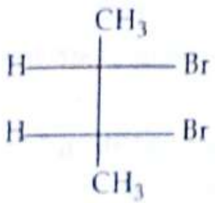
(b) 

(c) 

(d) none of these. *(2010)*

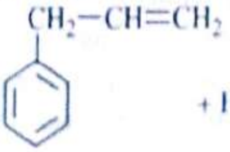
44. When *trans*-2-butene is reacted with Br_2 then product formed is

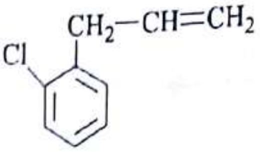
(a) 

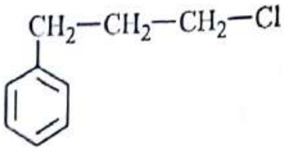
(b) 

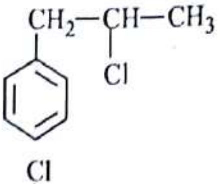
(c) Meso compounds (d) both (b) and (c) *(2013)*

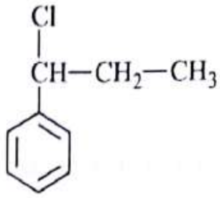
45. What is 'A' in the following reaction?

 + HCl ⟶ A

(a) 

(b) 

(c) 

(d)  *(2014)*

46. Which of the following is aromatic?

(a) 

(b) 

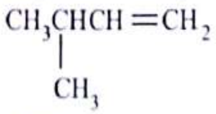
(c) 

(d)  *(2015)*

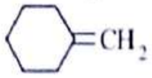
47. Which of the following species is not aromatic?
(a) Benzene
(b) Cyclooctatetraenyl dianion
(c) Tropylium ion
(d) Cyclopentadienyl cation *(2016)*

48. Which of the following alkenes will give same product by any method out of hydration, hydroboration-oxidation and oxymercuration-demercuration?

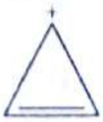
(a) $CH_3CH=CH_2$ (b) $CH_3CH=CHCH_3$

(c) 

$CH_3\underset{\displaystyle CH_3}{\underset{|}{C}H}CH=CH_2$

(d)  *(2016)*

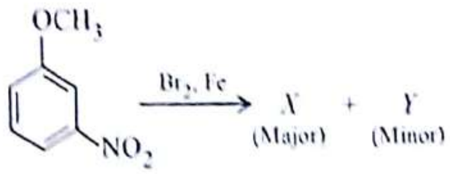
49. Which of the following compounds is aromatic in nature?

(a) 

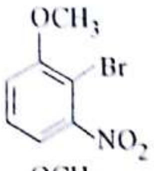
(b) 

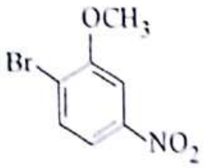
(c) 

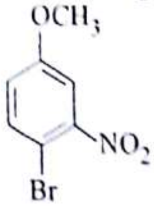
(d)  *(2017)*

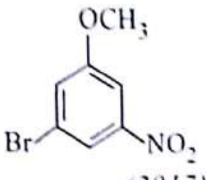
50. 

Identify X.

(a) 

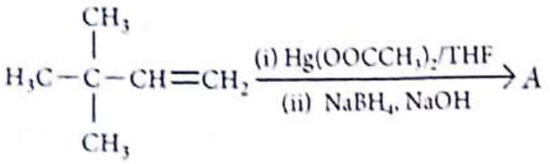
(b) 

(c) 

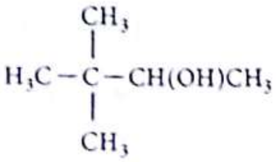
(d) 

(2017)

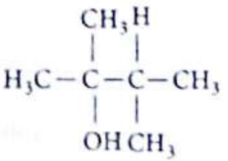
51. What will be compound A in the following reaction?



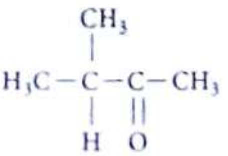
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH=CH_2 \xrightarrow[\text{(ii) NaBH}_4\text{, NaOH}]{\text{(i) Hg(OOCCH}_3)_2\text{/THF}} A$$

(a) 

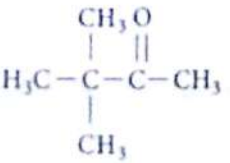
$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-CH(OH)CH_3$$

(b) 

$$H_3C-\underset{OH}{\overset{CH_3}{C}}-\underset{CH_3}{\overset{H}{C}}-CH_3$$

(c) 

$$H_3C-\underset{H}{\overset{CH_3}{C}}-\underset{}{\overset{}{\underset{O}{\underset{\|}{C}}}}-CH_3$$

(d) 

$$H_3C-\underset{CH_3}{\overset{CH_3}{C}}-\overset{O}{\overset{\|}{C}}-CH_3$$

(2017)

ASSERTION AND REASON

52. **Assertion** : Aniline hydrogen sulphate, on heating, forms a mixture of *ortho* and *para* aminobenzene sulphonic acids.
Reason : The sulphonic acid group is electron withdrawing. (1996)

53. **Assertion** : Alkenes and cycloalkanes series of hydrocarbons have same general formula.
Reason : Either insertion of a double bond or formation of a ring reduce the number of hydrogen atoms of corresponding alkane by 2. (2000)

54. **Assertion** : The carbon atoms of the benzene ring may be numbered for identification of substituent groups, just as a continuous chains of carbon atoms are numbered.
Reason : Smallest set of numbers designating the substituents is the preferred set. (2000)

55. **Assertion** : *Trans*-2-butene on reaction with Br_2 gives *meso*-2,3-dibromobutane.
Reason : The reaction involves *syn*-addition of bromine. (2003)

56. **Assertion** : Alkyl benzene is not prepared by Friedel-Crafts alkylation of benzene.
Reason : Alkyl halides are less reactive than acyl halides. (2003)

57. **Assertion** : 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 1-butene as a major product.
Reason : 1-Butene is more stable than 2-butene. (2004)

58. **Assertion** : Styrene on reaction with HBr gives 2-bromo-2-phenylethane.
Reason : Benzyl radical is more stable than alkyl radical. (2004)

59. **Assertion** : Rates of nitration of benzene and hexadeuterobenzene are different.
Reason : C – H bond is stronger than C – D bond. (2005)

60. **Assertion** : Cyclopentadienyl anion is much more stable than allyl anion.
Reason : Cyclopentadienyl anion is aromatic in character. (2005)

61. **Assertion** : Addition of HBr on 2-butene gives two isomeric products.
Reason : Addition of HBr on 2-butene follows Markownikoff's rule. (2006)

62. **Assertion** : *trans*-Butene on reaction with bromine forms racemic mixture.
Reason : *trans*-Compound in *trans* addition forms two types of stereoisomers. (2007)

63. **Assertion**
sodamide gi
Reason : s
acetylene a

64. **Assertion**
3-butanediol
Reason : I
gives *trans*

65. **Assertion** :
solubility o
Reason : A

66. **Assertion**
H_2SO_4 gi
when heat
pressure g
Reason : S

67. **Assertion**
stable tha
Reason :
be written
2-ene has

68. **Assertio**
electrolys
Reason :
cathode.

69. **Assertion**
Reason :
$H_2C=CH$

1. (a)
9. (b)
17. (d)
25. (c)
33. (b)
41. (c)
49. (a)
57. (d)
65. (b)
73. (b)

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63. ***Assertion*** : Acetylene on reacting with sodamide gives sodium acetylide and ammonia.
Reason : *sp* hybridised carbon atoms of acetylene are considerably electronegative. *(2007)*

64. ***Assertion*** : *Cis*-2-butene gives *meso*-2, 3-butanediol with dilute alkaline $KMnO_4$ solution.
Reason : Dilute alkaline $KMnO_4$ solution gives *trans* addition with alkenes. *(2009)*

65. ***Assertion*** : The presence of Ag^+ enhances the solubility of alkenes in water.
Reason : Alkenes are weakly polar in nature. *(2009)*

66. ***Assertion*** : Benzene on heating with conc. H_2SO_4 gives benzenesulphonic acid which when heated with superheated steam under pressure gives benzene.
Reason : Sulphonation is a reversible process. *(2010)*

67. ***Assertion*** : 2,3-Dimethylbut-2-ene is more stable than but-2-ene.
Reason : Six hyperconjugation structures can be written for 2,3-dimethylbut-2-ene while but-2-ene has twelve. *(2010)*

68. ***Assertion*** : Sodium acetate on Kolbe's electrolysis gives methane.
Reason : Methyl free radical is formed at cathode. *(2012)*

69. ***Assertion*** : $HC\equiv C^-$ is more stable than $H_2C=CH^-$.
Reason : $HC\equiv C^-$ has more *s*-character than $H_2C=CH^-$. *(2012)*

70. ***Assertion*** : Saturated hydrocarbons are chemically less reactive.
Reason : All isomeric paraffins have same parent name. *(2014, 2015)*

71. ***Assertion*** : All the hydrogen atoms in $CH_2=C=CH_2$ lie in one plane.
Reason : All the carbon atoms in its are sp^2 hybridized. *(2014)*

72. ***Assertion*** : Staggered conformation of ethane is 12.5 kJ mol^{-1} more stable than the eclipsed conformation.
Reason : The two conformations of ethane cannot be separated at room temperature. *(2016)*

73. ***Assertion*** : *trans*-Pent-2-ene is polar but *trans*-but-2-ene is non-polar.
Reason : The polarity of *cis*-isomer is more than *trans*-isomer, which are either non-polar or less polar. *(2017)*

74. ***Assertion*** : Oxidation of 1-nitro naphthalene gives *o*-nitro phthalic acid whereas 1-amino naphthalene on oxidation gives phthalic acid.
Reason : An amino group attached to the benzene ring makes it resistant to oxidation whereas nitro group makes the benzene ring susceptible to oxidation. *(2017)*

75. ***Assertion*** : Benzene reacts with iodine monochloride in presence of anhyd. $AlCl_3$ to form iodobenzene.
Reason : Iodine monochloride reacts with anhyd. $AlCl_3$ to produce I^+ which attacks the benzene ring. *(2017)*

Answer Key

1.	(a)	**2.**	(b)	**3.**	(d)	**4.**	(a)	**5.**	(b)	**6.**	(c)	**7.**	(b)	**8.**	(d)
9.	(b)	**10.**	(d)	**11.**	(d)	**12.**	(a)	**13.**	(d)	**14.**	(d)	**15.**	(b)	**16.**	(a)
17.	(d)	**18.**	(d)	**19.**	(d)	**20.**	(d)	**21.**	(b)	**22.**	(b)	**23.**	(b)	**24.**	(d)
25.	(c)	**26.**	(a)	**27.**	(d)	**28.**	(b)	**29.**	(a)	**30.**	(d)	**31.**	(a)	**32.**	(b)
33.	(b)	**34.**	(a)	**35.**	(a)	**36.**	(b)	**37.**	(b)	**38.**	(b)	**39.**	(d)	**40.**	(c)
41.	(c)	**42.**	(a)	**43.**	(c)	**44.**	(d)	**45.**	(c)	**46.**	(d)	**47.**	(d)	**48.**	(b)
49.	(a)	**50.**	(c)	**51.**	(a)	**52.**	(d)	**53.**	(a)	**54.**	(b)	**55.**	(c)	**56.**	(b)
57.	(d)	**58.**	(None)	**59.**	(d)	**60.**	(a)	**61.**	(d)	**62.**	(d)	**63.**	(a)	**64.**	(c)
65.	(b)	**66.**	(a)	**67.**	(c)	**68.**	(d)	**69.**	(a)	**70.**	(b)	**71.**	(d)	**72.**	(b)
73.	(b)	**74.**	(c)	**75.**	(a)										

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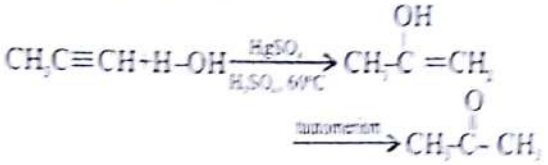
EXPLANATIONS

1. **(a) :** Ketones are formed on hydration of alkynes (other than acetylene) by following Markownikoff's rule.

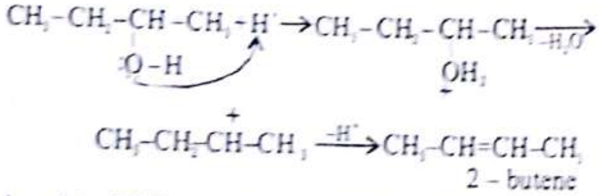


$$CH_3C\equiv CH + H-OH \xrightarrow[H_2SO_4,\ 60°C]{HgSO_4} CH_3-\overset{OH}{C}=CH_2 \xrightarrow{\text{tautomerism}} CH_3-\overset{O}{\overset{\|}{C}}-CH_3$$

2. **(b) :** Metamerism is due to presence of different alkyl groups attached to the same polyvalent functional group or atom.

∴ This kind of isomerism is not possible in case of alkenes.

3. **(d) :** According to Saytzeff's rule, in the dehydration of secondary and tertiary alcohols, when there is a possibility of formation of two isomers, the hydrogen atom is preferentially eliminated from the adjacent carbon atom with the fewer number of hydrogen atoms.



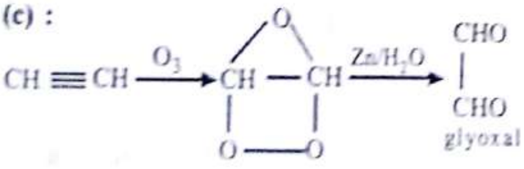
$$CH_3-CH_2-\underset{:O-H}{CH}-CH_3 + H^+ \rightarrow CH_3-CH_2-\underset{OH_2}{CH}-CH_3 \xrightarrow[-H_2O]{}$$

$$CH_3-CH_2-\overset{+}{C}H-CH_3 \xrightarrow{-H^+} \underset{\text{2 - butene}}{CH_3-CH=CH-CH_3}$$

4. **(a) :** $2CH_4 + \underset{\text{(limited)}}{3O_2} \rightarrow 2CO + 4H_2O$

5. **(b) :** $CH\equiv CH \xrightarrow[H_2O]{H_2SO_4/HgSO_4} CH_3CHO$

6. **(c) :**



7. **(b) :** $CH_3COOH \xrightarrow{NaOH/CaO} CH_4 + Na_2CO_3$

When sodium salt of carboxylic acids are heated with (NaOH + CaO), alkane is obtained with one less carbon atom than the acid, and the process is called decarboxylation.

8. **(d) :** $CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2$

mol. wt. of CaC_2 → 64 g

$\Rightarrow$ 64g CaC_2 ≡ 26g C_2H_2

$\Rightarrow$ 64100g CaC_2 ≡ $\frac{26}{64}$ × 64100g C_2H_2

= 26040.625 g C_2H_2

= 26.04 kg C_2H_2

$C_2H_2 + H_2 \longrightarrow C_2H_4$

Mol. wt. 26 g   28 g

$\Rightarrow$ 26 g C_2H_2 ≡ 28 g C_2H_4

$\Rightarrow$ 26.04 kg C_2H_2 ≡ $\frac{28}{26}$ × 26.04 kg C_2H_4

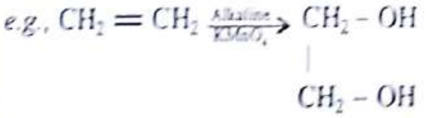
= 28.04 kg C_2H_4

$nC_2H_4 \rightarrow (CH_2-CH_2)_n$

Therefore, amount of polythene obtained is 28.04 kg.

9. **(b) :** Aromatic compounds are characterised by their unusual stability, delocalisation of π-electrons in a planar ring. They undergo substitution reactions more favourably than addition reactions, these properties are not present in cyclohexane.

10. **(d) :** Baeyer's reagent is alkaline $KMnO_4$ solution and it is used for oxidation at double bonds

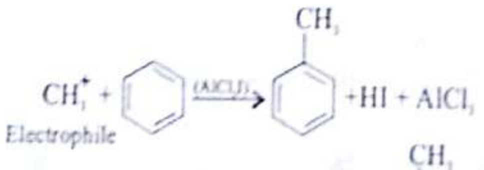


e.g., $CH_2=CH_2 \xrightarrow[KMnO_4]{\text{Alkaline}} \begin{array}{l} CH_2-OH \\ | \\ CH_2-OH \end{array}$

This reaction is used as a test for unsaturated compounds.

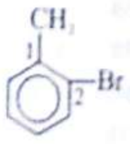
11. **(d) :** Benzene reacts with methyl iodide in the presence of anhydrous $AlCl_3$ to form toluene. Reaction is called as Friedel–Crafts reaction. It is used for alkylation and acylation of benzene nucleus.

$CH_3I + AlCl_3 \rightarrow CH_3^+[AlCl_3I]^-$



12. **(a) :** Toluene is methylbenzene

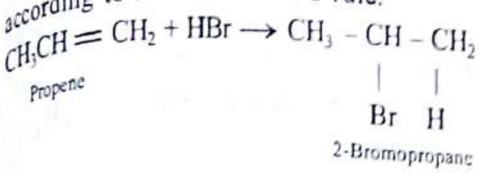
∴ 2-bromotoluene is



13. **(d) :** Methyl group is an electron releasing group due to which there is greater electron density in the ring, due to which electrophilic attack is favoured.

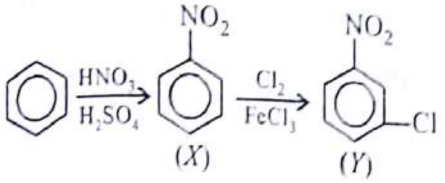
14. **(d) :** Alkenes are reactive due to the presence of double bond. The π-electrons are loosely held and are therefore, easily polarisable. So more the number of electron releasing alkyl group on the double bond, lesser is the stability.

15. **(b) :** HBr adds on the double bond of propene according to Markownikoff's rule.



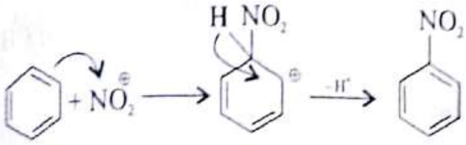
$$\underset{\text{Propene}}{CH_3CH=CH_2} + HBr \rightarrow \underset{\text{2-Bromopropane}}{CH_3-\underset{Br}{\underset{|}{C}H}-\underset{H}{\underset{|}{C}H_2}}$$

16. **(a) :**



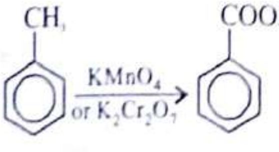
(HNO_3 + H_2SO_4) reagent is the agent for nitration in aromatic rings.

$$HNO_3 + 2H_2SO_4 \rightarrow NO_2^+ + HSO_4^- + H_3O^+$$



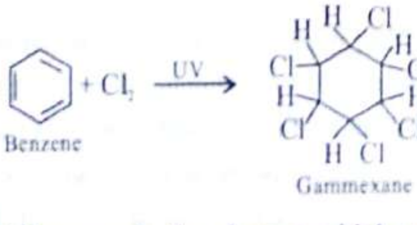
NO_2 group is a *meta* directing group so chlorine atom goes to *meta* position of the ring.

17. **(d) :**



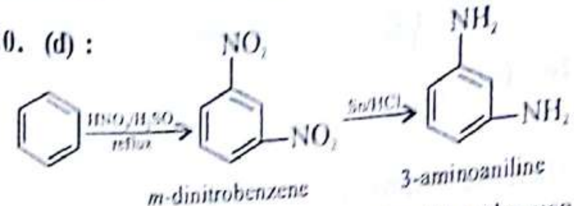
Both $KMnO_4$ and $K_2Cr_2O_7$ are strong oxidising agents therefore can oxidise any alkyl benzene to benzoic acid.

18. **(d) :**



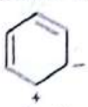
19. **(d) :** NO_2 group is the electron withdrawing group due to which electron density in the ring decreases. Therefore *meta* positions are preferred over *ortho* / *para* positions.

20. **(d) :**



21. **(b) :** Aromaticity can be predicted by the use of Huckel's rule which says that $(4n + 2)$ π-electrons are required in delocalisation system to give it aromaticity.

$(4n + 2)$ π electrons means 2, 6, 10 .....π electrons.



Here total number of electrons available for delocalisation = 6

∴ it is expected to be aromatic.

22. **(b) :** The nitration of benzene takes places in three steps, *i.e.*

(i) Generation of electrophile (NO_2^+)

(ii) Attack of an electrophile to benzene ring forming the carbocation

(iii) Loss of proton from carbocation giving nitrobenzene.

The attack of an electrophile to benzene ring forming the carbocation is the slowest and rate determining step.

23. **(b) :** Acetylene is converted to acetaldehyde when acetylene is treated with dil. H_2SO_4 and small amount of $HgSO_4$.

$$\underset{\text{Acetylene}}{CH\equiv CH} + H_2O \xrightarrow[Hg^{2+}]{\text{dil. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3-CHO}$$

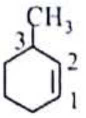
24. **(d) :** $\underset{\text{(2-butene)}}{CH_3-CH=CH-CH_3}$, $\underset{\text{(1-butene)}}{CH_3-CH_2-CH=CH_2}$

$\underset{\text{(1-pentene)}}{CH_3-CH_2-CH_2-CH=CH_2}$,

$\underset{\text{(2-pentene)}}{CH_3-CH_2-CH=CH-CH_3}$

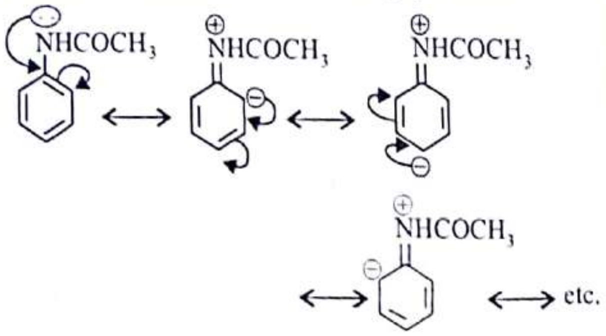
According to Saytzeff's rule, stability of alkenes depends upon the substitution on C=C bond. More the substitution by alkyl group, more stable is the alkene.

25. **(c) :** The bond length C – C (single bond as in ethane) is 1.54 Å and C = C (double bond as in ethene is 1.33 Å. The C – C bond length in benzene has been found to be 1.39Å which lies between single and double bond length values.

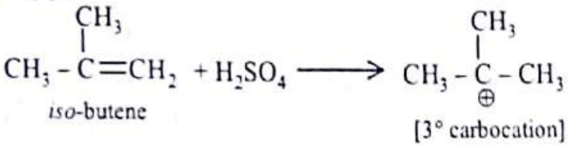
26. **(a) :** 

Therefore, IUPAC name is 3-methylcyclohex-1-ene or simply, 3-methylcyclohexene.

27. **(d) :** For *o*/*p* directing group, there should be partial –ve charge at the *o*-and *p*-positions.

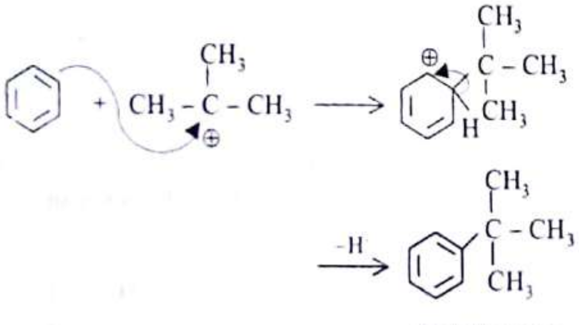


28. **(b) :**



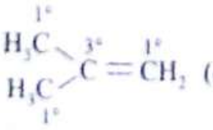
$$CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2+H_2SO_4\longrightarrow CH_3-\overset{\overset{CH_3}{|}}{\underset{\oplus}{C}}-CH_3$$

iso-butene [3° carbocation]

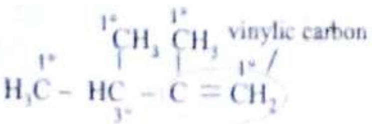


t-butylbenzene

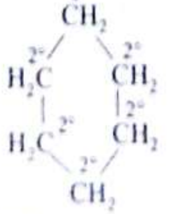
29. **(a) :** A 1° hydrogen atom is one that is bonded to a 1° carbon atom; a 2° hydrogen atom is one that is connected to a 2° carbon atom; etc.



(only 1° hydrogen atoms)



(1° and 3° H-atoms)

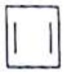


(2° hydrogen atoms)

30. **(d) :** In all other compounds the groups present on doubly bonded carbons are identical.

31. **(a) :** (a)  ; $4n+2=2$, $n=0$ (integer)

(b)  ; $4n+2=4$, $n=0.5$

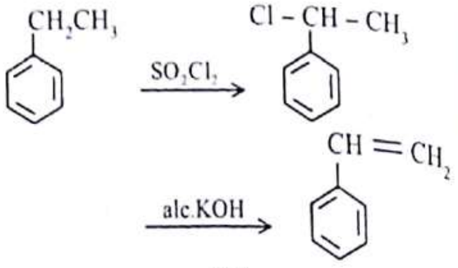
(c)  ; $4n+2=4$, $n=0.5$

(d)  ; $4n+2=4$, $n=0.5$

Only (a) obeys Huckel's rule.

32. **(b) :** Propyne can be prepared by the hydrolysis of magnesium carbide.

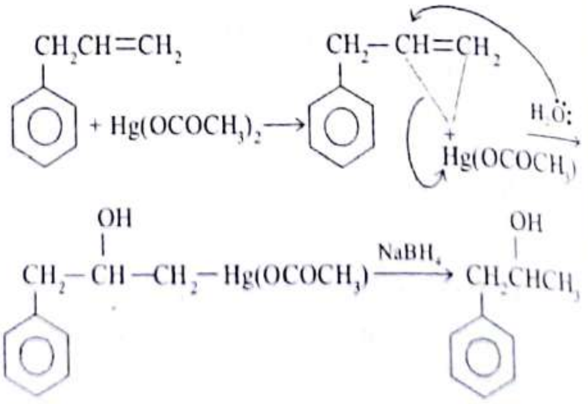
$$Mg_2C_3+4H_2O\longrightarrow 2Mg(OH)_2+HC\equiv C-CH_3$$

33. **(b) :** 

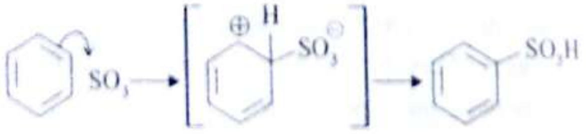
34. **(a) :** $3CH_3-CH=CH_2\xrightarrow[THF]{BH_3}(CH_3CH_2CH_2)_3B$

$$\xrightarrow[OH^-]{H_2O_2}3CH_3CH_2CH_2OH$$

35. **(a) :**



36. **(b) :** Most electrophilic substitution reactions are irreversible but sulphonation is an exception. Treatment of benzene with "oleum" (a solution of SO_3 in conc. sulphuric acid) will give the sulphonic acid, the electrophile is sulphur trioxide (SO_3).



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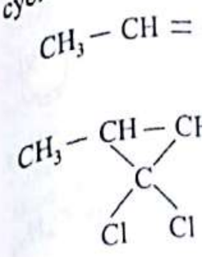
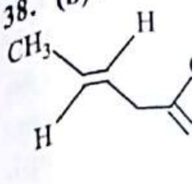
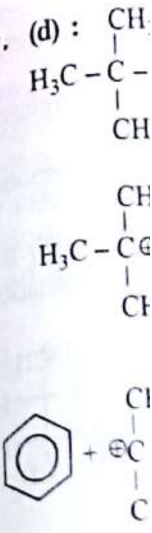
37. **(b) :** It is
cycloalkanes.



38. **(b) :**



39. **(d) :**



40. **(c) :** CH

41. **(c) :**
H₃C–(

42. **(a) :** B
of long cha
under high

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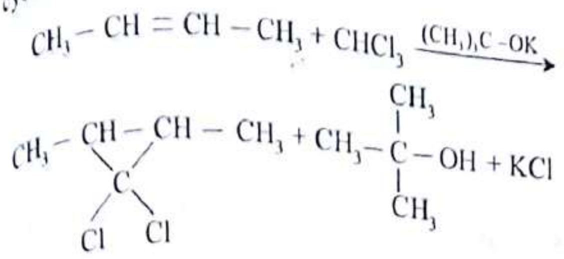
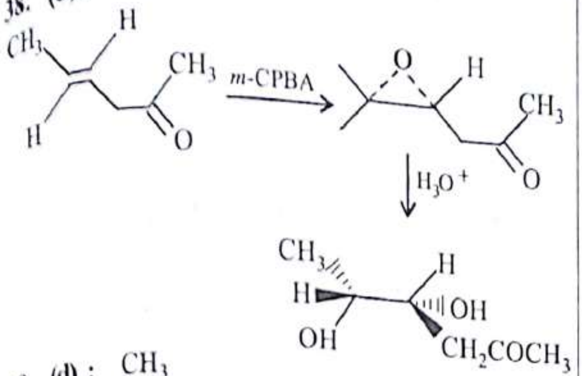
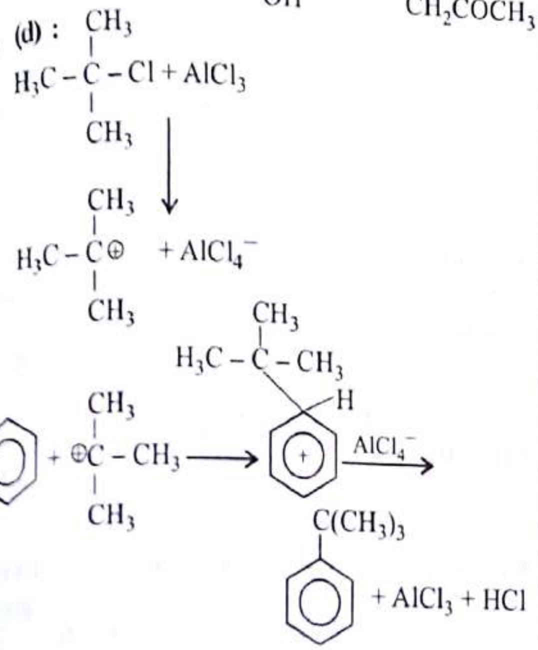
37. **(b)** : It is a method of preparation of cycloalkanes.



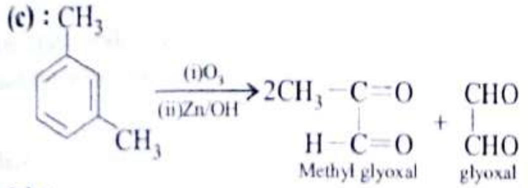
38. **(b)** :



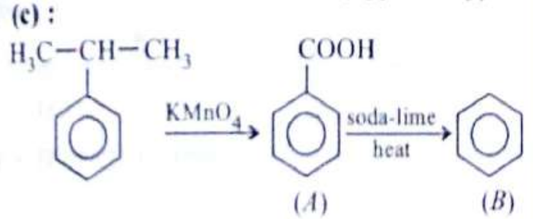
39. **(d)** :



40. **(c)** :

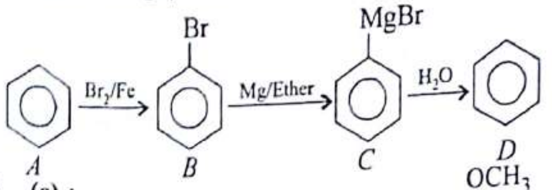


41. **(c)** :

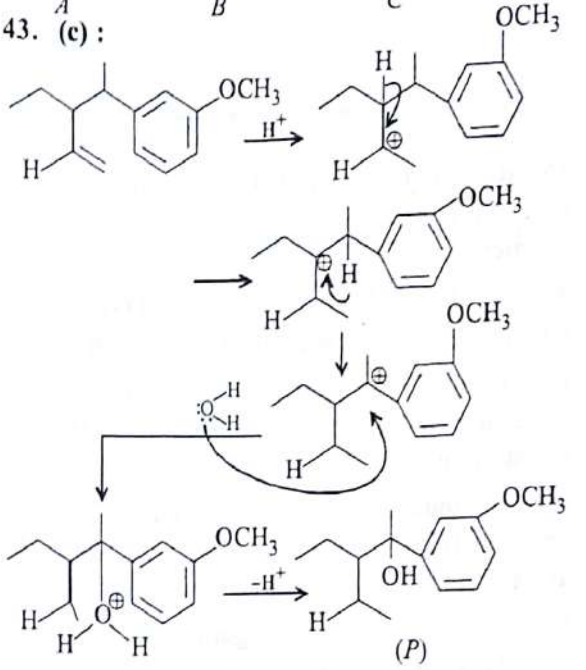


42. **(a)** : Benzene can be prepared by cyclization of long chain alkanes on heating at 500 - 550°C under high pressure in presence of catalyst Cr_2O_3 supported on alumina or $Pt - Al_2O_3$ (*i.e.*, catalytic reforming)

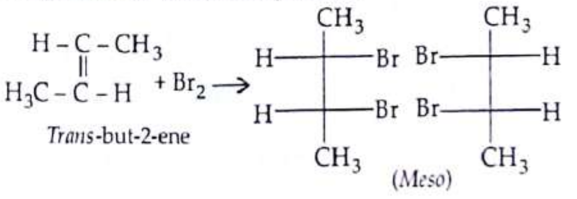
$$\underset{n\text{-hexane}}{C_6H_{14}} \xrightarrow[\text{773 K at high pressure}]{Cr_2O_3/Al_2O_3} \underset{A}{C_6H_6} + 4H_2$$



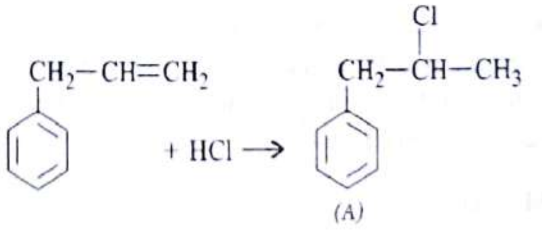
43. **(c)** :



44. **(d)** : With *trans*-but-2-ene, the product of Br_2 addition is optically inactive due to the formation of symmetric meso-compounds.



45. **(c)** : According to Markovnikov's rule,



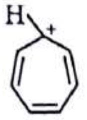
46. **(d)** : Any planar cyclic system containing $(4n + 2)\pi$ electrons and having a single cyclic π-electron cloud encompassing all the carbon atoms in the ring is aromatic.

(Planar, 6π-electrons)

47. (d) : On applying the Hückel rule, $[(4n + 2)\pi$ electron] system,

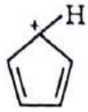

Benzene
[$n = 1$, 6π-electrons, aromatic]

;


Cycloheptatrienyl cation
(Tropylium ion)
[$n = 1$, 6π-electrons, aromatic]


Cyclooctatetraenyl dianion
[$n = 2$, 10π-electrons, aromatic]

;


Cyclopentadienyl cation
[4π-electrons, antiaromatic]

48. (b) : $CH_3CH = CHCH_3$ is symmetrical and gives same product by any of the given methods adopted.

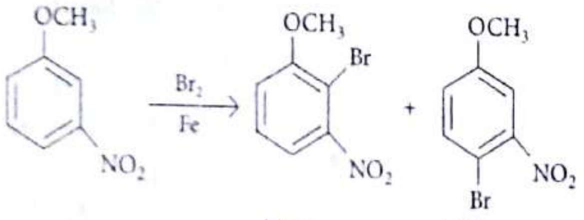
49. (a) : In (a), due to the presence of $(4n + 2)\pi e^-$ it follows Huckel's rule and therefore, it is aromatic.

In (b), due to the presence of extra lone pair of electrons, total e^- comes out to be $4\pi e^-$. Thus, it is anti-aromatic.

In (c), although it is cyclic and has conjugated $8\pi e^-$ but Huckel's $(4n + 2)\pi$ rule is not followed and also ring is not planar. Hence, it is non-aromatic.

In (d), it has $6\pi e^-$ in conjugation but not in the ring, hence it is non-aromatic.

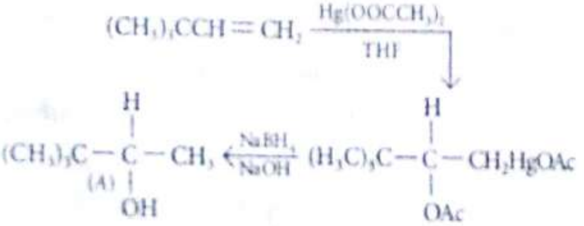
50. (c) :



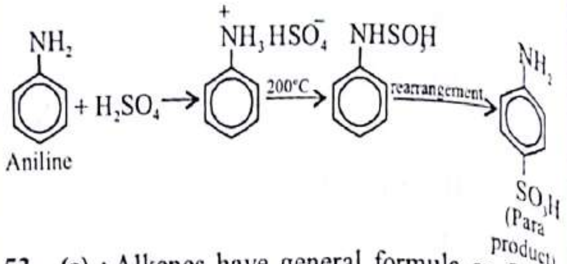
Minor (*Y*) Major (*X*)

Strong electron releasing group (—OCH_3)generally win over the deactivating group. Thus, *o* and *p*-products will be formed. Due to steric hindrance *ortho* product will be formed in lesser amount than *para* product.

51. (a) :

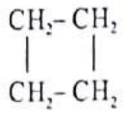


52. (d) :



53. (a) : Alkenes have general formula as C_nH_{2n} same as that of cycloalkanes.

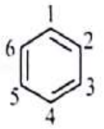
e.g. $CH_3CH = CHCH_3 \Rightarrow C_4H_8 \ (\equiv C_nH_{2n})$
2-butene



$$\begin{matrix} CH_2-CH_2 \\ | \quad\quad | \\ CH_2-CH_2 \end{matrix} \Rightarrow C_4H_8 \ (= C_nH_{2n})$$

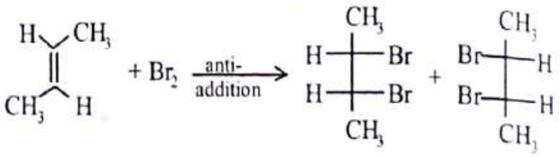
Cyclobutane

54. (b) : Nomenclature in benzene ring :



For only one substituent, no numbering is required. According to latest IUPAC system of nomenclature, the lowest set of locants is preferred even if it violates the lowest sum rule. 1, 3-dimethylbenzene is preferred as it corresponds to smallest total set of numbers.

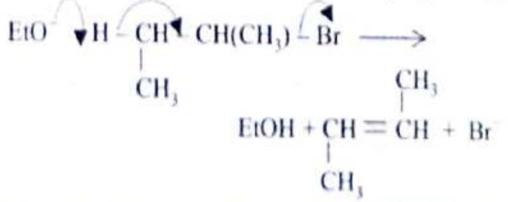
55. (c) : With *trans*-2-butene, the product of Br_2 addition is optically inactive due to the formation of symmetrical *meso* compounds.



(*meso*)

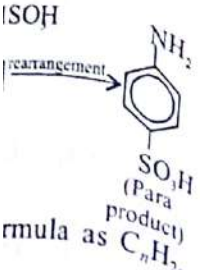
56. (b) : The monoalkyl derivative first formed readily undergoes further alkylation at a still greater speed to produce polysubstituted products, and alkyl halide employed may also undergo an isomeric change. Due to these difficulties alkyl benzene is not generally prepared by Friedel-Craft's alkylation of benzene.

57. (d) : 2-Bromobutane on reaction with sodium ethoxide in ethanol gives 2-butene as a major product.



This is according to Saytzeff's rule *i.e.* the predominant product is the most substituted

ISOH



rmula as C_nH_{2n}

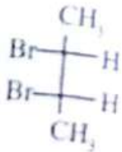
$\equiv C_nH_{2n}$)

C_nH_{2n})

ing :

g is required.
system of
is preferred
.
corresponds

duct of Br_2
: formation



)

t formed
ll greater
cts, and
isomeric
nzene is
kylation

sodium
product.

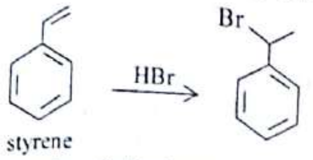
+ Br

the
tuted

---

alkene, 2-butene is more stable than 1-butene due to presence of large number of hyperconjugating structures in 2-butene.

58. **(None) :** HBr adds to the double bond of the styrene forming 1-bromo-1-phenylethane.



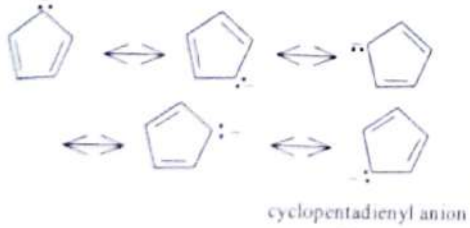
This is an example of elimination-addition reaction.

Note : Here given assertion is wrong.

59. **(d) :** Rates of nitration of benzene and hexadeutero benzene are same because nitration depends upon availability of electrophile.

C – D bond is stronger than C – H bond. Here changing a hydrogen atom to deuterium in C – H bond represents a 100% increase in mass. Here the mass of an atom affects the vibration frequency of the chemical bond that it forms, even if the electron configuration is nearly identical. Heavier atoms will lead to lower vibration frequencies or will have lower zero-point energy. With a lower zero-point energy, more energy must be supplied to break the bond, resulting in a higher activation energy for bond cleavage, thus C – D bond is stronger than C – H bond.

60. **(a) :**

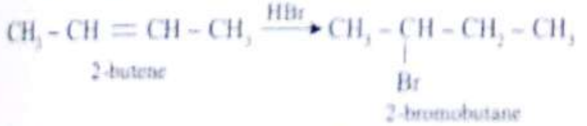


$$\bar{C}H_2CH=CH_2 \longleftrightarrow CH_2=CH\bar{C}H_2$$

allyl anion

Here the resonance approach is a poor predictor of stability. The Huckel rule, based on molecular orbital theory, is a much better predictor of stability for these aromatic and antiaromatic system.

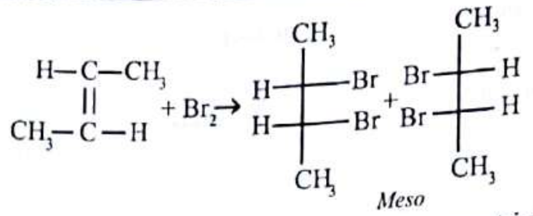
61. **(d) :** Addition of HBr on 2-butene gives only one product, 2-bromobutane.



$$\underset{\text{2-butene}}{CH_3-CH=CH-CH_3} \xrightarrow{HBr} \underset{\text{2-bromobutane}}{CH_3-\underset{\underset{Br}{|}}{C}H-CH_2-CH_3}$$

As 2-butene is a symmetrical alkene, it does not follow Markownikoff's rule.

62. **(d) :** With *trans*-but-2-ene, the product of Br_2 addition is optically inactive due to the formation of symmetric *meso* compounds.



In general, for symmetrical alkenes and symmetrical reagents, the addition takes place as :

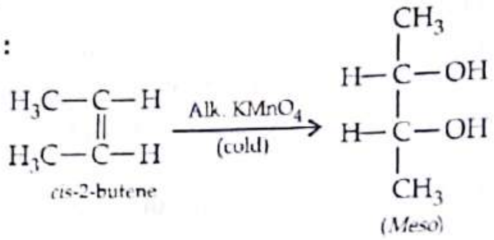
cis-alkene + syn-addition → meso
trans-alkene + syn-addition → racemic
cis-alkene + anti-addition → racemic
trans-alkene + anti-addition → meso

63. **(a) :**

$$HC\equiv CH + NaNH_2 \xrightarrow{\text{Ether}} HC\equiv C^-Na^+ + NH_3$$

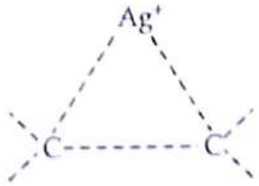
C–H bond is strongly polar due to high electronegativity of carbon atom. Hence it gives H^+ ion on reacting with a base or acetylene behaves as an acid.

64. **(c) :**



Alkaline $KMnO_4$ always gives *cis*-addition on olefins.

65. **(b) :** Ag^+ forms complex with the alkene by $p\pi$-$d\pi$ bonding giving an ion and the solubility increases.



66. **(a) :** Sulphonation of benzene is an electrophilic substitution reaction in which SO_3 acts as the electrophile.

67. **(c) :** Greater the number of hyperconjugating structures, greater is the stability of the compound.

68. **(d) :** Sodium acetate on Kolbe's electrolysis gives ethane. It is formed at anode.

69. **(a) :** $HC\equiv C^-$ has 50% s-character and $H_2C=CH^-$ has 33% s-character. Stability of carbanions increases with an increase in the s-character

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at the carbanion. So $HC\equiv C^-$ is more stable than $H_2C=CH^-$.

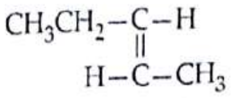
70. **(b)** : Less reactivity of saturated hydrocarbons are due to presence of single bonds between carbon atoms. Paraffins (alkanes) may have straight chain or branched chain isomers which have different parent names.

71. **(d)** : The two H-atoms on first carbon and the two H-atoms on the third carbon atom lie in perpendicular planes. The central carbon atom is *sp*-hybridized while terminal carbon atoms are sp^2-hybridized.

72. **(b)** : Staggered conformation is more stable because in this conformation any two hydrogen atoms on adjacent carbon atoms are as far apart as possible and the repulsion between the electron clouds of σ-bonds of two non-bonded hydrogen atoms is minimum.

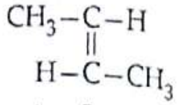
The energy difference of 12.55 kJ mol^{-1} is not large enough to prevent rotation at room temperature as a result it is not possible to seperate the two conformations of ethane.

73. **(b)** : The vector sum of all polar bonds in *trans*-pent-2-ene is not zero while in *trans*-but-2-ene it is zero.



$$\begin{array}{l} CH_3CH_2-C-H \\ \qquad\qquad\quad \| \\ \qquad\qquad H-C-CH_3 \end{array}$$

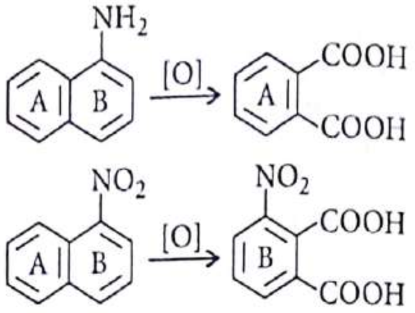
trans-Pent-2-ene
($\mu \neq 0$)



$$\begin{array}{l} CH_3-C-H \\ \qquad\quad \| \\ \qquad H-C-CH_3 \end{array}$$

trans-But-2-ene
($\mu = 0$)

74. **(c)** : An amino group increases the electron density in the benzene ring to which it is attached thereby making it susceptible to oxidation while a nitro group decreases the electron density in the benzene ring to which it is attached thereby making it resistant to oxidation. Instead, the other benzene ring gets oxidised giving *o*-nitrophthalic acid as shown below :



75. **(a)**

CHAPTER 14

Environmental Chemistry

1. Ozone in stratosphere is depleted by
   - (a) CF_2Cl_2
   - (b) C_7F_{16}
   - (c) $C_6H_6Cl_6$
   - (d) C_6F_6

   (2004)

2. Green chemistry means such reactions which
   - (a) are related to the depletion of ozone layer
   - (b) study the reactions in plants
   - (c) produce colour during reactions
   - (d) reduce the use and production of hazardous chemicals.

   (2008)

3. Living in the atmosphere of CO is dangerous, because it
   - (a) combines with O_2 present inside to form CO_2
   - (b) reduces organic matter of tissues
   - (c) combines with haemoglobin and makes it incapable to absorb oxygen
   - (d) dries up the blood.

   (2012)

4. Which of the following is not a greenhouse gas?
   - (a) Hydrogen
   - (b) Carbon dioxide
   - (c) Methane
   - (d) Nitrous oxide or N_2O

   (2013)

5. Which of the following has highest concentration of PAN?
   - (a) Smoke
   - (b) Ozone
   - (c) Photochemical smog
   - (d) Reducing smog

   (2014)

6. Which of the following is not a greenhouse gas?
   - (a) Carbon dioxide
   - (b) Water vapours
   - (c) Methane
   - (d) Oxygen

   (2015, 2003)

ASSERTION AND REASON

7. ***Assertion :*** Photochemical smog is produced by nitrogen oxides.

   Reason : Vehicular pollution is a major source of nitrogen oxides. *(2003)*

Answer Key

1.	(a)	**2.**	(d)	**3.**	(c)	**4**	(a)	**5.**	(c)	**6.**	(d)	**7.**	(b)

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EXPLANATIONS

1. **(a) :** Ozone depletion is caused by a number of pollutants like chlorofluorocarbons (14% of total depletion), nitrogen oxides, sulphur oxides, CCl_4, Cl_2, etc. Maximum ozone depleting potential or ODP is of chlorofluorocarbons (CF_2Cl_2) as it releases chlorine. A single chlorine atom converts 1 lakh molecules of ozone to oxygen.

2. **(d)**

3. **(c) :** Carbon monoxide combines with haemoglobin of blood to form a complex called carboxy-haemoglobin. Formation of this complex makes the haemoglobin incapable of oxygen transport. Due to which there will be oxygen deficiency in the blood.

4. **(a) :** Carbon dioxide, methane, water vapou nitrous oxide, CFCs and ozone are greenhouse gases

5. **(c) :** The main component of photochemica smog is peroxyacetyl nitrate, (PAN). The othe components are ozone, nitric oxide, acrolein an formaldehyde.

6. **(d) :** Carbon dioxide, water vapours and methane are greenhouse gases.

7. **(b) :** NO_2 + U.V. light → NO + O
Atomic oxygen produced as above reacts with hydrocarbons to give a variety of free hydrocarbon radicals, aldehydes, ketones, O_3, peroxyacetyl nitrate (PAN), etc. PAN mixes with the fog and gets condensed on smoke or dust particles in the air to form a smog which is called photochemical smog.

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CHAPTER 15

Solid State

1. Sodium metal crystallises as a body centred cubic lattice with the cell edge 4.29 Å. What is the radius of sodium atom (in cm)?
(a) 9.312×10^{-7} (b) 1.857×10^{-8}
(c) 2.371×10^{-7} (d) 3.817×10^{-8}
(1999)

2. A molecule contains atoms x and y so that x occurs at the corners of the cube while y at the face centres. The formula of the molecule can be
(a) xy_3 (b) x_3y
(c) xy_2 (d) x_2y *(2000)*

3. The edge length of face centred cubic unit cell is 508 pm. If the radius of the cation is 110 pm, the radius of the anion is
(a) 288 pm (b) 398 pm
(c) 144 pm (d) 618 pm *(2000)*

4. A solid AB has NaCl type structure. The radius of A^+ is 100 pm. What is the radius of B^-?
(a) 190.47 (b) 540.13
(c) 525 (d) 78.12 *(2001)*

5. Crystalline solids have
(a) short range order (b) long range order
(c) anisotropic distribution
(d) both (b) and (c). *(2001)*

6. Schottky defect defines imperfection in the lattice structure of a
(a) solid (b) gas
(c) liquid (d) plasma. *(2002)*

7. An AB_2 type structure is found in
(a) NaCl (b) CaF_2
(c) Al_2O_3 (d) N_2O *(2002)*

8. An element (atomic mass 100 g/mol) having *bcc* structure has unit cell edge 400 pm. The density of element is (No. of atom in *bcc* (Z) = 2).
(a) 2.144 g/cm^3 (b) 7.289 g/cm^3
(c) 5.188 g/cm^3 (d) 10.376 g/cm^3
(2002)

9. The crystal system of a compound with unit cell dimensions $a = 0.387$, $b = 0.387$ and $c = 0.504$ nm and $\alpha = \beta = 90°$ and $\gamma = 120°$ is
(a) cubic (b) hexagonal
(c) orthorhombic (d) rhombohedral.
(2004)

10. If Z is the number of atoms in the unit cell that represents the closest packing sequence ... $ABCAB\ C$ ..., the number of tetrahedral voids in the unit cell is equal to
(a) Z (b) $2Z$
(c) $Z/2$ (d) $Z/4$ *(2005)*

11. Ca^{2+} and F^- are located in CaF_2 crystal, respectively at face centred cubic lattice points and in
(a) tetrahedral voids
(b) half of tetrahedral voids
(c) octahedral voids
(d) half of octahedral voids. *(2006, 2015)*

12. The energy gaps (E_g) between valence band and conduction band for diamond, silicon and germanium are in the order
(a) E_g (diamond) > E_g (silicon) > E_g (germanium)
(b) E_g (diamond) < E_g (silicon) < E_g (germanium)
(c) E_g (diamond) = E_g (silicon) = E_g (germanium)
(d) E_g (diamond) > E_g (germanium) > E_g (silicon).
(2006)

13. The coordination number in *hcp* is
(a) 6 (b) 12
(c) 18 (d) 24 *(2007)*

14. The flame colours of metal ions are due to
(a) Frenkel defect
(b) Schottky defect
(c) metal deficiency defect
(d) metal excess defect. *(2008)*

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15. A unit cell of sodium chloride has four formula units. The edge length of the unit cell is 0.564 nm. What is the density of sodium chloride?

(a) 1.2 g/cm^3 (b) 2.165 g/cm^3

(c) 3.64 g/cm^3 (d) 4.56 g/cm^3

(2008)

16. Schottky defect in crystals is observed when

(a) unequal number of cations and anions are missing from the lattice

(b) equal number of cations and anions are missing from the lattice

(c) an ion leaves its normal site and occupies an interstitial site

(d) density of the crystal is increased.

(2009)

17. In tetragonal crystal system, which of the following is not true?

(a) All axial lengths and all axial angles are equal.

(b) All three axial lengths are equal.

(c) All three axial angles are equal.

(d) Two axial angles are equal but the third is different. *(2010)*

18. Schottky defect is

(a) vacancy of ions

(b) delocalization of ions

(c) interstitial vacancy of ions

(d) vacancy of only cations. *(2011)*

19. In *bcc* structure contribution of corner and central atom is

(a) $\frac{1}{8}, 1$ (b) $\frac{1}{4}, \frac{1}{8}$

(c) $\frac{1}{8}, \frac{1}{2}$ (d) $1, \frac{1}{2}$ *(2012)*

20. If Si is doped with B,

(a) *n*-type semiconductor is formed

(b) *p*-type semiconductor is formed

(c) insulator is formed

(d) polymer is formed. *(2012)*

21. CsCl has *bcc* arrangement. Its unit cell edge length is 400 pm. Its inter-ionic distance is

(a) 400 pm (b) 800 pm

(c) $\sqrt{3} \times 100$ pm (d) $\frac{\sqrt{3}}{2} \times 400$ pm

(2012)

22. In a solid, atom M occupies *ccp* lattice and 1/3rd of tetrahedral voids are occupied by atom N. Find the formula of solid formed by M and N.

(a) M_3N_2 (b) M_2N_3

(c) M_4N_3 (d) M_3N_4 *(2013)*

23. A forms *hcp* lattice and B are occupying 1/3rd of tetrahedral voids, then the formula of compound is

(a) AB (b) A_3B_2

(c) A_2B_3 (d) AB_4 *(2014)*

24. Which of the following is an amorphous solid?

(a) Iron (b) Graphite

(c) Diamond (d) Glass *(2015)*

25. The yellow colour in NaCl crystals is due to

(a) excitation of electrons in F-centres

(b) reflection of light from Cl$^-$ ions on the surface

(c) refraction of light from Na$^+$ ions

(d) all of the above. *(2015)*

26. Addition of group–13 elements to intrinsic semiconductors results in

(a) creation of conduction band slightly above the valence band

(b) creation of conduction band slightly below the valence band

(c) creation of valence band slightly above the conduction band

(d) overlapping of valence band and conduction band *(2015)*

27. If an atom crystallises in *bcc* lattice with $r = 4$ Å then the edge length will be

(a) 2 Å (b) 8 Å

(c) 2.39 Å (d) 9.23 Å *(2016)*

28. ZnO is white when cold and yellow when heated. It is due to the development of

(a) Frenkel defect

(b) metal excess defect

(c) Schottky defect

(d) metal deficiency defect. *(2017)*

ASSERTION AND REASON

29. ***Assertion:*** In crystal lattice, size of the cation is larger in a tetrahedral hole than in an octahedral hole.

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Reason: The cations occupy more space than anions in crystal packing. *(1996)*

30. ***Assertion :*** Graphite is an example of tetragonal crystal system.
Reason : For a tetragonal system, $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$. *(2006)*

31. ***Assertion :*** Conductivity of silicon increases by doping it with group-15 elements.
Reason : Doping means introduction of small amount of impurities like P, As or Bi into the pure crystal. *(2010, 2015)*

32. ***Assertion :*** Due to Frenkel defect, density of the crystalline solid decreases.
Reason : In Frenkel defect, a cation or an anion leaves the crystal. *(2010)*

33. ***Assertion :*** *bcc* and *hcp* has same packing efficiency.
Reason : Both have same number of atoms per unit cell and same arrangement. *(2011)*

34. ***Assertion :*** The presence of a large number of Schottky defects in NaCl lowers its density.
Reason : In NaCl, there are approximately 10^6 Schottky pairs per cm^3 at room temperature. *(2013)*

35. ***Assertion :*** Monoclinic sulphur is an example of monoclinic crystal system.
Reason : For a monoclinic system, $a \neq b \neq c$ and $\alpha = \gamma = 90°$, $\beta \neq 90°$. *(2014)*

36. ***Assertion :*** Diamagnetic substances are not attracted by magnetic field.
Reason : Diamagnetic substances have no unpaired electrons. *(2016)*

37. ***Assertion :*** The number of tetrahedral voids is double the number of octahedral voids.
Reason : The size of the tetrahedral voids is half of that of the octahedral void. *(2017)*

Answer Key

1.	(b)	**2.**	(a)	**3.**	(c)	**4.**	(a)	**5.**	(d)	**6.**	(a)	**7.**	(b)	**8.**	(c)
9.	(b)	**10.**	(b)	**11.**	(a)	**12.**	(a)	**13.**	(b)	**14.**	(d)	**15.**	(b)	**16.**	(b)
17.	(c)	**18.**	(a)	**19.**	(a)	**20.**	(b)	**21.**	(c)	**22.**	(a)	**23.**	(b)	**24.**	(d)
25.	(a)	**26.**	(a)	**27.**	(d)	**28.**	(b)	**29.**	(d)	**30.**	(d)	**31.**	(b)	**32.**	(d)
33.	(d)	**34.**	(b)	**35.**	(a)	**36.**	(a)	**37.**	(c)						

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EXPLANATIONS

1. (b) : In body-centred cubic crystals,

$$\text{radius} = \frac{\sqrt{3}}{4} \times \text{edge-length}$$

$$= \frac{\sqrt{3}}{4} \times 4.29 \times 10^{-8}\text{ cm}$$

$$= 1.857 \times 10^{-8}\text{ cm}$$

2. (a) : x atoms are at the corners of the cube, therefore,

number of x-atoms per unit cell $= \frac{1}{8} \times 8 = 1$

y-atoms are at the face centres of cube

$\therefore$ Number of y-atoms per unit cell $= \frac{1}{2} \times 6 = 3$

$\Rightarrow$ The formula of the molecule is xy_3

3. (c) : In face-centred cubic unit cell, the edge length can be written as :

$a = 2(r_+ + r_-)$

a = edge length, r_+ = radius of cation
r_- = radius of anion

$\Rightarrow 508 = 2(110 + r_-) \Rightarrow r_- = 144$ pm

4. (a) : NaCl type structure has face-centred cubic lattice. Here the radius ratio (r_c/r_a) ranges from 0.414 to 0.732.

$$\text{radius ratio} = \frac{r_c}{r_a} = \frac{\text{radius of cation}}{\text{radius of anion}}$$

$$\Rightarrow \quad \text{radius of anion } (B^-) = \frac{\text{radius of } A^+}{\text{radius ratio}}$$

$$= \frac{100}{0.414} \text{ to } \frac{100}{0.732}$$

$$= 241.5 \text{ to } 136.6$$

5. (d) : Crystalline solids are anisotropic therefore their physical properties *e.g.*, electrical conductivity, thermal conductivity, refractive index have different values in different directions.

6. (a) : It arises if some of the atoms or ions are missing from their normal lattice sites. The lattice sites which are unoccupied are called lattice vacancies or holes. Since the crystal is to remain electrically neutral, equal number of cations and anions are missing.

7. (b) : CaF_2 has AB_2 type structure in which Ca^{2+} ions have *fcc* arrangement and F^- ions are present in all the tetrahedral voids.

8. (c) : Atomic mass of element = 100 g/mol

Cell edge = 400 pm = $400 \times 10^{-12} = 4 \times 10^{-8}$ cm

and number of atoms in *bcc* $(Z) = 2$

As the atomic mass of the metal is 100 g/mol,

Therefore, mass of each atom $(m) = \dfrac{100}{6.023 \times 10^{23}}$

$= 16.6 \times 10^{-23}$ g

The volume of unit cell $= (4 \times 10^{-8})^3 = 64 \times 10^{-24}\text{ cm}^3$

And mass of unit cell $= Z \times m$

$= 2 \times (16.6 \times 10^{-23}) = 33.2 \times 10^{-23}$ g

$$\text{Therefore, density of element} = \frac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$$

$$= \frac{33.2 \times 10^{-23}}{64 \times 10^{-24}} \approx 5.188\text{ g/cm}^3$$

9. (b) : $a = b \neq c, \alpha = \beta = 90°, \gamma = 120°$

The given conditions represent hexagonal system.

10. (b) : Number of tetrahedral voids in the unit cell $= 2 \times$ number of atoms $= 2Z$

11. (a) : In CaF_2 crystal, Ca^{2+} ions are present at all corners and at the centre of each face of the cube while F^- ions occupy all the tetrahedral sites.

12. (a) : Semiconductors are solids where there is only a small difference in energy, called a 'band gap', between the filled valence band of electrons and the conduction band.

Compound	Energy gap (kJ mol^{-1})
Diamond	579
Silicon	106
Germanium	68

13. (b) : The number of nearest neighbours with which a given sphere is in contact is called coordination number. The C.N. in *hcp* and *ccp* arrangement is 12.

14. (d) : The crystals associated with metal excess defect contain free electron. These free electrons are called F-centres and impart colour to the metal ions.

15. (b) : $\text{Density} = \dfrac{nM}{N_A \times a^3}$

$$= \frac{4 \times 58.5}{6.023 \times 10^{23} \times (5.64 \times 10^{-8})^3} = 2.165\text{ g/cm}^3$$

16. (b)

17. (c) : In tetragonal system,

$a = b \neq c,\ \alpha = \beta = \gamma = 90°$

18. **(a) :** In Schottky defect, some of the lattice points are unoccupied (vacancies or holes). The number of missing cations and anions is the same, thus crystal remains neutral.

19. **(a) :** *bcc* has eight atoms at corners and each is shared by 8 unit cells so that the contribution of each atom at corner is $\frac{1}{8}$.

Central atom is not shared with any other unit cell hence, contribution of central atom is 1.

20. **(b) :** Silicon belongs to group 14, it is doped with a group 13 element like B which contains only three valence electrons. The place where the fourth valence e^- is missing is called electron hole. Under the electric field, e^- holes moves toward the negatively charged plate, as if they are positively charged thus, it is a *p*-type semiconductor.

21. **(c) :** In the body-centred cubic unit cell,

$$a\sqrt{3} = 4r$$

$$r = \frac{a\sqrt{3}}{4} = \frac{400\sqrt{3}}{4} = 100\sqrt{3} \text{ pm}$$

22. **(a) :** Suppose number of M atoms $= n$

Then number of tetrahedral sites $= 2n$

Number of N atoms $= \frac{1}{3}(2n)$

Ratio $M : N = n : \frac{2}{3}n = 3 : 2$,

i.e., formula is M_3N_2

23. **(b) :** Let no. of atoms of A used in close packing $= n$

Number of tetrahedral voids $= 2n$

Number of atoms of $B = \frac{1}{3} \times 2n = \frac{2}{3}n$

$A : B = n : \frac{2}{3}n = 3 : 2$

Formula of the compound $= A_3B_2$

24. **(d)** **25.** **(a)** **26.** **(a)**

27. **(d) :** For *bcc* lattice, $a = \frac{4r}{\sqrt{3}}$

$$\Rightarrow \quad a = \frac{4}{\sqrt{3}} \times 4 = 9.23 \text{ Å}$$

28. **(b) :** ZnO turns yellow on heating as Zn^{2+} ions move in interstitial sites and electrons also get entrapped in nearby interstitial sites to maintain electrical neutrality. As extra Zn^{2+} ions are present in interstitial sites thus, it is metal excess defect.

29. **(d) :** In crystal lattice tetrahedral void is smaller than the octahedral void as

Radius of tetrahedral void $= 0.225\ R$

Radius of octahedral void $= 0.414\ R$

Anions are larger in size than cations so anions occupy more space.

30. **(d) :** Graphite has a two dimensional sheet structure. Each C-atom is in sp^2 hybridised state and is linked to three other carbon atoms in a hexagonal planar structure.

For a tetragonal system, $a = b \neq c$, $\alpha = \beta = \gamma = 90°$.

For a hexagonal system, $a = b \neq c$, $\alpha = \beta = 90°$, $\gamma = 120°$.

31. **(b) :** When a silicon crystal is doped with a group-15 element, such as P, As, Sb or Bi the structure of the crystal lattice is left unchanged but an occasional atom with five valence electrons occupies a site that would normally be occupied by a silicon atom. The foreign atom uses four of its electrons in covalent bonding but the remaining fifth electron becomes delocalised and is thus free to contribute to electrical conduction.

32. **(d) :** In a Frenkel defect an ion leaves its position in the lattice and occupies normally vacant interstitial position which does not affect the density of crystal.

33. **(d) :** *bcc* has 68% and *hcp* has 74% packing efficiency.

bcc arrangement has 2 atoms per unit cell, while *hcp* has 4 atoms per unit cell.

Also, *bcc* and *hcp* have different arrangements of particles.

34. **(b) :** When an atom or an ion is missing from its normal lattice site, a lattice vacancy or defect is created, which is called Schottky defect. Due to missing atoms or ions, density of the crystal will be lowered.

35. **(a)** **36.** **(a)**

37. **(c) :** The size of tetrahedral voids is smaller but not half of that of the octahedral voids.

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CHAPTER 16

Solutions

1. The molality of a solution having 18 g of glucose (mol. wt = 180) dissolved in 500 g of water is
(a) 0.2 m (b) 0.1 m
(c) 2.2m (d) 0.5 m *(1995)*

2. The molarity of pure water is
(a) 18.36 M (b) 1.16 M
(c) 55.56 M (d) 5.56 M *(1995)*

3. Which of the following is the correct representation of relative lowering of vapour pressure ?
(a) $\frac{P^o}{\Delta P} = \frac{P^o - P}{P^o}$ (b) $\frac{P^o - P}{P^o}$
(c) $\frac{P^o}{P^o - P}$ (d) $\frac{\Delta P}{P^o} = \frac{P^o - P}{P^o}$ *(1996)*

4. The boiling point of a compound is raised by
(a) intermolecular hydrogen bonding
(b) volatility of compound
(c) intramolecular hydrogen bonding
(d) non-polarity in the molecules. *(1996)*

5. Vapour pressure of benzene at 30°C is 121.8 mm. When 15 g of a non-volatile solute is dissolved in 250 g of benzene, its vapour pressure is decreased to 120.2 mm. The molecular weight of the solute is
(a) 35.67 g (b) 355.5 g
(c) 432.8 g (d) 502.7 g *(1997)*

6. Which of the following is not affected by the temperature?
(a) Molarity (b) Molality
D (c) Normality (d) Formality *(1997)*

7. Which of the following salt has the same value of vant's Hoff factor as that of $K_3[Fe(CN)_6]$?
(a) Na_2SO_4 (b) $Al(NO_3)_3$
(c) $Al_2(SO_4)_3$ (d) Fe_3O_4 *(1998)*

8. The boiling point of water (100°C) becomes 100.52°C, if 3 g of a non-volatile solute is dissolved in 200 mL of water. The molecular weight of solute is (K_b for water = 0.6 K/m)
(a) 17.3 g mol^{-1} (b) 15.4 g mol^{-1}
(c) 12.2 g mol^{-1} (d) 20.4 g mol^{-1} *(1998)*

9. Which of the following is a colligative property?
(a) Surface tension (b) Viscosity
(c) Refractive index (d) Osmotic pressure *(1999)*

10. The vapour pressure of benzene at a certain temperature is 640 mm of Hg. When a non-volatile and non-electrolyte solid weighing 2.175 g is added to 39.08 g of benzene, the vapour pressure of the solution becomes 600 mm of Hg. What is the molecular weight of solid substance?
(a) 69.60 (b) 49.59
(c) 59.60 (d) 108.30 *(1999)*

11. D Which of the following 0.1 M solution will show maximum boiling point?
(a) Sodium chloride (b) Copper chloride
(c) Magnesium sulphate
(d) Chromium sulphate *(2000)*

12. A certain aqueous solution of $FeCl_3$ [formula mass = 162] has a density of 1.1 g/mL and contains 20.0% $FeCl_3$. Molar concentration of this solution is
(a) 0.028 (b) 0.163
(c) 1.357 (d) 1.47 *(2000)*

13. How many litres of ammonia gas at S.T.P. would be needed to prepare 100 mL of 2.5 M ammonium hydroxide solution ?
(a) 5.6 L (b) 0.056 L
(c) 11.2 L (d) 0.56 L. *(2001)*

14. Which one of the following statements given below regarding properties of solutions, describes a colligative effect?
(a) Boiling point of pure water decreases by the addition of ethanol.
(b) Vapour pressure of pure water decreases by the addition of nitric acid.
(c) Vapour pressure of pure benzene decreases by the addition of naphthalene.
(d) Boiling point of pure benzene increases by the addition of toluene. *(2003)*

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15. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream?
(a) 0.16 mol/L
(b) 0.31 mol/L
(c) 0.60 mol/L
(d) 0.45 mol/L.
(2004)

16. A 5% solution (by mass) of cane sugar in water has freezing point of 271 K and freezing point of pure water is 273.15 K. The freezing point of a 5% solution (by mass) of glucose in water is
(a) 271 K
(b) 273.15 K
(c) 269.07 K
(d) 277.23 K *(2006)*

17. 1 mol each of the following compounds is dissolved in 1L of solution. Which will have the largest ΔT_b value?
(a) HF
(b) HCl
(c) HBr
(d) HI *(2007)*

18. The vapour pressure of pure benzene at a certain temperature is 0.850 bar. A non-volatile, non-electrolyte solid weighing 0.5 g is added to 39.0 g of benzene (molar mass 78 g/mol). The vapour pressure of the solution then is 0.845 bar. What is the molecular mass of the solid substance?
(a) 58
(b) 180
(c) 170
(d) 145 *(2007)*

19. For a dilute solution, Raoult's law states that
(a) the relative lowering of vapour pressure is proportional to the amount of solute in solution
(b) the relative lowering of vapour pressure is equal to the mole fraction of solute
(c) the lowering of vapour pressure is equal to the mole fraction of the solute
(d) the vapour pressure of the solution is equal to the mole fraction of the solvent.
(2009)

20. A 0.1 molal solution of an acid is 4.5% ionized. Calculate freezing point. (molecular weight of the acid is 300). $K_f = 1.86$ K mol^{-1} kg.
(a) -0.194°C
(b) 2.00°C
(c) 0°C
(d) -0.269°C
(2009)

21. A mixture of two miscible liquids A and B is distilled under equilibrium conditions at 1 atm pressure. The mole fraction of A in solution and vapour phase are 0.30 and 0.60 respectively. Assuming ideal behaviour of the solution and the vapour, calculate the ratio of the vapour pressure of pure A to that of pure B.
(a) 4.0
(b) 3.5
(c) 2.5
(d) 1.85 *(2009)*

22. When 25 g of Na_2SO_4 is dissolved in 10^3 kg of solution, its concentration will be
(a) 2.5 ppm
(b) 25 ppm
(c) 250 ppm
(d) 100 ppm *(2010)*

23. Which of the following is true for an ideal solution?
(a) $\Delta H_{(mix)} = 0$
(b) $\Delta S_{(mix)} = 0$
(c) $\Delta G_{(mix)} = 0$
(d) None of these
(2013)

24. Boiling point of benzene is 353.23 K. When 1.8 g of non-volatile solute is dissolved in 90 g of benzene, boiling point is raised to 354.11 K. If K_b (benzene) = 2.53 kg mol^{-1} the molecular mass of non-volatile substance is
(a) 58 g mol^{-1}
(b) 120 g mol^{-1}
(c) 116 g mol^{-1}
(d) 60 g mol^{-1}
(2013)

25. The value of Henry's constant K_H is
(a) greater for gases with higher solubility
(b) greater for gases with lower solubility
(c) constant for all gases
(d) not related to the solubility of gases. *(2014)*

26. The relationship between osmotic pressure at 273 K when 10 g glucose (P_1), 10 g urea (P_2) and 10 g sucrose (P_3) are dissolved in 250 mL of water is
(a) $P_1 > P_2 > P_3$
(b) $P_3 > P_1 > P_2$
(c) $P_2 > P_1 > P_3$
(d) $P_2 > P_3 > P_1$
(2015)

27. Two elements A and B form compounds of formula AB_2 and AB_4. When dissolved in 20.0 g of benzene 1.0 g of AB_2 lowers f. pt. by 2.3°C whereas 1.0 g of AB_4 lowers f. pt. by 1.3°C. The K_f for benzene is 5.1. The atomic masses of A and B are
(a) 25, 42
(b) 42, 25
(c) 52, 48
(d) 48, 52 *(2016)*

28. The freezing point of a solution containing 0.2 g of acetic acid in 20.0 g benzene is lowered by 0.45°C. The degree of association of acetic acid in benzene is (Assume acetic acid dimerises in benzene and K_f for benzene = 5.12 K kg mol^{-1})
M_{observed} of acetic acid = 113.78
(a) 94.5%
(b) 54.9%
(c) 78.2%
(d) 100% *(2016)*

29. The depression in freezing point of 0.1 M aqueous solutions of HCl, $CuSO_4$ and K_2SO_4 are in the ratio
(a) 1 : 1 : 1.5
(b) 1 : 2 : 3
(c) 1 : 1 : 1
(d) 2 : 4 : 3 *(2017)*

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ASSERTION AND REASON

30. ***Assertion:*** 0.1 M solution of glucose has same depression in the freezing point as 0.1 M solution of urea.

Reason: K_f for both has same value. *(2000)*

31. ***Assertion :*** Increasing pressure on pure water decreases its freezing point.

Reason : Density of water is maximum at 273 K. *(2003)*

32. ***Assertion :*** The molecular weight of acetic acid determined by depression in freezing point method in benzene and water was found to be different.

Reason : Water is polar and benzene is non-polar. *(2005)*

33. ***Assertion :*** The water pouch of instant cold pack for treating athletic injuries breaks when squeezed and NH_4NO_3 dissolves thus lowering the temperature.

Reason : Addition of non-volatile solute into solvent results into depression of freezing point of solvent. *(2006)*

34. ***Assertion :*** If red blood cells were removed from the body and placed in pure water, pressure inside the cells increases.

Reason : The concentration of salt content in the cells increases. *(2006)*

35. ***Assertion :*** When a concentrated solution is diluted by adding more water, molarity of the solution remains unchanged.

Reason : Product of moles of a solute and volume is equal to the molarity. *(2008)*

36. ***Assertion :*** The molality of the solution does not change with change in temperature.

Reason : The molality is expressed in units of moles per 1000 g of solvent. *(2010)*

37. ***Assertion :*** A non volatile solute is mixed in a solution then elevation in boiling point and depression in freezing point both are 2 K.

Reason : Elevation in boiling point and depression in freezing point both depend on melting point of non-volatile solute. *(2011)*

38. ***Assertion :*** The solubility of a gas in a liquid increases with increase of pressure.

Reason : The solubility of a gas in a liquid is directly proportional to the pressure of the gas. *(2012)*

39. ***Assertion :*** In a pressure cooker, the water is brought to boil. The cooker is then removed from the stove. Now on removing the lid of pressure cooker, the water starts boiling again.

Reason : The impurities in water bring down its boiling point. *(2012)*

40. ***Assertion :*** An ideal solution obeys Raoult's law.

Reason : In an ideal solution, solute-solute as well as solvent-solvent interactions are similar to solute-solvent interactions. *(2014)*

41. ***Assertion :*** Acetone and aniline show negative deviations.

Reason : H–bonding between acetone and aniline is stronger than that between acetone-acetone and aniline-aniline. *(2016)*

42. ***Assertion :*** Azeotropic mixtures are formed only by non-ideal solutions and they may have boiling points either greater than both the components or lesser than both the components.

Reason : The composition of the vapour phase is same as that of the liquid phase of an azeotropic mixture. *(2017)*

Answer Key

1.	(a)	**2.**	(c)	**3.**	(d)	**4.**	(a)	**5.**	(b)	**6.**	(b)	**7.**	(b)	**8.**	(a)
9.	(d)	**10.**	(a)	**11.**	(d)	**12.**	(c)	**13.**	(a)	**14.**	(d)	**15.**	(b)	**16.**	(c)
17.	(d)	**18.**	(c)	**19.**	(b)	**20.**	(a)	**21.**	(b)	**22.**	(b)	**23.**	(a)	**24.**	(a)
25.	(b)	**26.**	(c)	**27.**	(a)	**28.**	(a)	**29.**	(a)	**30.**	**(b)**	**31.**	(c)	**32.**	(a)
33.	(a)	**34.**	(c)	**35.**	(d)	**36.**	(b)	**37.**	(d)	**38.**	(a)	**39.**	(c)	**40.**	(a)
41.	(a)	**42.**	(b)												

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EXPLANATIONS

1. **(a) :** Moles of glucose $= \dfrac{\text{Given mass}}{\text{Molecular mass}} = \dfrac{18}{180}$

$\Rightarrow$ Molality $= \dfrac{0.1}{500} \times 1000 = 0.2\text{m}$

2. **(c) :** Density of water = 1 g/cm^3 and its molecular weight = 18. Therefore, 1000 cm^3 of water will weigh 1000 g of water. We know that

$$\text{Molarity} = \frac{\text{Mass of water}}{\text{Molecular weight}} \times \frac{1000}{V(\text{cm}^3)} = \frac{1000}{18} = 55.56\text{ M}$$

3. **(d) :** Relative lowering of vapour pressure is written as : $\dfrac{\Delta P}{P^\circ} = \dfrac{P^\circ - P}{P^\circ}$

P^0 = Vapour pressure of pure component

P = Vapour pressure of component in solution

4. **(a) :** Intermolecular H-bonding increases the boiling point of a compound as more energy is required to break the hydrogen bonding between the molecules.

5. **(b) :** As, $\dfrac{P^\circ - P}{P^\circ} = \dfrac{\frac{w}{m}}{\frac{w}{m} + \frac{W}{M}}$

P° = vap. pressure of pure component

P = vap. pressure in solution

w = mass of solute, m = mol. wt. of solute

W = mass of solvent, M = mol. wt. of solvent

$$\Rightarrow \frac{121.8 - 120.2}{121.8} = \frac{\frac{15}{M}}{\frac{15}{M} + \frac{250}{78}} \Rightarrow M = 355.5g$$

6. **(b) :** Molality is not affected by temperature because volume does not involve in molality which changes with temperature.

$$\text{Molality} = \frac{\text{Moles of solute}}{\text{Weight of solvent (kg)}}$$

7. **(b) :** $K_3[Fe(CN)_6]$ on ionisation gives 4 species ($3K^+$ and $1\ [Fe(CN)_6]^{3-}$) and $Al(NO_3)_3$ also gives 4 species ($1Al^{3+}$ and $3NO_3^-$), thus both will have same value of van't Hoff factor.

8. **(a) :** As elevation in boiling point is given by :

$\Delta T_b = K_b \times$ molality

Putting the values, we get :

$$100.52 - 100.00 = 0.6 \times \frac{3/M}{200/1000}$$

$\Rightarrow M = 17.3\text{ g mol}^{-1}$

9. **(d) :** Colligative properties are those properties that depend only on the number of particles (ions, atoms, molecules) present in the solution *e.g.*, elevation in boiling point, depression in freezing point, osmotic pressure etc.

10. **(a) :** Relative lowering of vapour pressure is given by :

$\dfrac{P^\circ - P_s}{P^\circ} = x_B$; x_B = mole fraction of solute

P° = vapour pressure of pure solvent

P_s = vapour pressure of solution

$$\Rightarrow \quad \frac{P^\circ - P_s}{P^\circ} = \frac{1}{16} = x_B$$

$$\frac{1}{16} = \frac{2.175/M_B}{\frac{39.08}{78} + \frac{2.175}{M_B}} \Rightarrow M_B = 69.45$$

11. **(d) :** Sodium chloride : NaCl

Copper chloride : Cu_2Cl_2

Magnesium sulphate : $MgSO_4$

Chromium sulphate : $Cr_2(SO_4)_3$

Maximum number of particles (*i.e.* ions) will be obtained when $Cr_2(SO_4)_3$ is dissolved in water hence, 0.1 M solution of chromium sulphate will show maximum elevation in boiling point.

12. **(c) :** 20% $FeCl_3$ solution means 100 g of solution contains 20 g $FeCl_3$.

$\Rightarrow$ Volume of 100 g solution $= \dfrac{100\text{ g}}{1.1\text{ g/mL}} = 90.91$ mL

moles of 20 g $FeCl_3$ $= \dfrac{20}{162} = 0.1234$ mole

$\Rightarrow$ Molar concentration of solution

$$= \frac{0.1234}{90.91} \times 1000 = 1.357\text{ M}$$

13. **(a) :** Molecular weight of NH_4OH = 35

Now, 35 g of NH_4OH is needed to prepare 1 M solution in 1 litre

$\Rightarrow$ 35 g NH_4OH in 1 L solution $\equiv$ 1 molar solution

$\Rightarrow$ 2.5×35 g NH_4OH in 1 L solution $\equiv$ 2.5 molar solution

$\Rightarrow$ $\dfrac{2.5 \times 35}{10}$ g NH_4OH in 100 mL solution $\equiv$ 2.5 molar solution

$\Rightarrow$ 8.75 g NH_4OH was dissolved.

$NH_3 + H_2O \rightarrow NH_4OH$

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For 35 g NH_4OH, NH_3 needed = 22.4 L at S.T.P

$\Rightarrow$ for 8.75 g NH_4OH, NH_3 needed $= \frac{22.4}{35} \times 8.75$ L

$= 5.6$ L

14. **(d) :** Boiling point of a pure solvent increases by increase in number of soluble particles present in it. So by addition of toluene, boiling point of pure benzene increases.

15. **(b) :** $\pi = CRT$

$$C = \frac{\pi}{RT} = \frac{7.8}{0.082 \times 310} = 0.31 \text{ mol/L}$$

16. **(c) :** K_f for water $= \frac{\Delta T_f \times W \times m}{1000 \times w}$

(where W = wt. of water, w = wt. of cane sugar, m = molecular wt. of cane sugar)

$$= \frac{2.15 \times 100 \times 342}{1000 \times 5} = 14.7$$

Now, for 5% glucose,

$\Delta T_f = \frac{K_f \times 1000 \times w_B}{W \times M_B}$ (where w_2 = wt. of glucose, M_B = molecular wt. of glucose)

$$= \frac{14.7 \times 1000 \times 5}{100 \times 180} = 4.08$$

$\therefore$ Freezing point of glucose solution $= 273.15 - 4.08 = 269.07$ K

17. **(d) :** Bond dissociation energy increases in the order : HI < HBr < HCl < HF

HF is most stable halogen acid and HI is the least. Higher the bond dissociation energy, lower is the degree of ionisation.

As we know $\Delta T_b = iK_bm$.

Hence ΔT_b value is largest for HI. All colligative properties depend upon number of particles.

18. **(c) :** $P^\circ = 0.850$ bar, $P_s = 0.845$ bar

$w = 0.5$ g, $M_B = ?$

weight of solvent (benzene) = 39.0 g

and molecular weight of benzene = 78 g

As we know, $\frac{P^\circ - P_s}{P^\circ} = x_B = \frac{n_B}{n_A}$

$$\frac{0.850 - 0.845}{0.850} = \frac{\frac{w_B}{M_B}}{\frac{w_A}{M_A}} = \frac{\frac{0.5}{m}}{\frac{39}{78}}$$

On solving, we get

molecular mass of solid structure (m) = 170 g

19. **(b)**

20. **(a) :** If acid is 4.5% ionized then $\alpha = 0.045$

ΔT_f = molality $\times K_f = 0.1 \times 1.86 = 0.186$

$\Delta T_{exp} = \Delta T_f(1 + \alpha) = 0.186(1 + 0.045) = 0.194$ °C

21. **(b) :** In solution, $x_A = 0.30$; $x_B = 0.70$

In vapour phase, $x'_A = 0.60$; $x'_B = 0.40$

Using Dalton's law and Raoult's law

$$x'_A = 0.60 = \frac{p_A}{P} = \frac{p_A}{p_A + p_B} = \frac{0.30\ p_A^\circ}{0.30\ p_A^\circ + 0.70\ p_B^\circ}$$

$$x'_B = 0.40 = \frac{p_B}{P} = \frac{p_B}{p_A + p_B} = \frac{0.70\ p_B^\circ}{0.30\ p_A^\circ + 0.70\ p_B^\circ}$$

$$\frac{x'_A}{x'_B} = \frac{0.60}{0.40} = \frac{0.30\ p_A^\circ}{0.70\ p_B^\circ}$$

$$\frac{p_A^\circ}{p_B^\circ} = \frac{0.60 \times 0.70}{0.40 \times 0.30} = \frac{7}{2} = 3.5$$

22. **(b) :** When a solute is present in very minute amount (trace quantities), the concentration is expressed in ppm.

$$\text{ppm of } A = \frac{\text{mass of component } A}{\text{total mass of solution}} \times 10^6$$

$$= \frac{0.025}{10^3} \times 10^6 = 25 \text{ ppm}$$

23. **(a) :** For an ideal solution, $\Delta H_{mix} = 0$ and $\Delta V_{mix} = 0$.

24. **(a) :** $T_b^\circ = 353.23$ K, $W_B = 1.8$ g, $W_A = 90$ g, $T_b = 354.11$ K, $K_b = 2.53$ kg mol^{-1}

$\Delta T_b = T_b - T_b^\circ = 354.11 - 353.23 = 0.88$ K

$$M_B = \frac{W_B \times K_b \times 1000}{\Delta T_b \times W_A} = \frac{1.8 \times 2.53 \times 1000}{0.88 \times 90}$$

$= 57.5 \approx 58$ g mol^{-1}

25. **(b) :** $p = K_H x$

Higher the value of K_H at a given pressure, lower is the solubility of the gas in the liquid.

26. **(c) :** $P = \frac{w}{MV}RT$; since w, V and T are same

thus $P \propto (1/M)$.

27. **(a) :** Let the masses of A and B be a and b. The mass of AB_2 will be $(a + 2b)$ g mol^{-1} and AB_4 will be $(a + 4b)$ g mol^{-1}.

$$\Delta T_f = \frac{K_f \times W_B \times 1000}{M_B \times W_A}$$

For AB_2, $2.3 = \frac{5.1 \times 1 \times 1000}{(a + 2b) \times 20}$ ...(i)

For AB_4, $1.3 = \frac{5.1 \times 1 \times 1000}{(a + 4b) \times 20}$ ...(ii)

On solving (i) and (ii), we get
$a = 25.59$ and $b = 42.64$

28. **(a) :** Given : $w_2 = 0.2$ g, $w_1 = 20$ g, $\Delta T_f = 0.45$ °C

$$\Delta T_f = \frac{1000 \times K_f \times w_2}{w_1 \times M}$$

$$\Rightarrow 0.45 = \frac{1000 \times 5.12 \times 0.2}{20 \times M}$$

$\therefore$ $M_{(\text{observed})} = 113.78$ (acetic acid)

$$\begin{array}{lcc} & 2CH_3COOH \rightleftharpoons & (CH_3COOH)_2 \\ \text{Before association} & 1 & 0 \\ \text{After association} & 1 - \alpha & \alpha/2 \end{array}$$

(where α is degree of association)

Molecular weight of acetic acid = 60

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$\therefore \frac{M_{(\text{normal})}}{M_{(\text{observed})}} = 1 - \alpha + \frac{\alpha}{2}$$

or, $\frac{60}{113.78} = 1 - \alpha + \frac{\alpha}{2}$ $\therefore \alpha = 0.945$ or 94.5%

29. **(a) :** $\Delta T_f = iK_f m$
Thus, $\Delta T_f \propto i$ (as concentration is same for all solutions)
i for HCl = 2, i for $CuSO_4$ = 2, i for K_2SO_4 = 3
Thus, ratio of depression in freezing point
= 2 : 2 : 3 = 1 : 1 : 1.5

30. **(b) :** Depression in freezing point is a colligative property which depends on the number of particles present in the solution. As both 0.1 M solution of glucose and 0.1 M solution of urea contain same number of moles (number of particles) therefore, both will have same depression in freezing point.

31. **(c) :** Density of water is maximum at 4°C *i.e.*, 277 K.

32. **(a) :** Depression in freezing point is a colligative property which depends upon the number of particles. The number of particles are different in case of benzene and water because acetic acid undergoes association in benzene and dissociation in water. That is why molecular weight of acetic acid determined by depression in freezing point method is also different.

33. **(a) :** Freezing point of a substance is defined as the temperature at which the vapour pressure of its liquid is equal to the vapour pressure of the corresponding solid. Since the addition of a non-volatile solute always lowers the vapour pressure of solvent, therefore it will be in equilibrium with solid phase at a lower pressure and hence at a lower temperature.

34. **(c) :** If the red blood cells are placed in pure water, pressure inside the cells increases as the water is drawn in and the cell swells.

35. **(d) :** Molarity equation is written as
$M_1V_1 = M_2V_2$ thus if the V_2 changes M_2 also changes.

$$\text{Molarity} = \frac{\text{moles of solute}}{\text{volume of solution in litre}}$$

36. **(b) :** Molality does not depend upon volume thus it does not depend on temperature.

37. **(d) :** Elevation in boiling point $(\Delta T_b) = K_b \times m$
Depression in freezing point $(\Delta T_f) = K_f \times m$
Elevation in boiling point and depression in freezing point are colligative properties *i.e.*, they depend only on the number of particles of the solute. Value of K_b and K_f are different, so ΔT_b and ΔT_f are also different.

38. **(a) :** This is according to Henry's law which states that the solubility of a gas in given volume of a liquid at a particular temperature is directly proportional to the pressure of gas above the liquid. $m \propto p$, $m = Kp$ where K = Henry's constant.

39. **(c) :** In pressure cooker, water boils above 100°C. When the lid of cooker is opened, pressure is lowered so that boiling point decreases and water boils again.

40. **(a)** 41. **(a)**

42. **(b) :** Non-ideal solutions with positive deviation i.e., having more vapour pressure than expected, boil at lower temperature while those with negative deviation boil at higher temperature than those of the components.

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CHAPTER

17

Electrochemistry

1. Which of the following is not true about e.m.f. of a cell?
- (a) Work calculated from it is not the maximum work obtainable from the cell.
- (b) It is maximum voltage obtainable from the cell.
- (c) It is the potential difference between two electrodes when no current is flowing in circuit.
- (d) It is responsible for the flow of steady current in the cell. *(1994)*

2. In which cell the free energy of a chemical reaction is directly converted into electricity?
- (a) Concentration cell (b) Fuel cell
- (c) Lead storage battery (d) Lechlanche cell *(1994)*

3. By the electrolysis of aqueous solution of $CuSO_4$, the products obtained at both the electrodes are
- (a) O_2 at anode and H_2 at cathode
- (b) H_2 at anode and Cu at cathode
- (c) O_2 at anode and Cu at cathode
- (d) $H_2S_2O_8$ at anode and O_2 at cathode. *(1995)*

4. How many grams of silver will be displaced from a solution of $AgNO_3$ by 4 g of magnesium?
- (a) 18 g (b) 4 g
- (c) 36 g (d) 16 g *(1995)*

5. How many electrons flow when a current of 5 amperes is passed through a conductor for 200 seconds?
- (a) 6.25×10^{21} (b) 6.025×10^{21}
- (c) 6.25×10^{22} (d) 6.025×10^{22} *(1997)*

6. A current of 9.95 amperes flowing for 10 minutes, deposits 3 g of a metal. Equivalent weight of the metal is
- (a) 12.5 (b) 18.5
- (c) 21.5 (d) 48.5 *(1997)*

7. Which of the following has been universally accepted as a reference electrode at all temperatures and has been assigned a value of zero volt?
- (a) Platinum electrode
- (b) Copper electrode
- (c) Graphite electrode
- (d) Standard hydrogen electrode *(1998)*

8. A certain current liberated 0.504 g of hydrogen in 2 hours. How many grams of copper can be liberated by the same current flowing for the same time in copper sulphate solution?
- (a) 31.8 g (b) 16.0 g
- (c) 12.7 g (d) 63.5 g *(1995)*

9. The specific conductance of a *N*/10 KCl at 25°C is 0.0112 ohm^{-1} cm^{-1}. The resistance of cell containing solution at the same temperature was found to be 55 ohm. The cell constant will be
- (a) 6.16 cm^{-1} (b) 0.616 cm^{-1}
- (c) 0.0616 cm^{-1} (d) 616 cm^{-1} *(1998, 2009)*

10. Which of the following statement is true for an electrochemical cell?
- (a) H_2 is anode and Cu is cathode.
- (b) H_2 is cathode and Cu is anode.
- (c) Reduction occurs at H_2 electrode.
- (d) Oxidation occurs at Cu electrode. *(1999)*

11. What is the amount of chlorine evolved, when 2 A of current is passed for 30 minutes in an aqueous solution of NaCl?
- (a) 9.81 g (b) 1.32 g
- (c) 4.56 g (d) 12.6 g *(1999)*

12. The specific conductivity of *N*/10 KCl solution at 20°C is 0.0212 ohm^{-1} cm^{-1} and the resistance of cell containing this solution at 20°C is 55 ohm. The cell constant is
- (a) 2.173 cm^{-1} (b) 1.166 cm^{-1}
- (c) 4.616 cm^{-1} (d) 3.324 cm^{-1} *(1999)*

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13. A spoon to be electroplated with gold should be
(a) cathode (b) anode
(c) electrolyte (d) none of these.
(1995, 2001)

14. How many electrons are delivered at the cathode during electrolysis by a current of 1 A in 60 seconds?
(a) 3.74×10^{20} (b) 6.0×10^{23}
(c) 7.48×10^{21} (d) 6.0×10^{20} *(2001)*

15. The number of mole of electrons required to deposit 1 g equivalent aluminium (atomic wt. = 27) from a solution of aluminium chloride will be
(a) 3 (b) 1
(c) 4 (d) 2 *(1995, 2001)*

16. Which of the following reactions is used to make a fuel cell?
(a) $Cd_{(s)} + 2Ni(OH)_{3(s)} \rightarrow CdO_{(s)} + 2Ni(OH)_{2(s)} + H_2O_{(l)}$
(b) $Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$
(c) $2H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$
(d) $2Fe_{(s)} + O_{2(g)} + 4H^+_{(aq)} \rightarrow 2Fe^{2+}_{(aq)} + 2H_2O_{(l)}$
(2003)

17. Time required to deposit one millimole of aluminium metal by the passage of 9.65 amperes through aqueous solution of aluminium ion is
(a) 30 s (b) 10 s
(c) 30,000 s (d) 10,000 s.
(2003)

18. Which of the following statements is true for the electrochemical Daniell cell?
(a) Electrons flow from copper electrode to zinc electrode.
(b) Current flows from zinc electrode to copper electrode.
(c) Cations move towards copper electrode.
(d) Cations move towards zinc electrode.
(2004)

19. The chemical reaction,
$2AgCl_{(aq)} + H_{2(g)} \rightarrow 2HCl_{(aq)} + 2Ag_{(s)}$
taking place in a galvanic cell is represented by the notation
(a) $Pt_{(s)} | H_{2(g)}$, 1 bar | 1 M $KCl_{(aq)} | AgCl_{(s)} | Ag_{(s)}$
(b) $Pt_{(s)} | H_{2(g)}$, 1 bar | 1 M $HCl_{(aq)}$ | 1 M $Ag^+_{(aq)} | Ag_{(s)}$
(c) $Pt_{(s)} | H_{2(g)}$, 1 bar | 1 M $HCl_{(aq)} | AgCl_{(s)} | Ag_{(s)}$
(d) $Pt_{(s)} | H_{2(g)}$, 1 bar | 1 M $HCl_{(aq)} | Ag_{(s)} | AgCl_{(s)}$
(2005)

20. The charge required for the reduction of 1 mol of MnO_4^- to MnO_2 is
(a) 1 F (b) 3 F
(c) 5 F (d) 6 F. *(2006)*

21. The products formed when an aqueous solution of NaBr is electrolysed in a cell having inert electrodes are
(a) Na and Br_2 (b) Na and O_2
(c) H_2, Br_2 and NaOH (d) H_2 and O_2.
(2006)

22. The time period to coat a metal surface of 80 cm² with 5×10^{-3} cm thick layer of silver (density 1.05 g cm^{-3}) with the passage of 3 A current through a silver nitrate solution is
(a) 115 sec (b) 125 sec
(c) 135 sec (d) 145 sec. *(2008)*

23. For the following concentration cell, to be spontaneous $Pt(H_2)P_1$ atm $|HCl|Pt(H_2)P_2$ atm, which of the following is correct?
(a) $P_1 = P_2$
(b) $P_1 < P_2$
(c) $P_1 > P_2$
(d) cannot be predicted *(2008)*

24. To observe the effect of concentration on the conductivity electrolytes of different nature were taken in two vessels *A* and *B*. *A* contains weak electrolyte NH_4OH and *B* contains strong electrolyte NaCl. In both containers, concentration of respective electrolyte was increased and the observation is
(a) in *A* conductivity increases, in *B* conductivity decreases
(b) in *A* conductivity decreases, while in *B* conductivity increases
(c) in both *A* and *B* conductivity increase
(d) in both *A* and *B* conductivity decrease.
(2008)

25. The standard oxidation potential E° for the half cell reaction are
$Zn \rightarrow Zn^{2+} + 2e$; $E^\circ = +0.76V$
$Fe \rightarrow Fe^{2+} + 2e$; $E^\circ = +0.41V$
EMF of the cell reaction is
$Zn + Fe^{2+} \rightarrow Zn^{2+} + Fe$
(a) − 0.35 V (b) + 0.35 V
(c) 0.17 V (d) 1.17 V
(2008)

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26. Hydrofluoric acid is a weak acid. At 25 °C, the molar conductivity of 0.002 M HF is 176.2 Ω^{-1} cm^2 mol^{-1}. If its Λ_m^o = 405.2 Ω^{-1} cm^2 mol^{-1}, Equilibrium constant at the given concentration is

(a) 6.7×10^{-4} M (b) 3.2×10^{-4} M

(c) 6.7×10^{-5} M (d) 3.2×10^{-5} M

(2009)

27. A factory produces 40 kg of calcium in two hours by electrolysis. How much aluminium can be produced by same current in 2 hours if current efficiency is 50%?

(a) 22 kg (b) 18 kg

(c) 9 kg (d) 27 kg *(2010)*

28.

Electrolyte	KCl	KNO_3	HCl	NaOAc	NaCl
Λ^∞ (S cm^2 mol^{-1})	149.9	145.0	426.2	91.0	126.5

Calculate Λ_{HOAc}^∞ (in s cm^2 mol^{-1}) using appropriate molar conductances of the electrolytes listed above at infinite dilution in H_2O at 25 °C.

(a) 517.2 (b) 552.7

(c) 390.7 (d) 217.5

(2010, 2017)

29. The standard half-cell reduction potential for $Ag^+|Ag$ is 0.7991 V at 25°C. Given the experimental value $K_{sp} = 1.56 \times 10^{-10}$ for AgCl, calculate the standard half-cell reduction potential for the Ag|AgCl electrode.

(a) 0.2192 V (b) – 0.2192 V

(c) –1.2192 V (d) 1.2192 V

(2010)

30. For the electrochemical cell, $X^- \mid X \parallel M^+ \mid M$, $E^\circ(M^+ \mid M) = 0.44$ V and $E^\circ(X \mid X^-) = 0.33$ V. From this data one can deduce that

(a) $M + X \rightarrow M^+ + X^-$ is the spontaneous reaction

(b) $M^+ + X^- \rightarrow M + X$ is the spontaneous reaction

(c) $E_{cell} = 0.77$ V

(d) $E_{cell} = -0.77$ V *(2010)*

31. For $Zn^{2+} \mid Zn$, $E^\circ = -0.76$ V then EMF of the cell

$Zn \mid Zn^{2+}$ (1 M) $\parallel$ $2H^+$ (1 M)| H_2 (1 atm) will be

(a) – 0.76 V (b) 0.76 V

(c) 0.38 V (d) – 0.38 V

(2012)

32. Electrode potential of hydrogen electrode is 18 mV, then $[H^+]$ is

(a) 0.2 M (b) 1 M

(c) 2 M (d) 5 M *(2013)*

33. Which cell will measure standard electrode potential of copper electrode?

(a) $Pt_{(s)} \mid H_{2(g,\ 0.1\ bar)} \mid H^+_{(aq,\ 1\ M)} \parallel Cu^{2+}_{(aq,\ 1\ M)} \mid Cu_{(s)}$

(b) $Pt_{(s)} \mid H_{2(g,\ 1\ bar)} \mid H^+_{(aq,\ 1\ M)} \parallel Cu^{2+}_{(aq,\ 2\ M)} \mid Cu_{(s)}$

(c) $Pt_{(s)} \mid H_{2(g,\ 1\ bar)} \mid H^+_{(aq,\ 1\ M)} \parallel Cu^{2+}_{(aq,\ 1\ M)} \mid Cu_{(s)}$

(d) $Pt_{(s)} \mid H_{2(g,\ 1\ bar)} \mid H^+_{(aq,\ 0.1\ M)} \parallel Cu^{2+}_{(aq,\ 1\ M)} \mid Cu_{(s)}$

(2014)

34. What is the amount of chlorine liberated when 2 A of current is passed for 60 minutes in an aqueous solution of NaCl?

(a) 2.507 g (b) 1.364 g

(c) 2.648 g (d) 3.469 g *(2015)*

35. How many Faradays of electricity are required for the given reaction to occur?

$$MnO_4^- \longrightarrow Mn^{2+}$$

(a) 5F (b) 3F

(c) 1F (d) 7F *(2016)*

36. A conductivity cell has a cell constant of 0.5 cm^{-1}. This cell when filled with 0.01 M NaCl solution has a resistance of 384 ohms at 25 °C. Calculate the equivalent conductance of the given solution.

(a) 130.2 Ω^{-1} cm^2 $(g\ eq)^{-1}$

(b) 137.4 Ω^{-1} cm^2 $(g\ eq)^{-1}$

(c) 154.6 Ω^{-1} cm^2 $(g\ eq)^{-1}$

(d) 169.2 Ω^{-1} cm^2 $(g\ eq)^{-1}$ *(2016)*

ASSERTION AND REASON

37. ***Assertion*:** In electrolysis, the quantity of electricity needed for depositing 1 mole of silver is different from that required for 1 mole of copper.

***Reason*:** The atomic weights of silver and copper are different. *(1996, 2016)*

38. ***Assertion*:** Sodium ions are discharged in preference to hydrogen ions at mercury electrode.

***Reason*:** The nature of cathode can affect the order of discharge of cations. *(1996)*

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39. ***Assertion:*** Identification of cathode and anode is done by the use of a thermometer.
Reason: Higher the value of reduction potential, greater would be its reducing power. *(1999)*

40. ***Assertion:*** Zinc displaces copper from copper sulphate solution.
Reason: The $E^\circ_{298\text{ K}}$ of Zn is –0.76 volts and that of Cu is +0.34 volts. *(1999, 2010, 2015)*

41. ***Assertion:*** Equivalent conductance of all electrolytes decreases with increasing concentration.
Reason: Lesser number of ions are available per gram equivalent at higher concentration. *(1999)*

42. ***Assertion :*** Galvanised iron does not rust.
Reason : Zinc has a more negative electrode potential than iron. *(2005)*

43. ***Assertion :*** For the Daniell cell, $Zn|Zn^{2+} || Cu^{2+}|Cu$ with E°_{cell} = 1.1 V, the application of opposite potential greater than 1.1 V results into flow of electrons from cathode to anode.
Reason : Zn is deposited at anode and Cu is dissolved at cathode. *(2006)*

44. ***Assertion :*** A reaction is spontaneous if E_{cell} = +ve.
Reason : For E_{cell} = +ve, ΔG is always –ve. *(2011)*

45. ***Assertion :*** Conductivity of all electrolytes decreases on dilution.
Reason : On dilution number of ions per unit volume decreases. *(2014)*

46. ***Assertion :*** Pure iron when heated in dry air is covered with a layer of rust.
Reason : Rust has the composition Fe_3O_4. *(2015)*

47. ***Assertion :*** If standard reduction potential for the reaction $Ag^+ + e^- \rightarrow Ag$ is 0.80 volt, then for the reaction $2Ag^+ + 2e^- \rightarrow 2Ag$, it will be 1.60 volt.
Reason : If concentration of Ag^+ ions is doubled, the standard electrode potential is also doubled. *(2017)*

Answer Key

1.	(a)	**2.**	(b)	**3.**	(c)	**4.**	(c)	**5.**	(a)	**6.**	(d)	**7.**	(d)	**8.**	(b)
9.	(b)	**10.**	(a)	**11.**	(b)	**12.**	(b)	**13.**	(a)	**14.**	(a)	**15.**	(a)	**16.**	(c)
17.	(b)	**18.**	(c)	**19.**	(b)	**20.**	(b)	**21.**	(c)	**22.**	(b)	**23.**	(c)	**24.**	(d)
25.	(b)	**26.**	(a)	**27.**	(c)	**28.**	(c)	**29.**	(a)	**30.**	(b)	**31.**	(b)	**32.**	(c)
33.	(c)	**34.**	(c)	**35.**	(a)	**36.**	(a)	**37.**	(b)	**38.**	(a)	**39.**	(d)	**40.**	(a)
41.	(a)	**42.**	(a)	**43.**	(b)	**44.**	(a)	**45.**	(a)	**46.**	(d)	**47.**	(d)		

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EXPLANATIONS

1. **(a) :** E.M.F. is defined as the potential difference between two electrodes when current is flowing in circuit. It is the maximum work obtainable from the cell.

2. **(b) :** Fuel cell *e.g.*, $H_{2(g)} + O_{2(g)} \rightarrow 2H_2O_{(l)}$

3. **(c) :** Oxygen is oxidised at anode while Cu^{2+} is reduced at cathode. Therefore, copper deposits on cathode and oxygen is evolved at anode.

4. **(c) :** Weight of magnesium = 4 g

We know that, $\dfrac{\text{Weight of silver displaced }(M)}{\text{Weight of magnesium}}$

$= \dfrac{\text{Equivalent weight of silver}}{\text{Equivalent weight of magnesium}}$ or $\dfrac{M}{4} = \dfrac{108}{12}$

or $M = \dfrac{108 \times 4}{12} = 36$ g

5. **(a) :** $Q = It = 5 \times 200 = 1000$ coulombs

Charge carried by 1 electron = 1.6×10^{-19}C

$\Rightarrow$ No. of electrons in 1000 C = $\dfrac{1000}{1.6 \times 10^{-19}}$
= 6.25×10^{21}

6. **(d) :** Charge = Current × time
= 9.95 × 10 × 60 = 5970 C

$\therefore$ 5970 C deposits 3 g of metal.

$\Rightarrow$ 96500 C will deposit = $\dfrac{3}{5970} \times 96500$ g metal
= 48.49 g metal

Therefore, equivalent weight is 48.49 g

7. **(d) :** Hydrogen electrode is the primary standard electrode. The hydrogen electrode can act as cathode or anode with respect to other electrode.

$H_2 \rightarrow 2H^+ + 2e^-$ (Anode)

$2H^+ + 2e^- \rightarrow H_2$ (cathode)

8. **(b) :** $\dfrac{\text{Mass of Hydrogen}}{\text{Mass of copper}}$

$= \dfrac{\text{Equivalent mass of hydrogen}}{\text{Equivalent mass of copper}}$

$\Rightarrow \dfrac{0.504}{\text{Mass of copper}} = \dfrac{1}{63.5/2}$

$\Rightarrow$ Mass of copper deposited = 16.0 g

9. **(b) :** We know that,

Specific conductance = Cell constant × Conductance

$\Rightarrow$ Cell constant = Resitance × *sp.* conductance
= $55 \times 0.0112 = 0.616$ cm^{-1}

10. **(a)**

11. **(b) :** As $Q = It$

$\Rightarrow$ Total charge carried = $2 \times 30 \times 60 = 3600$ C

Now, 96500 C of charge deposits 35.5 g chlorine

$\Rightarrow$ 3600 C of charge will deposit

$= \dfrac{35.5}{96500} \times 3600 = 1.32$ g

12. **(b) :** We know that,

Specific conductance = Cell constant × Conductance

$\Rightarrow$ Cell constant = Resistance × specific conductance
= $0.0212 \times 55 = 1.166$ cm^{-1}

13. **(a) :** Standard electrode potential for gold is 1.50 volt. Therefore, gold gets easily reduced. So to electroplate gold on the spoon, spoon should be made cathode as reduction takes place on cathode.

14. **(a) :** Charge = Current × Time

Charge, $Q = 1$ A × 60 sec = 60 coulombs

Now, 96500 C charge is carried by 6.023×10^{23} electrons

$\Rightarrow$ 60 C charge = $\dfrac{6.023 \times 10^{23}}{96500} \times 60$ electrons
= 3.74×10^{20} electrons

15. **(a) :** $Al^{3+} + 3e^- \rightarrow Al$

Therefore, 3 moles of electrons are required to deposit 1 g equivalent of aluminium.

16. **(c) :** Fuel cells are galvanic cells in which chemical energy of fuel is directly converted into electrical energy.

e.g., Hydrogen - oxygen fuel cell.

17. **(b) :** $Al^{3+} + 3e^- \rightarrow Al$

For deposition of 1g equivalent, charge required ≡ 96500 C

For deposition of 1 millimole, charge required ≡ 96.500 C

As $Q = It \Rightarrow t = \dfrac{Q}{I} = \dfrac{96.5}{9.65} = 10$ s

18. **(c) :** In Daniell cell, during the passage of electric current through external circuit, electrons flow from the zinc electrode to the copper electrode. At the zinc electrode, the zinc metal is oxidised to Zn^{2+} which goes into the solution. The electrons released at the electrode travel through the external circuit to the copper electrode where they are used in the reduction of Cu^{2+} ions to metallic copper which is deposited

---

on the electrode.
19. (b) : 2AgC
The cell reactior
$Pt_{(s)}|H_{2(g)}$, 1
or $Pt_{(s)}|H_{2(g)}$,
20. (b) : MnO
Charge required
to MnO_2 = 3 F
21. (c) : NaBr
At cathode : 2I
At anode : 2Br
In solution : N
As discharge p
of Na^+ ions ar
lower than that
and Br_2 is libe
22. (b) : Wei
= 80 × 5
$\because$ $w = \dfrac{Ei}{965}$
$\therefore$ 0.42 =
23. (c) : Pt(
For spontaneo
$P_1 > P_2$.
E_{cell} =
Also, if P_1 >
and reductio
24. (d) : S
ions comp
concentratio
conductance
The one wh
called weak
electrolyte
decreases in
conductanc
25. (b) :
26. (a) :
$\alpha = \dfrac{\Lambda_c}{\Lambda^\circ_m}$ =
$K = \dfrac{[H^+][}{[HF}$

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on the electrode.

19. **(b) :** $2AgCl_{(aq)} + H_{2\,(g)} \rightarrow 2HCl_{(aq)} + 2Ag_{(s)}$

The cell reaction will be

$$Pt_{(s)}|H_{2(g)}, 1\text{ bar}|H^+_{(aq)}\, 1\text{ M}|AgCl_{(aq)}\, 1\text{ M}\,|Ag_{(s)}$$

or $$Pt_{(s)}|H_{2(g)}, 1\text{ bar}\,|1\text{ M } HCl_{(aq)}\,||1\text{ M } Ag^+_{(aq)}|Ag_{(s)}$$

20. **(b) :** $MnO_4^- + 2H_2O + 3e^- \rightarrow MnO_2 + 4OH^-$

Charge required for the reduction of 1 mol of MnO_4^- to $MnO_2 = 3$ F

21. **(c) :** $NaBr \rightleftharpoons Na^+ + Br^-$, $H_2O \rightleftharpoons H^+ + OH^-$

At cathode : $2H^+ + 2e^- \rightarrow H_2$

At anode : $2Br^- \rightarrow Br_2 + 2e^-$

In solution : $Na^+ + OH^- \rightarrow NaOH$

As discharge potential of H^+ ions is lower than that of Na^+ ions and discharge potential of Br^- ions is lower than that of OH^- ions, H_2 is liberated at cathode and Br_2 is liberated at anode.

22. **(b) :** Weight of Ag required $= V \times d$

$= 80 \times 5 \times 10^{-3} \times 1.05 = 0.42$ g

$\because \quad w = \dfrac{Eit}{96500}$

$\therefore \quad 0.42 = \dfrac{108 \times 3 \times t}{96500} \Rightarrow t = 125$ sec

23. **(c) :** $Pt(H_2)\ P_1$ atm | $Pt(H_2)\ P_2$ atm

For spontaneous reaction, E_{cell} should be positive, so $P_1 > P_2$.

$$E_{cell} = \frac{0.059}{2}\log\frac{P_1}{P_2}$$

Also, if $P_1 > P_2$, oxidation occurs at L.H.S. electrode and reduction occurs at R.H.S. electrode.

24. **(d) :** Solution which contains large number of ions compared to another solution of same concentration at the same temperature has more conductance and is said to be stronger electrolyte. The one which has relatively small number of ions is called weak electrolyte. If concentration of respective electrolyte is increased, the equivalent conductance decreases in each case, but rapid decrease in equivalent conductance is seen in weak electrolyte.

25. **(b) :** $E^\circ_{cell} = 0.76 - 0.41 = 0.35$ V

26. **(a) :**

$$\alpha = \frac{\Lambda_c}{\Lambda^\circ_m} = \frac{176.2\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}}{405.2\ \Omega^{-1}\text{ cm}^2\text{ mol}^{-1}} = 0.435$$

$$K = \frac{[H^+][F^-]}{[HF]} = \frac{C\alpha^2}{1-\alpha} = \frac{(0.002\text{ M})(0.435)^2}{1-0.435}$$

$= 6.70 \times 10^{-4}$ M

27. **(c) :** $\dfrac{W_{Ca}}{E_{Ca}} = \dfrac{W_{Al}}{E_{Al}} \Rightarrow \dfrac{40}{20} = \dfrac{W_{Al}}{9} \Rightarrow W_{Al} = 18$ kg

As current efficiency is 50% so, $W_{Al} = 9$ kg

28. **(c) :** $\Lambda^\infty_{HOAc} = \Lambda^\infty_{NaOAc} + \Lambda^\infty_{HCl} - \Lambda^\infty_{NaCl}$

$= 91.0 + 426.2 - 126.5$ S cm^2 mol^{-1}

$= 390.7$ S cm^2 mol^{-1}

29. **(a) :** For the desired reaction,

$$AgCl + 1e^- \rightarrow Ag + Cl^-,\ E^\circ = \frac{-\Delta_r G^\circ}{(1)F}$$

The needed $\Delta_r G^\circ$ can be obtained by adding the values of $\Delta_r G^\circ$ for the reactions,

$Ag^+ + 1e^- \rightarrow Ag;\ \Delta_r G^\circ = -nFE^\circ$

$AgCl \rightarrow Ag^+ + Cl^-;\ \Delta_r G^\circ = -RT\ln K_{sp}$

$$\Delta_r G^\circ = -(1\text{ mol})(9.648\times10^4\text{ J mol}^{-1}\text{ V}^{-1})(0.7991\text{ V})$$
$$-(8.314\text{ JK}^{-1}\text{mol}^{-1})(298\text{ K})\ln(1.56\times10^{-10})$$
$$= -77.10\text{ kJ} + 55.95\text{ kJ} = -21.15\text{ kJ}$$

$$\therefore\ E^\circ = \frac{-(-21.15)}{(1)(96.485)} = +0.2192\text{ V}$$

30. **(b) :** $M^+ + X^- \rightarrow M + X$ is spontaneous because for the cell represented by $X^-|X||M^+|M$, the value of E° is positive *i.e.*, $(0.44 - 0.33)$ V = 0.11 V.

31. **(b) :** $\overset{\circ}{E}_{cell} = \overset{\circ}{E}_{right} - \overset{\circ}{E}_{left}$

$\overset{\circ}{E}_{cell} = 0 - (-0.76) = 0.76$

32. **(c) :** Given : $E_{H^+/H_2} = 18\times10^{-3}$ V, $[H^+] = ?$

Applying Nernst equation,

$$E_{H^+/H_2} = E^\circ_{H^+/H_2} - \frac{0.0591}{1}\log\frac{1}{[H^+]}$$

18×10^{-3} V $= 0 + 0.0591 \log [H^+]$

18×10^{-3} V $= 0.0591 \log [H^+]$

$\log [H^+] = 0.3046$

$\therefore\quad [H^+] = \text{antilog}\ (0.3046) = 2.02 = 2.0$ M

33. **(c) :** To calculate the standard electrode potential of the given cell it is coupled with the standard hydrogen electrode in which pressure of hydrogen gas is one bar and the concentration of H^+ ions in the solution is one molar and also the concentrations of the oxidised and the reduced forms of the species in the right hand half-cell are unity.

34. **(c) :** According to Faraday's law,

$$w = Zit = \frac{35.5}{96,500}\times2\times\frac{3600}{1} = 2.648\text{ g}$$

35. **(a) :** $\overset{+7}{\text{Mn}}\text{O}_4^- \longrightarrow \text{Mn}^{2+}$

The reaction can be written as :

$$MnO_4^- + 5e^- \rightarrow Mn^{2+}$$

Hence, 5 moles of electrons or 5F of electricity are required for the given reaction.

36. **(a) :** Equivalent conductance, $\Lambda_{eq} = \frac{\kappa \times 1000}{\text{Normality}}$

where, κ (Specific conductance) $= C \times \frac{l}{a}$

$$= \frac{1}{R} \times \frac{l}{a} = \frac{1}{384} \times 0.5 = 1.302 \times 10^{-3}\ \text{ohm}^{-1}\ \text{cm}^{-1}$$

$$\therefore \quad \Lambda_{eq} = \frac{1.302 \times 10^{-3} \times 1000}{0.01}$$

$$= 130.2\ \text{ohm}^{-1}\ \text{cm}^2\ (\text{g eq})^{-1}$$

37. **(b) :** $Ag^+ + e^- \rightarrow Ag$, $Cu^{2+} + 2e^- \rightarrow Cu$

For deposition of Ag, 1 mole of electrons is required while for Cu, 2 moles of electrons are required. So quantity of electricity needed for depositing 1 mole of silver is different from 1 mole of copper.

38. **(a) :** Hydrogen ions are discharged in preference to sodium normally but at mercury electrode, sodium ions are discharged first due to the formation of amalgam (Na / Hg).

39. **(d) :** Identification of cathode and anode is done by using ammeter Higher the value of reduction potential, greater would be its oxidising power.

40. **(a) :** $Zn + Cu^{2+}_{(aq)} \rightarrow Zn^{2+}_{(aq)} + Cu$

$E^\circ_{Cu^{2+}/Cu} = 0.34\ \text{V}, \qquad E^\circ_{Zn^{2+}/Zn} = -0.76\ \text{V}$

The above values show that zinc will release electrons and copper will be reduced.

41. **(a) :** Equivalent conductance is defined as the conducting power of all the ions produced by one gram equivalent of the electrolyte in a given solution. Therefore, at higher concentration, degree of dissociation of electrolyte is less. Degree of dissociation can be increased by dilution.

42. **(a) :** Zinc metal which has a more negative electrode potential than iron will provide electrons in preference to the iron, and therefore corrodes first. Only when all the zinc has been oxidised, iron starts to rust.

43. **(b) :** If the opposing potential becomes slightly larger than that of the cell potential, the direction of current flow is reversed, and so is the cell reaction. Now, zinc ions are converted to zinc at one electrode and Cu is converted into copper ion and the overall cell reaction becomes

$$Zn^{++} + Cu \rightarrow Zn + Cu^{++}$$

44. **(a) :** For a redox reaction to be spontaneous, the EMF of the cell must be positive.

As, $-\Delta G = nFE_{\text{cell}}$

Therefore, for $E_{\text{cell}} = +\text{ve}$, ΔG is always negative.

45. **(a)**

46. **(d) :** Dry air has no action on pure iron. Rust has the composition $Fe_2O_3 \cdot xH_2O$.

47. **(d) :** Standard reduction potential of an electrode has a fixed value.

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CHAPTER 18

Chemical Kinetics

1. The rate, at which a substance reacts, depends upon its
   (a) equivalent mass (b) molecular mass
   (c) active mass (d) atomic mass.
   (1996)

2. The extra amount of energy, which the molecules of the reactants have to absorb, so that their energy becomes equal to the threshold energy, is called
   (a) kinetic energy
   (b) potential energy
   (c) chemical energy
   (d) activation energy. *(1997)*

3. A first order reaction, which is 30% complete in 30 minutes has a half-life period of
   (a) 102.2 min (b) 58.2 min
   (c) 24.2 min (d) 120.2 min
   (1998, 2016)

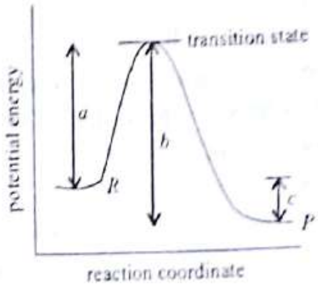
4. The rate constant of a reaction is 0.69×10^{-2} min^{-1} and the initial concentration is 0.2 mol L^{-1}. The half-life period is
   (a) 800 sec (b) 600 sec
   (c) 400 sec (d) 6024 sec
   (1998)

5. The rate constant of a first order reaction is 3×10^{-6} per sec. If the initial concentration is 0.10 M, the initial rate of reaction is
   (a) 3×10^{-6} M s^{-1} (b) 3×10^{-5} M s^{-1}
   (c) 3×10^{-8} M s^{-1} (d) 3×10^{-7} M s^{-1}
   (1999)

6. The salient feature of the theory of absolute reaction rates is the
   (a) formation of activated complex
   (b) collision of the reactant molecules
   (c) matching potential energy of the reactant molecules
   (d) decrease of entropy of the reactant molecules. *(2000)*

7. For the reaction :
   $H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$
   the order of reaction is
   (a) 0 (b) 2
   (c) 1 (d) 3. *(2002)*

8. The potential energy diagram for a reaction $R \rightarrow P$ is given in the figure. ΔH° of the reaction corresponds to the energy

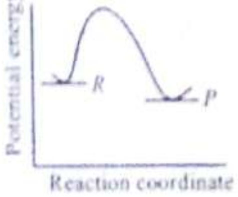


   (a) a (b) b
   (c) c (d) $a + b$ *(2003)*

9. The rate constant k, for the reaction
   $$N_2O_{5\,(g)} \rightarrow 2NO_{2\,(g)} + 1/2\ O_{2\,(g)}$$
   is 2.3×10^{-2} s^{-1}. Which equation given below describes the change of $[N_2O_5]$ with time? $[N_2O_5]_0$ and $[N_2O_5]_t$ correspond to concentration of N_2O_5 initially and at time t.
   (a) $[N_2O_5]_t = [N_2O_5]_0 + kt$
   (b) $[N_2O_5]_0 = [N_2O_5]_t e^{kt}$
   (c) $\log[N_2O_5]_t = \log[N_2O_5]_0 + kt$
   (d) $\ln\frac{[N_2O_5]_0}{[N_2O_5]_t} = kt$ *(2004)*

10. An endothermic reaction with high activation energy for the forward reaction is given by the diagram

   (a)



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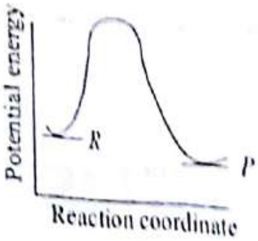
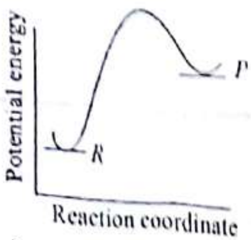
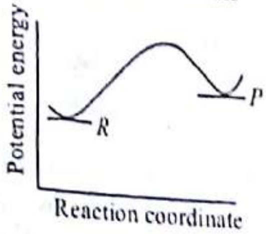
(b)



(c)



(d)



(2005)

11. For reaction $aA \rightarrow xP$, when $[A] = 2.2$ mM, the rate was found to be 2.4 mM s^{-1}. On reducing concentration of A to half, the rate changes to 0.6 mM s^{-1}. The order of reaction with respect to A is

(a) 1.5
(b) 2.0
(c) 2.5
(d) 3.0

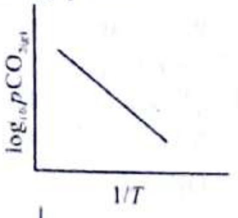
(2005, 2015)

12. For the chemical equilibrium,

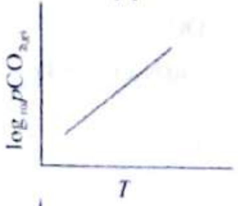
$$CaCO_{3\,(s)} \rightleftharpoons CaO_{(s)} + CO_{2\,(g)},$$

$\Delta H_r°$ can be determined from which one of the following plots?

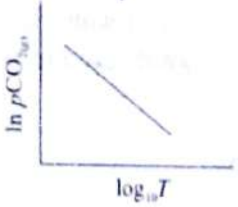
(a)



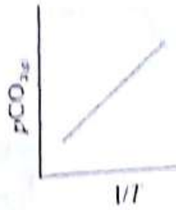
(b)



(c)



(d)



(2005)

13. For the reaction, $2N_2O_5 \rightarrow 4NO_2 + O_2$ rate of reaction is

(a) $\frac{1}{2}\frac{d}{dt}[N_2O_5]$
(b) $2\frac{d}{dt}[N_2O_5]$
(c) $\frac{1}{4}\frac{d}{dt}[NO_2]$
(d) $4\frac{d}{dt}[NO_2]$

(2006)

14. For the reaction, $2NO_2 + F_2 \rightarrow 2NO_2F$, following mechanism has been provided.

$$NO_2 + F_2 \xrightarrow{\text{Slow}} NO_2F + F$$

$$NO_2 + F \xrightarrow{\text{Fast}} NO_2F$$

Thus, rate expression of the above reaction can be written as

(a) $r = k[NO_2]_2[F_2]$
(b) $r = k[NO_2][F_2]$
(c) $r = k[NO_2]$
(d) $r = k[F_2]$

(2008)

15. Acid hydrolysis of sucrose is a

(a) pseudo first order reaction
(b) zero order reaction
(c) second order reaction
(d) unimolecular reaction.

(2008)

16. In a homogenous reaction $A \rightarrow B + C + D$ the initial pressure was P_0 and after time t it was P. Expression for rate constant k in terms of P_0, P and t will be

(a) $k = \frac{2.303}{t}\log\frac{2P_0}{3P_0 - P}$

(b) $k = \frac{2.303}{t}\log\frac{2P_0}{P_0 - P}$

(c) $k = \frac{2.303}{t}\log\frac{3P_0 - P}{2P_0}$

(d) $k = \frac{2.303}{t}\log\frac{2P_0}{3P_0 - 2P}$

(2009)

17. Which curve corresponds to the temperature dependance of the rate R of a simple one step reaction?

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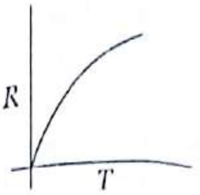
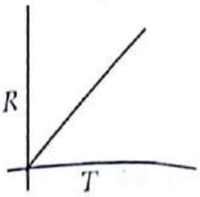
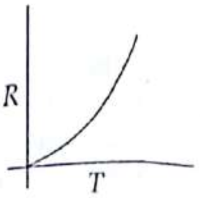
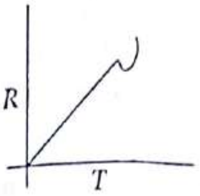
(a) 

(b) 

(c) 

(d) 

(2009)

18. For a 1st order reaction if concentration is doubled then rate of reaction becomes

(a) double (b) half
(c) four times (d) remains same. *(2010)*

19. For a reaction $X \rightarrow Y$, the graph of the product concentration (x) versus time (t) came out to be a straight line passing through the origin. Hence the graph of $\frac{-d[X]}{dt}$ and time would be

(a) straight line with a negative slope and an intercept on y-axis
(b) straight line with a positive slope and an intercept on y-axis
(c) a straight line parallel to x-axis
(d) a hyperbola. *(2010)*

20. For a first order gas phase reaction:
$A_{(g)} \rightarrow 2B_{(g)} + C_{(g)}$
P_0 be initial pressure of A and P_t the total pressure at time 't'. Integrated rate equation is

(a) $\frac{2.303}{t}\log\left(\frac{P_o}{P_o - P_t}\right)$

(b) $\frac{2.303}{t}\log\left(\frac{2P_o}{3P_o - P_t}\right)$

(c) $\frac{2.303}{t}\log\left(\frac{P_o}{2P_o - P_t}\right)$

(d) $\frac{2.303}{t}\log\left(\frac{2P_o}{2P_o - P_t}\right)$ *(2011)*

21. For a reaction, $r = k(CH_3COCH_3)^{3/2}$, then unit of rate of reaction and rate constant respectively is

(a) mol L^{-1} s^{-1}, mol$^{-1/2}$ $L^{1/2}$ s^{-1}
(b) mol^{-1} L^{-1} s^{-1}, mol$^{-1/2}$ $L^{-1/2}$ s^{-1}
(c) mol L^{-1} s^{-1}, mol$^{1/2}$ $L^{1/2}$ s^{-1}
(d) mol L s, mol$^{1/2}$ $L^{1/2}$ s *(2012)*

22. If $t_{1/2}$ *vs* $\frac{1}{a^2}$ is a straight line graph then determine the order of reaction.

(a) Zero order (b) First order
(c) Second order (d) Third order *(2012)*

23. The plot of a concentration of the reactant versus time for a reaction is a straight line with a negative slope. The reaction follows a

(a) first order rate equation
(b) zero order rate equation
(c) second order reaction
(d) third order rate equation. *(2013)*

24. Energy of activation of forward reaction for an endothermic process is 50 kJ. If enthalpy change for forward reaction is 20 kJ then enthalpy change for backward reaction will be

(a) 30 kJ (b) 20 kJ
(c) 70 kJ (d) 50 kJ *(2013)*

25. 75% of a first order reaction complete in 4 h, 87.5% of the same reaction completes in

(a) 6 h (b) 12 h
(c) 8 h (d) 2 h *(2014)*

26. For the reaction $A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$, the rate constant is given as (P_i is initial pressure and P_t is pressure at time t)

(a) $k = \frac{2.303}{t}\log\frac{P_i}{P_t}$

(b) $k = \frac{2.303}{t}\log\frac{P_i}{(2P_i - P_t)}$

(c) $k = \frac{2.303}{t}\log\frac{2P_i - P_t}{P_i}$

(d) $k = \frac{2.303}{t}\log\frac{P_i - P_t}{2P_i}$ *(2014)*

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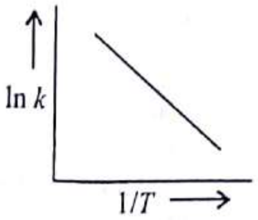
27. During the decomposition of H_2O_2 to give oxygen, 48 g O_2 is formed per minute at a certain point of time. The rate of formation of water at this point is
(a) 0.75 mol min^{-1} (b) 1.5 mol min^{-1}
(c) 2.25 mol min^{-1} (d) 3.0 mol min^{-1}
(2016)

28. The chemical reaction, $2O_3 \longrightarrow 3O_2$ proceeds as follows :
Step 1 : $O_3 \rightleftharpoons O_2 + O$ ....(fast)
Step 2 : $O + O_3 \longrightarrow 2O_2$ ....(slow)
The rate law expression should be
(a) $r = k'[O_3][O_2]$ (b) $r = k'[O_3]^2[O_2]^{-1}$
(c) $r = k'[O_3]^2$ (d) unpredictable.
(2017)

29. The temperature dependence of a reaction is represented by the Arrhenius equation :

$$\ln k = -\frac{E_a}{RT} + \ln A$$



Which among the following is wrong conclusion about the given plot?
(a) Intercept of the line = ln A
(b) Slope = $-\frac{E_a}{RT}$
(c) Reaction with high activation energy is more temperature sensitive than that of low activation energy (E_a).
(d) Slope = $-\frac{E_a}{R}$ *(2017)*

ASSERTION AND REASON

30. ***Assertion***: The molecularity of the reaction $H_2 + Br_2 = 2HBr$ is two.
Reason: The order of this reaction is 3/2.
(1995)

31. ***Assertion :*** According to transition state theory, for the formation of an activated complex, one of the vibrational degrees of freedom is converted into a translational degree of freedom.
Reason : Energy of the activated complex is higher than the energy of reactant molecules.
(2006)

32. ***Assertion :*** The kinetics of the reaction :
$mA + nB + pC \rightarrow m'X + n'Y + p'Z$
obeys the rate expression as
$$\frac{dx}{dt} = k[A]^m[B]^n$$
Reason : The rate of reaction does not depend upon the concentration of C.
(2007)

33. ***Assertion :*** In rate law, unlike in the expression for equilibrium constants, the exponents for concentrations do not necessarily match the stoichiometric coefficients.
Reason : It is the mechanism and not the balanced chemical equation for the overall change that governs the reaction rate.
(2009)

34. ***Assertion :*** The overall order of the reaction is the sum of the exponents of all the reactants in the rate expression.
Reason : There are many higher order reactions.
(2010)

35. ***Assertion :*** Two different reactions can never have same rate of reaction.
Reason : Rate of reaction always depends only on frequency of collision and Arrhenius factor.
(2011)

36. ***Assertion :*** Rate of reaction doubles when concentration of reactant is doubled if it is a first order reaction.
Reason : Rate constant also doubles.
(2012)

37. ***Assertion :*** Catalyst changes Gibbs free energy of system.
Reason : Catalyst changes pre-exponential factor of a chemical reaction.
(2013)

Answer Key

1.	(c)	**2.**	(d)	**3.**	(b)	**4.**	(d)	**5.**	(d)	**6.**	(a)	**7.**	(a)	**8.**	(c)
9.	(d)	**10.**	(c)	**11.**	(b)	**12.**	(a)	**13.**	(c)	**14.**	(b)	**15.**	(a)	**16.**	(a)
17.	(b)	**18.**	(a)	**19.**	(c)	**20.**	(b)	**21.**	(a)	**22.**	(d)	**23.**	(b)	**24.**	(a)
25.	(a)	**26.**	(b)	**27.**	(d)	**28.**	(b)	**29.**	(b)	**30.**	(b)	**31.**	(a)	**32.**	(a)
33.	(a)	**34.**	(c)	**35.**	(d)	**36.**	(c)	**37.**	(d)						

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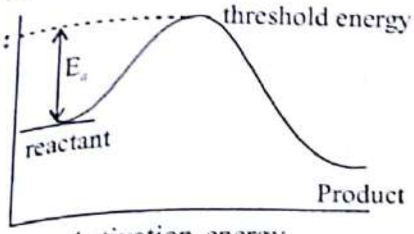
EXPLANATIONS

1. **(c) :** According to law of mass action, rate depends on active mass or simply concentration.

2. **(d) :**



E_a = Activation energy

3. **(b) :** For first order reaction

$t = \frac{1}{k}\log\frac{a}{a-x}$;

$$\frac{t_{30\%}}{t_{50\%}} = \frac{\frac{1}{k}\times 2.303\times\log\frac{100}{100-30}}{\frac{1}{k}\times 2.303\times\log\frac{100}{100-50}}$$

$$\frac{30}{t_{1/2}} = \frac{\log\frac{10}{7}}{\log 2};\quad \frac{30}{t_{1/2}} = \frac{0.1549}{0.3010};$$

$$t_{1/2} = \frac{0.3010\times 30}{0.1549} = 58.2956\text{ min} \approx 58.3\text{ min}$$

4. **(d) :** Rate constant = 0.69×10^{-2} min^{-1}

This unit (*i.e.* min^{-1}) is characteristics of first order reaction. For first order reaction, half-life time is given as :

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.69\times 10^{-2}} = 1.004\times 10^{2}\text{ min}$$

$t_{1/2}$ = 100.4 min = 6024 sec

5. **(d) :** For first order reaction,

rate = rate constant × concentration of reactant

∴ Initial rate = rate constant × Initial concentration

$= 3\times 10^{-6}\times 0.10 = 3\times 10^{-7}$ M s^{-1}

6. **(a) :** According to Absolute reaction rate theory, the bimolecular reaction between the two molecules A_2 and B_2 passes through the formation of the so called activated complex, which then decomposes to yield product AB.

$$A_2 + B_2 \rightleftharpoons (A_2B_2)^{*} \rightarrow 2AB$$

7. **(a) :** Photochemical reaction between H_2 and Cl_2 is zero order reaction.

8. **(c) :** ΔH = activation energy of forward reaction − activation energy of backward reaction

∴ $\Delta H = b - a = c$

9. **(d) :** $k = \frac{1}{t}\ln\frac{a\text{ (initial)}}{(a-x)\text{ (after time } t)}$;

$$kt = \ln\frac{[N_2O_5]_0}{[N_2O_5]_t}$$

10. **(c) :** Endothermic reactions are those which involve absorption of heat. High activation energy means potential energy of product must be much greater than reactants.

11. **(b) :** $aA \rightarrow xP$

Rate of reaction = $[A]^a$; Order of reaction = a.

$[A]_1 = 2.2$ mM, $r_1 = 2.4$ mM s^{-1} ... (i)

$[A]_2 = \frac{2.2}{2}$ mM, $r_2 = 0.6$ mM s^{-1} or $\frac{2.4}{4}$ ...(ii)

On reducing the concentration of A to half, the rate of reaction is decreased by four times.

Rate of reaction = $[A]^2$; Order of reaction = 2

12. **(a) :** For the reaction,

$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

$K_p = p_{CO_2}$ and $K_C = [CO_2]$

(∵ $[CaCO_3] = 1$ and $[CaO] = 1$ for solids]

According to Arrhenius equation, we have

$$K = Ae^{-\Delta H_r^\circ/RT}$$

Taking logarithm, we have

$$\log K_p = \log A - \frac{\Delta H_r^\circ}{RT(2.303)}$$

This is an equation of straight line. When $\log K_p$ is plotted against $1/T$, we get a straight line.

The intercept of this line = $\log A$, slope = $-\Delta H_r^\circ/2.303R$

Knowing the value of slope from the plot and universal gas constant R, ΔH_r° can be calculated.

13. **(c) :** In general for a reaction,

$$x_1A + x_2B \rightarrow y_1C + y_2D$$

The rate expression may be expressed as

$$-\frac{1}{x_1}\frac{d[A]}{dt} = -\frac{1}{x_2}\frac{d[B]}{dt} = \frac{1}{y_1}\frac{d[C]}{dt} = \frac{1}{y_2}\frac{d[D]}{dt}$$

For $2N_2O_5 \rightarrow 4NO_2 + O_2$

$$-\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}$$

14. **(b) :** Slowest step of mechanism decides the rate expression. Thus rate = $k[NO_2][F_2]$

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15. (a) : It is an example of pseudo unimolecular reaction where molecularity ≥ 2 but order of reaction is one.

Rate = k[Sugar] [H_2O]

In the reaction, water is present in excess and its concentration is taken to be constant, thus the reaction becomes independent of [H_2O] and is pseudo first order.

16. (a) :

$$\begin{array}{lcccc} & A \rightarrow & B + & C + & D \\ \text{Initial} & a & 0 & 0 & 0 \\ \text{After time } t & a-x & x & x & x \end{array}$$

It is given that $a = P_0$ ...(i)

$a - x + x + x + x = P$

or $a + 2x = P$ ...(ii)

From (i), $P_0 + 2x = P$ or $x = \frac{P - P_0}{2}$

From rate equation, $k = \frac{2.303}{t}\log\frac{a}{a-x}$

$$= \frac{2.303}{t}\log\frac{P_0}{P_0 - \left(\frac{P-P_0}{2}\right)} = \frac{2.303}{t}\log\frac{2P_0}{3P_0 - P}$$

17. (b)

18. (a) : For a first order reaction, rate = $k[A]$, when concentration of A is doubled, the rate becomes double.

19. (c) : If product concentration is x.

For a zero order reaction $\frac{x}{t} = k$

Thus graph would be a straight line passing through origin. So the given information is for zero order reaction. For a zero order reaction, rate of the reaction is constant. Thus, plot of rate *vs* time, *i.e.*, $-\frac{d[X]}{dt}$ *vs* time will be a straight line parallel to x-axis.

20. (b) :

$$\begin{array}{lccc} & A_{(g)} \longrightarrow & 2B_{(g)} + & C_{(g)} \\ \text{Initial :} & P_0 & 0 & 0 \\ & P_0 - P & 2P & P \end{array}$$

Total pressure at time (t) = $P_0 - P + 2P + P = P_t$

$\Rightarrow \quad P_t = P_0 + 2P$

$P_t - P_0 = 2P \quad \Rightarrow \quad P = \frac{P_t - P_0}{2}$

$$k = \frac{2.303}{t}\log\left[\frac{P_0}{P_0 - P}\right] = \frac{2.303}{t}\log\left[\frac{P_0}{P_0 - \left(\frac{P_t - P_0}{2}\right)}\right]$$

$$= \frac{2.303}{t}\log\left(\frac{2P_0}{2P_0 - P_t + P_0}\right) = \frac{2.303}{t}\log\left(\frac{2P_0}{3P_0 - P_t}\right)$$

21. (a) : Rate $= \frac{\text{concentration}}{\text{time}} = \frac{\text{mol L}^{-1}}{\text{s}}$

$= \text{mol L}^{-1}\,\text{s}^{-1}$

The units of rate constant for the reaction of the n^{th} order = $(\text{mol L}^{-1})^{1-n}\,\text{s}^{-1}$

here, $n = \frac{3}{2}$

∴ Unit of rate constant $= (\text{mol L}^{-1})^{1-3/2}\,\text{s}^{-1}$

$= (\text{mol L}^{-1})^{-1/2}\,\text{s}^{-1} = \text{mol}^{-1/2}\,\text{L}^{1/2}\,\text{s}^{-1}$

22. (d) : For a n^{th} order reaction,

$t_{1/2} \propto \frac{1}{[a]^{n-1}}$

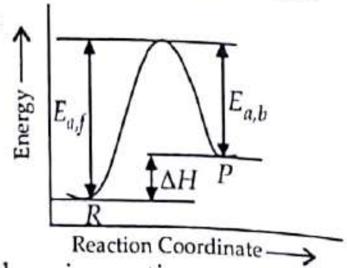
where n = order of reaction

$t_{1/2} \propto \frac{1}{[a]^{3-1}}$ $[\because n = 3]$

$t_{1/2} \propto \frac{1}{[a]^2}$

23. (b) : A straight line plot of $[A]$ *vs* t with negative slope is for a reaction of zero order.

24. (a) :



For endothermic reaction,

$E_{a,b} = E_{a,f} - \Delta H° = 50\text{ kJ} - 20\text{ kJ} = 30\text{ kJ}$

25. (a) : Using the relation, $t_{87.5\%} = \frac{3}{2}t_{75\%}$

$t_{87.5\%} = \frac{3}{2} \times \frac{4}{1} = 6\text{ h}$

26. (b) : For the reaction,

$$\begin{array}{lccc} & A_{(g)} \longrightarrow & B_{(g)} + & C_{(g)} \\ t = 0 & P_i & 0 & 0 \\ t & (P_i - x) & x & x \end{array}$$

Given: P_i is initial pressure at time, $t = 0$ and P_t is pressure at time 't'.

$P_t = (P_i - x) + x + x = P_i + x$

$x = P_t - P_i$

Here, $P_A = P_i - x \quad \Rightarrow \quad P_i - (P_t - P_i)$

$P_A = 2P_i - P_t$

$$k = \frac{2.303}{t}\log\frac{P_i}{P_A} \Rightarrow k = \frac{2.303}{t}\log\frac{P_i}{(2P_i - P_t)}$$

27. (d) : $2H_2O_2 \longrightarrow 2H_2O + O_2$

$$\text{Rate} = -\frac{1}{2}\frac{d[H_2O_2]}{dt} = \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$$

Rate of formation

$= \frac{48}{32}$ mol m

Rate of forn

∴ $\frac{1}{2}\frac{d[H_2O]}{dt} =$

⇒ $\frac{d[H_2O]}{dt} = 2$

⇒

28. (b) : As

determining step

$r = k[O_3][O]$

From step 1, K_{eq}

or $[O] = \frac{K_{eq}}{[C}$

From eq. (i) and

$r = kK_{eq}\frac{[O_3]^2}{[O_2]}$

29. (b)

30. (b) : Mol

molecules actin

order of reactic

which concent

expression. So

31. (a) : A +

The activated

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Rate of formation of oxygen = 48 g min^{-1}

$= \frac{48}{32}$ mol min^{-1} = 1.5 mol min^{-1}

Rate of formation of H_2O

$\therefore \quad \frac{1}{2}\frac{d[H_2O]}{dt} = \frac{d[O_2]}{dt}$

$\Rightarrow \quad \frac{d[H_2O]}{dt} = \frac{2d[O_2]}{dt} = 2 \times 1.5 = 3 \text{ mol min}^{-1}$

28. **(b)** : As the slowest step is the rate determining step, hence from ste 2,

$r = k[O_3][O]$ ...(i)

From step 1, $K_{eq} = \frac{[O_2][O]}{[O_3]}$

or $[O] = \frac{K_{eq}[O_3]}{[O_2]}$ ...(ii)

From eq. (i) and (ii),

$r = kK_{eq}\frac{[O_3]^2}{[O_2]} = k'[O_3]^2[O_2]^{-1}$ $[\because k' = kK_{eq}]$

29. **(b)**

30. **(b)** : Molecularity of reaction is the no. of molecules acting in the rate determing step while order of reaction is the sum total of all powers to which concentration are raised in the rate law expression. So both may or may not be same.

31. **(a)** : $A + B \rightleftharpoons (AB)^{\ddagger} \rightarrow$ products.

The activated complex can also be treated as a distinct chemical species in equilibrium with the reactants which then decompose into products. It is, however, a special molecule in which one vibrational degree of freedom has been converted to a translational degree of freedom along the reaction coordinate. It must be remembered that the activated complex is not merely an intermediate in process of breaking or forming of chemical bonds. It is unstable because it is situated at the maximum of the potential energy barrier separating the products from the reactants. The difference between the energy of the activated complex (E_1) and the energy of the reactants (E_2) is the activation energy, E_a.

$$E_1 - E_2 = E_a,\ E_1 >> E_2$$

32. **(a)** : Rate expression $\frac{dx}{dt} = k[A]^m[B]^n$ shows that the total order of reactions is $m + n + 0 = m + n$ as the rate of reaction is independent of concentration of C, *i.e.* the order with respect to C is zero. This is the reason that C does not figure in the rate expression.

33. **(a)**

34. **(c)** : Reactions of higher order are rare because chances for larger number of molecules to come simultaneously for collision are less.

35. **(d)** : Two different reactions can have same rate of reaction. Rate of reaction depends upon many factors like nature and concentration of reactants, temperature, catalyst, energy factors, orientation factor, etc.

36. **(c)** : For first order reaction,

Rate$_1$ = $k[A_1]$

According to question,

$[A_2] = [2A_1]$

$\therefore$ Rate$_2$ = $k[2A_1]$

$\Rightarrow$ Rate$_2$ = 2 Rate$_1$

For a given reaction, rate constant is constant and independent of the concentration of reactant.

37. **(d)** : Catalyst have no effects on Gibb's free energy of system and pre-exponential factor of a chemical reaction.

CHAPTER

19

Surface Chemistry

1. A catalyst is used to
(a) increase the rate of reaction
(b) increase the equilibrium constant
(c) decrease the product
(d) none of these. *(1994)*

2. Which of the following kinds of catalysis can be explained by the adsorption theory?
(a) Heterogeneous catalysis
(b) Enzyme catalysis
(c) Homogeneous catalysis
(d) Acid base catalysis *(1995)*

3. The physical adsorption of gases on the solid surface is due to
(a) van der Waals' forces
(b) covalent bonding
(c) hydrogen bonding
(d) all of these. *(1998)*

4. The size of colloidal particle is
(a) 10^{-3} to 10^{-9} m (b) 10^{-9} to 10^{-12} m
(c) 10^{-7} to 10^{-9} m (d) 10^{-12} to 10^{-19} m
(1999, 2002)

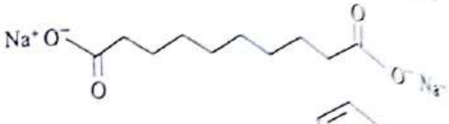
5. A packet of colloidal system is taken in which colloidal particles are still. Two electrodes are taken in system and voltage is applied so that liquid medium moves under the influence of electric field. This phenomenon is called
(a) Tyndall effect (b) electro-osmosis
(c) electrophoresis (d) electrodialysis.
(2001)

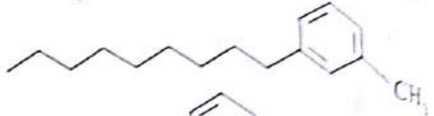
6. Correct equation of Freundlich isotherm is
(a) $\log\left(\frac{x}{m}\right) = \log K + \frac{1}{n}\log C$
(b) $\log\left(\frac{m}{x}\right) = \log K + \frac{1}{n}\log C$
(c) $\log\left(\frac{x}{m}\right) = \log C + \frac{1}{K}\log C$
(d) $\log\left(\frac{x}{m}\right) = \log C + \frac{1}{n}\log K$

(2001, 2003)

7. Which of the following molecule is most suitable to disperse benzene in water?

(a) 

(b) 

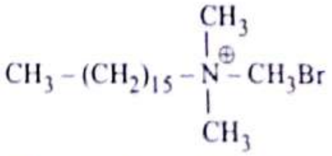
(c) 

(d) 

(2005)

8. Which of the following does not represent the correct match of catalyst and corresponding process/reaction?
(a) $[RhCl(PPh_3)_3]$: Hydrogenation
(b) $TiCl_4 + Al(C_2H_5)_3$: Polymerization
(c) V_2O_5 : Haber-Bosch process
(d) Nickel : Hydrogenation *(2006)*

9. A catalyst
(a) changes the equilibrium constant
(b) lowers the activation energy
(c) increases the forward and backward reactions at different speeds
(d) follows same mechanism for the reaction. *(2007)*

10. Which one of the following is not a surfactant?
(a) 
$CH_3-(CH_2)_{15}-\overset{\oplus}{N}(CH_3)_2-CH_3Br$
(b) $CH_3-(CH_2)_{14}-CH_2-NH_2$
(c) $CH_3-(CH_2)_{16}-CH_2OSO_2^- Na^+$
(d) $OHC-(CH_2)_{14}-CH_2-COO^- Na^+$
(2008)

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11. Butter is an exa
(a) Solid in liq
(c) Liquid in li

12. Which of the
physisorption
(a) Reversible
(b) Increases
(c) Low heat
(d) Increases

13. A colloidal s
illuminated b
appears at the
This effect is
(a) Tyndall
(b) Brownian
(c) Hardy-Sc
(d) none of

14. Hair cream is
(a) gel
(c) solid so
(2013)

15. According
flocculating
(a) decrease
(c) decrease
(d) increase

16. Purification
(a) dialysis
(c) electro

17. Which one
homogene
(a) Manu
proces
(b) Manu
proces
(c) Hydro
(d) Hydro
dilute

18. Paints and
(a) sol a
(c) emuls

1. (a) 2.
9. (b) 1
17. (d) 1
25. (a) 2

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11. Butter is an example of which type of colloid?
(a) Solid in liquid (b) Liquid in solid
(c) Liquid in liquid (d) Gas in liquid
(2010)

12. Which of the following is incorrect for physisorption?
(a) Reversible
(b) Increases with increase in temperature
(c) Low heat of adsorption
(d) Increases with increase in surface area
(2011)

13. A colloidal solution is kept in dark and is illuminated by a beam of light. Brightness appears at the right angle of direction of light. This effect is called
(a) Tyndall effect
(b) Brownian effect
(c) Hardy-Schulze effect
(d) none of these. *(2012, 2015)*

14. Hair cream is a/an
(a) gel (b) emulsion
(c) solid sol (d) sol.
(2013)

15. According to Hardy schulze law, the flocculating power of an ion increases with
(a) decrease in size (b) increase in size
(c) decrease in charge
(d) increase in charge. *(2013)*

16. Purification of colloids is done by
(a) dialysis (b) peptisation
(c) electrophoresis (d) coagulation.
(2014)

17. Which one of the following is an example of homogeneous catalysis?
(a) Manufacture of ammonia by Haber's process
(b) Manufacture of sulphuric acid by Contact process
(c) Hydrogenation of oil
(d) Hydrolysis of sucrose in presence of dilute hydrochloric acid *(2014)*

18. Paints and hair creams are respectively
(a) sol and emulsion (b) aerosol and foam
(c) emulsion and sol (d) foam and gel.
(2016)

19. The coagulation of 200 mL of a positive colloid took place when 0.73 g HCl was added to it without changing the volume much. The flocculation value of HCl for the colloid is
(a) 100 (b) 36.5 *(2017)*
(c) 0.365 (d) 150

ASSERTION AND REASON

20. ***Assertion***: Chemical adsorption of molecules on surface requires activation energy.
Reason: Because the bonds of the adsorbed molecules are broken. *(1994, 2002)*

21. ***Assertion :*** An increase in surface area increases the rate of evaporation.
Reason : Stronger the inter-molecular attractive forces, faster is the rate of evaporation at a given temperature.
(2002)

22. ***Assertion***: Alcohols are dehydrated to hydrocarbons in the presence of acidic zeolites.
Reason : Zeolites are porous catalysts.
(2004)

23. ***Assertion*** : Aqueous gold colloidal solution is red in colour.
Reason : The colour arises due to scattering of light by colloidal gold particles. *(2004)*

24. ***Assertion :*** Fe^{3+} can be used for coagulation of As_2S_3 sol.
Reason : Fe^{3+} reacts with As_2S_3 to give Fe_2S_3.
(2006, 2015)

25. ***Assertion :*** Coagulation power of Al^{3+} is more than Na^+.
Reason : Greater the valency of the flocculating ion added, greater is its power to cause precipitation (Hardy-Schulze rule).
(2014)

26. ***Assertion :*** Activity of an enzyme is pH-dependent.
Reason : Change in pH affects the solubility of the enzyme in water. *(2017)*

Answer Key

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

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EXPLANATIONS

1. **(a) :** A catalyst speeds up the reaction both in forward and backward direction, maintaining the equilibrium constant.

2. **(a)** **3.** **(a)**

4. **(c)** The colloidal solution is a heterogeneous solution which contains particles of size 10^{-7} m to 10^{-9} m (intermediate of true solution and suspension). Particles are visible only with an ultra microscope.

5. **(b) :** Movement of dispersion medium particles under the influence of potential gradient is called electro-osmosis.

6. **(a) :** Freundlich gave an empirical relationship between the quantity of gas adsorbed by unit mass of solid adsorbent and concentration at a particular temperature.

$$\log x/m = \log K + \frac{1}{n}\log C$$

x = mass of gas adsorbed, m = mass of adsorbent
C = concentration, K, n = constants.

7. **(c) :** Benzene is non-polar in nature. As we know that non-polar compounds disperse more in non-polar substances.

8. **(c) :** Haber-Bosch process is used for the synthesis of ammonia.

$$N_2 + 3H_2 \rightleftharpoons 2NH_3\ ;\ \Delta H = -92.0\ kJ$$

The best catalyst for this reaction is highly porous finely divided iron containing small amounts of promoters usually molybdenum or oxides of potassium and aluminium.

9. **(b) :** A substance which increases the speed of a reaction without being consumed in the reaction is called a catalyst. Catalyst reduces the height of barrier by providing an alternative path for the reaction and lowers the activation energy.

10. **(b)** **11.** **(b)**

12. **(b) :** Since, the adsorption process is exothermic, the physical adsorption occurs readily at low temperature and decreases with increase in temperature (Le-Chatelier's principle).

13. **(a)**

14. **(b) :** Hair cream is an emulsion in which both dispersed phase and dispersion medium are liquids.

15. **(d) :** Greater the valency of the flocculating ion, greater is its flocculating power.

16. **(a) :** Peptisation is the method of preparation of colloidal solution while coagulation and electrophoresis are the properties of colloidal solution.

17. **(d) :** $\underset{\text{Sucrose}}{C_{12}H_{22}O_{11(aq)}} + H_2O_{(l)} \xrightarrow{HCl_{(aq)}} \underset{\text{Glucose}}{C_6H_{12}O_{6(aq)}} + \underset{\text{Fructose}}{C_6H_{12}O_{6(aq)}}$

18. **(a) :** Paints – Solid in liquid type colloid
Hair cream – Liquid in liquid type colloid

19. **(a) :** 200 mL of the sol required = 0.73 g HCl

$$= \frac{0.73}{36.5} = 0.02\ \text{mol} = 20\ \text{mmol}$$

∴ 1000 mL (1L) of the sol will require

$$= \frac{20}{200} \times 1000 = 100\ \text{mmol}$$

Thus, the flocculation value of HCl for the colloid is 100.

20. **(a)**

21. **(c) :** Greater is the surface area, faster is the rate of evaporation at a given temperature. This is due to the fact that more surface area means more number of molecules are present at the surface which can then be evaporated easily. Strong inter-molecular forces of attraction slow down the rate of evaporation.

22. **(b) :** Zeolites are shape-selective porous solid acid catalysts. Their catalytic activity originates from the presence of highly acidic [Al–O(H)–Si] hydroxyl in the framework.

23. **(a) :** The colour of colloidal solution depends on the wavelength of light scattered by the dispersed particles. The wavelength of light further depends on the size and nature of the particles. Finest gold sol is red in colour. As size of the particles increases, it becomes purple, then blue and finally golden yellow.

24. **(c) :** When oppositely charged sols are mixed in almost equal proportions, their charges are neutralised. Both sols may be partially or completely precipitated. When negatively charged As_2S_3 sol is added to positively charged $Fe(OH)_3$ sol in suitable amounts, precipitation of both the sols take place simultaneously.

25. **(a)**

26. **(b) :** Activity of enzyme is maximum at pH = 7.4 (physiological pH). In fact, as pH is increased, the rate rises to a maximum and then falls off.

CHAPTER 20

1. The important ore
(a) kaolin
(c) bauxite

2. Lithopone, a whi
(a) ZnS and BaS
(c) Al_2O_3 and Ca

3. Bauxite, an ore
(a) Hall's proce
(c) Baeyer's pr

4. Thermite is a m
(a) Zn + Mg
(c) Fe_2O_3 + Al

5. Which of the
(a) Carnallite
(c) Copper py

6. The purificati
(a) Baeyer's
(c) Castuer

7. An ore of po
(a) carnallite
(c) bauxite

8. The compos
(a) KCl·Mg
(c) Fe_3O_4

9. Which of th
(a) Limoni
(c) Magne

CHAPTER 20

General Principles and Processes of Isolation of Elements

1. The important ore of aluminium is
(a) kaolin (b) corundum
(c) bauxite (d) ruby. *(1995)*

2. Lithopone, a white pigment, consists of
(a) ZnS and $BaSO_4$ (b) PbS and MgO
(c) Al_2O_3 and $CaCO_3$ (d) $BaSO_4$ and $PbSO_4$.
(1995)

3. Bauxite, an ore of aluminium is purified by
(a) Hall's process (b) Serpek's process
(c) Baeyer's process (d) all of these.
(1996)

4. Thermite is a mixture of
(a) Zn + Mg (b) Fe + Al
(c) Fe_2O_3 + Al (d) Cu + Mg
(1996)

5. Which of the following is a sulphide ore?
(a) Carnallite (b) Magnetite
(c) Copper pyrites (d) Malachite
(1996)

6. The purification of alumina is called
(a) Baeyer's process (b) Bosch process
(c) Castuer process (d) Hoop's process.
(1998, 2008)

7. An ore of potassium is
(a) carnallite (b) cryolite
(c) bauxite (d) dolomite.
(2000)

8. The composition of carnallite is
(a) $KCl{\cdot}MgCl_2{\cdot}6H_2O$ (b) $Na_2Al_2O_3$
(c) Fe_3O_4 (d) Na_3AlF_6
(2001, 2015)

9. Which of the following is not an ore of iron?
(a) Limonite (b) Cassiterite
(c) Magnetite (d) None of these
(2002)

10. In the extraction of copper from sulphide ore the metal is formed by reduction of Cu_2O with
(a) FeS (b) CO
(c) CuS (d) SO_2 *(2003)*

11. Which of the following is a carbonate ore?
(a) Pyrolusite (b) Malachite
(c) Diaspore (d) Cassiterite
(2005)

12. Carbon and CO gas are used to reduce which of the following pairs of metal oxides for extraction of metals?
(a) FeO, SnO (b) SnO, ZnO
(c) BaO, Na_2O_2 (d) FeO, ZnO
(2007)

13. What is the role of aniline or cresol when added in a froth floatation process?
(a) Stabilizer (b) Depressant
(c) Wetting agent (d) All of these
(2013)

14. Slag formed in blast furnace, removes the impurity of
(a) SiO_2 (b) CaO
(c) CO_2 (d) FeO *(2014)*

15. When CO_2 is passed through solution of sodium meta aluminate, precipitate of which compound is formed?
(a) $Al(OH)_3$ (b) Al_2O_3
(c) Na_2CO_3 (d) No ppt. *(2014)*

16. Which of the following is not the correct match?
(a) Leaching : Ag
(b) Zone refining : Sn
(c) Liquation : Pb
(d) van Arkel : Zr *(2015)*

17. Oil used as frothing agent in froth-floatation process is

(a) pine oil
(b) mustard oil
(c) coconut oil
(d) olive oil.

(2016)

ASSERTION AND REASON

18. ***Assertion :*** Extraction of iron metal from iron oxide ore is carried out by heating with coke only.

Reason : The reaction $Fe_2O_{3(s)} \rightarrow Fe_{(s)} + 3/2O_{2(g)}$ is a spontaneous process. *(2005)*

19. ***Assertion :*** Magnesium is extracted by the electrolysis of fused mixture of $MgCl_2$, NaCl and $CaCl_2$.

Reason : Calcium chloride acts as a reducing agent. *(2013)*

20. ***Assertion :*** Hydrometallurgy involves dissolving the ore in a suitable reagent followed by precipitation by a more electropositive metal.

Reason : Copper is extracted by hydrometallurgy. *(2017)*

Answer Key

1.	(c)	**2.**	(a)	**3.**	(d)	**4.**	(c)	**5.**	(c)	**6.**	(a)	**7.**	(a)	**8.**	(a)
9.	(b)	**10.**	(a)	**11.**	(b)	**12.**	(d)	**13.**	(a)	**14.**	(a)	**15.**	(a)	**16.**	(b)
17.	(a)	**18.**	(d)	**19.**	(c)	**20.**	(b)								

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EXPLANATIONS

1. **(c) :** Bauxite is an important ore of aluminium ($Al_2O_3.2H_2O$.)

2. **(a) :** Lithopone is ($ZnS + BaSO_4$). It is used as a filler in rubber and paper industry.

3. **(d) :** Hall's and Baeyer's processes are used if aluminium ore contains iron oxide as impurity, while Serpek's process is used when SiO_2 is present as an impurity.

4. **(c)**

5. **(c) :** Chemical formula for magnetite is Fe_3O_4, malachite is $CuCO_3{\cdot}Cu(OH)_2$, carnallite is $KCl{\cdot}MgCl_2{\cdot}6H_2O$ and copper pyrites is $CuFeS_2$. Therefore, copper pyrites is a sulphide ore.

6. **(a)**

7. **(a) :** Carnallite is an ore of potassium *i.e.*, $KCl.MgCl_2.6H_2O$.

8. **(a)**

9. **(b) :** Magnetite – Fe_2O_3
   Limonite – $FeO(OH)$
   Cassiterite – SnO_2

10. **(a) :** Iron has greater affinity for oxygen than copper.

$$Cu_2O + FeS \rightarrow FeO + Cu_2S$$
$$FeO + SiO_2 \rightarrow \underset{(slag)}{FeSiO_3}$$
$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2$$
$$2Cu_2O + Cu_2S \xrightarrow[\text{reduction}]{\text{auto}} 6Cu + SO_2$$

11. **(b) :** Pyrolusite - MnO_2
    Malachite - $CuCO_3{\cdot}Cu(OH)_2$
    Diaspore - $Al_2O_3{\cdot}H_2O$
    Cassiterite - SnO_2

12. **(d) :** $\overset{+2}{Fe}O + C \rightarrow \overset{0}{Fe} + CO$ (reduction)

$$FeO + CO \rightarrow Fe + CO_2$$

Similarly, $\overset{+2}{Zn}O + C \rightarrow \overset{0}{Zn} + CO$ (reduction)

$$ZnO + CO \rightarrow Zn + CO_2$$

13. **(a)**

14. **(a) :** In the blast furnace, SiO_2 is removed as calcium silicate.

$$\underset{\text{Flux}}{CaO} + \underset{\substack{\text{Gangue}\\ \text{(Impurity)}}}{SiO_2} \longrightarrow \underset{\text{(Slag)}}{CaSiO_3}$$

15. **(a) :** In Hall's process, for purifying the bauxite ore, the solution containing sodium metaaluminate is warmed to 50-60°C and carbon dioxide is circulated through it, $Al(OH)_3$ separates out as precipitate.

$$2NaAlO_2 + CO_2 + 3H_2O \longrightarrow 2Al(OH)_3 + Na_2CO_3$$

16. **(b) :** Zone refining method is used for the elements like Si, Ge, Ga etc. which are used as semiconductors and are required in highly pure form.

17. **(a)**

18. **(d) :** Extraction of iron metal from iron oxide ore is carried out by heating with coke and flux (calcium carbonate). Flux is a slag forming substance. It converts infusible impurities into fusible slag.

The reaction : $Fe_2O_{3\,(s)} \rightarrow Fe_{(s)} + 3/2\ O_{2\,(g)}$ is not a spontaneous process. Fe_2O_3 is converted to FeO at about 400°C.

19. **(c) :** NaCl and $CaCl_2$ are added to provide conductivity to the electrolyte and also to lower the fusion temperature of anhydrous $MgCl_2$.

20. **(b)**

CHAPTER

21

THE p-BLOCK ELEMENTS (GROUP 15 TO 18)

1. Which of the following gas is produced in the reaction: $KO_2 + CO_2$?

(a) O_2 (b) H_2
(c) CO (d) N_2 *(1994)*

2. The oxidation number of phosphorus and basicity of acid in pyrophosphoric acid respectively are

(a) + 4 and three (b) + 1 and four
(c) + 5 and four (d) + 3 and one. *(1995)*

3. Nessler's reagent is used in the test of

(a) NH_4Cl (b) NH_3
(c) NH_4^+ (d) all of these. *(1995)*

4. Euchlorine is produced by heating a mixture of

(a) KCl + conc. H_2SO_4
(b) KCl + conc. HCl
(c) K_2ClO_3 + conc.H_2SO_4
(d) $KClO_3$ + conc. HCl *(1995)*

5. Which of the following molecule has regular geometry?

(a) H_2O (b) PF_3
(c) XeF_4 (d) SF_6 *(1995)*

6. Which of the following oxyacids does not exist?

(a) H_3SbO_3 (b) $HBiO_3$
(c) H_3AsO_4 (d) H_3BiO_4 *(1995)*

7. Bismuth chloride ($BiCl_3$), on hydrolysis, yields a white precipitate of

(a) bismuth hydroxide (b) bismuth oxyacid
[✓ (c)] bismuth oxychloride
(d) none of these. *(1996)*

8. Chlorine oxidises sodium thiosulphate to form

(a) Na_2SO_3 (b) Na_2O
[✓ (c)] Na_2SO_4 (d) Na_2CO_3 *(1996, 2016)*

9. Which of the following molecules is paramagnetic?

(a) P_2O_5 (b) NO_2
(c) $H_2S_2O_7$ (d) N_2O_5 *(1996)*

10. Which of the following is strongest Bronsted base?

(a) ClO^- (b) ClO_2^-
(c) ClO_3^- (d) ClO_4^- *(1996, 2001)*

11. Which of the following, on reaction with H_2S, does not produce metallic sulphide?

(a) $CdCl_2$ (b) $ZnCl_2$
(c) $COCl_2$ (d) $CuCl_2$ *(1997)*

12. Ammonia, on reaction with excess of chlorine, gives

(a) NCl_3 and HCl (b) N_4 and NH_4Cl
(c) NCl_3 and NH_4Cl (d) N_2 and HCl *(1997)*

13. Which of the following exhibits the weakest intermolecular forces?

(a) He (b) HCl
(c) NH_3 (d) H_2O *(1999)*

14. The radii of F, F^-, O and O^{2-} are in the order of

(a) $O^{2-} > O > F^- > F$ (b) $F^- > O^{2-} > F > O$
(c) $O^{2-} > F^- > F > O$ (d) $O^{2-} > F^- > O > F$ *(1999)*

15. Which oxide of nitrogen is obtained on heating ammonium nitrate at 250°C?

(a) Nitrous oxide
(b) Nitric oxide
(c) Nitrogen dioxide
(d) Dinitrogen tetraoxide *(1999)*

16. Which of the following atoms would be paramagnetic?
(a) Zn (b) Be
(c) Ca (d) N *(1999)*

17. Which of the following is the correct statement for PH_3?
(a) It is less poisonous than NH_3.
(b) It is less basic than NH_3.
(c) Electronegativity of $PH_3 > NH_3$.
(d) It does not show reducing properties. *(1999, 2012)*

18. Which of the following is the strongest acid?
(a) $HClO$ (b) $HClO_3$
(c) $HClO_2$ (d) $HClO_4$ *(1999)*

19. Which of the following is paramagnetic?
(a) NO_2 (b) N_2O
(c) N_2O_3 (d) N_2O_5 *(2000)*

20. Which of the following is true about ClO_2?
(a) It is paramagnetic.
(b) It dimerizes in liquid phase.
(c) It is a linear molecule.
(d) It is very reactive. *(2000)*

21. Which is not hydrolysed?
(a) PCl_3 (b) NCl_3
(c) $AsCl_3$ (d) $SbCl_3$ *(2000)*

22. Nitrogen and oxygen exist as diatomic but their congeners are P_4 and S_8 respectively. This is due to
(a) phosphorus and sulphur are solids
(b) phosphorus and sulphur polymerise as soon as they are formed
(c) phosphorus and sulphur catenate due to the existence of *d*-orbitals and form strainless structures
(d) none of these. *(2000)*

23. The AsF_5 molecule is trigonal pyramidal. The hybrid orbitals used by the As atoms for bonding are
(a) $d_{x^2-y^2}, d_{z^2}, s, p_x, p_y$ (b) d_{xy}, s, p_x, p_y, p_z
(c) $s, p_x, p_y, p_z, d_{z^2}$ (d) $d_{x^2-y^2}, s, p_x, p_y, p_z$ *(2000)*

24. Which of the following hydrogen halide is most basic?
(a) HF (b) HCl
(c) HBr (d) HI *(2001)*

25. Which of the following order of basic strength is correct?
(a) $NH_3 < NH_2OH < HN_3 < NH_2NH_2$
(b) $NH_2OH < HN_3 < NH_2NH_2 < NH_3$
(c) $HN_3 < NH_3 < NH_2OH < NH_2NH_2$
(d) $HN_3 < NH_2OH < NH_2NH_2 < NH_3$ *(2001)*

26. Which one forms KHX_2 type compound?
(a) HF (b) HCl
(c) HI (d) HBr *(2001)*

27. The correct order of solubility in water for He, Ne, Ar, Kr, Xe is
(a) He > Ne > Ar > Kr > Xe
(b) Xe > Kr > Ar > Ne > He
(c) Ne > Ar > Kr > He > Xe
(d) Ar > Ne > He > Kr > Xe *(2002)*

28. Which of the following compound is a tribasic acid?
(a) H_3PO_2 (b) H_3PO_4
(c) H_3PO_3 (d) $H_4P_2O_7$ *(2002)*

29. The paramagnetic species is
(a) KO_2 (b) SiO_2
(c) TiO_2 (d) BaO_2 *(2003)*

30. The true statement for the acids of phosphorus, H_3PO_2, H_3PO_3 and H_3PO_4 is
(a) the order of their acidity is $H_3PO_4 > H_3PO_3 > H_3PO_2$
(b) all of them are reducing in nature
(c) all of them are tribasic acids
(d) the geometry of phosphorus is tetrahedral in all the three. *(2003, 2016)*

31. The mixture of concentrated HCl and HNO_3 made in 3 : 1 ratio contains
(a) ClO_2 (b) NOCl
(c) NCl_3 (d) N_2O_4 *(2003)*

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32. On dissolving moderate amount of sodium metal in liquid NH_3 at low temperature, which one of the following does not occur?
(a) Blue coloured solution is obtained.
(b) Na^+ ions are formed in the solution.
(c) Liquid NH_3 becomes good conductor of electricity.
(d) Liquid ammonia remains diamagnetic.
(2003)

33. The element which forms oxides in all oxidation states +I to +V is
(a) N (b) P
(c) As (d) Sb
(2004)

34. The statement true for N_3^- is
(a) it has a non-linear structure
(b) it is called pseudohalogen
(c) the formal oxidation state of nitrogen in this anion is −1
(d) it is isoelectronic with NO_2.
(2004)

35. For electron affinity of halogens which of the following is correct?
(a) Br > F (b) F > Cl
(c) Br > Cl (d) F > I
(2004)

36. Shape of O_2F_2 is similar to that of
(a) C_2F_2 (b) H_2O_2
(c) H_2F_2 (d) C_2H_2
(2004)

37. Which of the following is arranged in the increasing order of enthalpy of vaporization?
(a) NH_3, PH_3, AsH_3 (b) AsH_3, PH_3, NH_3
(c) NH_3, AsH_3, PH_3 (d) PH_3, AsH_3, NH_3
(2004)

38. Among the following molecules
(i) XeO_3 (ii) $XeOF_4$ (iii) XeF_6
Those having same number of lone pairs on Xe are
(a) (i) and (ii) only (b) (i) and (iii) only
(c) (ii) and (iii) only (d) (i), (ii) and (iii)
(2005)

39. The number of P – O – P bridges in the structure of phosphorus pentoxide and phosphorus trioxide are respectively
(a) 6, 6 (b) 5, 5
(c) 5, 6 (d) 6, 5 *(2005)*

40. F_2 formed by reacting K_2MnF_6 with
(a) SbF_5 (b) MnF_3
(c) $KSbF_6$ (d) MnF_4 *(2005)*

41. Tincture of iodine is
(a) aqueous solution of I_2
(b) solution of I_2 in aqueous KI
(c) alcoholic solution of I_2
(d) aqueous solution of KI. *(2006, 2009)*

42. The compound molecular in nature in gas phase but ionic in solid state is
(a) PCl_5 (b) CCl_4
(c) PCl_3 (d) $POCl_3$
(2006)

43. Which two of the following salts are used for preparing iodized salt?
(i) KIO_3, (ii) KI, (iii) I_2, (iv) HI
(a) (i) and (ii) (b) (i) and (iii)
(c) (ii) and (iv) (d) (iii) and (iv)
(2006)

44. The compound used in enrichment of uranium for nuclear power plant is
(a) U_3O_8 (b) UF_6
(c) $UO_2(NO_3)_2$ (d) UCl_4 *(2006)*

45. The incorrect statement among the following is
(a) C_{60} is an allotropic form of carbon
(b) O_3 is an allotropic form of oxygen
(c) S_8 is only allotropic form of sulphur
(d) red phosphorus is more stable in air than white phosphorus. *(2006)*

46. Inert gases are mixed in iodine vapours. Then there are _____ between them.
(a) H-bonding
(b) van der Waals forces
(c) electrostatic forces
(d) metallic bonds *(2007)*

47. XeF_6 on complete hydrolysis produces
(a) $XeOF_4$ (b) XeO_2F_2
(c) XeO_3 (d) XeO_2
(2007, 2015)

48. The element which is the most abundant in the earth crust is
(a) O (b) S
(c) Al (d) H *(2007)*

49. What is the correct relationship between the pHs of isomolar solutions of sodium oxide (pH_1),

sodium sulphid
and sodium tel
(a) $pH_1 > pH$
(b) $pH_1 < pH$
(c) $pH_1 < pH$
(d) $pH_1 > pH$

50. The number o
trimer (S_3O_9)
(a) three
(c) one

51. Which acid h
(a) Hypopho
(b) Pyropho
(c) Metaph
(d) Orthoph

52. KF combine
compound c
(a) K^+, F^-
(c) K^+ and

53. The *M* – O
is halogen)
(a) Br_2O
(b) $F_2O >$
(c) $F_2O >$
(d) Cl_2O

54. Bromine is
of NaOH.
the follow
(a) Duri
four
(b) The
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(c) On
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55. The sha
oxyfluor
(a) Xe
(b) X
(c) Xe
(d) X

56. PCl_3 or

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sodium sulphide (pH_2), sodium selenide (pH_3) and sodium telluride (pH_4)?
(a) $pH_1 > pH_2 = pH_3 = pH_4$
(b) $pH_1 < pH_2 < pH_3 < pH_4$
(c) $pH_1 < pH_2 > pH_3 < pH_4$
(d) $pH_1 > pH_2 > pH_3 > pH_4$ *(2008)*

50. The number of S – S bonds in sulphur trioxide trimer (S_3O_9) is
(a) three (b) two
(c) one (d) zero. *(2008)*

51. Which acid has P – P linkage?
(a) Hypophosphoric acid
(b) Pyrophosphoric acid
(c) Metaphosphoric acid
(d) Orthophosphoric acid *(2008)*

52. KF combines with HF to form KHF_2. This compound contains the species
(a) K^+, F^- and H^+ (b) K^+, F^- and HF
(c) K^+ and $[HF_2]^-$ (d) $[KHF]^-$ and F_2 *(2009)*

53. The *M* – *O* – *M* bond angles in M_2O (where *M* is halogen) is in the order
(a) $Br_2O > Cl_2O > F_2O$
(b) $F_2O > Br_2O > Cl_2O$
(c) $F_2O > Cl_2O > Br_2O$
(d) $Cl_2O > F_2O > Br_2O$ *(2009)*

54. Bromine is added to cold dilute aqueous solution of NaOH. Then the mixture is boiled. Which of the following statements is not true?
(a) During the reaction bromine is present in four different oxidation states.
(b) The greatest difference between the various oxidation states of bromine is 5.
(c) On acidification of the final mixture bromine is formed.
(d) Disproportionation of bromine occurs during the reaction. *(2010)*

55. The shape and hybridisation of some xenon oxyfluorides are given. Choose the wrong set.
(a) $XeOF_2$ -T-Shape-sp^3d
(b) $XeOF_4$ - Square pyramidal-sp^3d^2
(c) XeO_2F_2 -Distorted trigonal bipyramidal-sp^3d
(d) XeO_3F_2 - Octahedral - sp^3d *(2010)*

56. PCl_3 on hydrolysis gives fumes of
(a) $H_3PO_3 + HCl$ (b) $H_3PO_4 + HCl$
(c) H_3PO_2 and H_3PO_3 (d) $H_3PO_2 + HCl$ *(2011)*

57. First compound of Xe synthesized was
(a) $[XeF]^+ [XePtF_5]^-$ (b) $[XeO_2]$
(c) $Xe[PtF_6]$ (d) $O_2[XeF_6]$ *(2011)*

58. How many P $=$ O bond present in $(HPO_3)_3$?
(a) 0 (b) 3
(c) 6 (d) 9 *(2012)*

59. $S_2O_8^{2-}$ have
(a) S–S bond (b) S–O bridge
(c) O–O bridge
(d) all S–O bond lengths are same. *(2012)*

60. N—N bond length is minimum in
(a) N_2O (b) N_2O_3
(c) N_2O_4 (d) N_2O_5 *(2012)*

61. Which of the following statement is not true for hydrolysis of XeF_6?
(a) $XeOF_4$ is formed.
(b) XeO_2F_2 is formed.
(c) It is a redox reaction.
(d) XeO_3 is formed. *(2013)*

62. Rhombic sulphur dissolves best in
(a) CS_2 (b) H_2O
(c) ethanol (d) ether. *(2014)*

63. Enrichment of U^{235} is done by
(a) IF_7 (b) ClF_3
(c) IF_5 (d) ClF_5 *(2014)*

64. Which halogen forms only one oxoacid (HO*X*)?
(a) F (b) Cl
(c) Br (d) I *(2014)*

65. Which is correct regarding acidity?
(a) $H_2S < H_2Se$ (b) $H_2S > H_2Se$
(c) $H_2Se > H_2Te$ (d) None of these *(2014)*

66. For which of the following elements it is difficult to disproportionate in +3 oxidation state?
(a) N (b) As
(c) Sb (d) Bi *(2016)*

67. Best reagent for the conversion of $AgNO_3$ to Ag is
(a) $HClO_4$ (b) H_3PO_2
(c) HIO_4 (d) I_2 *(2016)*

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68. Large difference in boiling points is observed in
(a) N and P (b) P and As
(c) As and Sb (d) Sb and Bi *(2016)*

69. Which of the following can be oxidised by SO_2?
(a) $K_2Cr_2O_7$ (b) Mg
(c) H_2O (d) All of these *(2016)*

70. Which of the following oxoacids of phosphorus is a reducing agent and a monobasic acid as well?
(a) $H_4P_2O_5$ (b) HPO_3
(c) H_3PO_3 (d) H_3PO_2 *(2017)*

ASSERTION AND REASON

71. ***Assertion***: A solution of $KMnO_4$ is decolourized by SO_2.
Reason: SO_2 is acidic in character. *(1994)*

72. ***Assertion***: Halogens do not occur in free state.
Reason: Halogens are highly reactive. *(1994)*

73. ***Assertion***: Nitrogen is unreactive at room temperature but becomes reactive at elevated temperatures (on heating) or in the presence of catalysts.
Reason: In nitrogen molecules, there is extensive delocalization of electrons. *(1996)*

74. ***Assertion***: The bond angle of PBr_3 is greater than PH_3 but the bond angle of NBr_3 is less than NH_3.
Reason: Size of Br is less than hydrogen. *(1997)*

75. ***Assertion***: Liquid ammonia is used for refrigeration.
Reason: It vaporises quickly. *(1997, 2008)*

76. ***Assertion***: NO_3^- is planar while NH_3 is pyramidal.
Reason: N in NO_3^- is sp^2 and in NH_3 is sp^3 hybridized. *(1997)*

77. ***Assertion*** : Both chlorine and sulphur dioxide act as bleaching agents.
Reason: Chlorine bleaches by vigorous oxidation, while sulphur dioxide bleaches by mild reduction. *(1998)*

78. ***Assertion*** : Xenon forms fluorides.
Reason: Because 5*d*-orbitals are available for valence shell expansion. *(1999)*

79. ***Assertion*** : Reaction of conc. H_2SO_4 on NaBr and NaI does not give HBr and HI.
Reason: HBr and HI are oxidised by conc. H_2SO_4 to Br_2 and I_2. *(1994, 1999)*

80. ***Assertion*** : H_3PO_3 is dibasic acid.
Reason: Two hydrogen atoms are directly attached to the P. *(2000, 2014)*

81. ***Assertion*** : Dinegative anion of oxygen (O^{2-}) is quite common but dinegative anion of sulphur (S^{2-}) is less common.
Reason : Covalency of oxygen is two. *(2002)*

82. ***Assertion*** : All halogens are coloured.
Reason : The halogens absorb visible light. *(2002)*

83. ***Assertion*** : F – F bond has low bond dissociation energy.
Reason : The fluorine has lower reactivity. *(2002)*

84. ***Assertion*** : $BaCO_3$ is more soluble in HNO_3 than in plain water.
Reason : Carbonate is a weak base and reacts with the H^+ from the strong acid, causing the barium salt to dissociate. *(2003)*

85. ***Assertion*** : Sb (III) is not precipitated as sulphide when in its alkaline solution H_2S is passed.
Reason : The concentration of S^{2-} ion in alkaline medium is inadequate for precipitation. *(2004)*

86. ***Assertion*** : $HClO_4$ is a stronger acid than $HClO_3$.
Reason : Oxidation state of Cl in $HClO_4$ is +8 and in $HClO_3$ is +5. *(2004)*

87. ***Assertion*** : Ozone is a powerful oxidising agent in comparison to O_2.
Reason : Ozone is diamagnetic but O_2 is paramagnetic. *(2005)*

88. ***Assertion*** : $SeCl_4$ does not have a tetrahedral structure.
Reason : Se in $SeCl_4$ has two lone pairs. *(2005)*

89. ***Assertion*** : Ozone is an allotrope of oxygen.
Reason : Oxygen is bluish colour liquid and in singlet state it is more paramagnetic. *(2007)*

90. ***Assertion*** : Bleaching powder reacts with dilute acids to evolve chlorine.
Reason : The chlorine liberated by the action of dilute acids on bleaching powder is called available chlorine. *(2008)*

91. ***Assertion*** : The S-S-S bond angle in S_8 molecule is 105°.
Reason : S_8 has a V-shape. *(2009)*

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92. ***Assertion :*** PCl_5 is covalent in gaseous and liquid states but ionic in solid state.
Reason : PCl_5 in solid state consists of tetrahedral PCl_4^+ cation and octahedral PCl_6^- anion. *(2010)*

93. ***Assertion :*** H_2S is less acidic than H_2Te.
Reason : Te has larger radius than S. *(2011)*

4. ***Assertion :*** $R_3P{=}O$ exists but $R_3N{=}O$ does not exist.
Reason : P is more electronegative than N. *(2011)*

95. ***Assertion :*** AgCl is more soluble in NH_3 than in water.
Reason : Ammonia is more polar than water. *(2011)*

96. ***Assertion :*** Helium is used in diving apparatus.
Reason : Solubility of helium is less in blood. *(2011)*

97. ***Assertion :*** Chlorine undergoes disproportionation reaction in alkaline medium.
Reason : Cl_2 is an oxidising agent. *(2011)*

98. ***Assertion :*** H_3PO_2 has strong reducing property but H_3PO_4 does not.
Reason : P-OH bond present in H_3PO_4. *(2012)*

99. ***Assertion :*** H_2Se is less acidic than H_2S.
Reason : S is less electronegative than Se. *(2012)*

100. ***Assertion :*** Bond dissociation energy is $F_2 > Cl_2$.
Reason : Cl_2 has more electronic repulsion than F_2. *(2013)*

101. ***Assertion :*** Bond lengths of P—Cl bonds in gaseous PCl_5 and solid PCl_5 are not equal.
Reason : Because in solid state two PCl_5 molecules are associated. *(2013)*

102. ***Assertion :*** Phosphoric acid has no reducing properties.
Reason : Phosphoric acid does not contain P—H bonds. *(2013)*

103. ***Assertion :*** O_2 has higher bond length than O_3.
Reason : O_3 is paramagnetic. *(2014)*

104. ***Assertion :*** Sb_2S_3 is not soluble in yellow ammonium sulphide.
Reason : The common ion effect due to S^{2-} ions reduces the solubility of Sb_2S_3. *(2015)*

105. ***Assertion :*** Charcoal is used in separation of noble gases.
Reason : Charcoal has porous structure. *(2016)*

106. ***Assertion :*** H_2S is stronger acid than PH_3.
Reason : S is more electronegative than P, conjugate base HS^- is more stable than H_2P^-. *(2016)*

107. ***Assertion :*** Hydrides of group-16 elements show volatility in the order :
$H_2O > H_2S > H_2Se > H_2Te$
Reason : Electronegativity of group-16 elements increases down the group from oxygen to tellurium. *(2017)*

Answer Key

1.	(a)	**2.**	(c)	**3.**	(d)	**4.**	(d)	**5.**	(d)	**6.**	(d)	**7.**	(c)	**8.**	(c)
9.	(b)	**10.**	(a)	**11.**	(c)	**12.**	(a)	**13.**	(a)	**14.**	(d)	**15.**	(a)	**16.**	(d)
17.	(b)	**18.**	(d)	**19.**	(a)	**20.**	(a)	**21.**	(b)	**22.**	(c)	**23.**	(c)	**24.**	(a)
25.	(b)	**26.**	(a)	**27.**	(b)	**28.**	(b)	**29.**	(a)	**30.**	(d)	**31.**	(b)	**32.**	(d)
33.	(a)	**34.**	(c)	**35.**	(d)	**36.**	(b)	**37.**	(d)	**38.**	(d)	**39.**	(a)	**40.**	(a)
41.	(b)	**42.**	(a)	**43.**	(a)	**44.**	(b)	**45.**	(c)	**46.**	(b)	**47.**	(c)	**48.**	(a)
49.	(d)	**50.**	(d)	**51.**	(a)	**52.**	(c)	**53.**	(a)	**54.**	(b)	**55.**	(d)	**56.**	(a)
57.	(c)	**58.**	(b)	**59.**	(c)	**60.**	(a)	**61.**	(c)	**62.**	(a)	**63.**	(b)	**64.**	(a)
65.	(a)	**66.**	(d)	**67.**	(b)	**68.**	(c)	**69.**	(b)	**70.**	(d)	**71.**	(a)	**72.**	(a)
73.	(c)	**74.**	(d)	**75.**	(b)	**76.**	(a)	**77.**	(a)	**78.**	(a)	**79.**	(a)	**80.**	(c)
81.	(b)	**82.**	(a)	**83.**	(c)	**84.**	(a)	**85.**	(c)	**86.**	(c)	**87.**	(b)	**88.**	(c)
89.	(c)	**90.**	(b)	**91.**	(c)	**92.**	(a)	**93.**	(b)	**94.**	(c)	**95.**	(c)	**96.**	(a)
97.	(b)	**98.**	(b)	**99.**	(c)	**100.**	(d)	**101.**	(a)	**102.**	(a)	**103.**	(d)	**104.**	(d)
105.	(a)	**106.**	(a)	**107.**	(d)										

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EXPLANATIONS

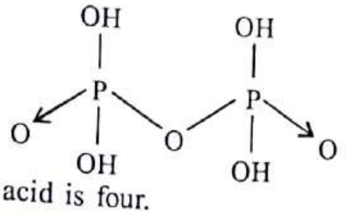
1. **(a)** : $2KO_2 + CO_2 \rightarrow K_2CO_3 + \frac{3}{2}O_2$

2. **(c)** : Pyrophosphoric acid : $H_4P_2O_7$
Let Oxidation state of P be x

$\Rightarrow 4 \times (+1) + 2x + 7 \times (-2) = 0$

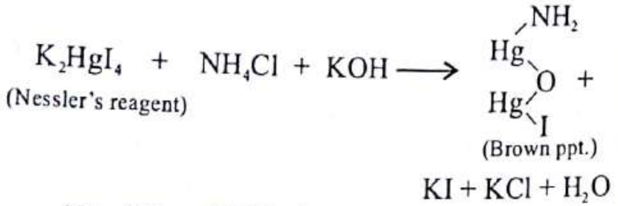
$\Rightarrow 4 + 2x - 14 = 0$

$\Rightarrow x = +5$



Basicity of acid is four.

3. **(d)** : $NH_4^+ + OH^- \rightarrow NH_3 + H_2O$
To the aqueous solution of ammonium salt when Nessler's reagent is added, brown coloured precipitate is formed.

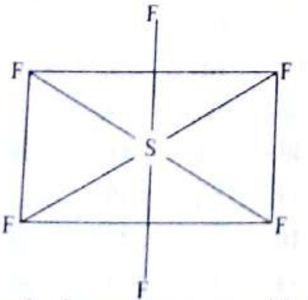


4. **(d)** : When $KClO_3$ is heated with conc.HCl, a mixture of chlorine and chlorine dioxide is obtained called euchlorine.

$$[KClO_3 + HCl \rightarrow KCl + HClO_3] \times 2$$
$$\underline{2HClO_3 + 2HCl \rightarrow 2ClO_2 + Cl_2 + 2H_2O}$$
$$2KClO_3 + 4HCl \rightarrow 2KCl + 2ClO_2 + Cl_2 + 2H_2O$$

5. **(d)** : S : $\boxed{\uparrow\downarrow}\ \boxed{\uparrow\downarrow|\uparrow|\uparrow}$ ground state
S : $\boxed{\uparrow}\ \boxed{\uparrow|\uparrow|\uparrow}\ \boxed{\uparrow|\uparrow|\ |\ |\ }$ excited state

Six unpaired electrons, form bonds with six fluorine atoms. It has regular octahedral shape.

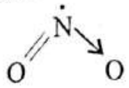


6. **(d)** : Arsenic forms two oxyacids H_3AsO_3 and H_3AsO_4. Antimony forms only one oxyacid H_3SbO_3 and bismuth forms only one oxyacid $HBiO_3$. Therefore, H_3BiO_4 does not exist.

7. **(c)** : Except NF_3 and BF_3, all other trihalides of this group are hydrolysed by water to form oxychloride.
$BiCl_3 + H_2O \rightarrow BiOCl + 2HCl$

8. **(c)** : $Cl_2 + 2Na_2S_2O_3 \rightarrow Na_2SO_4 + 2NaCl + SO_2$

9. **(b)** : NO_2 contains an unpaired electron so exhibit paramagnetism.



10. **(a)** : $HClO_4$ is the strongest acid among HClO, $HClO_2$, $HClO_3$ and $HClO_4$ as more the number of oxygen atoms attached, more is the acidity of the molecule. Order of acidity is :
$HClO < HClO_2 < HClO_3 < HClO_4$
So the conjugate base order will be just the reverse:
$ClO^- > ClO_2^- > ClO_3^- > ClO_4^-$

11. **(c)** : H_2S is the group reagent for II and IV group of basic radicals (cations). So, with $COCl_2$ (no metal here), no metallic sulphide will be produced.

12. **(a)** : $NH_3 + 3Cl_2 \rightarrow NCl_3 + 3HCl$
NCl_3 is an explosive material.

13. **(a)** : Helium is a noble gas. Weak van der Waal's forces operate between the gaseous molecules of helium. In NH_3, H_2O and HCl, there is strong hydrogen bonding between the molecules.

14. **(d)** : We know that anion is always larger than the corresponding atom therefore $F^- > F$ and $O^{2-} > O$.
Also, in a period, size of the atom decreases from left to right due to greater forces of attraction. Hence, correct order is :
$O^{2-} > F^- > O > F$

15. **(a)** : On heating ammonium nitrate,
$NH_4NO_3 \rightarrow N_2O + 2H_2O$
Nitrous oxide is evolved.

16. **(d)** : N ($Z = 7$) : $\underset{1s^2}{\boxed{\uparrow\downarrow}}\ \underset{2s^2}{\boxed{\uparrow\downarrow}}\ \underset{2p^3}{\boxed{\uparrow|\uparrow|\uparrow}}$

Due to the presence of three unpaired electrons, N atom will be paramagnetic in nature.

17. **(b)** : Nitrogen is more electronegative than the phosphorus atom. In NH_3, nitrogen attracts the bonded pair of electrons between N and H atoms towards it, and this effect is more in NH_3 than in PH_3. Due to this effect, the lone pair of electrons in NH_3 can participate more than that of PH_3.

18. **(d)** : More the number of oxygen atoms attached to the central atom, more is the electron withdrawal effect towards oxygen atom, which in turn makes central atom electron deficient so the hydrogen attached becomes more and more acidic with increasing number of oxygen atoms.

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19. **(a) :** NO_2 is paramagnetic due to the presence of unpaired electron on the nitrogen atom.

20. **(a) :** ClO_2 molecule has an angular structure with O–Cl–O bond angle of 117.6°. Cl–O bond has appreciable double bond character due to $p\pi$-$d\pi$ bonding. The molecule is paramagnetic since it has one odd electron in a *p*-orbital.

21. **(b) :** NCl_3 cannot be hydrolysed as there is no vacant *d*-orbitals available. All other, group V elements can expand their coordination sphere due to the availability of *d*-vacant orbital.

22. **(c) :** As nitrogen and oxygen atoms are small and highly electronegative with no vacant *d*-orbitals available for bonding thus, multiple bonds are formed between oxygen-oxygen and nitrogen-nitrogen atoms.

$N \equiv N \qquad O = O$

As the size of P and S atoms is large so multiple bonds are not strong enough, also catenation is possible due to vacant *d*-orbitals.

23. **(c) :** Hybridisation involved is sp^3d involving s, p_x, p_y, p_z and d_{z^2} orbitals.

24. **(a) :** The bond strength H–*X* decreases from HF to HI. Thus, HF is the most stable and hence weakest acid while HI is least stable and most acidic. In aqueous solutions, HF is only slightly ionised but HCl, HBr and HI are almost completely ionised. As basicity is the reverse of acidity. Therefore, HF is the most basic of all H–*X*.

25. **(b) :** Basicity in nitrogen compounds is attributed to the availability of lone pair of electrons. The order of availability of e^- pair on N-atom is :

$NH_3 > NH_2NH_2 > HN_3 > NH_2OH$.

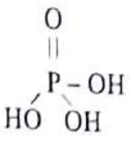
Therefore, same is the order of basicity of these compounds.

26. **(a) :** Hydrogen fluoride is an associated molecule and can be represented by H_2F_2. This is due to the fact that strong hydrogen bonding exist between the molecules. (as F is highly electronegative element)

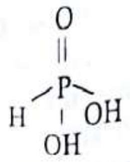
$H_2F_2 + KF \rightarrow KHF_2 + HF$

27. **(b) :** As the size of the noble gas atoms increases down the group, the polarisation of the electron cloud becomes easier. So, heavier noble gas atoms are easily polarised in polar water. Thus, solubility increases down the group.

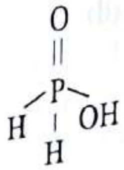
28. **(b) :** H_3PO_4 is a tetrahedral structure molecule. It contains three –OH groups so that three protons can be released. So, it acts as a tribasic acid.



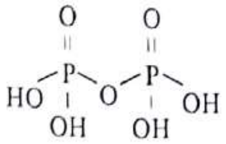
$(H_3PO)_4$
(Tribasic acid)



$(H_3PO)_3$
(Dibasic acid)

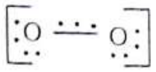


$(H_3PO)_2$
(Monobasic acid)



$H_4P_2O_7$ (Tetrabasic acid)

29. **(a) :** KO_2 is a superoxide of potassium containing superoxide ion, O^{2-} which has three electron bond. Thus, this ion can be represented as

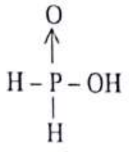


The presence of one unpaired electron in three electron bond makes this ion paramagnetic.

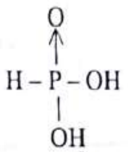
30. **(d) :** H_3PO_2, H_3PO_3 and H_3PO_4 contain one, two and three ionisable hydrogen atoms respectively.

$$H_3PO_2 \rightleftharpoons H^+ + H_2PO_2^-$$
$$H_3PO_3 \rightleftharpoons H^+ + H_2PO_3^- \rightleftharpoons 2H^+ + HPO_3^{2-}$$
$$H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^- \rightleftharpoons 2H^+ + HPO_4^{2-}$$
$$\rightleftharpoons 3H^+ + PO_4^{3-}$$

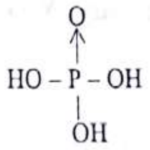
But there is very little difference in acidity.



sp^3
H_3PO_2



sp^3
H_3PO_3



sp^3
H_3PO_4

As sp^3 hybridised, therefore all are tetrahedral.

31. **(b) :** $\underbrace{3HCl + HNO_3}_{\text{Aqua regia}} \longrightarrow \underset{\text{Nitrosyl chloride}}{NOCl} + 2H_2O + 2Cl$

32. **(d) :** The alkali metals dissolve in liquid ammonia without evolution of hydrogen. The colour of the dilute solution is blue and is paramagnetic in nature.

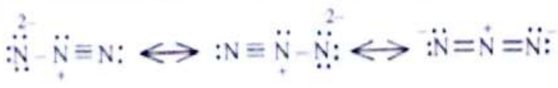
$M \rightarrow M^+$ (in liquid ammonia) + e^- (ammoniated)

$M + (x + y)NH_3 \rightarrow [M(NH_3)_x]^+ + e^-(NH_3)_y$

solvated electron

33. **(a) :** Stability of oxides of higher oxidation states decreases with increasing atomic number. Nitrogen exhibits a large number of oxidation states such as +1, +2, +3, +4, +5 in N_2O, NO, N_2O_3, N_2O_4 and N_2O_5.

34. **(c) :** Azide ion is a linear molecule, it is a pseudo halide and formal oxidation state of N in azide ion is –1. Resonance structures of N_3^- ion are :



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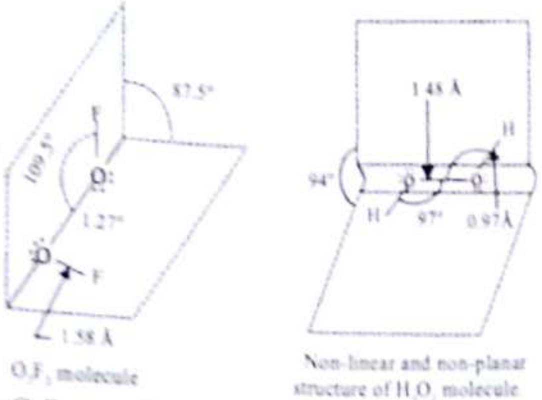
35. **(d) :**

	F	Cl	Br	I
Electron affinity	–3.6	–3.8	–3.5	–3.2

The low value of electron affinity of fluorine is probably due to small size of fluorine atom, *i.e.* electron density is high which hinders the addition of an extra electron.

36. **(b) :** O_2F_2 and H_2O_2, both have open book type structure.



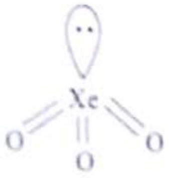
O_2F_2 molecule

Non-linear and non-planar structure of H_2O_2 molecule

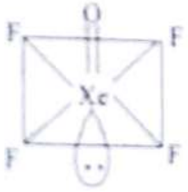
In O_2F_2, one O – O bond and two O – F bonds are lying in different planes, *i.e.* this molecule like H_2O_2 has non-linear and non-planar structure.

37. **(d)**

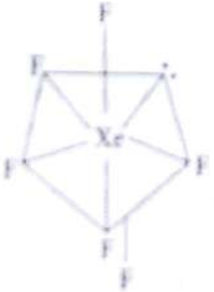
38. **(d) :** XeO_3 :



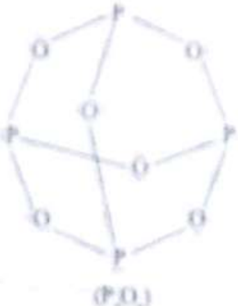
$XeOF_4$:



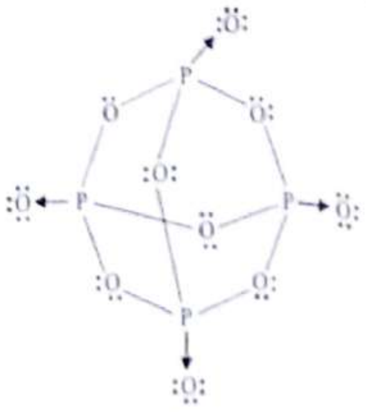
XeF_6 :



39. **(a) :**



(P_4O_6)



(P_4O_{10})

40. **(a) :** $K_2MnF_6 + 2SbF_5 \rightarrow 2KSbF_6 + MnF_3 + \frac{1}{2}F_2$

In this reaction, the stronger Lewis acid SbF_5 displaces the weaker one, MnF_4 from its salt. MnF_4 is unstable and readily decomposes to give MnF_3 and fluorine.

41. **(b) :** Tincture of iodine is an aqueous solution of I_2 in KI, and French iodine is a solution in alcohol.

42. **(a) :** PCl_5 is molecular in the gas phase but exists as $[PCl_4]^+[PCl_6]^-$ in the crystalline solid.

43. **(a) :** When traces of iodide in the form of KIO_3/KI is added to the salt, iodised salt is obtained.

44. **(b)**

45 **(c) :** The different allotropic forms of sulphur arises partly from the extent to which S has polymerised and partly from the crystal structures adopted.

The two common crystalline forms are α-rhombic sulphur and β-monoclinic sulphur. A third modification is γ-monoclinic sulphur. All three forms contain puckered S_8 rings with a crown conformation. Engel's sulphur (ε-sulphur) contains S_6 rings.

S_7, S_9, S_{10}, S_{11}, S_{12}, S_{18} and S_{20} rings have been made by Schmidt and his group.

Plastic or γ-sulphur contains spiral chains and sometimes S_8 and other rings.

The other allotropic forms of sulphur are milk of sulphur and colloidal or δ-sulphur.

46. **(b) :** There are several types of van der Waals attraction : dipole-dipole, dipole-induced-dipole and spontaneous-dipole-induced-dipole. The spontaneous-dipole-induced-dipole attractions are also known as *London dispersion forces*. LDF are surprisingly strong but are only short range forces *e.g.* surface of neutral molecules or inert gases. All molecules have LDF and strength increases with the size/surface area of the molecule. In case of halogens, LDF increases as $F_2 < Cl_2 < Br_2 < I_2$.

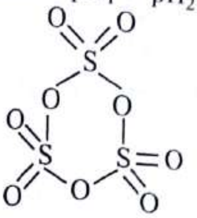
47. **(c) :** $XeF_{6(s)} + 3H_2O_{(l)} \longrightarrow \underset{\text{Highly explosive}}{XeO_{3(s)}} + 6HF_{(aq)}$

48. **(a) :** Oxygen is the most abundant element in the earth's crust. (above 45.5 wt %)

49. **(d) :**
I $Na_2O + H_2O \rightarrow 2NaOH$
II $Na_2S + H_2O \rightarrow 2NaOH + H_2S$
III $Na_2Se + H_2O \rightarrow 2NaOH + H_2Se$
IV $Na_2Te + H_2O \rightarrow 2NaOH + H_2Te$

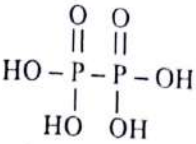
I will have the highest pH. Among H_2S, H_2Se, H_2Te, acidity goes on increasing on going down the group as bond length increases on increasing size of central atom. So, $pH_4 < pH_3 < pH_2$.
Overall order is $pH_1 > pH_2 > pH_3 > pH_4$.

50. **(d) :**



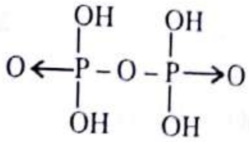
Cyclic trimer

51. **(a) :** Hypophosphoric acid is



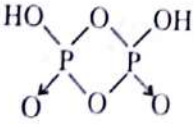
$HO-\overset{\overset{O}{\|}}{\underset{\underset{HO}{|}}{P}}-\overset{\overset{O}{\|}}{\underset{\underset{OH}{|}}{P}}-OH$

Pyrophosphoric acid

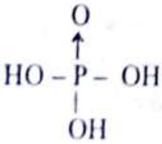


$O\leftarrow\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}-O-\overset{\overset{OH}{|}}{\underset{\underset{OH}{|}}{P}}\rightarrow O$

Metaphosphoric acid



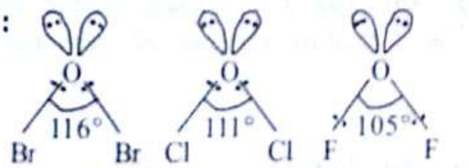
Orthophosphoric acid



$HO-\overset{\overset{O}{\uparrow}}{\underset{\underset{OH}{|}}{P}}-OH$

52. **(c) :** The fluoride ion, by a process of hydrogen bonding, forms the anion, HF_2^-. The compound is written as $K^+[HF_2]^-$

53. **(a) :**



In OF_2 repulsion between lone pairs is greater than that between bond pair since electrons are away from O and nearer to F. In Cl_2O, bonding electrons are nearer to O than to Cl, so the bond angle is greater than 109°28′. In Br_2O, the bonding electrons are more closer to oxygen than in Cl_2O, so the bond angle is largest (116°).

54. **(b) :** $2NaOH_{(dilute)} + Br_2 \xrightarrow{cold} NaBrO + NaBr + H_2O$

$\underset{\text{Sodium hypobromide}}{3NaBrO} \xrightarrow{300\ K} NaBrO_3$

On acidification, the final mixture gives bromine.

$5NaBrO + NaBrO_3 + 6HCl \longrightarrow 6NaCl + 3Br_2 + 3H_2O$

Thus, during the reaction, bromine is present in four different oxidation states *i.e.*, zero in Br_2, +1 in NaBrO, –1 in NaBr and +5 in $NaBrO_3$. The greatest difference between various oxidation states of bromine is 6 and not 5. On acidification of the final mixture, Br_2 is formed and disproportionation of Br_2 occurs during the reaction giving BrO^-, Br^- and BrO_3^- ions.

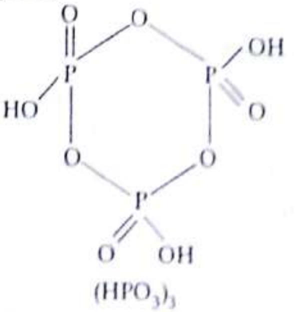
55. **(d) :** The structure of XeO_3F_2 -

No. of lone pair of Xe = 0 and no. of bond pair = 5
Hybridisation of Xe = sp^3d
Hence, shape of XeO_3F_2 should be trigonal bipyramidal and not octahedral.

56. **(a) :** Phosphorus trichloride reacts violently with water forming phosphorous acid.
$PCl_3 + 3HOH \longrightarrow H_3PO_3 + 3HCl$

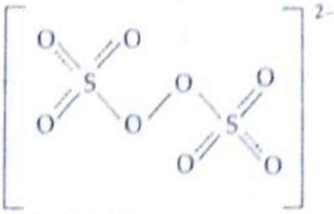
57. **(c) :** $XePtF_6$ was first real compound of any of the noble gases.

58. **(b) :**



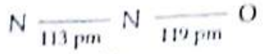
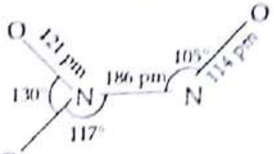
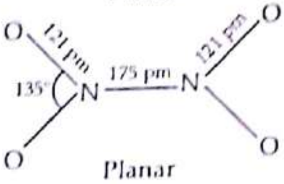
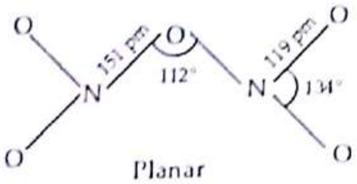
$(HPO_3)_3$

59. **(c) :** The structure of peroxodisulfate anion is:



It has a O–O bridge.

60. **(a)** : N—N bond length is minimum in N_2O.

Compound	**Structure**
N_2O	 Linear
N_2O_3	 Planar
N_2O_4	 Planar
N_2O_5	 Planar

61. **(c)** : Hydrolysis of XeF_6 is not a redox reaction. XeF_6 reacts violently with water, but slow hydrolysis by atmospheric moisture gives highly explosive solid, XeO_3.

$XeF_{6(s)} + 3H_2O_{(l)} \rightarrow XeO_{3(s)} + 6HF_{(aq)}$

Partial hydrolysis of XeF_6 yields $XeOF_4$ and XeO_2F_2.

$XeF_6 + H_2O \rightarrow XeOF_4 + 2HF$

$XeF_6 + 2H_2O \rightarrow XeO_2F_2 + 4HF$

62. **(a)** : Rhombic sulphur is insoluble in water but readily soluble in carbon disulphide, CS_2. It dissolves to some extent in benzene, alcohol and ether also.

63. **(b)** : ClF_3 and BrF_3 are used for the production of UF_6 in the enrichment of U^{235}.

$U_{(s)} + 3ClF_{3(l)} \longrightarrow UF_{6(g)} + 3ClF_{(g)}$

64. **(a)** : Due to high electronegativity and small size, fluorine forms only one oxoacid, HOF known as fluoric(I) acid or hypofluorous acid.

65. **(a)** : Due to decrease in bond (H—*E*, where *E* = O, S, Se, Te) dissociation enthalpy down the group, acidic character increases.

Hence, the order is :

$H_2O < H_2S < H_2Se < H_2Te$

66. **(d)** : In nitrogen family, due to inert pair effect as the tendency to show +3 oxidation state increases down the group from As to Bi, tendency to disproportionate decreases.

67. **(b)** : H_3PO_2 is a good reducing agent as it contains two P-H bonds and thus reduces $AgNO_3$ to Ag.

$$4AgNO_3 + H_3PO_2 + 2H_2O \longrightarrow 4Ag\downarrow + H_3PO_4 + 4HNO_3$$

68. **(c)** :

Element	**Boiling point (K)**	**Difference**
N	772	→ 476.8
P	554	→ 334
As	888	→ 972
Sb	1860	→ 23
Bi	1837	

69. **(b)** : With $K_2Cr_2O_7$, SO_2 works as reducing agent.

$$K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + H_2O$$

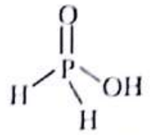
With water the reaction is not a redox reaction,

$SO_2 + H_2O \longrightarrow H_2SO_3$

$2Mg + SO_2 \longrightarrow 2MgO + S$

$3Mg + SO_2 \longrightarrow 2MgO + MgS$

70. **(d)** : Acids which contain P—H bonds have strong reducing properties. Hypophosphorus acid (H_3PO_2) is a good reducing agent as it contains two P—H bonds. It has one P—OH bond, so it is monobasic.



(Monobasic)

71. **(a)** : Acidified $KMnO_4$ is reduced by acidic SO_2.

$[SO_2 + 2H_2O \rightarrow H_2SO_4 + 2H] \times 5$

$[2H + O \rightarrow H_2O] \times 5$

$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$

$2KMnO_4 + 5SO_2 + 2H_2O \rightarrow K_2SO_4 + 2MnSO_4 + 2H_2SO_4$

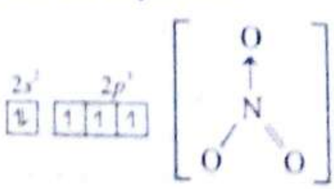
72. **(a)** : Due to their high reactivity, halogens are not found in free state.

73. **(c)** : At elevated temperature or in the presence of catalyst, strong bonds between two N-atoms rupture, and make N_2 molecule reactive.

74. **(d)** : The bond angle of PBr_3 is lesser than PH_3 but the bond angle of NBr_3 is greater than NH_3. Size of Br is larger than hydrogen.

75. **(b)** : Liquid ammonia is used in refrigeration on account of its large heat of evaporation.

76. **(a)** : NO_3^- : N →



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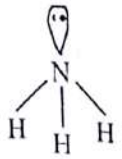
Hybridisation is sp^2 here and therefore planar structure is expected.

NH_3 : N → $1s^2, 2s^2, 2p^3$

Hybridisation is sp^3, therefore tetrahedral structure is expected but there is pyramidal structure as lone pair of electron occupy one of the corners of tetrahedral.



77. **(a) :** SO_2 in presence of moisture acts as a bleaching agent. This is due to the reducing nature of SO_2. But bleaching action is only temporary.

$SO_2 + 2H_2O \rightarrow H_2SO_4 + 2[H]$

Similarily, Cl_2 in presence of moisture give out nascent oxygen and causes bleaching.

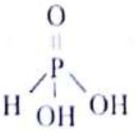
$Cl_2 + H_2O \rightarrow 2HCl + [O]$

here bleaching action is permanent.

78. **(a) :** Xenon belongs to noble gases which are considered to be very unreactive. In xenon atom, the ionisation potential of Xe to lose one electron was found to be nearly equivalent that of $O_2 \rightarrow O_2^+ + e^-$. Also, due to the presence of empty 5*d*-orbitals, electrons can be excited and higher valency of xenon can be produced. *e.g.*, XeF_2, XeF_4, XeF_6 etc.

79. **(a) :** H_2SO_4 when react with NaBr and NaI, give out Br_2 and I_2 as concentrated H_2SO_4 is a strong oxidising agent.

80. **(c) :** Structure of H_3PO_3 is :



Due to the presence of two hydroxyl protons, H_3PO_3 is dibasic acid.

81. **(b) :** Oxygen is second most electronegative element after fluorine. So, it can easily gain electrons to form dinegative anion (O^{2-}) while sulphur is not so electronegative element as oxygen.

82. **(a) :** All the halogens are coloured. The colour deepens with the rise of atomic number from fluorine to iodine.

The colour is due to the absorption of energy from visible light by their molecules on excitation of outer electrons to higher energy levels.

F	Cl	Br	I
Light yellow	Yellow green	Reddish brown	Deep violet

83. **(c) :** Lower value of bond dissociation energy of fluorine is due to the high interelectronic repulsions between non-bonding electrons of the 2*p*-orbital of small sized fluorine. As a result F–F bond is weaker as comparison to Cl–Cl and Br–Br bonds.

	Bond dissociation energy
F–F	38 kcal/mole
Cl–Cl	57 kcal/mole
Br–Br	45.5 kcal/mole
I–I	35.6 kcal/mole

84. **(a) :** $BaCO_3 + 2HNO_3 \rightarrow Ba(NO_3)_2 + H_2O + CO_2$

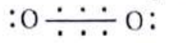
85. **(c) :** Sb(III) is a basic radical of IIB group for which group reagent is H_2S in presence of dilute HCl. It is necessary to maintain the proper hydrogen ion concentration for the precipitation of IInd group cations and to check the precipitation of IV group cations.

86. **(c) :** Greater the number of negative ions present in the oxy-acid, greater the acidic strength.

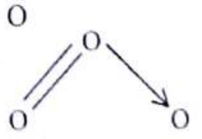
In general, the strengths of acids that have general formula, $(HO)_mZO_n$ can be related to the value of n. As the value of n increases, acidic character also increases. The negative ions draw electrons away from the Z-atom and make it more positive. The Z-atom, therefore, becomes more effective in withdrawing electron density away from the oxygen atom that bonded to hydrogen. In turn, the electrons of O – H bond are drawn more strongly away from the H-atom. The net effect is it makes proton release easier and thus increases the acidic strength.

87. **(b) :** Due to the ease with which it can liberate nascent oxygen, O_3 acts as a powerful oxidising agent.

$O_3 \rightarrow O_2 + O$



Paramagnetic
(due to presence of
two unpaired electrons)



Diamagnetic

88. **(c) :** $SeCl_4$ possess see-saw geometry, which can be regarded as a distorted trigonal bipyramidal structure, having one lone pair (lp) of electrons in the basal position of the trigonal bipyramidal. See-saw geometry of $SeCl_4$ molecules arises due to the sp^3d hybridisation of the central atom. The distortion in shape is due to the presence of one lone pair of electrons.

89. **(c) :** Oxygen is a colourless, odourless and tasteless gas. It is paramagnetic in gaseous, liquid and solid states. It can be liquefied to a pale blue liquid by compressing the gas at a very low temperature. Its allotropic modification is ozone.

90. **(b) :** The reaction involved is

$CaOCl_2 + H_2SO_4 \rightarrow CaSO_4 + H_2O + Cl_2$

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The available chlorine may be defined as the % of chlorine liberated when one mole of bleaching powder (127 g) is treated with excess of dilute H_2SO_4.

91. **(c)** : As atoms in S_8 molecule undergo sp^3 hybridisation and contain two lone pairs of electrons on each and exists as staggered 8 atoms-rings.

92. **(a)** : PCl_5 is trigonal bipyramidal containing sp^3d hybridized P atom in liquid and gaseous states whereas in solid state it consists of tetrahedral PCl_4^+ cation and octahedral PCl_6^- anion.

93. **(b)** : As the size of the atom M in H_2M increases, the strength of the H – M bond decreases.

94. **(c)** : Due to small size and absence of d-orbital, N cannot form R_3 N = O. The electronegativity of N (3.0) is much higher than P (2.1).

95. **(c)** : Solubility of AgCl (at 25°C) in H_2O

= 0.0020 g AgCl per litre of H_2O

Solubility of AgCl in NH_3 (at 25°C)

= 14.00 g AgCl dissolved per kg of NH_3

Solubility of AgCl is more in NH_3 due to formation of soluble stable complex $[Ag(NH_3)_2]^+$.

Ammonia is less polar than water, as oxygen is more electronegative than nitrogen.

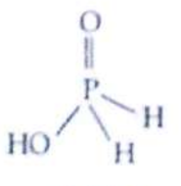
96. **(a)** : A mixture of oxygen and helium is used in diving apparatus which gives the same partial pressure of O_2 as in normal air at 1 atm. Due to high partial pressure and greater solubility, N_2 gets dissolved in blood and form bubbles (bends or decompression sickness). Hence, N_2 is replaced by helium which is much less soluble in biological fluids.

97. **(b)** : $Cl_2 + 2NaOH\ (dil.) \xrightarrow{cold} NaCl + NaOCl + H_2O$

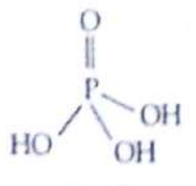
$3Cl_2 + 6NaOH\ (conc.) \xrightarrow{heat} 5NaCl + NaClO_3 + 3H_2O$

Chlorine undergoes the simultaneous oxidation-reduction. Chlorine is simultaneously reduced to chloride ion (Cl^-) and is oxidised to either ClO^- or ClO_3^- ion. Halogens (*e.g.* Cl) have a strong tendency to accept electrons, so they act as strong oxidising agents.

98. **(b)** :



(H_3PO_2)



(H_3PO_4)

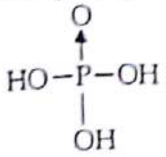
Oxoacids of phosphorus which contain P — H bond act as reducing agents and reduce metal salts to free metals. Thus, H_3PO_2 act as reducing agent while H_3PO_4 does not.

99. **(c)** : S is more electronegative than Se.

100. **(d)** : Bond dissociation energy is $F_2 < Cl_2$ because of relatively large electron-electron repulsion among the lone pairs in F_2 molecule where they are much closer to each other than in Cl_2.

101. **(a)** : As in solid state, PCl_5 exists as an ionic solid $[PCl_4]^+[PCl_6]^-$ in which the cation, $[PCl_4]^+$ is tetrahedral and the anion, $[PCl_6]^-$ is octahedral. PCl_5 in gaseous state has trigonal bipyramidal structure in which three equatorial bonds are equivalent, while the two axial bonds are longer than equatorial bonds due to more bond pair repulsion.

102. **(a)** : Phosphoric acid is a tribasic acid, *i.e.*, three hydroxyl groups are present.

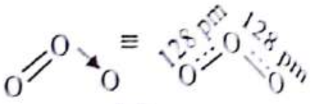


$$HO-\overset{\overset{\displaystyle O}{\uparrow}}{\underset{\underset{\displaystyle OH}{|}}{P}}-OH$$

103. **(d)** :

Str. $O=O$

121 pm



B.O. 2.0 1.5

The bond length decreases as bond order increases. Hence, bond length of O_3 is higher than O_2.

The resonance forms do not show any unshared electrons. Hence, O_3 molecule is not paramagnetic.

104. **(d)** : Sb_2S_3 is soluble in yellow ammonium sulphide.

$Sb_2S_3 + 3(NH_4)_2S \rightarrow 2(NH_4)_3SbS_3$

105. **(a)** : Inert gases are adsorbed on the charcoal.

106. **(a)** : $H_2S_{(g)} + aq \rightarrow HS^-_{(aq)} + H^+_{(aq)}$

$PH_{3(g)} + aq \rightarrow H_2P^-_{(aq)} + H^+_{(aq)}$

As S is more electronegative than P, conjugate base HS^- is more stable than H_2P^-. Hence, H_2S is stronger acid than PH_3.

107. **(d)**: Hydrides of group-16 elements show volatility in the order :

$H_2S > H_2Se > H_2Te > H_2O$

Oxygen is most electronegative than other elements of group-16, it undergoes hydrogen bonding. Due to strong intermolecular hydrogen bonding in H_2O, it shows lowest volatility.

As the size of the atom increases regularly from sulphur to tellurium, van der Waals' forces of attraction increase and hence volatility decreases from H_2S to H_2Te.

* * *

CHAPTER

22

1. Number of v
(a) 7
(c) 8

2. In order to
is coated w
(a) zinc
(c) tin

3. Which of
configurati
(a) [Ar]3d
(c) [Ar]4s

4. Which c
photogra
(a) Ag_2S
(c) Ag_2C

5. Which o
black on t
(a) CuCl
(c) AgC

6. Blister c
(a) allo
(c) cop
(d) ore

7. Which
as whit
(a) Zn
(c) Na

8. Whicl
reactio
colour
(a) Z
(c) C

9. Brass
(a) A
(c) Z

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CHAPTER

22

THE *d*- and *f*-BLOCK ELEMENTS

1. Number of water molecules in Mohr's salt is
(a) 7 (b) 5
(c) 8 (d) 6 *(1994)*

2. In order to protect iron from corrosion, iron is coated with
(a) zinc (b) nickel
(c) tin (d) copper. *(1995)*

3. Which of the following is the electronic configuration of Cu^{2+} ($Z = 29$)?
(a) $[Ar]3d^9$ (b) $[Ar]4s^1 3d^8$
(c) $[Ar]4s^2 3d^{10} 4p^1$ (d) $[Ar]4s^1 3d^{10}$ *(1995)*

4. Which of the following is used in photography?
(a) Ag_2S (b) $AgCl$
(c) $Ag_2C_2O_4$ (d) $AgBr$ *(1995)*

5. Which of the following compounds turns black on the addition of ammonium hydroxide?
(a) $CuCl_2$ (b) $PbCl_2$
(c) $AgCl$ (d) Hg_2Cl_2 *(1995)*

6. Blister copper is
(a) alloy of copper (b) pure copper
(c) copper containing 1% impurity
(d) ore of copper. *(1996)*

7. Which of the following compounds is known as white vitriol ?
(a) $ZnSO_4 \cdot 7H_2O$ (b) $CaSO_4 \cdot 2H_2O$
(c) $Na_2SO_4 \cdot 7H_2O$ (d) $MgSO_4 \cdot 7H_2O$ *(1996)*

8. Which of the following compounds on reaction with NaOH and Na_2O_2, gives yellow colour?
(a) $Zn(OH)_2$ (b) $Al(OH)_3$
(c) $Cr(OH)_3$ (d) $CaCO_3$ *(1997)*

9. Brass is an alloy of copper (Cu) and
(a) Al (b) Sn
(c) Zn (d) Ag *(1997)*

10. Which of the following can give iodometric titration?
(a) Fe^{3+} (b) Cu^{2+}
(c) Pb^{2+} (d) Ag^{2+} *(1997)*

11. Which of the following does not react with AgCl?
(a) $NaNO_3$ (b) NH_4OH
(c) Na_2CO_3 (d) $Na_2S_2O_3$ *(1997)*

12. Which of the following elements are analogous to the lanthanides?
(a) Carbides (b) Borides
(c) Actinides (d) Hydrides *(1998)*

13. Which of the following transition elements shows the highest oxidation state?
(a) Fe (b) Cr
(c) Mn (d) V *(1999)*

14. Which of the following metal is present in brass, bronze and german-silver?
(a) Cu (b) Na
(c) Mg (d) Al *(1994, 1999)*

15. In dichromate dimer
(a) 4 Cr – O bonds are equal
(b) 6 Cr – O bonds are equal
(c) all Cr – O bonds are equal
(d) all Cr – O bonds are unequal. *(2000)*

16. Tempering steel is a process of heating
(a) steel in contact with carbon and quenching it
(b) steel in the presence of ammonia and quenching it
(c) the hardened steel to a temperature below redness and cooling it slowly
(d) steel to bright redness and quenching it. *(2000)*

17. Philosopher's wool when heated with BaO at 1100°C gives a compound. Identify the compound.

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(a) $BaZnO_2$ (b) $Ba + ZnO_2$
(c) $BaCdO_2$ (d) $BaO_2 + Zn$
(2000)

18. Identify the transition element :
(a) $1s^2, 2s^22p^6, 3s^23p^6, 4s^2$
(b) $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^1$
(c) $1s^2, 2s^22p^6, 3s^23p^63d^{10}, 4s^24p^6$
(d) $1s^2, 2s^22p^6, 3s^23p^63d^2, 4s^2$ *(2000)*

19. Which of the following is the correct sequence of atomic weights of the given elements?
(a) Ni > Co > Fe (b) Fe > Co > Ni
(c) Co > Fe > Ni (d) Co > Ni > Fe
(1996, 2001)

20. Which of the following does not have valence electron in 3*d*-subshell?
(a) Fe (III) (b) Cr (I)
(c) Mn (II) (d) P (0) *(2002)*

21. Thermite is a mixture of iron oxide and
(a) zinc powder (b) potassium metal
(c) sodium shavings (d) aluminium powder.
(2002)

22. The colourless species is
(a) VCl_3 (b) $VOSO_4$
(c) Na_3VO_4
(d) $[V(H_2O)_6]SO_4 \cdot H_2O$ *(2003)*

23. Lanthanide for which +II and +III oxidation states are common is
(a) La (b) Nd
(c) Ce (d) Eu *(2003)*

24. The liquefied metal expanding on solidification is
(a) Ga (b) Al
(c) Zn (d) Cu *(2004)*

25. Among the following pair of ions, the lower oxidation state in aqueous solution is more stable than the other, in
(a) Tl^+, Tl^{3+} (b) Cu^+, Cu^{2+}
(c) Cr^{2+}, Cr^{3+} (d) V^{2+}, VO^{2+} *(2005)*

26. The colour imparted by Co (II) compounds to glass is
(a) green (b) deep-blue
(c) yellow (d) red. *(2006)*

27. During estimation of nickel, we prepare nickel dimethylglyoxime, a scarlet red solid. This compound is ....
(a) ionic (b) covalent
(c) metallic (d) non-ionic complex.
(2007)

28. Mercurous chloride exists in the form of
(a) Hg^+ (b) Hg_2^{2+}
(c) Hg^{2+} (d) Hg_3^{2+} *(2009)*

29. What are constituents of 'Mischmetal'?
(a) La, Fe (b) La, Ce
(c) Fe, Ce (d) Ce, Cu *(2010)*

30. Match list I with list II and select the correct answer using the codes given below the lists.

	List I Metal ion		List II Magnetic moment(BM)
A.	Cr^{3+}	1.	$\sqrt{35}$
B.	Fe^{2+}	2.	$\sqrt{30}$
C.	Ni^{2+}	3.	$\sqrt{24}$
D.	Mn^{2+}	4.	$\sqrt{15}$
		5.	$\sqrt{8}$

Codes
(a) A-1, B-3, C-5, D-4 (b) A-2, B-3, C-5, D-1
(c) A-4, B-3, C-5, D-1 (d) A-4, B-5, C-3, D-1
(2010)

31. Which is not stable under ambient condition?
(a) Fe^{3+} (b) Mn^{2+}
(c) Ti^{4+} (d) Cu^+ *(2012)*

32. MnO_3 in an acidic medium dissociates into
(a) MnO_2 and MnO_4^- (b) MnO and MnO_4^-
(c) MnO_2 and MnO (d) MnO_2 and MnO_3
(2012)

33. Magnetic moment of Cr^{2+} is nearest to
(a) Fe^{2+} (b) Mn^{2+}
(c) Co^{2+} (d) Ni^{2+} *(2012)*

34. Which of the following elements has lowest melting point?
(a) Cr (b) Fe
(c) Ni (d) Cu *(2013)*

35. Maximum number of unpaired electrons are present in
(a) Gd^{3+} (b) Yb^{2+}
(c) Tb^{2+} (d) Pm^{3+} *(2013)*

36. When calomel is treated with ammonium hydroxide, a black substance is formed. The black substance is
(a) Hg + HgO (b) $HgO.HgCl_2$
(c) $H_2N - Hg - Cl + Hg$
(d) $Hg(NH_2)_2 + HgO$ *(2013)*

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37. Which of the following is most basic?
(a) $Al(OH)_3$ (b) $Cr(OH)_3$
(c) $La(OH)_3$ (d) $Fe(OH)_3$ *(2013)*

38. Which of the following ion does not exist?
(a) $[CuI_4]^{2-}$ (b) VO_4^{3-}
(c) WO_4^{2-} (d) CrO_4^{2-} *(2013)*

39. $KMnO_4$ in alkaline medium changes to
(a) Mn^{3+} (b) MnO_2
(c) MnO_4^{2-} (d) $Mn(OH)_4^-$ *(2014)*

40. Choose the correctly paired gaseous cation and its magnetic (spin only) moment (in B.M.)
(a) Ti^{2+}, 3.87 B.M. (b) Cr^{2+}, 4.90 B.M.
(c) Co^{3+}, 3.87 B.M. (d) Mn^{2+}, 4.90 B.M. *(2014)*

1. In presence of acidic medium, $KMnO_4$ converts H_2S into
(a) Mn only (b) MnS only
(c) MnS + S (d) S only *(2014)*

42. Copper sulphate is dissolved in water containing ________ for making Bordeaux mixture.
(a) NaOH (b) KCN
(c) $Ca(OH)_2$ (d) All of these *(2015)*

43. Colour imparted by Co(II) compounds to glass is
(a) green (b) brown
(c) violet (d) blue. *(2015)*

44. The colourless species is
(a) VCl_3 (b) $VOSO_4$
(c) Na_3VO_4
(d) $[V(H_2O)_6]SO_4 \cdot H_2O$ *(2017)*

45. Among the following, the compound that is both paramagnetic and coloured is
(a) $K_2Cr_2O_7$ (b) $(NH_4)_2[TiCl_6]$
(c) $VOSO_4$ (d) $K_3[Cu(CN)_4]$ *(2017)*

ASSERTION AND REASON

46. ***Assertion*** : Tungsten has very high melting point.
Reason: Tungsten is a covalent compound. *(1997)*

47. ***Assertion:*** Tailing of mercury occurs on passing ozone through it.
Reason: Due to oxidation of mercury. *(1999)*

48. ***Assertion*** : Cuprous ion (Cu^+) is colourless whereas cupric ion (Cu^{++}) is blue in the aqueous solution.
Reason : Cuprous ion (Cu^+) has unpaired electrons while cupric ion (Cu^{++}) does not. *(2002)*

49. ***Assertion*** : Solution of Na_2CrO_4 in water is intensely coloured.
Reason : Oxidation state of Cr in Na_2CrO_4 is +VI. *(2003)*

50. ***Assertion*** : Potassium ferrocyanide is diamagnetic whereas potassium ferricyanide is paramagnetic.
Reason : Crystal field splitting in ferrocyanide ion is greater than that of ferricyanide ion. *(2005)*

51. ***Assertion*** : $K_2Cr_2O_7$ is used as primary standard in volumetric analysis.
Reason : It has a good solubility in water. *(2006, 2015)*

52. ***Assertion*** : Change in colour of acidic solution of potassium dichromate by breath is used to test drunk drivers.
Reason : Change in colour is due to the complexation of alcohol with potassium dichromate. *(2006, 2015)*

53. ***Assertion*** : Copper sulphate solution is not stored in zinc vessel.
Reason : Zinc forms complex with $CuSO_4$. *(2007)*

54. ***Assertion*** : Magnetic moment of Dy is the highest among the lanthanoids.
Reason : Orbital motion contributes magnetic moment. *(2007)*

55. ***Assertion*** : Copper metal gets readily corroded in acidic aqueous solution.
Reason : Free energy change for this process is negative. *(2008, 2004)*

56. ***Assertion*** : Transition metals are poor reducing agents.
Reason : Transition metals form numerous alloys with other metals. *(2010)*

57. ***Assertion*** : The degree of complex formation in actinides decreases in the order

$$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}.$$

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Reason : Actinides form complexes with π-bonding ligands such as alkyl phosphines and thioethers. *(2010)*

58. **Assertion :** Reduction potential of Mn (+3 to +2) is more positive than Fe (+3 to +2).
Reason : Ionisation potential of Mn is more than that of Fe. *(2011)*

59. **Assertion :** Ce^{4+} is used as an oxidising agent in volumetric analysis.
Reason : Ce^{4+} has the tendency of attaining +3 oxidation state. *(2012)*

60. **Assertion :** $La(OH)_3$ is more basic than $Lu(OH)_3$.
Reason : Size of Lu^{3+} increases and shows less covalent character. *(2012)*

61. **Assertion :** Co (IV) is known but Ni (IV) is not.
Reason : Ni (IV) has d^4 electronic configuration. *(2014)*

62. **Assertion :** The correct order of oxidising power is : $VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$.
Reason : The oxidation state of Mn is +7. *(2014)*

63. **Assertion :** Chemistry of actinoids is more complicated than lanthanoids.
Reason : Actinoid elements are radioactive. *(2014)*

Answer Key

1.	(d)	**2.**	(a)	**3.**	(a)	**4.**	(d)	**5.**	(d)	**6.**	(c)	**7.**	(a)	**8.**	(c)
9.	(c)	**10.**	(b)	**11.**	(c)	**12.**	(c)	**13.**	(c)	**14.**	(a)	**15.**	(b)	**16.**	(c)
17.	(a)	**18.**	(d)	**19.**	(d)	**20.**	(d)	**21.**	(d)	**22.**	(c)	**23.**	(d)	**24.**	(a)
25.	(a)	**26.**	(b)	**27.**	(d)	**28.**	(b)	**29.**	(b)	**30.**	(c)	**31.**	(d)	**32.**	(a)
33.	(a)	**34.**	(d)	**35.**	(a)	**36.**	(c)	**37.**	(c)	**38.**	(a)	**39.**	(b)	**40.**	(b)
41.	(d)	**42.**	(c)	**43.**	(d)	**44.**	(c)	**45.**	(c)	**46.**	(c)	**47.**	(a)	**48.**	(c)
49.	(b)	**50.**	(c)	**51.**	(c)	**52.**	(c)	**53.**	(a)	**54.**	(a)	**55.**	(d)	**56.**	(b)
57.	(b)	**58.**	(c)	**59.**	(a)	**60.**	(c)	**61.**	(d)	**62.**	(b)	**63.**	(b)		

---

1. (d) : Mohr
2. (a) : Co
phenomenon a
it with a thin f
iron by a pro
3. (a) : Cu
4. (d) : As
making photo
Solution of s
forms a solu
AgBr + 2Na
5. (d) : Th
of mercury a

Hg_2Cl_2 + 2N

6. (c) :
(98–99% C
7. (a) : V
8. (c) :
CrO_4^{2-} ion.
$2Cr(OH)_3$

9. (c) :
10. (b) :
$2S_2$C
(thi
11. (c) :
2N
Na_2
12. (c)
the inne
consist
consists
13. (c)
i.e., KM
14. (a
an allo
Cu, Zr
15. (

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EXPLANATIONS

1. **(d) :** Mohr's salt is $Fe(SO_4)\cdot(NH_4)_2SO_4\cdot 6H_2O$.

2. **(a) :** Corrosion or rusting is a surface phenomenon and thus iron is protected by coating it with a thin film of zinc which is more active than iron by a process called galvanisation.

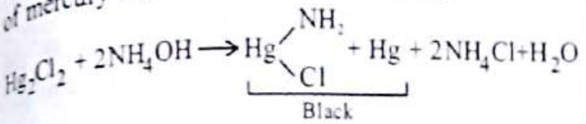
3. **(a) :** Cu ($Z = 29$) : $[Ar]4s^1 3d^{10}$, Cu^{2+} : $[Ar]3d^9$.

4. **(d) :** As AgBr is sensitive to light, it is used for making photographic films.

Solution of sodium thiosulphate is used as fixer. It forms a soluble complex with silver halides.

$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

5. **(d) :** The black substance obtained is a mixture of mercury and mercuric aminochloride.



$$Hg_2Cl_2 + 2NH_4OH \longrightarrow \underbrace{Hg\begin{matrix}NH_2\\Cl\end{matrix} + Hg}_{\text{Black}} + 2NH_4Cl + H_2O$$

6. **(c) :** 'Blister copper' is impure copper (98-99% Cu).

7. **(a) :** White vitriol : $ZnSO_4.7H_2O$.

8. **(c) :** Yellow colour is due to the formation of CrO_4^{2-} ion.

$$2Cr(OH)_3 + \underset{\substack{\text{(From}\\ Na_2O_2)}}{3[O]} + 4NaOH \rightarrow 2Na_2CrO_4 + 5H_2O$$

9. **(c) :** Copper and zinc are the components of brass.

10. **(b) :** $2Cu^{2+} + 2I^- \rightarrow Cu_2I_2 + I_2\uparrow$

$\underset{\text{(thiosulphate)}}{2S_2O_3^{2-}} + I_2 \rightarrow S_4O_6^{2-} + 2I^-$

11. **(c) :** $NaNO_3 + AgCl \rightarrow AgNO_3 + NaCl$

$2NH_4OH + AgCl \rightarrow Ag(NH_3)_2Cl + 2H_2O$

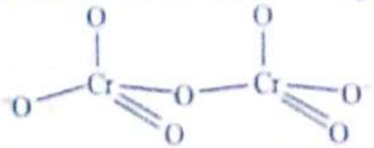
$Na_2S_2O_3 + 2AgCl \rightarrow Ag_2S_2O_3 + 2NaCl$

12. **(c) :** Lanthanides and actinides are called as the inner-transition metals. Lanthanide elements consists of 4*f*-series while actinide elements consists of 5*f*-series.

13. **(c) :** Mn shows highest oxidation state of +7, *i.e.*, $KMnO_4$.

14. **(a) :** Brass is an alloy of Cu and Zn. Bronze is an alloy of Cu and Sn. German-silver is an alloy of Cu, Zn and Ni.

15. **(b) :** Dichromate has the following structure,



6 Cr – O bond lengths are found to be equal.

16. **(c) :** Tempering of steel is a process of heating the steel to a temperature below redness and then cooling it slowly. A thin film of the oxide is formed on the surface of steel.

17. **(a) :** When Philosopher's wool (*i.e.*, ZnO) is heated with BaO at 1100°C, it gives

$BaO + ZnO \rightarrow BaZnO_2$

18. **(d) :** Transition elements are those elements which possess partly filled *d*-subshells in their elementaryform or their commonly occurring ions *i.e.*, $(n-1)d^{1-10}ns^{1-2}$.

19. **(d) :** Fe ($Z = 26$); Atomic weight = 55.85

Co ($Z = 27$); Atomic weight = 58.93

Ni ($Z = 28$); Atomic weight = 58.69

The correct order of Atomic weights is :

Co > Ni > Fe

20. **(d) :** Phosphorus (P) has electronic configuration

$1s^2, 2s^2, 2p^6, 3s^2, 3p^3$

Therefore, no valence electron is present in the 3*d*-subshell.

Fe (III) has electronic configuration : $3d^5 4s^0$

Cr(I) : $3d^5 4s^0$

Mn (II) : $3d^5 4s^0$

21. **(d) :** Thermite process involves the reduction of metal oxides by the use of aluminium powder.

$Fe_2O_3 + 2Al \rightarrow Al_2O_3 + 2Fe$

22. **(c) :** Na_3VO_4 contains colourless *ortho*-vanadate VO_4^{3-} ion.

23. **(d) :** La = +3, Nd = +2, +3, +4

Ce = +3, +4, Eu = +2, +3

24. **(a) :** Gallium is brittle at low temperature but is liquid above room temperature and can indeed melt in the hand.

Gallium metal expands by 3.1 percent when it solidifies, and therefore should not be stored in either glass or metal containers. Gallium also corrodes most other metals by diffusing into their metal lattice.

25. **(a) :** Tl^+ ions are more stable than Tl^{3+} and thus, Tl^{3+} ions change to Tl^+ ions thereby acting as oxidising agents.

$\underset{\text{(less stable, oxidising agent)}}{Tl^{3+}\text{ compounds}} + 2e^- \rightarrow \underset{\text{(more stable, reducing agent)}}{Tl^+\text{ compounds}}$

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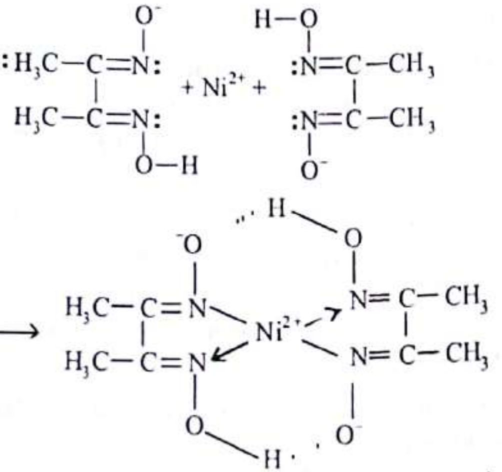
26. (b) : Glass is an amorphous and transparent or translucent solid obtained by solidification of a mixture of silicates of different metals, one of which is always an alkali metal. Addition of small amounts of transition metal salts to the glass mixture imparts colour to the glass. For example, addition of small amounts of Fe^{3+}, Fe^{2+}, Co^{2+}, Cr^{3+} and Mn^{4+} salts imparts yellow-brown, light blue, deep blue, green or violet colour respectively.

27. (d) :



Bis-(dimethylglyoximato) nickel (II) chelated comple (red ppt)

This planar complex is very poorly soluble and is used for the gravimetric determination of nickel *e.g.*, ores.

28. (b)

29. (b) : The constituents of Mischmetal is approximately 50% cerium and 25% lanthanum with small amounts of neodymium and praseodymium.

30. (c) : For $Cr^{3+} = 3d^3$, $\mu = \sqrt{3(3+2)} = \sqrt{15}$ B.M.

For $Fe^{2+} = 3d^6$, $\mu = \sqrt{4(4+2)} = \sqrt{24}$ B.M.

For $Ni^{2+} = 3d^8$, $\mu = \sqrt{2(2+2)} = \sqrt{8}$ B.M.

For $Mn^{2+} = 3d^5$, $\mu = \sqrt{5(5+2)} = \sqrt{35}$ B.M.

31. (d) : Copper (I) compounds are unstable in aqueous solution and undergo disproportionation.

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

The greater stability of $Cu^{2+}_{(aq)}$ than $Cu^+_{(aq)}$ is due to much more $-ve$ $\Delta_{hyd}H$ of $Cu^{2+}_{(aq)}$ than $Cu^+_{(aq)}$, which is more than compensates for the second ionisation enthalpy of Cu.

32. (a) : In acidic solution, manganese (VI) becomes unstable and undergoes disproportionation to form manganese (VII) and manganese (IV)

$$5\overset{VI}{Mn}O_3 + 2H^+ + 4e^- \longrightarrow 3\overset{IV}{Mn}O_2 + 2\overset{VII}{Mn}O_4^- + H_2O$$

33. (a) : $Cr^{2+} = 3d^4$, No. of unpaired electrons $(n) = 4$

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

$= \sqrt{4(4+2)} = \sqrt{24} = 4.89$ B.M.

$Fe^{2+} = 3d^6$, No. of unpaired electrons $(n) = 4$

Magnetic moment $= \sqrt{4(4+2)}$ B.M.

$= \sqrt{24} = 4.89$ B.M.

$Mn^{2+} = 3d^5$, No. of unpaired electrons $(n) = 5$

Magnetic moment $= \sqrt{5(5+2)}$ B.M.

$= \sqrt{35} = 5.91$ B.M.

$Co^{2+} = 3d^7$, No. of unpaired electrons $(n) = 3$

Magnetic moment $= \sqrt{3(3+2)}$ B.M.

$= \sqrt{15} = 3.87$ B.M.

$Ni^{2+} = 3d^8$, No. of unpaired electrons $(n) = 2$

Magnetic moment $= \sqrt{2(2+2)}$ B.M.

$= \sqrt{8} = 2.82$ B.M.

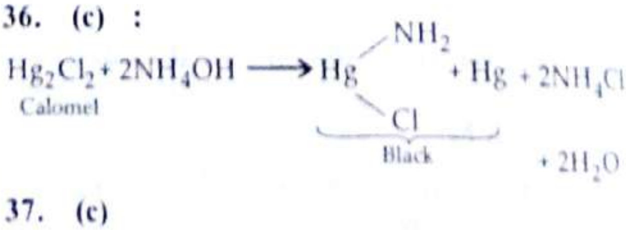
34. (d) : Cu has lowest melting point because it has lowest enthalpy of atomisation (*i.e.*, heat required to break the metal lattice to get free atoms) among the elements.

	Ni >	Fe >	Cr >	Cu
Enthalpy of atomisation : (in kJ mol^{-1})	430	416	397	339

35. (a) :

	No. of unpaired electrons
$Gd^{3+} : [Xe]4f^7$	↿ ↿ ↿ ↿ ↿ ↿ ↿
7	
$Yb^{2+} : [Xe]4f^{14}$	⇅ ⇅ ⇅ ⇅ ⇅ ⇅ ⇅
0	
$Tb^{2+} : [Xe]4f^9$	⇅ ⇅ ↿ ↿ ↿ ↿ ↿
5	
$Pm^{3+} : [Xe]4f^4$	↿ ↿ ↿ ↿ ☐ ☐ ☐
4	

36. (c) :



$$\underset{\text{Calomel}}{Hg_2Cl_2} + 2NH_4OH \longrightarrow \underbrace{Hg\begin{matrix} NH_2 \\ Cl \end{matrix}}_{\text{Black}} + Hg + 2NH_4Cl + 2H_2O$$

37. (c)

38. (a) : $[CuI_4]^{2-}$ does not exist because I^- being a stronger reducing agent reduces Cu^{2+} to Cu^+.

$2CuI_2 \longrightarrow 2CuI + I_2$

---

39. (b) : In alkalin
reduced to mangan
manganese dioxide.
$2KMnO_4 + H_2O \xrightarrow{alk}$

40. (b) : Using exp
(where, n

Ion
Co

$_{22}Ti^{2+}$
$_{24}Cr^{2+}$
$_{27}Co^{3+}$
$_{25}Mn^{2+}$

41. (d) : Acidifie
$2KMnO_4 + 3H_2SO$

42. (c) : Bordea
sulphate ($CuSO_4$)

43. (d)

44. (c) : In Na_3
oxidation state.
$V^{5+} : 3d^0 4s^0$, doe
Na_3VO_4, is colo

45. (c) : K_2Cr_2
$(NH_4)_2[TiCl_6]$ –
$VOSO_4 \rightarrow V^{+4}$
$K_3[Cu(CN)_4]$ –
$VOSO_4$, due
electron, is pa

46. (c) : Tun
very hard du
Tungsten (W)

47. (a) : Wh
superficially
sticks to th

48. (c) : C
it has no un
has $3d^{10}$ co
unpaired e
absorbing t
migrate fro
cupric ion
colour.

49. (b) :
colour, w
(due to t
$2Na_2CrO$

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39. (b) : In alkaline solution, $KMnO_4$ is first reduced to manganate and then to insoluble manganese dioxide.

$$2KMnO_4 + H_2O \xrightarrow{\text{alkaline}} 2MnO_2 + 2KOH + 3[O]$$

40. (b) : Using expression, $\mu = \sqrt{n(n+2)}$ B.M.
(where, n = No. of unpaired electrons)

Ion	Outer Configuration	n	μ
$_{22}Ti^{2+}$	$3d^2$	2	2.84
$_{24}Cr^{2+}$	$3d^4$	4	4.90
$_{27}Co^{3+}$	$3d^6$	4	4.90
$_{25}Mn^{2+}$	$3d^5$	5	5.92

41. (d) : Acidified $KMnO_4$ oxidises H_2S to S only.

$$2KMnO_4 + 3H_2SO_4 + 5H_2S \longrightarrow K_2SO_4 + 2MnSO_4 + 5S + 8H_2O$$

42. (c) : Bordeaux mixture consists of copper sulphate ($CuSO_4$) and lime [$Ca(OH)_2$].

43. (d)

44. (c) : In Na_3VO_4, vanadium is present in +5 oxidation state.
$V^{5+}: 3d^0 4s^0$, does not have unpaired electron. Hence, Na_3VO_4, is colourless species.

45. (c) : $K_2Cr_2O_7 \rightarrow Cr^{+6} : 3d^0$
$(NH_4)_2[TiCl_6] \rightarrow Ti^{+4} : 3d^0$
$VOSO_4 \rightarrow V^{+4} : 3d^1$
$K_3[Cu(CN)_4] \rightarrow Cu^+ : 3d^{10}$
$VOSO_4$, due to the presence of one unpaired electron, is paramagnetic and coloured.

46. (c) : Tungsten is a transition element and is very hard due to high metallic bonding.
Tungsten (W); Z = 74;

47. (a) : When mercury is exposed to ozone it gets superficially oxidised and loses its meniscus and sticks to the glass.

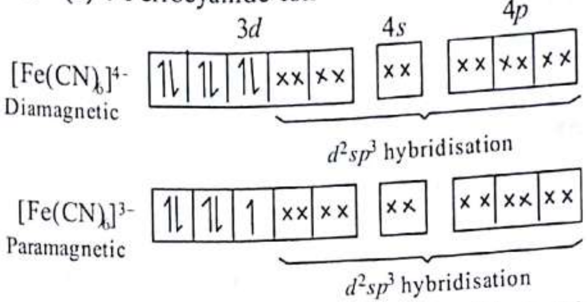
48. (c) : Cuprous ions (Cu^+) is colourless because it has no unpaired electrons in the $3d$ sub-shell as it has $3d^{10}$ configuration. The cupric ion (Cu^{++}) has one unpaired electron as it has $3d^9$ configuration. By absorbing the visible light, the unpaired electron can migrate from one set of d-orbitals to another. Hence cupric ion (Cu^{++}) in aqueous solution shows blue colour.

49. (b) : Na_2CrO_4 solution in water is yellow in colour, when acidified it changes to orange colour (due to the formation of $Cr_2O_7^{2-}$ ions).

$$2Na_2CrO_4 + H_2SO_4 \rightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

Let oxidation state of Cr in Na_2CrO_4 be x.
$\Rightarrow \quad 2(+1) + x + 4(-2) = 0 \Rightarrow x = +6$

50. (c) : Ferrocyanide ion



In ferrocyanide ion, the oxidation state of Fe is +2 however in ferricyanide ion, the oxidation number of Fe is +3.
Generally, the higher the oxidation state of the metal, the greater the crystal field splitting. It means crystal field splitting in ferrocyanide ion is lower than that of ferricyanide ion.

51. (c) : $K_2Cr_2O_7$ is less soluble in water. $K_2Cr_2O_7$ can be found in pure state and can be accurately weighed. It is not hygroscopic in nature. So, $K_2Cr_2O_7$ is used as a primary standard solution.

52. (c) : Change in colour is due to the oxidation of alcohol with potassium dichromate.
$K_2Cr_2O_7$ in presence of dilute H_2SO_4 acts as an oxidising agent. It is converted into chromic sulphate which is green in colour.

$$\underset{\text{(orange)}}{K_2Cr_2O_7} + 4H_2SO_4 \rightarrow K_2SO_4 + \underset{\text{(green)}}{Cr_2(SO_4)_3} + 4H_2O + 3O$$

53. (a) : Electropositive element like zinc precipitates copper from a solution of copper sulphate and finally forms a complex.

$$CuSO_4 + Zn \rightarrow Cu + ZnSO_{4(aq)} \rightarrow [Zn(H_2O)_4]SO_4$$

54. (a)

55. (d) : Non-oxidising acids (HCl and dil. H_2SO_4) do not have any effect on copper. However they dissolve the metal in presence of air. As it is a non-spontaneous process so, ΔG cannot be –ve.

56. (b) : In actual practice transition metals react with acid very slowly and act as poor reducing agents. This is due to the protection of metal as a result of formation of thin oxide protective film. Further, their poor tendency as reducing agent is due to high ionisation energy, high heat of vapourisation and low heat of hydration.

57. (b) : Higher the charge on the metal ion, smaller is the ionic size and more is the complex forming

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ability. Thus, the degree of complex formation decreases in the order

$M^{4+} > MO_2^{2+} > M^{3+} > MO_2^{+}$

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

58. (c) : Mn^{2+} = [Ar] $3d^5$, Mn^{3+} = [Ar] $3d^4$
Fe^{2+} = [Ar] $3d^6$, Fe^{3+} = [Ar] $3d^5$

Thus, Mn^{2+} has more stable configuration than Mn^{3+} while Fe^{3+} has more stable configuration than Fe^{2+}.

Hence, reduction potential for Mn^{3+}/Mn^{2+} couple is more positive than Fe^{3+}/Fe^{2+}.

59. (a) : The element which can reduce itself acts as an oxidising agent.

60. (c) : Due to lanthanide contraction, the size of Lu^{3+} is decreased, then, covalent character of hydroxides increases and hence the basic strength decreases. Thus, $La(OH)_3$ is more ionic and thus more basic.

61. (d) : Both Co and Ni have (IV) oxidation state. Ni (IV) has $3d^6$ electronic configuration.

Metals	**Outer electronic configuration**	**Oxi. states**
Co	$3d^7 4s^2$	+2, +3, +4
Ni	$3d^8 4s^2$	+2, +3, +4

62. (b) : The oxidation states of the given compounds are

$VO_2^+ : x + 2(-2) = +1$
$\Rightarrow x = +5$
$Cr_2O_7^{2-} : 2x + 7(-2) = -2$
$\Rightarrow 2x = +12$
$\Rightarrow x = +6$
$MnO_4^- : x + 4(-2) = -1$
$x = -1 + 8 = +7$

The correct order of oxidising power is :

$VO_2^+ < Cr_2O_7^{2-} < MnO_4^-$

63. (b) : Chemistry of actinoids is more complicated due to the possibility of large number of oxidation states.

CHAPTER 23

COORDINATION COMPOUNDS

Which of the following complex has square planar structure?
(a) $[Ni(CN)_4]^{2-}$ (b) $Ni(CO)_4$
(c) $[Zn(NH_3)_4]^{2-}$ (d) $[NiCl_4]^{2-}$ *(1995)*

2. In the compound lithium tetrahydroaluminate, the ligand is
(a) H (b) H^+
(c) H^- (d) F^- *(1997)*

3. Which of the following compound is not coloured?
(a) $Na_2[CuCl_4]$ (b) $Na_2[CdCl_4]$
(c) $K_4[Fe(CN)_6]$ (d) $K_3[Fe(CN)_6]$
(1997)

4. Which one of the following shows maximum paramagnetic character?
(a) $[Fe(CN)_6]^{3-}$ (b) $[Fe(CN)_6]^{4-}$
(c) $[Cr(H_2O)_6]^{3+}$ (d) $[Cu(H_2O)_6]^{2+}$
(1998)

5. $CuSO_4$ reacts with KCN solution and forms
(a) $K_3[Cu(CN)_4]$ (b) CuCN
(c) $Cu(CN)_2$ (d) $[K_4Cu(CN)_6]$
(1999)

6. $CuSO_4$ dissolves in NH_3 due to the formation of
(a) $Cu(OH)_2$ (b) $[Cu(NH_3)_4]SO_4$
(c) $Cu[(NH_3)_4(OH)_2]$ (d) CuO *(2000)*

7. In the formation of $[Ni(CN)_4]^{2-}$, the type of hybridisation involved is
(a) sp^2 (b) sp^3d^2
(c) dsp^2 (d) sp^3d. *(2000)*

8. Sodium thiosulphate is used in photography to
(a) reduce AgBr grains to metallic Ag
(b) dissolve out Ag produced by reduction
(c) remove unaffected AgBr in the photographic film or plate
(d) none of these. *(2000)*

9. dsp^2 hybridisation is found in
(a) $[Ni(CN)_4]^{2-}$ (b) $[CoCl_4]^{2-}$
(c) $[CuCl_4]^{3-}$ (d) $[CuCl_4]^{2-}$ *(2001)*

10. Which of the following molecule or ions is a bidentate ligand?
(a) $C_2O_4^{2-}$ (b) Br_2^+
(c) CH_3NH_2 (d) $CH_3-C\equiv N$
(1995, 2001)

11. The ion which is not tetrahedral in shape is
(a) BF_4^- (b) NH_4^+
(c) $[Cu(NH_3)_4]^{2+}$ (d) $[NiCl_4]^{2-}$ *(2003)*

12. The complex used as an anti-cancer agent is
(a) *mer*-$[Co(NH_3)_3Cl_3]$ (b) *cis*-$[PtCl_2(NH_3)_2]$
(c) *cis*-$K_2[PtCl_2Br_2]$ (d) $Na_2[CoCl_4]$
(2003)

13. The ligand called π-acid is
(a) CO (b) NH_3
(c) $C_2O_4^{2-}$ (d) ethylenediamine.
(2003)

14. Which one of the following forms with an excess of CN^- (cyanide) a complex having coordination number two?
(a) Cu^+ (b) Ag^+
(c) Ni^{2+} (d) Fe^{2+} *(2004)*

15. Which of the following is not considered as an organometallic compound?
(a) *cis*-Platin (b) Ferrocene
(c) Zeise's salt (d) Grignard reagent
(2004)

16. Which of the following does not have optical isomerism?
(a) $[Co(NH_3)_3Cl_3]$ (b) $[Co(en)_3]Cl_3$
(c) $[Co(en)_2Cl_2]Cl$
(d) $[Co(en)(NH_3)_2Cl_2]Cl$ *(2004)*

17. An aqueous solution of $CoCl_2$ on addition of excess of concentrated HCl turns blue due to formation of
(a) $[Co(H_2O)_4Cl_2]$ (b) $[Co(H_2O)_2Cl_4]^{2-}$
(c) $[CoCl_4]^{2-}$ (d) $[Co(H_2O)_2Cl_2]$
(2005)

18. In which of the following pairs both the complexes show optical isomerism?
(a) *cis*-$[Cr(C_2O_4)_2Cl_2]^{3-}$, *cis*-$[Co(NH_3)_4Cl_2]$

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(b) $[Co(en)_3]Cl_3$, *cis*-$[Co(en)_2Cl_2]Cl$
(c) $[PtCl(dien)]Cl$, $[NiCl_2Br_2]^{2-}$
(d) $[Co(NO_2)_3(NH_3)_3]$, *cis*-$[Pt(en)_2Cl_2]$
(2005, 2015)

19. The diamagnetic species is
(a) $[Ni(CN)_4]^{2-}$ (b) $[NiCl_4]^{2-}$
(c) $[CoCl_4]^{2-}$ (d) $[CoF_6]^{3-}$
(2005, 2015)

20. The correct order for the wavelength of absorption in the visible region is
(a) $[Ni(NO_2)_6]^{4-} < [Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+}$
(b) $[Ni(NO_2)_6]^{4-} < [Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+}$
(c) $[Ni(H_2O)_6]^{2+} < [Ni(NH_3)_6]^{2+} < [Ni(NO_2)_6]^{4-}$
(d) $[Ni(NH_3)_6]^{2+} < [Ni(H_2O)_6]^{2+} < [Ni(NO_2)_6]^{4-}$
(2005)

21. The pair in which both species have same magnetic moment (spin only value) is
(a) $[Cr(H_2O)_6]^{2+}$, $[CoCl_4]^{2-}$
(b) $[Cr(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{2+}$
(c) $[Mn(H_2O)_6]^{2+}$, $[Cr(H_2O)_6]^{2+}$
(d) $[CoCl_4]^{2-}$, $[Fe(H_2O)_6]^{2+}$ *(2006)*

22. The number of possible isomers of an octahedral complex $[Co(C_2O_4)_2(NH_3)_2]^-$ is
(a) 1 (b) 2
(c) 3 (d) 4 *(2006)*

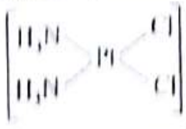
23. Which of the following metal ions will form complexes with the same magnetic moment and geometry irrespective of the nature of ligands?
(a) Ni^{2+} (b) Fe^{2+}
(c) Cu^{2+} (d) Co^{2+} *(2007)*

24. Wavelength of red light is absorbed by the complex
(a) $[Cu(CN)_4]^{3-}$ (b) $[Cu(NH_3)_4]^{2+}$
(c) $CuSO_4$ (d) $Cu(CN)_2$
(2007)

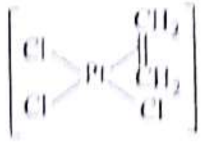
25. In the change $[Cu(H_2O)_6]^{2+} \xrightarrow{HCl} [CuCl(H_2O)_5]^+$, the colour changes from
(a) blue to green (b) blue to pink
(c) pink to green (d) pink to blue.
(2007)

26. Which statement is true for ferrocene?
(a) All Fe-C are of equal length.
(b) C are sp^2 hybridized.
(c) It was the first discovered organometallic compound.
(d) All of these *(2007)*

27. Which of the following is considered as an anticancer species?

(a) 

(b) 

(c) 

(d) 

(2008)

28. A complex $PtCl_4 \cdot 5NH_3$ shows a molar conductance of 402 ohm^{-1} cm^2 mol^{-1} in water and precipitates three moles of AgCl with $AgNO_3$ solution. The formula of the complex is
(a) $[Pt(NH_3)_6]Cl_4$ (b) $[Pt(NH_3)_4Cl_2]Cl_2$
(c) $[Pt(NH_3)_5Cl]Cl_3$ (d) $[Pt(NH_3)_3Cl_3]Cl$
(2010)

29. The wavelength of light absorbed is highest in
(a) $[Co(NH_3)_5Cl]^{2+}$ (b) $[Co(NH_3)_5H_2O]^{3+}$
(c) $[Co(NH_3)_6]^{3+}$ (d) $[Co(en)_3]^{3+}$
(2011)

30. Which of the following is diamagnetic?
(a) $[Cu(NH_3)_4]^{2+}$ (b) $[NiCl_4]^{2-}$
(c) $[PtCl_4]^{2-}$ (d) $[Cu(H_2O)_4]^{2+}$
(2011)

31. Which of the following metal ion forms unstable complex with CN^-?
(a) Ag(I) (b) Zn(II)
(c) Cu(II) (d) Cr(II) *(2013)*

32. Least coordination number is shown by
(a) $Co_2(CO)_8$ (b) $Mn_2(CO)_{10}$
(c) $[Fe(en)_2NH_3]$ (d) $[Cr(OH)_3(NH_3)_3]$
(2014)

33. Amongst the following, the most stable complex is
(a) $[Fe(H_2O)_6]^{3+}$ (b) $[Fe(NH_3)_6]^{3+}$
(c) $[Fe(C_2O_4)_3]^{3-}$ (d) $[FeCl_6]^{3-}$ *(2015)*

34. Select the correct statement.
(a) Geometrical isomer may differ in dipole moment and visible/UV spectra.
(b) Complexes of the type $[Ma_3b_3]$ can also have facial (*fac*) and meridional (*mer*) isomer.
(c) No optical isomer exists for the complex *trans*-$[Co(en)_2Cl_2]^+$.
(d) All of these. *(2016)*

---

35. Calculate th
equilibrium c
given that s
complex is 2
(a) 8.27 × 1
(c) 2.39 × 1

ASSE

36. ***Assertion***
$N(CH_3)_3$.
Reason :
aqueous sol

37. ***Assertion***
ethylenedi
$[Ni(NH_3)_6]$
Reason :
trigonal bi

38. ***Assertion***
optical is
Reason :

39. ***Assertion***
longer, th
Reason :
from fille
the CO l

40. ***Asserti***
configur
Reason
is less

41. ***Asserti***
not in N
Reason
with N

42. ***Assert***
is na
μ-hyd

1. (a)
9. (a)
17. (c)
25. (b)
33. (c)
41. (a)
49. (c)

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35. Calculate the overall complex dissociation equilibrium constant for the $[Cu(NH_3)_4]^{2+}$ ions, given that stability constant (β_4) for this complex is 2.1×10^{13}.
(a) 8.27×10^{-13} (b) 4.76×10^{-14}
(c) 2.39×10^{-7} (d) 1.83×10^{14} *(2017)*

ASSERTION AND REASON

36. ***Assertion :*** NF_3 is a weaker ligand than $N(CH_3)_3$.
Reason : NF_3 ionizes to give F^- ions in aqueous solution. *(2003, 2015)*

7. ***Assertion :*** The $[Ni(en)_3]Cl_2$ (*en* = ethylenediamine) has lower stability than $[Ni(NH_3)_6]Cl_2$.
Reason : In $[Ni(en)_3]Cl_2$ the geometry of Ni is trigonal bipyramidal. *(2004)*

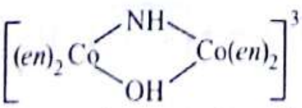
38. ***Assertion :*** $[Co(NO_2)_3(NH_3)_3]$ does not show optical isomerism.
Reason : It has a plane of symmetry. *(2006)*

39. ***Assertion :*** C – O bond in metal carbonyl is longer. than CO molecule
Reason : There is delocalisation of electrons from filled *d* orbitals into the empty orbitals on the CO ligands. *(2007)*

40. ***Assertion :*** In high spin situation, configuration of d^5 ions will be $t_{2g}^3\, e_g^2$.
Reason : In high spin situation, pairing energy is less than crystal field energy. *(2008)*

41. ***Assertion :*** $Cu(OH)_2$ is soluble in NH_4OH but not in NaOH.
Reason : $Cu(OH)_2$ forms a soluble complex with NH_3. *(2009)*

42. ***Assertion :***



is named as *tetrakis* (ethylenediamine) μ-hydroxo-μ-imido dicobalt (III) ion.
Reason : In naming polynuclear complexes *i.e.*, containing two or more metal atoms joined by bridging ligands, the word μ is added with hyphen before the name of such ligands. *(2010)*

43. ***Assertion :*** F^- ion is a weak ligand and forms outer orbital complex.
Reason : F^- ion cannot force the electrons of d_{z^2} and $d_{x^2-y^2}$ orbitals of the inner shell to occupy d_{xy}, d_{yz} and d_{zx} orbitals of the same shell. *(2012)*

44. ***Assertion :*** $[Fe(H_2O)_5NO]SO_4$ is paramagnetic.
Reason : The Fe in $[Fe(H_2O)_5NO]SO_4$ has three unpaired electrons. *(2012)*

45. ***Assertion :*** EDTA forms complex with divalent metals of 3*d*-series in the ratio of 1:1.
Reason : EDTA has 4 —COOH groups. *(2013)*

46. ***Assertion :*** In a mixture of Cd(II) and Cu(II), Cd^{2+} gets precipitated in presence of KCN by H_2S.
Reason : The stability constant of $[Cu(CN)_4]^{3-}$ is greater than $[Cd(CN)_4]^{2-}$. *(2013)*

47. ***Assertion :*** Linkage isomerism arises in coordination compounds containing ambidentate ligand.
Reason : Ambidentate ligand has two different donor atoms. *(2014)*

48. ***Assertion :*** $Co[Hg(SCN)_6]$ and $Hg[Co(SCN)_6]$ are isomers.
Reason : SCN^- is a stronger ligand as compared to NCS^-. *(2016)*

49. ***Assertion :*** $[Fe(CN)_6]^{3-}$ has d^2sp^3 type hybridisation.
Reason : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to two unpaired electrons.

Answer Key

1.	(a)	**2.**	(c)	**3.**	(b)	**4.**	(c)	**5.**	(a)	**6.**	(b)	**7.**	(c)	**8.**	(c)
9.	(a)	**10.**	(a)	**11.**	(c)	**12.**	(b)	**13.**	(a)	**14.**	(b)	**15.**	(a)	**16.**	(a)
17.	(c)	**18.**	(b)	**19.**	(a)	**20.**	(a)	**21.**	(b)	**22.**	(c)	**23.**	(c)	**24.**	(b)
25.	(b)	**26.**	(d)	**27.**	(a)	**28.**	(c)	**29.**	(a)	**30.**	(c)	**31.**	(a)	**32.**	(a)
33.	(c)	**34.**	(d)	**35.**	(b)	**36.**	(c)	**37.**	(d)	**38.**	(a)	**39.**	(a)	**40.**	(c)
41.	(a)	**42.**	(a)	**43.**	(a)	**44.**	(a)	**45.**	(b)	**46.**	(a)	**47.**	(a)	**48.**	(c)
49.	(c)														

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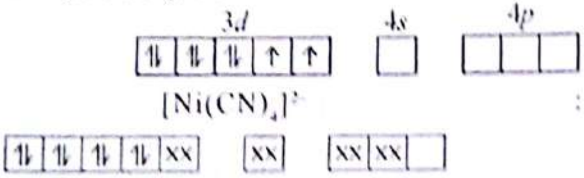
EXPLANATIONS

1. **(a) :** $Ni^{2+}(d^8)$:



∴ dsp^2 hybridisation and square planar structure.

2. **(c)**

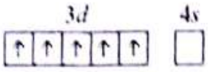
3. **(b) :** $Na_2[CdCl_4]$

Cd : $4d^{10}\,5s^2$

Cd^{2+} : $4d^{10}$

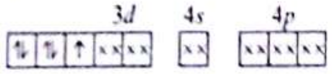
As there is no scope for d–d transition in Cd^{2+} ion, therefore, it does not exhibit any colour.

4. **(c) :** $[Fe(CN)_6]^{3-}$; Fe^{3+}:

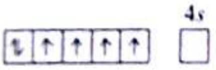


Due to strong ligand *i.e.*, cyanide ion, 3d electrons pair up so, only one unpaired electron remains.

$[Fe(CN)_6]^{3-} \rightarrow$



$[Fe(CN)_6]^{4-}$; Fe^{2+} :

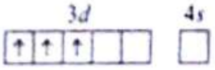


Due to strong ligand CN^-, all electrons pair up.

$[Fe(CN)_6]^{4-} \rightarrow$

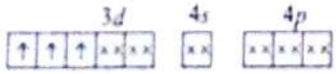
∴ No unpaired electron

$[Cr(H_2O)_6]^{3+}$; Cr^{3+} :



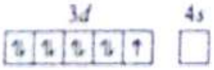
As H_2O is weak ligand, no electron pairing takes place.

$[Cr(H_2O)_6]^{3+} \rightarrow$



∴ Three unpaired electrons.

$[Cu(H_2O)_6]^{2+}$; Cu^{2+} :



Only one unpaired electron.

5. **(a) :** $(CuSO_4 + 2KCN \rightarrow Cu(CN)_2 + K_2SO_4) \times 2$

$2Cu(CN)_2 \rightarrow Cu_2(CN)_2 + (CN)_2$

$Cu_2(CN)_2 + 6KCN \rightarrow 2K_3[Cu(CN)_4]$

$2CuSO_4 + 10KCN \rightarrow 2K_3[Cu(CN)_4] + 2K_2SO_4 + (CN)_2$

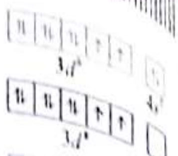
6. **(b) :** $NH_3 + H_2O \rightarrow NH_4OH$

$CuSO_4 + 2NH_4OH \rightarrow Cu(OH)_2 + (NH_4)_2SO_4$

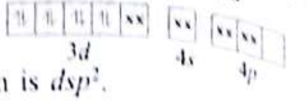
$Cu(OH)_2 + 2NH_4OH + (NH_4)_2SO_4 \rightarrow$
$[Cu(NH_3)_4]\,SO_4 + 4H_2O$

7. **(c) :** Ni :

Ni^{2+} :



$[Ni(CN)_4^{2-}]$:



⇒ Hybridisation is dsp^2.

8. **(c) :** In photography, AgBr is mainly used as the light sensitive material. The unchanged AgBr after developing the film is treated with $Na_2S_2O_3$. Solution of sodium thiosulphate is used as fixer and forms a soluble complex with silver halide.

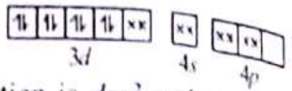
$AgBr + 2Na_2S_2O_3 \rightarrow Na_3[Ag(S_2O_3)_2] + NaBr$

9. **(a) :** Electronic configuration of Ni :

Ni ($Z = 28$) : $4s^2\,3d^8$

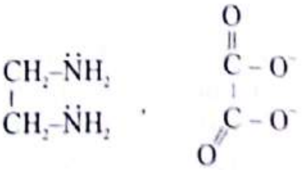
Ni^{2+} : $3d^8$

$[Ni(CN)_4]^{2-}$:

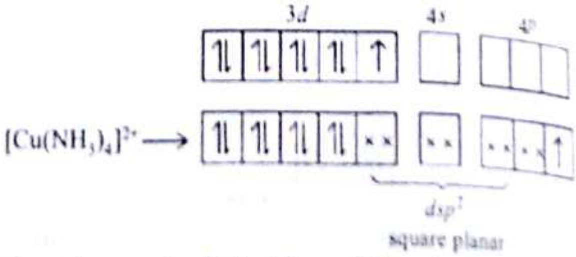


Therefore, hybridisation is dsp^2 and structure is square planar.

10. **(a) :** Bidentate ligands are those ligand which can coordinate to metal atom by two donor atoms. e.g.



11. **(c) :** $[Cu(NH_3)_4]^{2+}$, $Cu^{2+} \rightarrow 3d^9\,4s^0$



One electron is shifted from 3d to 4p orbital.

12. **(b) :** *cis*-$[PtCl_2(NH_3)_2]$ is used as an anti-cancer agent, called as *cis*-platin.

13. **(a) :** Carbon monoxide is π -acid ligand as it characterises both metal to carbon and carbon to metal bonding. The latter is known as π-acidic character.

14. **(b) :** Ag^+ of AgCN is soluble in excess cyanide ion to form $[Ag(CN)_2]^-$ complex.

Coordination Compo

15. (a) : H_3N

compound as it

16. (a) : Opti

octahedral com

where AA is sy

is unsymmetric

Octahedral com

exhibit geomet

17. (c) : CoCl

chloride ion

tetrahedral [C

anhydrous, a

hydrated, for

indicator for

18. (b) : [Co

cis-[Co(*en*)$_2$C

19. (a) :

$[Ni(CN)_4]^{2-}$

$[NiCl_4]^{2-}$

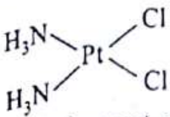
$[CoCl_4]^{2-}$

$[CoF_6]^{3-}$

20. (a)

observati

depends

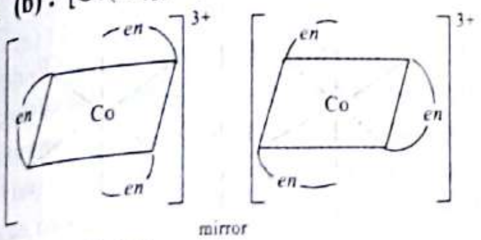
15. **(a) :**  is not an organometallic compound as it does not contain carbon-metal bond.

16. **(a) :** Optical isomerism is very common in octahedral complexes of general formulae, $[Ma_2b_2c_2]^{n\pm}$, $[Mabcdef]$, $[M(AA)_3]^{n\pm}$, $[M(AA)_2a_2]^{n\pm}$, $[M(AA)a_2b_2]^{n\pm}$, $[M(AA)_2ab]^{n\pm}$ and $[M(AB)_3]^{n\pm}$, where AA is symmetrical bidentate ligand and AB is unsymmetrical bidentate ligand.

Octahedral complex of the type Ma_4b_2 and Ma_3b_3 exhibit geometrical isomerism.

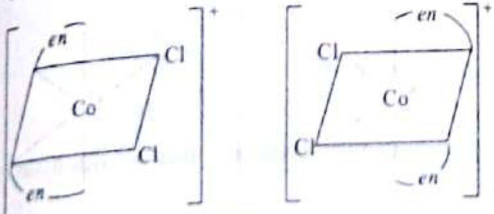
17. **(c) :** $CoCl_2$ is a weak Lewis acid, reacting with chloride ion to produce salt containing the tetrahedral $[CoCl_4]^{2-}$ ion. $CoCl_2$ is blue when anhydrous, and a deep magenta colour when hydrated, for this reason it is widely used as an indicator for water.

18. **(b) :** $[Co(en)_3]Cl_3$



mirror

cis-$[Co(en)_2Cl_2]Cl$

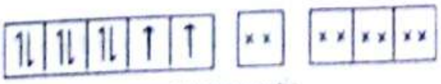


mirror

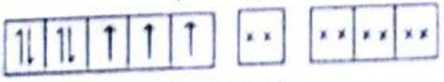
19. **(a) :**

$[Ni(CN)_4]^{2-}$ 

diamagnetic

$[NiCl_4]^{2-}$ 

paramagnetic

$[CoCl_4]^{2-}$ 

paramagnetic

$[CoF_6]^{3-}$ 

paramagnetic

20. **(a) :** The absorption of energy or the observation of colour in a complex compound depends on the charge of the metal ion and the nature of the ligands attached. The same metal ion with different ligands shows different absorption depending upon the type of ligand. The presence of weak field ligands make the central metal ion to absorb low energies *i.e.*, of higher wavelength. The field strength of ligands can be obtained from spectrochemical series. *i.e.*

(Weak field) $I^- < Br^- < S^{2-} < Cl^- < NO_3^- < F^- < OH^- < H_2O < NH_3 < NO_2^- < CN^- < CO$ (strong field)

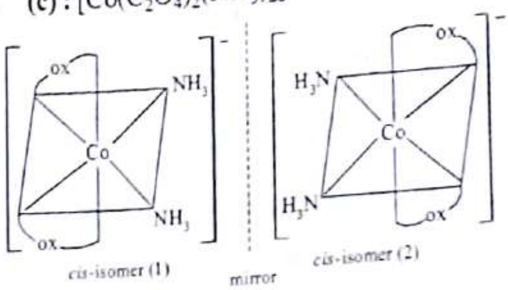
21. **(b) :** Spin only magnetic moment, $\mu_s = \sqrt{n(n+2)}$

where, n = number of unpaired electrons.

Number of unpaired electrons in Cr^{2+} ([Ar] $3d^4$) is 4, in Co^{2+} ([Ar] $3d^7$) is 3, in Fe^{2+} ([Ar] $3d^6$) is 4, in Mn^{2+} ([Ar] $3d^5$) is 5.

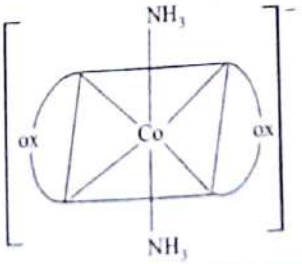
As the number of unpaired electrons in Cr^{2+} and Fe^{2+} are same, hence $[Cr(H_2O)_6]^{2+}$ and $[Fe(H_2O)_6]^{2+}$ will have same magnetic moment.

22. **(c) :** $[Co(C_2O_4)_2(NH_3)_2]^-$



cis-isomer (1) mirror cis-isomer (2)

(d-and l-form)

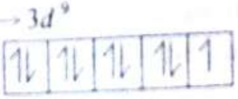


trans-isomer (3)

23. **(c) :** In presence of either strong field or weak field, the number of unpaired electron remains the same in case of Cu^{2+} ion.

$$Cu \longrightarrow 3d^{10}4s^1$$

$$Cu^{2+} \longrightarrow 3d^9$$



24. **(b) :** When NH_4OH is added to the solution containing Cu^{2+} ions, deep blue solution is obtained.

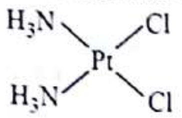
$$Cu^{2+} + 4NH_4OH \rightarrow \underset{\text{deep blue solution}}{[Cu(NH_3)_4]^{2+}} + 4OH^-$$

Hydrated cupric compounds absorb radiations corresponding to red light and the transmitted colour is greenish blue (which is complementary to red colour). Thus, cupric compounds give greenish-blue colour.

25. **(b)**

26. **(d)**

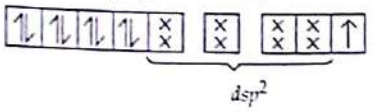
27. **(a) :** *Cis*-Platin is effective in curing cancer



28. **(c) :** The complex $PtCl_4.5NH_3$ is designated as $[Pt(NH_3)_5Cl]Cl_3$ which ionizes to $[Pt(NH_3)_5Cl]^{3-}$ + $3Cl^-$ ions. Thus, three moles of AgCl are produced from $3Cl^-$ ions with $AgNO_3$.

29. **(a) :** As in complex $[Co(NH_3)_5Cl]^{2+}$, Cl^- is present as ligand which is weakest among ligands present in other complexes, so it requires less energy for excitation. Thus, the wavelength of light absorbed will be highest (*i.e.*, $E \propto 1/\lambda$).

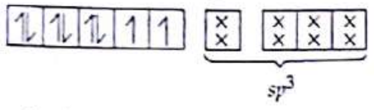
30. **(c) :** $[Cu(NH_3)_4]^{2+}$



No. of unpaired electron = 1

So, $[Cu(NH_3)_4]^{2+}$ is paramagnetic.

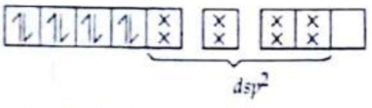
$[NiCl_4]^{2-}$:



No. of unpaired electrons = 2

So, $[NiCl_4]^{2-}$ is paramagnetic.

$[PtCl_4]^{2-}$:

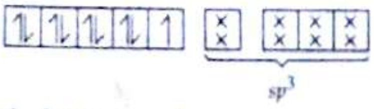


No. of unpaired electrons = 0

So, $[PtCl_4]^{2-}$ is diamagnetic.

Pt is large in size thus it forms strong bond with the ligands. Due to which strong repulsion between the electrons of Pt and ligand takes place which result in strong crystal field splitting. The strong filed splitting breaks the degeneracy of $d_{x^2-y^2}$ and d_{z^2}. Hence stabilises the square planar arrangement.

$[Cu(H_2O)_4]^{2+}$:



No. of unpaired electrons = 1

So, $[Cu(H_2O)_4]^{2+}$ is paramagnetic.

31. **(a) :** Except Ag(I), all ions form stable complexes with CN^-.

32. **(a) :**

Complex	Coordination no.
$Co_2(CO)_8$	4
$Mn_2(CO)_{10}$	5
$[Fe(en)_2NH_3]$	5
$[Cr(OH)_3(NH_3)_3]$	6

33. **(c) :** $[Fe(C_2O_4)_3]^{3-}$ is the most stable complex due to chelate formation as $C_2O_4^{2-}$ is a bidentate chelating ligand.

34. **(d)**

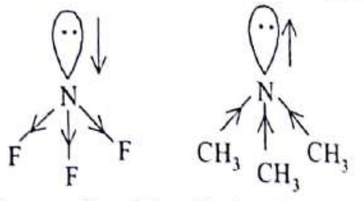
35. **(b) :** Dissociation constant is the reciprocal of the stability constant ($\beta = 1/K$).

Overall complex dissociation equilibrium constant,

$$K = \frac{1}{\beta_4}$$

$$= \frac{1}{2.1\times10^{13}} = 4.76\times10^{-14}$$

36. **(c) :** Due to high electronegativity of F-atoms, the lone pair of N-atom in NF_3 molecule cannot be ligated easily. Whereas in $N(CH_3)_3$, CH_3 group is a electron releasing group, thus lone pair of N-atom in $N(CH_3)$ molecule can be ligated easily.



Except, nitrogen fluoride, all other halides hydrolyse in water.

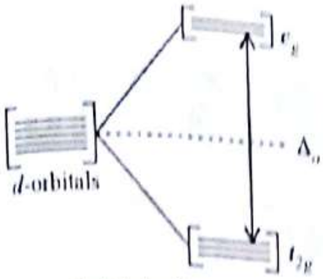
37. **(d) :** $[Ni(en)_3]Cl_2$ is a chelating compound and chelated complexes are more stable than similar complexes with unidentate ligands as dissociation of the complex involves breaking of two bonds rather than one.

In $[Ni(en)_3]Cl_2$, Ni with d^8 configuration shows octahedral geometry.

38. **(a) :** The essential requirement for a substance to be optically active is that the substance should not have a plane of symmetry in its structure.

39. **(a) :** C – O bond in metal carbonyl is long as ligated CO has lower bond order. The lower B.O. is due to the transfer of metal $d\pi$ electrons into the π^* orbitals of ligated CO.

40. (c) :

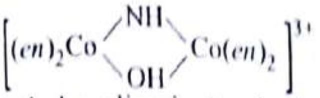


d-orbital splitting in an octahedral crystal field

$\therefore$ In high spin situation, $\Delta_o < P$, in d^5 configuration, 4th and 5th electron are added to e_g rather than t_{2g}. So, configuration of d^5 ion will be $t_{2g}^3\ e_g^2$.

41. (a)

42. (a) :



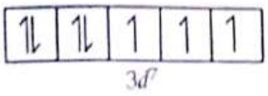
$\left[(en)_2Co\begin{matrix}NH\\OH\end{matrix}Co(en)_2\right]^{3+}$ is named as *tetrakis* (ethylenediamine)-μ-hydroxo-μ-imido dicobalt (III) ion. For more than one bridging group the word μ is repeated before each bridging group.

43. (a)

44. (a) : Fe^+ : [Ar] $3d^6\ 4s^1$

When the weak field ligand H_2O and strong field ligand NO attack, the configuration changes as follows:

Fe^+ : [Ar] $3d^7\ 4s^0$



$\therefore$ Fe^+ has 3 unpaired electrons.

45. (b) : EDTA is a hexadentate ligand. It forms complex with central metal in the ratio 1 : 1 in which it binds through two nitrogen atoms and four oxygen atoms.

46. (a) : $Cd^{2+} + 2CN^- \rightarrow Cd(CN)_2$

$Cd(CN)_2 + 2CN^- \rightarrow [Cd(CN)_4]^{2-}$

$[Cd(CN)_4]^{2-}$ is colourless compound and not too stable. When hydrogen sulphide gas is added, cadmium sulphide is precipitated.

$[Cd(CN)_4]^{2-} + H_2S \rightarrow CdS\downarrow + 2H^+ + 4CN^-$

But in case of Cu^{2+},

$Cu^{2+} + 2CN^- \rightarrow Cu(CN)_2\downarrow$

$2Cu(CN)_2 \xrightarrow[\text{decomposes}]{\text{Quickly}} 2CuCN\downarrow + (CN)_2\uparrow$

$CuCN\downarrow + 3CN^- \rightarrow [Cu(CN)_4]^{3-}$

This complex is so stable (*i.e.*, $[Cu^+]$ is too low) that H_2S cannot precipitate Cu(I) sulphide (Cu_2S).

47. (a)

48. (c) : $Co[Hg(SCN)_6]$ and $Hg[Co(SCN)_6]$ are ionisation isomers. NCS^- is stronger than SCN^-.

49. (c) : $[Fe(CN)_6]^{3-}$ ion shows magnetic moment corresponding to one unpaired electron.

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CHAPTER

24

HALOALKANES AND HALOARENES

1. When alkyl halides are heated, with dry Ag_2O, they give
   (a) diethyl ether (b) ester
   (c) benzene (d) ketone. *(1994)*

2. When chloroform is exposed to air and sunlight, it gives
   (a) mustard gas (b) phosgene
   (c) carbon tetrachloride
   (d) lewisite. *(1994)*

3. Chloroform by reacting with conc. HNO_3 produces
   (a) tear gas (b) water gas
   (c) producer gas (d) laughing gas. *(1995)*

4. What happens when chloroform is left open in air in the presence of sunlight?
   (a) Polymerisation takes place.
   (b) Explosion takes place.
   (c) No reaction takes place.
   (d) Phosgene, a poisonous gas is formed. *(1996,2015)*

5. An acyl halide is formed when PCl_5 reacts with
   (a) amide (b) alcohol
   (c) acid (d) ester. *(1998)*

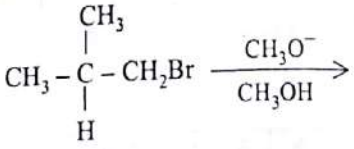
6. Which of the following is involved in Sandmeyer's reaction?
   (a) Ferrous salt (b) Diazonium salt
   (c) Ammonium salt
   (d) Cuprammonium salt *(2002)*

7. The reaction:
   $C_2H_5OH + SOCl_2 \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2 + HCl$
   is known as
   (a) Kharasch effect
   (b) Williamson's synthesis
   (c) Darzen's halogenation
   (d) Hunsdiecker reaction. *(2002)*

8. Among the following the most reactive towards alcoholic KOH is
   (a) $CH_2{=}CHBr$ (b) $CH_3COCH_2CH_2Br$
   (c) CH_3CH_2Br (d) $CH_3CH_2CH_2Br$ *(2004)*

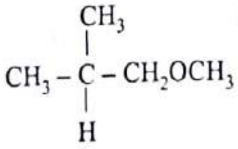
9. Among the following, the one which reacts most readily with ethanol is
   (a) *p*-nitrobenzyl bromide
   (b) *p*-chlorobenzyl bromide
   (c) *p*-methoxybenzyl bromide
   (d) *p*-methylbenzyl bromide. *(2004)*

10. The major product formed in the following reaction is



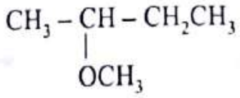
$$\mathrm{CH_3-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}-CH_2Br \xrightarrow[CH_3OH]{CH_3O^-}}$$

(a)



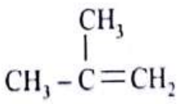
$$\mathrm{CH_3-\underset{\displaystyle H}{\overset{\displaystyle CH_3}{C}}-CH_2OCH_3}$$

(b)



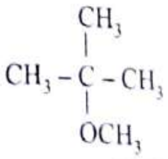
$$\mathrm{CH_3-\underset{\displaystyle OCH_3}{CH}-CH_2CH_3}$$

(c)



$$\mathrm{CH_3-\overset{\displaystyle CH_3}{C}{=}CH_2}$$

(d)



$$\mathrm{CH_3-\underset{\displaystyle OCH_3}{\overset{\displaystyle CH_3}{C}}-CH_3}$$

(2005)

11. The major product obtained on treatment of $CH_3CH_2CH(F)CH_3$ with CH_3O^-/CH_3OH is
    (a) $CH_3CH_2CH(OCH_3)CH_3$
    (b) $CH_3CH = CHCH_3$
    (c) $CH_3CH_2CH = CH_2$
    (d) $CH_3CH_2CH_2CH_2OCH_3$ *(2005)*

12. 3-Phenylpropene on reaction with HBr gives (as a major product)
    (a) $C_6H_5CH_2CH(Br)CH_3$
    (b) $C_6H_5CH(Br)CH_2CH_3$
    (c) $C_6H_5CH_2CH_2CH_2Br$
    (d) $C_6H_5CH(Br)CH = CH_2$ *(2005)*

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'OCH_2CH_2Br
'H_2CH_2Br
(2004)
hich reacts

(2004)
following

'H_3
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ves

5)

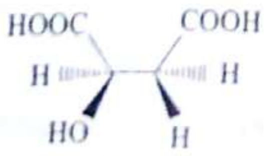
13. Which of the following compounds has the highest boiling point?
(a) $CH_3CH_2CH_2Cl$
(b) $CH_3CH_2CH_2CH_2Cl$
(c) $CH_3CH(CH_3)CH_2Cl$
(d) $(CH_3)_3CCl$
(2006)

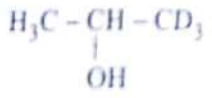
14. The correct increasing order of the reactivity of halides for S_N1 reaction is
(a) $CH_3-CH_2-X < (CH_3)_2CH-X < CH_2=CH-CH_2-X < PhCH_2-X$
(b) $(CH_3)_2CH-X < CH_3-CH_2-X < CH_2=CH-CH_2-X < PhCH_2-X$
(c) $PhCH_2-X < (CH_3)_2CH-X < CH_3-CH_2-X < CH_2=CH-CH_2-X$
(d) $CH_2=CH-CH_2-X < PhCH_2-X < (CH_3)_2CH-X < CH_3-CH_2-X$
(2006)

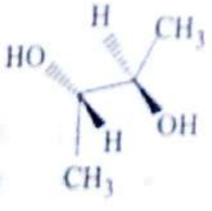
15. Which of these compounds is synthesised by chloral?
(a) DDT
(b) BHC
(c) Chloroform
(d) Michler's ketone.
(2008)

16. Which of the following compounds is not chiral?
(a) 1-Chloropentane
(b) 2-Chloropentane
(c) 1-Chloro-2-methylpentane
(d) 3-Chloro-2-methylpentane *(2008,2015)*

17. Which of the following molecules will not show optical activity?

(a) 

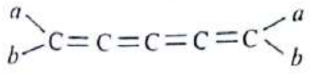
(b) 
$H_3C-\underset{\displaystyle OH}{\underset{|}{CH}}-CD_3$

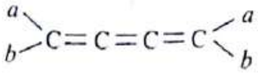
(c) 

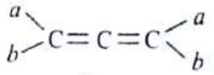
(d) 

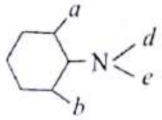
(2008)

18. Which is optically inactive?

(a) 

(b) 

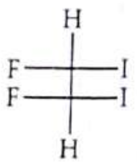
(c) 

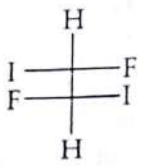
(d) 

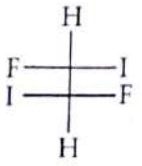
(2010)

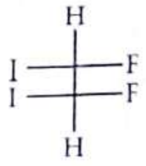
19. Which of the following is a chiral compound?
(a) Hexane
(b) *n*-Butane
(c) Methane
(d) 2,3,4-Trimethylhexane *(2012)*

20. Which of the following compounds are optically active?

(1) 

(2) 

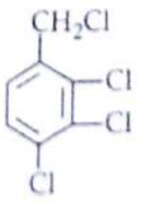
(3) 

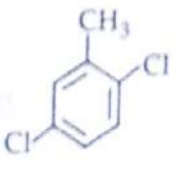
(4) 

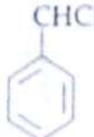
(a) 1 and 2
(b) 2 and 3
(c) 3 and 4
(d) 1 and 4 *(2012)*

21. An aromatic compound $C_7H_6Cl_2$ (*A*), gives AgCl on boiling with alcoholic $AgNO_3$ solution and yields C_7H_7OCl on treatment with sodium hydroxide. (*A*) on oxidation gives monochlorobenzoic acid. The compound (*A*) is

(a) 

(b) 

(c) 

(d) 

(2012)

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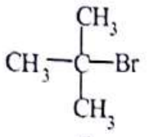
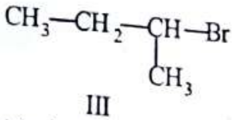
22. Arrange the given compounds in decreasing order of boiling points.

$CH_3CH_2CH_2CH_2Br$

I



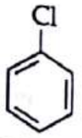
II



III

(a) I > III > II
(b) II > I > III
(c) I > II > III
(d) III > I > II *(2016)*

23. Which one of the following does not give white precipitate with acidified silver nitrate solution?

(a) 

(b) $CH_2 = CH—Cl$

(c) $CH_2 = CH—CH_2—Cl$

(d) Both (a) and (b) *(2016)*

24. (*R*)-2-Iodobutane is treated with NaI in acetone and allowed to stand for a long time. The product eventually formed is

(a) (*R*)-2-iodobutane
(b) (*S*)-2-iodobutane
(c) (±)-2-iodobutane
(d) (±)-1, 2-diiodobutane. *(2017)*

ASSERTION AND REASON

25. ***Assertion*** : Benzyl bromide when kept in acetone water it produces benzyl alcohol.
Reason : The reaction follows S_N2 mechanism. *(2003)*

26. ***Assertion*** : Rate of hydrolysis of methyl chloride to methanol is higher in DMF than in water.
Reason : Hydrolysis of methyl chloride follows second order kinetics. *(2005)*

27. ***Assertion*** : The presence of nitro group facilitates nucleophilic substitution reactions in aryl halides.
Reason : The intermediate carbanion is stabilised due to the presence of nitro group. *(2006)*

28. ***Assertion*** : Alkyl iodide can be prepared by treating alkyl chloride/bromide with NaI in acetone.
Reason : NaCl/NaBr are soluble in acetone while NaI is not. *(2007)*

29. ***Assertion*** : Chloral reacts with phenyl chloride to form DDT.
Reason : It is an electrophilic substitution reaction. *(2007)*

30. ***Assertion*** : Rate of reaction of alkyl halide in Williamson's synthesis reaction is 1°*RX* > 2°*RX* > 3°*RX*.
Reason : It is a type of bimolecular substitution reaction (S_N2). *(2011)*

31. ***Assertion*** : 1, 2-dichloroethane is optically active.
Reason : Meso compound is optically active. *(2012)*

32. ***Assertion*** : Chloroform is stored in dark coloured bottles.
Reason : Chronic chloroform exposure may cause damage to liver and kidneys. *(2014)*

33. ***Assertion*** : Chlorobenzene is more reactive than benzene towards the electrophilic substitution reaction.
Reason : Resonance destabilises the carbocation. *(2016)*

Answer Key

1.	(a)	**2.**	(b)	**3.**	(a)	**4.**	(d)	**5.**	(c)	**6.**	(b)	**7.**	(c)	**8.**	(d)
9.	(c)	**10.**	(d)	**11.**	(b)	**12.**	(a)	**13.**	(b)	**14.**	(a)	**15.**	(a)	**16.**	(a)
17.	(c)	**18.**	(b)	**19.**	(d)	**20.**	(b)	**21.**	(a)	**22.**	(a)	**23.**	(d)	**24.**	(c)
25.	(a)	**26.**	(a)	**27.**	(a)	**28.**	(c)	**29.**	(c)	**30.**	(a)	**31.**	(d)	**32.**	(b)
33.	(d)														

---

1. **(a)** : *R*–*X*

2. **(b)** : Whe
air, it slowly
hydrogen chlor

Cl
Cl – C – H
Cl

3. **(a)** : CHC

4. **(d)** : Ch
and air, under
forms poison

H
Cl – C –
Cl

5. **(c)** : Ac
with carbox
CH_3COOH +

6. **(b)** :
decomposit
of copper
correspond
replaced by
as Sandme

Dia

7. **(c)** :
prepared
refluxed i
R – OH +
Byproduct
can be ca

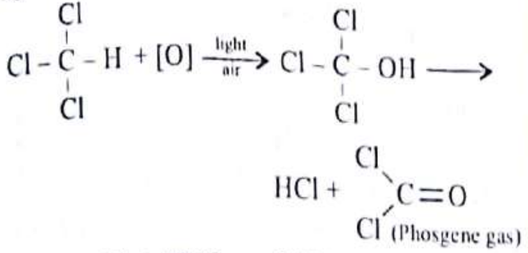
8. **(d)** :
increases

9. **(c)**

EXPLANATIONS

1. **(a) :** $R-X \xrightarrow[\Delta]{\text{Dry } Ag_2O} \underset{\text{Diethyl ether}}{R-O-R}$

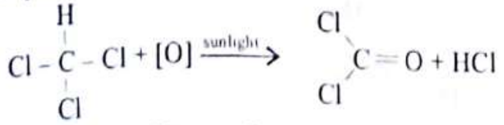
2. **(b) :** When $CHCl_3$ is exposed to sunlight and air, it slowly decomposes into phosgene and hydrogen chloride.



$$Cl-\underset{Cl}{\overset{Cl}{C}}-H+[O]\xrightarrow[\text{air}]{\text{light}}Cl-\underset{Cl}{\overset{Cl}{C}}-OH\longrightarrow HCl+\underbrace{Cl_2C=O}_{\text{(Phosgene gas)}}$$

3. **(a) :** $CHCl_3 + HNO_3 \rightarrow \underset{\text{Chloropicrin (Tear gas)}}{CCl_3NO_2}$

4. **(d) :** Chloroform in the presence of sunlight and air, undergoes reaction with oxygen (in air) and forms poisonous phosgene gas.

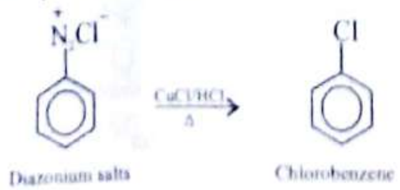


$$Cl-\underset{Cl}{\overset{H}{C}}-Cl+[O]\xrightarrow{\text{sunlight}}Cl_2C=O+HCl$$

5. **(c) :** Acid halides are formed when PCl_5 reacts with carboxylic acids.

$CH_3COOH + PCl_5 \rightarrow CH_3COCl + POCl_3 + HCl$

6. **(b) :** Aryl halides can be prepared by the decomposition of aryl diazonium salts in presence of copper halides solution dissolved in the corresponding halogen acid, the diazo group is replaced by a halogen atom. This reaction is known as Sandmeyer's reaction.



7. **(c) :** Darzen's halogenation : Alkyl halides are prepared when thionyl chloride and alcohols are refluxed in presence of pyridine.

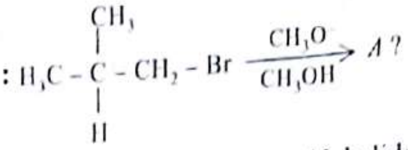
$R-OH + SOCl_2 \xrightarrow[\text{reflux}]{Py} R-Cl + SO_2 + HCl$

Byproducts of this reaction are gases (SO_2, HCl) so can be easily removed from the reaction mixture.

8. **(d) :** In alkyl halides, polarity of C–Br bond increases with increase in chain length.

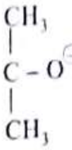
9. **(c)**

10. **(d) :**

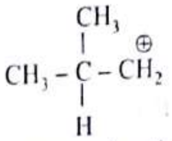


$$H_3C-\underset{H}{\overset{CH_3}{C}}-CH_2-Br\xrightarrow[CH_3OH]{CH_3O^-}A\,?$$

Alkyl halide is 1°. As we know, 1° halide gives product by S_N2/E-2 mechanism and 1° halide always gives substitution reaction except when strongly hindered base is used.

e.g., With  $CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O^{\ominus}$ it gives mainly elimination.

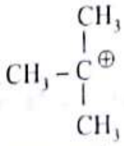
The reaction involves carbocation intermediate.

i.e., 

$$CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2$$

(primary carbocation)

but as it is a primary carbocation it will rearrange to give a tertiary carbocation, which completes the reaction



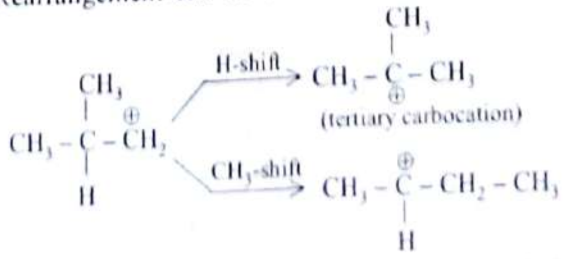
$$CH_3-\underset{CH_3}{\overset{CH_3}{C^{\oplus}}}$$

(tertiary carbocation)

Stability of carbocation : 3° > 2° > 1° > $\overset{\oplus}{C}H_3$

It is because the stability of a charged system is increased by dispersal of the charge. The more stable the carbocation, the faster it is formed.

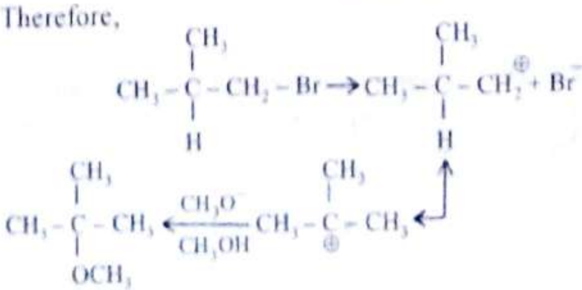
Rearrangement can be done in two ways :



$$CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2\xrightarrow{\text{H-shift}}CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_3 \text{ (tertiary carbocation)}$$

$$CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2\xrightarrow{CH_3\text{-shift}}CH_3-\underset{H}{\overset{\oplus}{C}}-CH_2-CH_3 \text{ (secondary carbocation)}$$

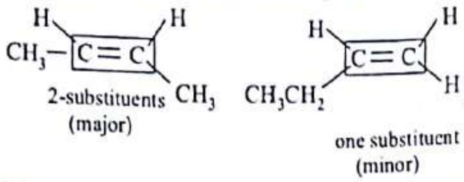
Therefore,



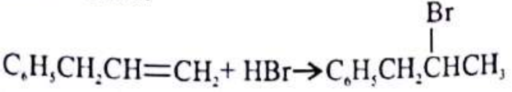
$$CH_3-\underset{H}{\overset{CH_3}{C}}-CH_2-Br\rightarrow CH_3-\underset{H}{\overset{CH_3}{C}}-\overset{\oplus}{C}H_2+Br^-$$

$$CH_3-\underset{\oplus}{\overset{CH_3}{C}}-CH_3\xrightarrow[CH_3OH]{CH_3O^-}CH_3-\underset{OCH_3}{\overset{CH_3}{C}}-CH_3$$

11. (b) : According to Saytzeff's rule, the major product will be that one which contains more number of substituents around the double bond.



12. (a) : According to Markownikoff's rule, the negative part of the attacking reagent adds to less hydrogenated (more substituted) carbon atom of the double bond.

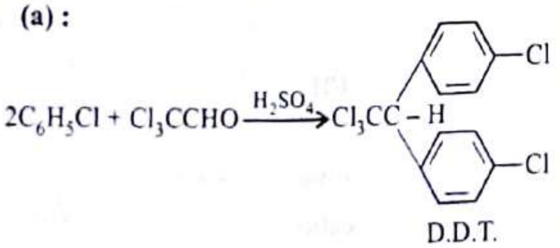


$$C_6H_5CH_2CH{=}CH_2 + HBr \rightarrow C_6H_5CH_2\overset{\overset{\displaystyle Br}{|}}{C}HCH_3$$

13. (b) : For the same halogen, boiling point of alkyl halide decreases as the size of the alkyl group decreases.
For isomeric alkyl halides, boiling point decreases as branching increases. So the decreasing order of boiling point is
$CH_3CH_2CH_2CH_2Cl > CH_3CH_2CH_2Cl$
$> CH_3CH(CH_3)CH_2Cl > (CH_3)_3CCl$.

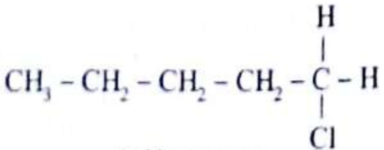
14. (a) : Reactivity of halides towards S_N1 mechanism is benzyl > allyl > 3° > 2° > 1°.

15. (a) :



D.D.T.

16. (a) :

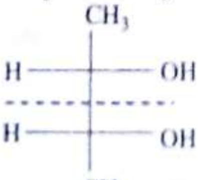


$$CH_3-CH_2-CH_2-CH_2-\underset{\underset{\displaystyle Cl}{|}}{\overset{\overset{\displaystyle H}{|}}{C}}-H$$

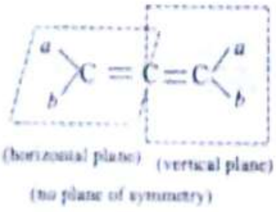
1-chloropentane

⇒ absence of asymmetric carbon atom.

17. (c) : As it has plane of symmetry



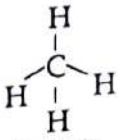
18. (b) : Allenes with even number of cumulative double bonds are optically active if both sides are disymmetric.



19. (d) : Chiral compound contains one or more 'chiral' carbon atom(s). Chiral carbon atoms are usually bonded to four different atoms or group of atoms.

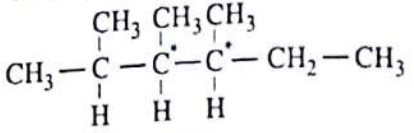
$CH_3-CH_2-CH_2-CH_2-CH_2-CH_3$ (Hexane)
(Achiral)

$CH_3-CH_2-CH_2-CH_3$ (n-Butane)
(Achiral)



(Methane)

(Achiral)

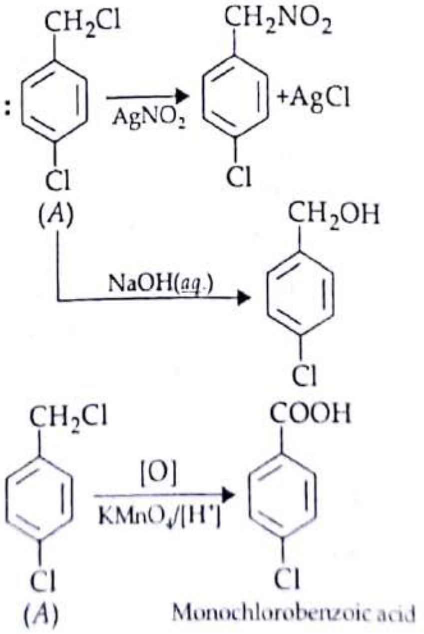


$$CH_3-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C^{\bullet}}}-\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C^{\bullet}}}-CH_2-CH_3$$

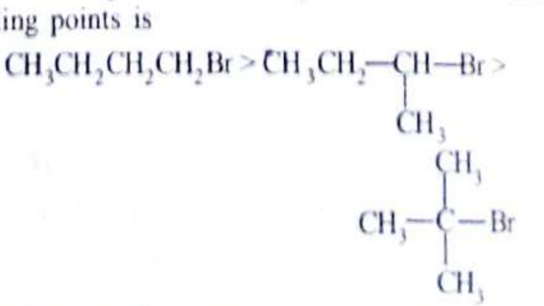
(Chiral)
(2, 3, 4-Trimethylhexane)

20. (b) : (1) and (4) compounds are *meso*-compounds, they possess a plane of symmetry and is consequently optically inactive and superimposes on its mirror image (*i.e.*, they are identical).

21. (a) :



22. (a) : Magnitude of van der Waals' forces goes on decreasing with branching. Hence, the order of boiling points is



$$CH_3CH_2CH_2CH_2Br > CH_3CH_2-\underset{\underset{\displaystyle CH_3}{|}}{CH}-Br > CH_3-\underset{\underset{\displaystyle CH_3}{|}}{\overset{\overset{\displaystyle CH_3}{|}}{C}}-Br$$

23. (d) : In (c), chlorine is attached to sp^3 hybridized C-atom and C—Cl bond is more polar thus, it easily gives AgCl precipitate. In case of

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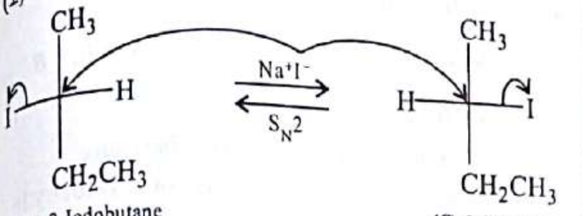
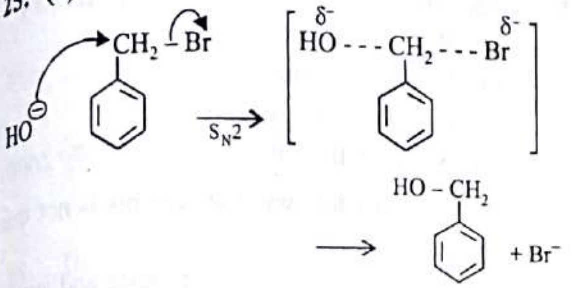
(a) and (b), chlorine is attached to sp^2 hybridized C-atom and there is double bond character between C—Cl bond due to resonance *i.e.*, C—Cl bond is stronger bond and hence chlorine cannot be easily replaced.

24. (c) : I^- is a good nucleophile as well as a good leaving group. Therefore, if (*R*)-2-iodobutane is treated with NaI, repeated S_N2 reactions occur. As a result, eventually a racemic mixture of (±)-2-iodobutane is obtained.



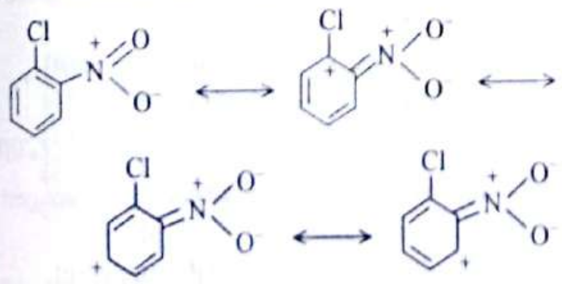
(*R*)-2-Iodobutane (*S*)-2-Iodobutane

25. (a) :

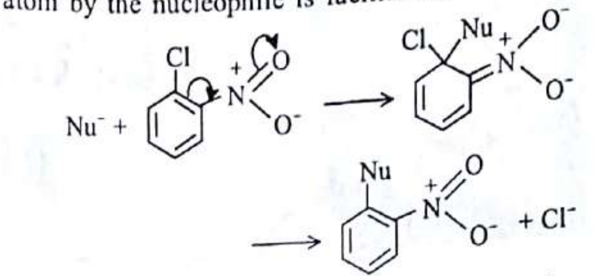


26. (a) : Hydrolysis of methyl chloride to methanol follows S_N2 reaction. The rates of many S_N2 reactions are affected by the solvent. Protic solvents are those that contain – OH or – NH_2 group, are generally the worst solvents for S_N2. Polar protic solvents, (like water, alcohols and carboxylic acids), which have strong dipoles but don't have – OH or – NH_2 groups are the best. In contrast to protic solvents, which decrease the rates of S_N2 reactants by lowering the ground state energy of nucleophile, polar aprotic solvents (DMF) increase the rates of S_N2 reactions by raising the ground state energy of nucleophile.

27. (a) : The C-atom of C – Cl in chloronitrobenzene carries a small +ve charge.



Because of the positive charge, attack at this carbon atom by the nucleophile is facilitated.

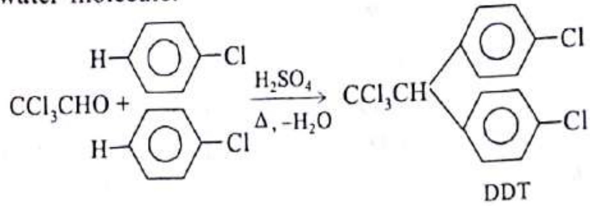


28. (c) : This is Finkelstein reaction which involves the conversion of an alkyl chloride/bromide to an alkyl iodide by the addition of sodium iodide in acetone. Because sodium iodide is soluble in acetone and NaCl and NaBr are not, the equilibrium is shifted by the precipitation of insoluble salt.

$$R-X \underset{MX}{\overset{MX'}{\rightleftharpoons}} R-X'$$

The equilibrium position of the reaction depends on the nucleophilicity of the anion, whether a good leaving group is present and whether one anion is better stabilised than the other in a given solvent.

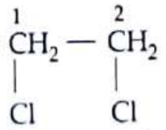
29. (c) : When chlorobenzene is heated with chloral in the presence of conc. H_2SO_4, a powerful insecticide, DDT is formed with the elimination of water molecule.



DDT

30. (a) : Williamson's synthesis occurs by S_N2 mechanism and primary alkyl halides are most reactive in S_N2 reactions.

31. (d) :



$$\overset{1}{\underset{\displaystyle Cl}{\underset{|}{CH_2}}} - \overset{2}{\underset{\displaystyle Cl}{\underset{|}{CH_2}}}$$

Since it has no chiral carbon, it is optically inactive. Meso compounds are optically inactive.

32. (b) : Chloroform is slowly oxidised by air in the presence of light to an extremely poisonous gas 'phosgene'. Therefore, it is stored in dark bottles, completely filled so that air is kept out.

33. (d) : Chlorobenzene is less reactive than benzene towards the electrophilic substitution reactions due to –*I*-effect.

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CHAPTER 25

ALCOHOLS, PHENOLS AND ETHERS

1. Ethyl alcohol exhibits acidic character on reacting with
(a) hydrogen iodide (b) acetic acid
(c) sodium metal (d) all of these
(1994)

2. Which one of the following can differentiate between C_2H_5OH and CH_3OH?
(a) H_2O (b) HCl
(c) $I_2 + KOH$ (d) NH_3 *(1994)*

3. What is the correct bond angle in dimethyl ether?
(a) 120° (b) 109°
(c) 180° (d) 110° *(1995)*

4. In the reaction sequence:

$$CaC_2 \xrightarrow{H_2O} A \xrightarrow[HgSO_4]{dil.H_2SO_4} B \xrightarrow{H_2/Ni} C,$$

the term C is
(a) CH_3CHO (b) $HCHO$
(c) C_2H_5OH (d) CH_3OH *(1996)*

5. Absolute ether is diethyl ether, which
(a) is obtained from Williamson's synthesis
(b) is mixed with absolute alcohol
(c) is totally free from moisture and peroxides
(d) contains traces of peroxide. *(1996)*

6. Which of the following compound is glycerine?
(a) One primary – OH group is present
(b) Two primary – OH groups are present
(c) One secondary – OH group is present
(d) both (b) and (c)
(1997)

7. Ethanol and dimethyl ether form a pair of functional isomers. The boiling point of ethanol is higher than that of dimethyl ether, due to the presence of
(a) $-CH_3$ group in ethanol
(b) H-bonding in dimethyl ether
(c) H-bonding in ethanol
(d) $-CH_3$ group in dimethyl ether. *(1998)*

8. In the reaction:

$$\text{Phenol} \xrightarrow[CHCl_3]{NaOH} A \xrightarrow{H^+} B,$$

B is identified as
(a) benzaldehyde (b) benzene
(c) benzoic acid (d) salicyaldehyde
(1999)

9. Salicylic acid is prepared from phenol by
(a) Reimer - Tiemann reaction
(b) Kolbe's synthesis
(c) Gattermann's reaction
(d) None of the above. *(1997, 2000)*

10. Which of the following statements is not true about alcohols?
(a) Lower alcohols have fiery taste and strong smell.
(b) As molecular mass increases the boiling point increases.
(c) Lower alcohols are water insoluble and their solubility increases with molecular weight.
(d) Lower alcohols are water soluble and their solubility decreases with molecular weight. *(1997, 2001)*

11. Lucas test is used for the determination of
(a) alcohols (b) alkyl halides
(c) phenols (d) aldehydes.
(2002)

12. Propan-1-ol can be prepared from propene by
(a) H_2O/H_2SO_4
(b) $Hg(OAc)_2/H_2O$ followed by $NaBH_4$
(c) B_2H_6 followed by H_2O_2
(d) CH_3CO_2H/H_2SO_4 *(2003)*

13. Intermolecular hydrogen bonding is strongest in
(a) methylamine (b) phenol
(c) formaldehyde (d) methanol.
(2003)

14. The most suitable reagent for the conversion of

$RCH_2OH \rightarrow RCHO$ is

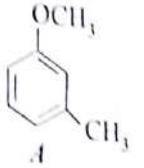
(a) $KMnO_4$ (b) $K_2Cr_2O_7$

(c) CrO_3

(d) PCC (pyridine chlorochromate).

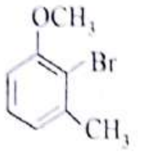
(2004)

15. The major product obtained on the monobromination (with $Br_2/FeBr_3$) of the following compound *A* is

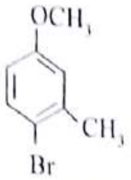


A

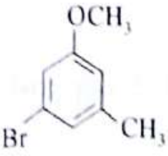
(a)



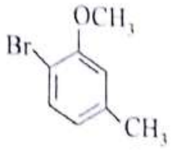
(b)



(c)



(d)



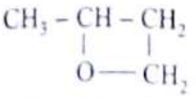
(2006)

16. The major product formed in the following reaction is $CH_3CH(Cl)CH_2-CH_2OH \xrightarrow{aq.KOH}$

(a) $CH_3CH=CH-CH_2OH$

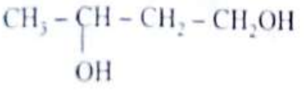
(b) $CH_2=CH-CH_2-CH_2OH$

(c)



$CH_3-CH-CH_2$ with $O-CH_2$ bridging (ring)

(d)



$CH_3-\underset{\underset{OH}{|}}{CH}-CH_2-CH_2OH$ *(2006)*

17. Isopropyl benzene on air oxidation in the presence of dilute acid gives

(a) C_6H_5COOH (b) $C_6H_5COCH_3$

(c) C_6H_5CHO (d) C_6H_5OH

(2006, 2015)

18. $CH_3OC_2H_5$ and $(CH_3)_3C-OCH_3$ are treated with hydroiodic acid. The fragments after reactions obtained are

(a) $CH_3I + HOC_2H_5$; $(CH_3)_3C-I + HOCH_3$

(b) $CH_3OH + C_2H_5I$; $(CH_3)_3CI + HOCH_3$

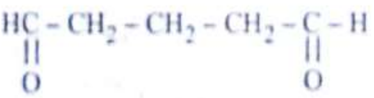
(c) $CH_3OH + C_2H_5$, $(CH_3)_3C-OH + CH_3I$

(d) $CH_3I + HOC_2H_5$; $CH_3I + (CH_3)_3C-OH$

(2007, 2017)

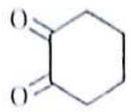
19. Oxidation of 1,2-cyclopentanediol with HIO_4 gives

(a)

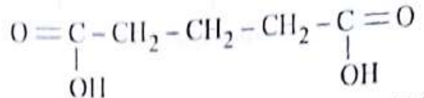


$H\underset{\underset{O}{\|}}{C}-CH_2-CH_2-CH_2-\underset{\underset{O}{\|}}{C}-H$

(b)



(c)



$O=\underset{\underset{OH}{|}}{C}-CH_2-CH_2-CH_2-\underset{\underset{OH}{|}}{C}=O$

(d) none of these. *(2008)*

20. When phenol reacts with phthalic anhydride in presence of H_2SO_4 and heated and hot reaction mixture is poured in NaOH solution, then product formed is

(a) alizarin (b) methyl orange

(c) fluorescein (d) phenolphthalein.

(2008)

21. Cumene process is the most important commercial method for the manufacture of phenol. Cumene is

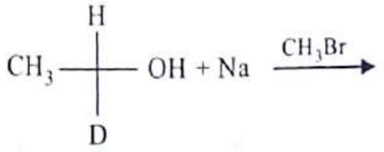
(a) *iso*-propyl benzene (b) ethyl benzene

(c) vinyl benzene (d) propyl benzene.

(2008)

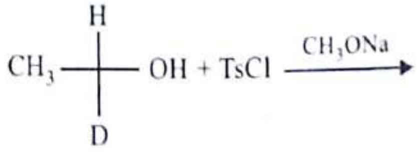
22. In which of the following preparations of ether, the configuration about chiral centre is not retained?

(a)



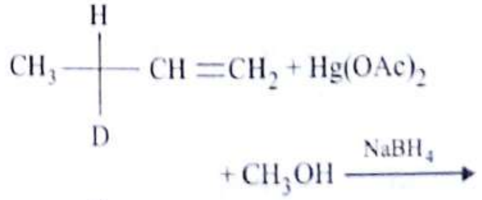
$CH_3-\overset{H}{\underset{D}{C}}-OH + Na \xrightarrow{CH_3Br}$

(b)



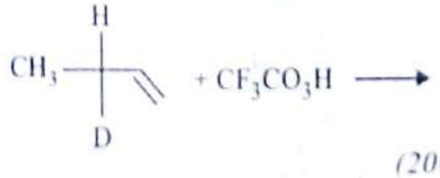
$CH_3-\overset{H}{\underset{D}{C}}-OH + TsCl \xrightarrow{CH_3ONa}$

(c)



$CH_3-\overset{H}{\underset{D}{C}}-CH=CH_2 + Hg(OAc)_2 + CH_3OH \xrightarrow{NaBH_4}$

(d)



$+ CF_3CO_3H \longrightarrow$

(2008)

23. In Oppenauer's oxidation,

(a) secondary alcohol is oxidised to carboxylic acid in acetone solvent using aluminium tertiary butoxide

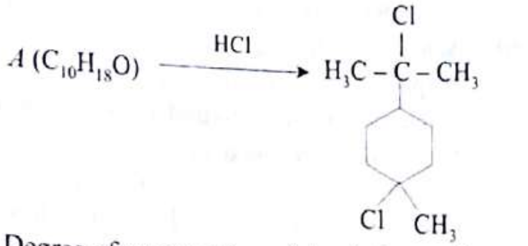
(b) secondary alcohol is oxidised to carboxylic acid without affecting the C=C or C≡C bond by aluminium tertiary butoxide in acetone solvent

(c) secondary alcohol is oxidised to ketone without affecting C=C or C≡C bond by aluminium tertiary butoxide

(d) secondary alcohol is oxidised to ketone by chromic acid - pyridine complex.

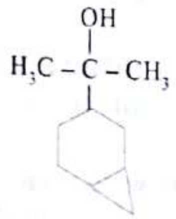
(2009)

24.

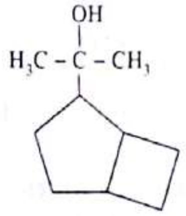


Degree of unsaturation of *A* = 2, it contains no double or triple bonds. *A* is

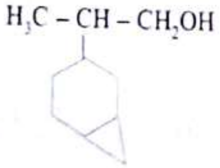
(a)



(b)



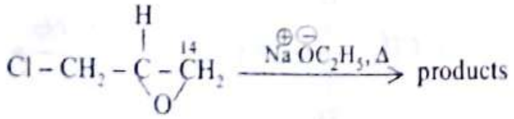
(c)



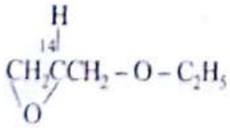
(d) none of these.

(2010)

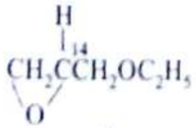
25. The major product of the following reaction is



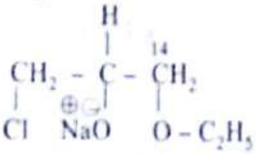
(a)



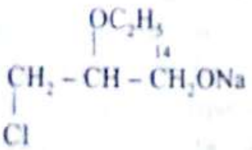
(b)



(c)



(d)



(2010)

26. Find the product for
$CH_3CH_2\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}CH_2\text{-}C_6H_5 + \underset{\text{(excess)}}{HI}$

(a) $HO\text{-}CH_2CH_2\text{-}OH, C_6H_5CH_2\text{-}I, CH_3CH_2\text{-}I$

(b) $C_6H_5CH_2\text{-}OH, CH_3CH_2\text{-}I, I\text{-}CH_2CH_2\text{-}OH$

(c) $I\text{-}CH_2CH_2\text{-}I, C_6H_5CH_2\text{-}I, CH_3CH_2\text{-}OH$

(d) $HO\text{-}CH_2CH_2\text{-}OH, C_6H_5CH_2\text{-}I, CH_3CH_2\text{-}OH$

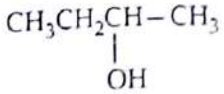
(2011)

27. But-1-ene $\xrightarrow[H_3O^+]{(CH_3COO)_2Hg}$?

The product in the above reaction is

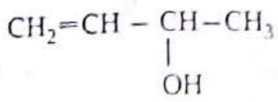
(a) $CH_3CH_2CH_2CH_2OH$

(b)



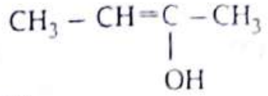
$CH_3CH_2\underset{\large OH}{\underset{|}{C}}H-CH_3$

(c)



$CH_2=CH-\underset{\large OH}{\underset{|}{C}}H-CH_3$

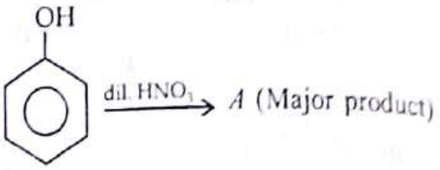
(d)



$CH_3-CH=\underset{\large OH}{\underset{|}{C}}-CH_3$

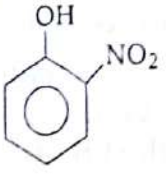
(2012)

28.



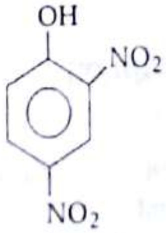
A is

(a)

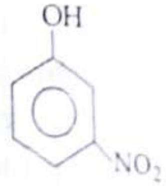


(b)

(c)

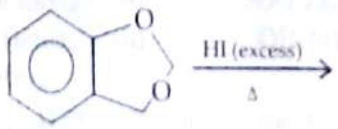


(d)

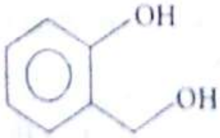


(2013)

29.

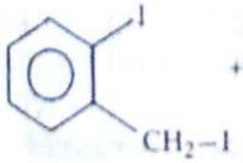


(a)



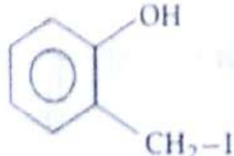
$+ CH_2I_2$

(b)



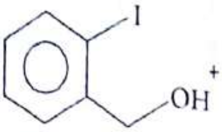
+ HCHO

(c)

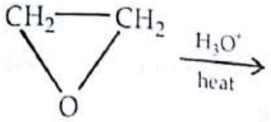


$+ I - CH_2 - OH$

Scanned by CamScanner

(d)  $+ I_2 + CH_3OH$ *(2013)*

30. Which of the following reaction will not produce ethylene glycol?

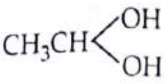
(a) 

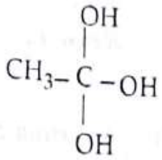
(b) $ClCH_2CH_2Cl \xrightarrow[\text{heat}]{OH^-}$

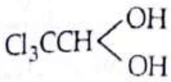
(c) $HO\text{-}CH_2\text{-}CH_2\text{-}OCH_3 \xrightarrow[\text{heat}]{OH^-}$

(d) $CH_2{=}CH_2 \xrightarrow[KMnO_4]{\text{alkaline}}$ *(2013)*

31. A compound containing two -OH groups attached with one carbon atom is unstable but which one of the following is stable?

(a)  $CH_3CH(OH)_2$

(b)  $CH_3\text{-}C(OH)_3$

(c)  $Cl_3CCH(OH)_2$

(d) None of these. *(2013)*

32. During the dehydration of alcohols to alkenes by heating with conc. H_2SO_4, the initiating step is

(a) elimination of water

(b) protonation of an alcohol molecule

(c) formation of an ester

(d) formation of carbocation. *(2014)*

33. The reaction,

$C_6H_5ONa + CO_2 + H_2O \rightarrow C_6H_5OH + NaHCO_3$

suggests that

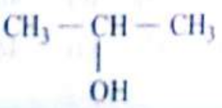
(a) phenol is a stronger acid than carbonic acid

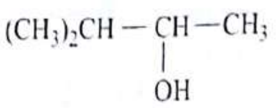
(b) carbonic acid is a stronger acid than phenol

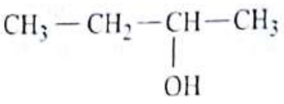
(c) water is a stronger acid than phenol

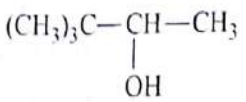
(d) none of these. *(2016)*

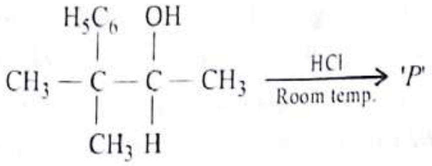
34. Lucas test is given by an alcohol within 5 minutes, 0.22 g of which liberates 56 mL of CH_4 at STP on treating with CH_3MgI. The structure of alcohol is

(a)  $CH_3-CH(OH)-CH_3$

(b)  $(CH_3)_2CH-CH(OH)-CH_3$

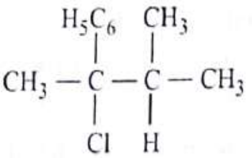
(c)  $CH_3-CH_2-CH(OH)-CH_3$

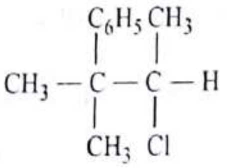
(d)  $(CH_3)_3C-CH(OH)-CH_3$ *(2017)*

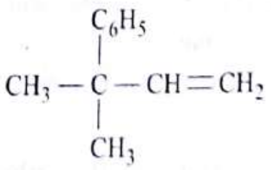
35. 

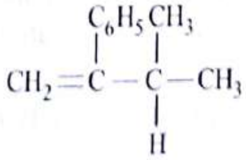
$CH_3-C(C_6H_5)(CH_3)-CH(OH)-CH_3 \xrightarrow[\text{Room temp.}]{HCl}$ 'P'

The product *P* is

(a)  $CH_3-C(C_6H_5)(Cl)-CH(CH_3)-CH_3$

(b)  $CH_3-C(C_6H_5)(CH_3)-CH(CH_3)(Cl)$

(c)  $CH_3-C(C_6H_5)(CH_3)-CH{=}CH_2$

(d)  $CH_2{=}C(C_6H_5)-CH(CH_3)-CH_3$ *(2017)*

36. Decreasing order of reactivity in Williamson synthesis of the following is

I. Me_3CCH_2Br II. $CH_3CH_2CH_2Br$

III. $CH_2{=}CHCH_2Cl$ IV. $CH_3CH_2CH_2Cl$

(a) III > II > IV > I (b) I > II > IV > III

(c) II > III > IV > I (d) I > III > II > IV

(2017)

ASSERTION AND REASON

37. ***Assertion*** : Phenol undergoes Kolbe reaction whereas ethanol does not.

Reason : Phenoxide ion is more basic than ethoxide ion. *(1995, 2015)*

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38. **Assertion :** *o*-nitrophenol is more volatile than *p*-nitrophenol.
Reason : Intramolecular hydrogen bonding is present in *o*-nitrophenol while intermolecular H - bonding is in *p*-nitrophenol. *(2001)*

39. **Assertion :** CH_3OCH_3 and C_2H_5OH has comparable molecular weight but boiling point of C_2H_5OH is more than dimethyl ether.
Reason : C_2H_5OH forms intermolecular H-bonding while CH_3OCH_3 forms intramolecular H-bonding. *(1994, 2001)*

40. **Assertion :** Phenol is a weak acid than ethanol.
Reason : Groups with $+M$ effect and $-I$ effect decreases acidity at *m*-position. *(2002)*

41. **Assertion :** Ethers behave as bases in the presence of mineral acids.
Reason : It is due to the presence of lone pair of electrons on the oxygen. *(2002, 2008)*

42. **Assertion :** The major products formed by heating $C_6H_5CH_2OCH_3$ with HI are $C_6H_5CH_2I$ and CH_3OH.
Reason : Benzyl cation is more stable than methyl cation. *(2003)*

43. **Assertion :** The pK_a of acetic acid is lower than that of phenol.
Reason : Phenoxide ion is more resonance stabilised. *(2004)*

44. **Assertion :** *t*-Butyl methyl ether is not prepared by the reaction of *t*-butyl bromide with sodium methoxide.
Reason : Sodium methoxide is a strong nucleophile. *(2005)*

45. **Assertion :** Phenol is more reactive than benzene towards electrophilic substitution reaction.
Reason : In the case of phenol, the intermediate carbocation is more resonance stabilised. *(2008, 2012)*

46. **Assertion :** 2-Butanol on heating with H_2SO_4 gives 1-butene and 2-butene.
Reason : Dehydration of 2-butanol follows Saytzeff's rule. *(2008)*

47. **Assertion :** Ethers can be dried by using sodium wire.
Reason : Ethers do not react with sodium. *(2009)*

48. **Assertion :** Dehydration of alcohols always takes place in basic medium.
Reason : OH^- is a better leaving group. *(2011)*

49. **Assertion :** *p*-Nitrophenol gives more electrophilic substituted compound than *m*-methoxyphenol.
Reason : Methoxy group shows only negative *I*-effect. *(2011)*

50. **Assertion :** Aryl sulphonic acid gives phenol on reacting with NaOH at high temperature.
Reason : This reaction is electrophilic substitution reaction. *(2013)*

51. **Assertion :** Phenol is more acidic than ethanol.
Reason : Phenoxide ion is resonance stabilised. *(2016)*

52. **Assertion :** $C{-}\ddot{O}{-}H$ bond angle is less than the normal tetrahedral bond angle.
Reason : Lone pair-lone pair repulsion decreases bond angle. *(2016)*

53. **Assertion :** Phenol forms 2, 4, 6-tribromophenol on treatment with Br_2-water at 273 K.
Reason : Phenol is *o*, *p*- directing group. *(2017)*

Answer Key

1.	(c)	2.	(c)	3.	(d)	4.	(c)	5.	(c)	6.	(d)	7.	(c)	8.	(d)
9.	(a)	10.	(c)	11.	(a)	12.	(c)	13.	(d)	14.	(d)	15.	(b)	16.	(d)
17.	(d)	18.	(a)	19.	(a)	20.	(d)	21.	(a)	22.	(b)	23.	(c)	24.	(a)
25.	(b)	26.	(a)	27.	(b)	28.	(a)	29.	(b)	30.	(c)	31.	(c)	32.	(b)
33.	(b)	34.	(b)	35.	(a)	36.	(c)	37.	(c)	38.	(a)	39.	(c)	40.	(d)
41.	(a)	42.	(a)	43.	(c)	44.	(b)	45.	(a)	46.	(a)	47.	(a)	48.	(d)
49.	(d)	50.	(c)	51.	(a)	52.	(a)	53.	(b)						

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EXPLANATIONS

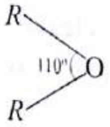
1. **(c)** : $2CH_3CH_2OH + \underset{\text{metal}}{Na} \longrightarrow 2CH_3CH_2O^-Na^+ + H_2$

Formation of alkoxide indicates the acidic nature of alcohols as alkoxides are electrovalent compounds and are written as RO^-M^+.

2. **(c)** : Iodoform test is positive for ethanol (not for methanol).

$$CH_3CH_2OH \xrightarrow[KOH]{I_2} \underset{\text{Iodoform}}{CHI_3} + HCOO^-K^+$$

3. **(d)** : The oxygen atom in ethers is sp^3 hybridized. Two of the hybrid orbitals overlap with hybrid orbitals of two carbon atoms to form sigma bonds and the bond angle is

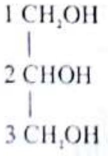


4. **(c)** : Reaction sequence is;

$$CaC_2 \xrightarrow{H_2O} \underset{\substack{(A)\\ \text{Acetylene}}}{C_2H_2} \xrightarrow[HgSO_4]{\text{dil. } H_2SO_4} \underset{\substack{(B)\\ \text{Acetaldehyde}}}{CH_3CHO} \xrightarrow{H_2/Ni} \underset{\substack{(C)\\ \text{Ethanol}}}{CH_3CH_2OH}$$

5. **(c)** : Absolute ether is 100% pure diethyl ether, totally free from any impurities.

6. **(d)** : Glycerine is

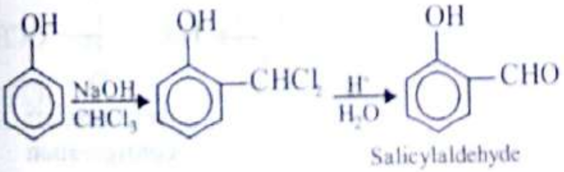


$$\begin{array}{l} 1\ CH_2OH \\ \quad | \\ 2\ CHOH \\ \quad | \\ 3\ CH_2OH \end{array}$$

1 and 3 C-atoms are primary.
2 C-atom is secondary .

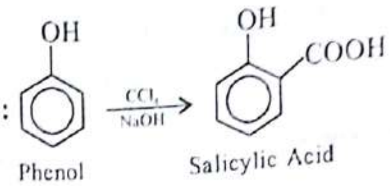
7. **(c)** : There is extensive hydrogen bonding in ethanol due to the presence of –OH groups, while it is not possible in dimethyl ether (no –OH group available).

8. **(d)** : The given reaction is Reimer-Tiemann reaction.



Salicylaldehyde

9. **(a)** :



Reaction is called as Reimer-Tiemann reaction. It involves the attack of dichlorocarbene on benzene ring.

10. **(c)** : All the alcohols are water soluble due to the formation of extensive hydrogen bonding between water molecules and alcohol molecules. Lower alcohols are highly soluble in water and their solubility decreases with an increase in the molecular weight.

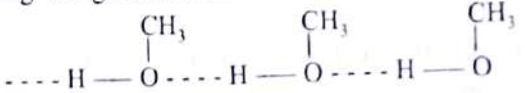
11. **(a)** : Lucas test – Alcohol reacts with concentrated hydrochloric acid in presence of anhydrous $ZnCl_2$ to form alkyl halides. The three types of alcohols undergo this reaction at different rates. Order of rate of reaction is :
tertiary > secondary > primary.

$$R-OH + HCl \xrightarrow{\text{anhy } ZnCl_2} \underset{\text{Alkyl chloride}}{R-Cl} + H_2O$$

12. **(c)** : Hydroboration yields 1° alcohol from alkenes.

$$3CH_3CH{=}CH_2 \xrightarrow[\text{or } B_2H_6]{BH_3 \text{ in THF}} (CH_3CH_2CH_2)_3B \xrightarrow{3H_2O_2} \underset{\text{1-propanol}}{3CH_3CH_2CH_2OH} + H_3BO_3$$

13. **(d)** : Methanol has – OH group due to which there will be more intermolecular hydrogen bonding among the given molecules.



$$----H-\overset{\overset{CH_3}{|}}{O}----H-\overset{\overset{CH_3}{|}}{O}----H-\overset{\overset{CH_3}{|}}{O}$$

We know that with the increase of electronegativity and decrease in size of the atom to which hydrogen is covalently linked, the strength of the hydrogen bond increases.

14. **(d)** : Pyridine chlorochromate (PCC) $[C_5H_5NH^+ClCrO_3^-]$ selectively oxidizes primary alcohols to aldehydes. Secondary alcohols can be oxidized to ketones with PCC.

15. **(b)** : The position taken up by a third group entering the ring depends on the nature of the two groups already present.

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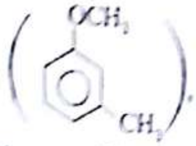
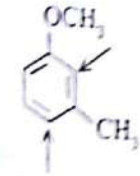
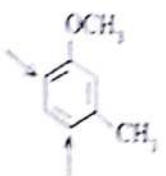
When both groups show *o*-and *p*-directing nature, the directive power of each group is generally in the following order :

$O^- > NH_2 > NR_2 > OH > OMe > NHAc > Me > X$

In case of compound *A* , the arrows are used to indicate the possible positions that may be taken up by an incoming group.

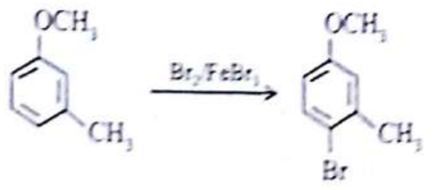


(with respect to - OCH$_3$ group)



(with respect to both - CH$_3$ group and - OCH$_3$ group)

Due to presence of bulky group, steric effect works, and the favourable product will be this.

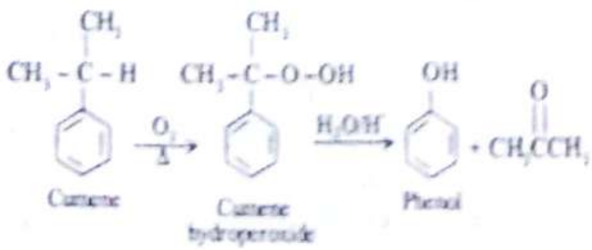


16. **(d)** : Halogenated compounds on treatment with aq. KOH form alcohols. The halogen atom is substituted by – OH group.

$$CH_3CH(Cl)CH_2-CH_2OH \xrightarrow{aq\,KOH} CH_3CH(OH)CH_2-CH_2OH$$

Here OH^- acts as a nucleophile.

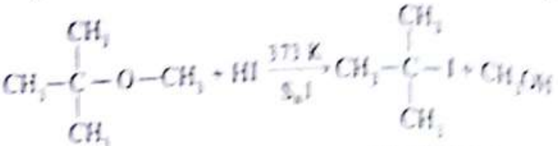
17. **(d)** : Isopropyl benzene or cumene on air oxidation in presence of dilute acid gives phenol.



18. **(a)** : When mixed ethers are used, the alkyl iodide produced depends on the nature of alkyl groups. If one group is Me and the other a pri- or sec-alkyl group, then methyl iodide is produced. Here reaction occurs via S_N2 mechanism and because of the steric effect of the larger group, I$^-$ attacks the smaller (Me) group.

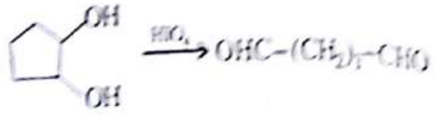
$$CH_3OC_2H_5 + HI \rightarrow CH_3I + C_2H_5OH$$

When the substrate is a methyl *t*-alkyl ether, the products are *t*-RI and MeOH. Here reaction occurs via S_N1 mechanism and formation of products is controlled by the stability of carbocation. Since carbocation stability order is $3^\circ > 2^\circ > 1^\circ > \overset{\oplus}{C}H_3$, alkyl halide is always derived from *tert*-alkyl group.



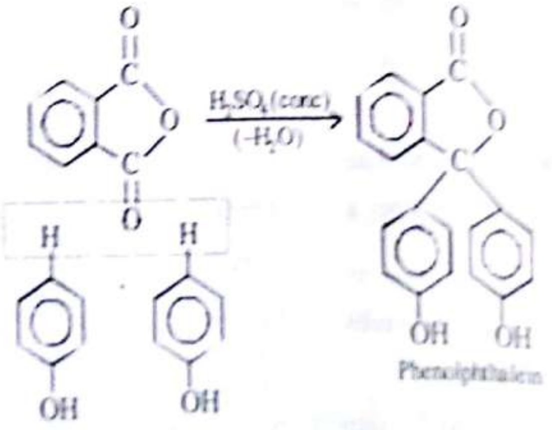
$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-O-CH_3 + HI \xrightarrow[S_N1]{373\,K} CH_3-\underset{CH_3}{\overset{CH_3}{C}}-I + CH_3OH$$

tert - Butyl methyl ether   *tert* - Butyl iodide

19. **(a)** : 

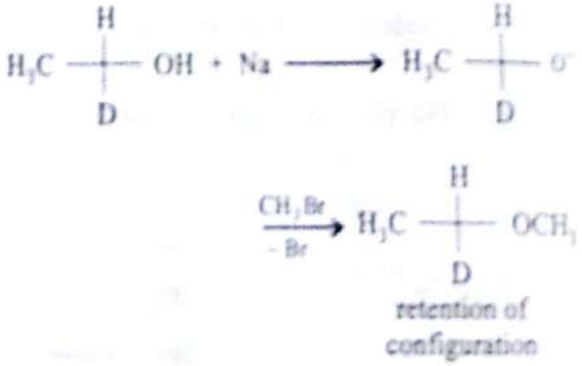
To cause oxidative cleavage of bonds carrying groups prone to undergo oxidation, one mole of reagent is required to cleave one bond.

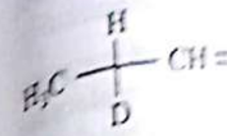
20. **(d)** : Phenol couples with phthalic anhydride in presence of conc. H_2SO_4 to form phenolphthalein which is used as an indicator.



21. **(a)**

22. **(b)** :





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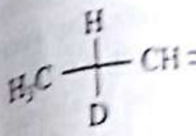
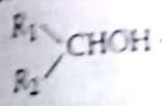
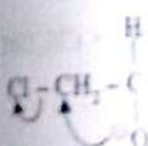


23. **(c)** : In Opp
alcohol is oxidis
presence of alu
oxidisable group



24. **(a)** : Degre
it contains no
are two rings
product and th
cleaved by HCl
structure.

25. **(b)** : Cl



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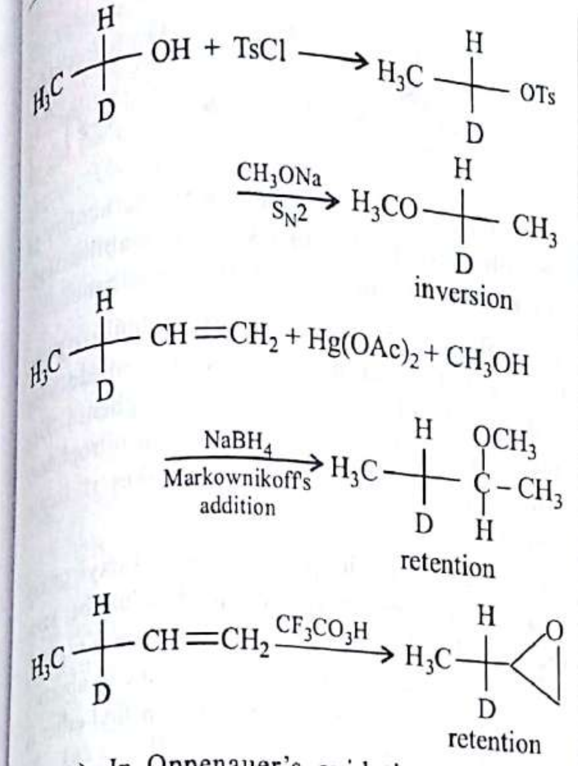
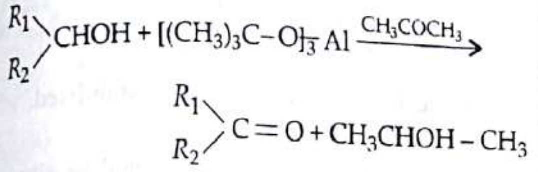
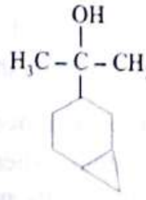


23. (c) : In Oppenauer's oxidation, secondary alcohol is oxidised to corresponding ketone in the presence of aluminium tertiary butoxide. Other oxidisable groups are not affected.

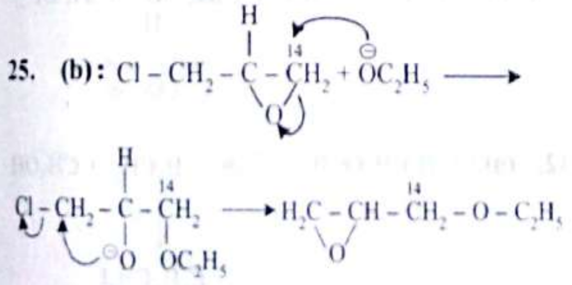


$$\begin{matrix}R_1\\R_2\end{matrix}\!\!>CHOH + [(CH_3)_3C-O]_3Al \xrightarrow{CH_3COCH_3} \begin{matrix}R_1\\R_2\end{matrix}\!\!>C=O + CH_3CHOH-CH_3$$

24. (a) : Degree of unsaturation of $C_{10}H_{18}O = 2$, but it contains no double or triple bond. Hence there are two rings – one six membered as indicated by product and the other three membered which is cleaved by HCl due to strain. Hence A has following structure.

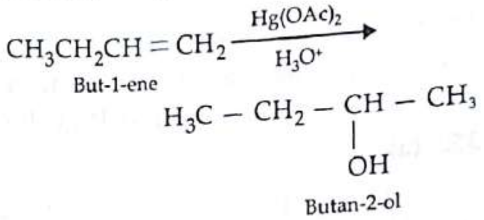


25. (b):



26. (a) : Presence of excess of HI favours S_N1 mechanism.
So, formation of products is controlled by the stability of the carbocation resulting in the cleavage of C – O bond in protonated ether.
Thus the product for given equation are $C_6H_5CH_2I$, CH_3CH_2I, $HOCH_2-CH_2OH$.

27. (b) :

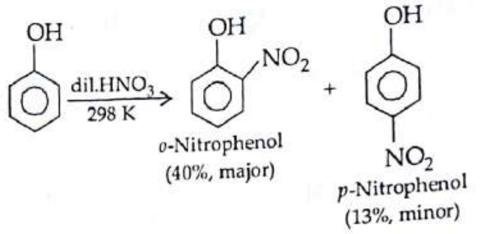


$$CH_3CH_2CH=CH_2 \xrightarrow[H_3O^+]{Hg(OAc)_2} H_3C-CH_2-\underset{\displaystyle OH}{\underset{|}{CH}}-CH_3$$

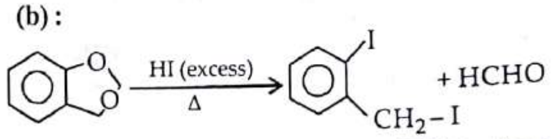
But-1-ene

Butan-2-ol

28. (a) :



29. (b) :



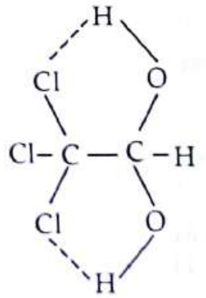
Ethers are readily cleaved by action of HI to form alcohol and alkyl halide.

$R-O-R + HX \rightarrow RX + R-OH$

If excess of halogen acid is used, then alcohol formed reacts further with halogen acid to produce alkyl halide.

30. (c)

31. (c) : Chloral hydrate is stable due to hydrogen bonding.



32. (b) : The mechanism of dehydration of alcohol involves the following steps-

1. Formation of protonated alcohol
2. Formation of carbocation
3. Formation of ethene by elimination of a proton.

33. (b) : Since a stronger acid displaces a weaker acid from its salts, therefore, carbonic acid ($CO_2 + H_2O \rightarrow H_2CO_3$) is a stronger acid than phenol.

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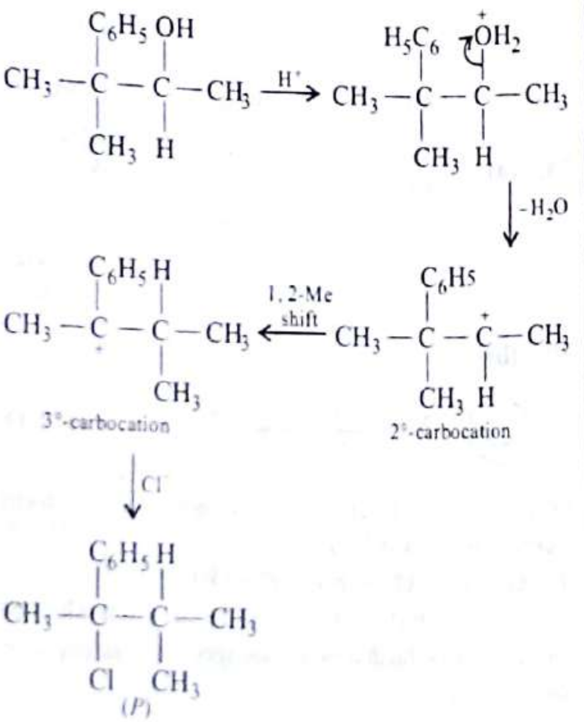
34. **(b) :** Lucas test will be given by all the given alcohols within 5 minutes as all are 2° alcohols. Exact structure can be known by molecular mass or formula of alcohol which will be obtained as follows :
Let molecular mass of alcohol be M.

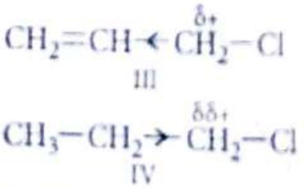
$$\frac{56}{22400} = \frac{0.22}{M} \text{ or, } M = \frac{22400 \times 0.22}{56} = 88$$

The general formula of alcohols is $C_nH_{2n+1}OH$.
The molecular mass 88 corresponds to the value of $n = 5$. Thus, the 2° alcohol is $(CH_3)_2CHCHOHCH_3$.

35. **(a) :**



36. **(c) :** C—Br bond is weaker than C—Cl bond, therefore, alkyl bromide (II) reacts faster than alkyl chlorides, (III) and (IV). Since $CH_2{=}CH{-}$ is electron withdrawing therefore, CH_2 has more +ve charge on III than on IV.

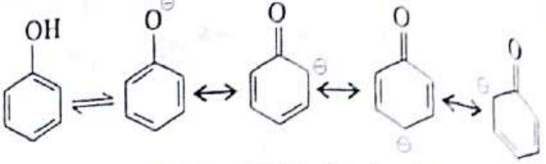


$$\underset{\text{III}}{CH_2{=}CH \leftarrow \overset{\delta+}{C}H_2{-}Cl}$$

$$\underset{\text{IV}}{CH_3{-}CH_2 \rightarrow \overset{\delta\delta+}{C}H_2{-}Cl}$$

In other words, nucleophilic attack occurs faster on III than on IV. Further, since Williamson synthesis occurs by S_N2 mechanism, therefore, due to steric hindrance alkyl bromide (I) is the least reactive. Thus, the decreasing order of reactivity is II > III > IV > I.

37. **(c) :**

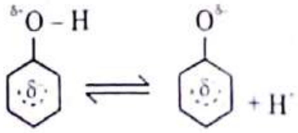


Phenol is acidic in nature due to the acidity of phenolic proton (due to resonance stabilisation) but there is no such stabilisation in ethanol.

38. **(a) :** *p*-nitrophenol has higher boiling point than *o*-nitrophenol, because intermolecular hydrogen bonding present in *p*-nitrophenol. But intramolecular hydrogen bonding in *o*-nitrophenol affects the boiling point which makes it steam volatile.

39. **(c) :** Due to the presence of hydroxyl group (–OH), there is extensive hydrogen bonding between the ethanol molecules (C_2H_5OH). But there is no such Hydrogen bonding in dimethyl ether (due to absence of –OH group). So boiling point of dimethyl ether is much lower than ethanol.

40. **(d) :** Phenols are more acidic than alcohols.

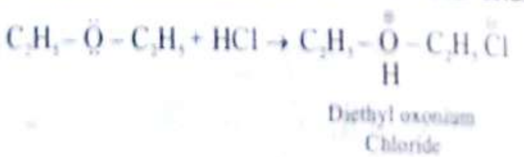


Phenoxide ion is more resonance stabilised.

$$R-O-H \rightleftharpoons R-O^- + H^+$$

No resonance stabilisation for alochol or alkoxide ion. Thus, phenols are more acidic than alcohols. Electron withdrawing group like. $-NO_2$, $-CN$ etc. disperse the negative charge and therefore stabilise the phenoxide ion. Thus, these groups will increase the acidic strength. The particular effect is more significant when the substituent is present in *o*- or *p*-position than *m*-position to the –OH group.

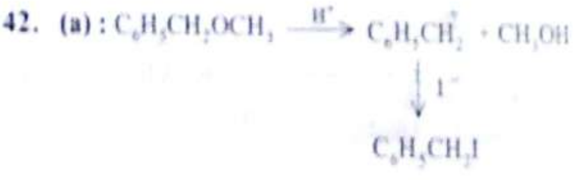
41. **(a) :** Due to the presence of lone pair of electrons on oxygen atom, ethers behave as base and form stable oxonium salts with mineral acids.



$$C_2H_5-\ddot{O}-C_2H_5 + HCl \rightarrow C_2H_5-\underset{H}{\overset{\oplus}{O}}-C_2H_5\,\overset{\ominus}{Cl}$$

Diethyl oxonium Chloride

42. **(a) :**



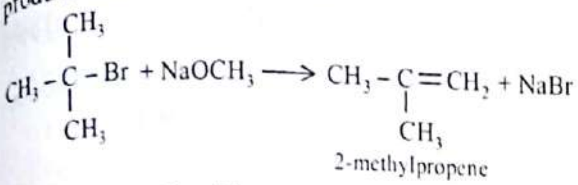
$$C_6H_5CH_2OCH_3 \xrightarrow{H^+} C_6H_5\overset{+}{C}H_2 + CH_3OH$$
$$\downarrow I^-$$
$$C_6H_5CH_2I$$

Scanned by CamScanner

This can be explained on the basis of S_N1 mechanism, the carbonium ion produced being benzylium ion, is more stable than alkylium ion.

43. (c) : Lower the value of pK_a, more acidic will be the compound. Acetic acid is more acidic than phenol. This indicates that carboxylate ion should be more stable than the phenoxide ion and it is clear that carboxylate ion has more equivalent resonating structures than the phenoxide ion.

44. (b) : In Williamson's synthesis, if a tertiary alkyl halide is used, an alkene is the only reaction product and no ether is formed.

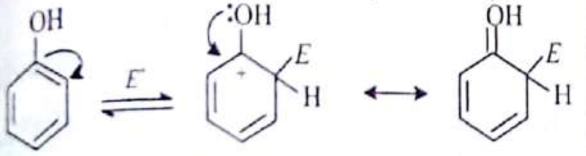


$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-Br + NaOCH_3 \longrightarrow CH_3-\underset{\underset{CH_3}{|}}{C}=CH_2 + NaBr$$

2-methylpropene

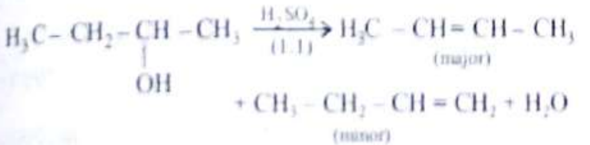
It is because alkoxides are not only nucleophiles but also strong bases as well. They react with alkyl halides leading to elimination reaction.

45. (a) : – OH group shows + *M* effect and is an activating group, moreover the arenium ion of phenolic substitution is more stable.



46. (a) : Saytzeff's rule : The alkene formed in greatest amount is the one that corresponds to removal of the hydrogen from the β-carbon having the fewest hydrogen substituent.

In case of 2° and 3° alcohol Saytzeff's rule is followed.



$$H_3C-CH_2-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[(1:1)]{H_2SO_4} \underset{(major)}{H_3C-CH=CH-CH_3} + \underset{(minor)}{CH_3-CH_2-CH=CH_2} + H_2O$$

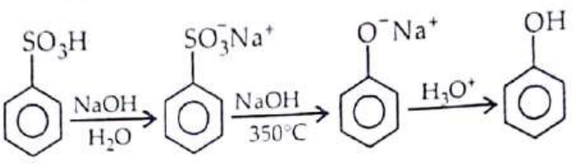
47. (a)

48. (d) : Dehydration of alcohols can be carried out either with protonic acids such as conc. H_2SO_4, H_3PO_4 or catalysts such as anhydrous zinc chloride or alumina.

49. (d) : In *p*-nitrophenol, – NO_2 group has –*I* effect, as a result of which electron density decreases on the benzene ring, hence reactivity towards electrophilic substitution decreases. Methoxy group shows both +*R* (due to lone pair of electrons on O) and –*I* effect (due to greater electronegativity of O).

– OCH_3 at *meta*-position shows only –*I* effect but lesser than –*I* effect of $-NO_2$ group.

50. (c) :



This is nucleophilic aromatic substitution reaction and occurs *via* the addition-elimination mechanism with SO_3^{2-} as the leaving group.

51. (a)

52. (a) : The $C-\ddot{O}-H$ bond angle in alcohols is slightly less than the tetrahedral angle 109°28′ due to repulsion between the unshared electron pairs of oxygen.

53. (b) : Phenol forms 2, 4, 6 tribromophenol on treatment with Br_2-water. In phenols, the polarisation of bromine takes place even in the absence of Lewis acid.

CHAPTER

26

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

1. When ethanal is treated with Fehling's solution, it gives a precipitate of
(a) Cu_2O (b) Cu
(c) Cu_3O (d) CuO *(1994)*

2. In Wolff–Kishner reduction, the carbonyl group of aldehydes and ketones is converted into
(a) $-CH_2OH$ (b) $-CH_2-$
(c) $-CH_3$ (d) $-CHOH-$
(1994)

3. Which of the following compounds gives Cannizzaro's reaction?
(a) CH_3CH_2CHO (b) HCHO
(c) $(CH_3)_2CHCHO$ (d) CH_3CHO
(1994)

4. Which of the following will not undergo aldol condensation?
(a) Propionaldehyde (b) Acetone
(c) Formaldehyde (d) Acetaldehyde
(1994)

5. Which one is the strongest of the following acids?
(a) CCl_3COOH (b) HCOOH
(c) $CH_2ClCOOH$ (d) CH_3COOH
(1994)

6. Which of the following is called an ethanoic acid?
(a) CH_3CH_2COOH (b) HCOOH
(c) $CH_3CH_2CH_2COOH$ (d) CH_3COOH
(1994)

7. Which of the following is formed, when benzaldehyde reacts with alcoholic KCN?
(a) Benzoin (b) Benzyl alcohol
(c) Benzoic acid (d) Ethyl benzoate
(1996)

8. R-CH_2-CH_2OH can be converted into RCH_2CH_2COOH. The correct sequence of the reagents is
(a) KCN and H^+
(b) PBr, KCN and H_2
(c) PBr_3, KCN and H^+
(d) HCN, PBr_3 and H^+ *(1997)*

9. In a reaction of C_6H_5Y, the major product (> 60%) is m-isomer. The group Y is
(a) – Cl (b) – OH
(c) – NH_2 (d) – COOH
(1997)

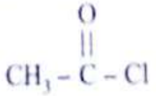
10. 1-Butyne reacts with cold alkaline $KMnO_4$ to produce
(a) CH_3CH_2COOH
(b) $CH_3CH_2CH_2COOH$
(c) $CH_3CH_2COOH + CO_2$
(d) $CH_3 - CH_2 - COOH + HCOOH$
(1997)

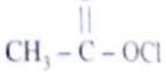
11. Reduction of benzoyl chloride with $Pd/BaSO_4$ produces
(a) benzene (b) benzaldehyde
(c) benzoic acid (d) benzoyl cyanide.
(1997)

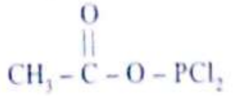
12. Which of the following compounds will not give Cannizzaro's reaction?
(a) $(Me)_3CCHO$ (b) HCHO
(c) CH_3CHO (d) C_6H_5CHO
(1998)

13. Benzaldehyde can be prepared by the hydrolysis of
(a) benzyl chloride (b) benzotrichloride
(c) benzal chloride (d) benzo nitrite.
(1998)

14. The product obtained when acetic acid is treated with phosphorus trichloride, is

(a) 
$CH_3-\overset{O}{\overset{||}{C}}-Cl$

(b) 
$CH_3-\overset{O}{\overset{||}{C}}-OCl$

(c) 
$CH_3-\overset{O}{\overset{||}{C}}-O-PCl_2$

(d) CH_3 – CH

15. Vinegar is
(a) HCOOH
(c) CH_3CH

16. CO_2 is libera
to a carboxyl
from
(a) carbox
(c) alkyl g

17. In the follo
CH_3CH_2CO
(a) CH_2=
(b) CH_2 –
(c) CH_3C
(d) CH_3C

18. Strongest
(a) CH_3C
(c) F_2CH

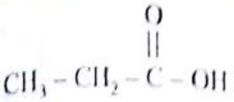
19. The intern
is
(a) aldo
(c) alco

20. The comp
of cyano
(a) C_2H
(c) C_2H

21. CH_3CO
by the
(a) HI
(c) Zn

22. In the
C_6H_5CH
the co
(a) a
(c) S

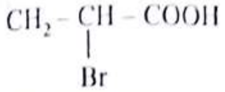
23. Amon
(a) (
(c)
(d)

(d) 

$CH_3-CH_2-\overset{\overset{O}{||}}{C}-OH$ *(1998)*

15. Vinegar is
(a) HCOOH (b) HCHO
(c) CH_3CHO (d) CH_3COOH
(1999)

16. CO_2 is liberated on adding sodium carbonate to a carboxylic acid. The carbon of CO_2 comes from
(a) carboxylic group (b) carbonate
(c) alkyl group (d) methyl. *(2000)*

17. In the following reaction order, B is
$CH_3CH_2COOH \xrightarrow{P/Br_2} A \xrightarrow[H^+]{alc.\ KOH} B$
(a) $CH_2{=}CH-COOH$
(b) 

$CH_3-\underset{\underset{Br}{|}}{CH}-COOH$

(c) CH_3CH_2COBr
(d) CH_3CH_2OH *(2001)*

18. Strongest acid among the following is
(a) CH_3COOH (b) FCH_2COOH
(c) $F_2CHCOOH$ (d) F_3CCOOH
(2001)

19. The intermediate formed in aldol condensation is
(a) aldol (b) carbanion
(c) alcohol (d) α-hydrogen ester.
(2002)

20. The compound most suitable for the preparation of cyanohydrin is
(a) C_2H_5COOH (b) $C_6H_5NH_2$
(c) $C_2H_5COC_2H_5$ (d) $C_2H_5-C_2H_5$
(2002)

21. CH_3COCH_3 can be converted to $CH_3CH_2CH_3$ by the action of
(a) HIO_3 (b) HNO_3
(c) Zn – Hg/HCl (d) H_3PO_3 *(2002)*

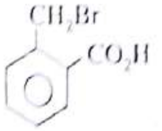
22. In the reaction :
$C_6H_5CHO + C_6H_5NH_2 \rightarrow C_6H_5N{=}CHC_6H_5 + H_2O$,
the compound $C_6H_5N{=}CHC_6H_5$ is known as
(a) aldol (b) Schiff's base
(c) Schiff's reagent (d) Benedict's reagent.
(2002)

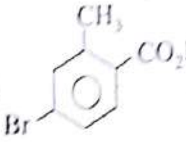
23. Among the following the strongest acid is
(a) CH_3COOH (b) C_6H_5COOH
(c) m-$CH_3OC_6H_4COOH$
(d) p-$CH_3OC_6H_4COOH$ *(2003)*

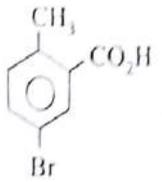
24. At higher temperature, iodoform reaction is given by
(a) $CH_3CO_2CH_3$ (b) $CH_3CO_2C_2H_5$
(c) $C_6H_5CO_2CH_3$ (d) $CH_3CO_2C_6H_5$
(2003)

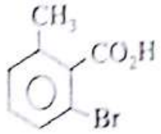
25. The reagent used for the separation of acetaldehyde from acetophenone is
(a) $NaHSO_3$ (b) $C_6H_5NHNH_2$
(c) NH_2OH (d) NaOH and I_2
(2004)

26. o-Toluic acid on reaction with Br_2 + Fe gives

(a) 

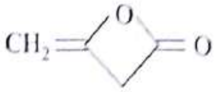
(b) 

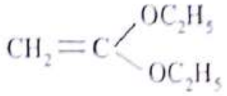
(c) 

(d) 

(2004)

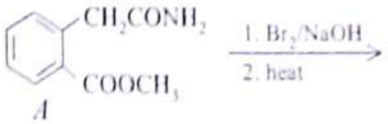
27. $CH_3CO_2C_2H_5$ on reaction with sodium ethoxide in ethanol gives A, which on heating in the presence of acid gives B. Compound B is
(a) CH_3COCH_2COOH (b) CH_3COCH_3

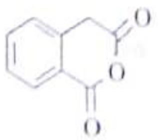
(c) 

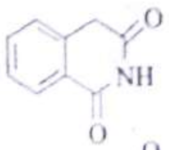
(d) 

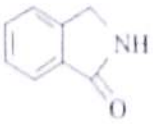
(2005)

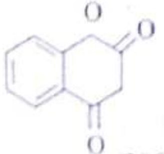
28. The following sequence of reactions on A gives



(a) 

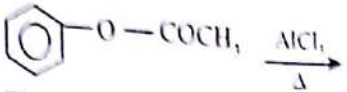
(b) 

(c) 

(d) 

(2006)

29. Benzoic acid is treated with lithium aluminium hydride. The compound obtained is
(a) benzaldehyde (b) benzyl alcohol
(c) toluene (d) benzene.
(2007, 2015)

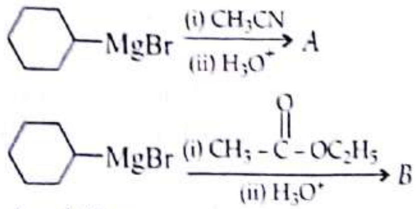
30. 

The product obtained is/are
(a) o-product
(b) m-product
(c) o- and p-products
(d) o-, m- and p-products. *(2007)*

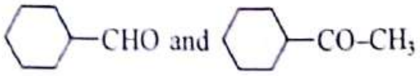
31. Prolonged exposure of fat or oil in moist air and light causes bad smell (rancidity). It is due to
(a) formation of $C_6 - C_{12}$ fatty acids
(b) formation of ketone and aldehyde
(c) both of these causes
(d) formation of glycerol. *(2008)*

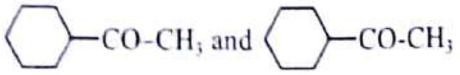
32. Toluene on treatment with CrO_3 and $(CH_3CO)_2O$ followed by hydrolysis with dil. HCl gives
(a) benzaldehyde
(b) benzoic acid
(c) phenol
(d) phenylacetaldehyde. *(2008)*

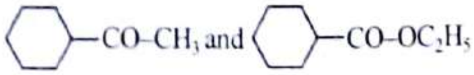
33. In the reactions,

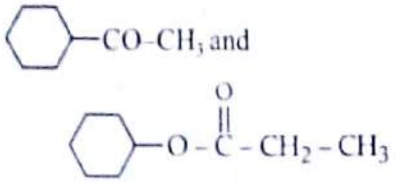


A and B are

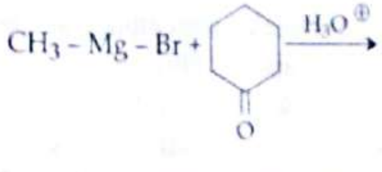
(a) 

(b) 

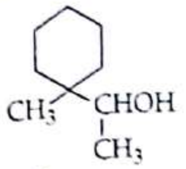
(c) 

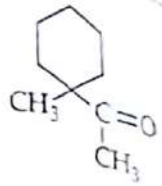
(d)  *(2009)*

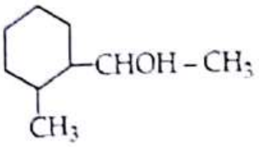
34. In the following sequence of the reactions, identify the final product.

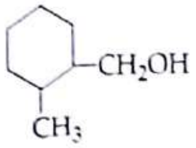


$$A \xrightarrow{HBr} B \xrightarrow{Mg,\ ether} C \xrightarrow[H_3O^{\oplus}]{CH_3CHO} D$$

(a) 

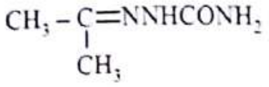
(b) 

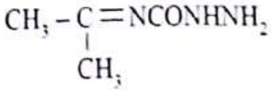
(c) 

(d)  *(2009)*

35. Compound *A* (molecular formula C_3H_8O) is treated with acidified potassium dichromate to form a product *B* (molecular formula C_3H_6O). *B* forms a shining silver mirror on warming with ammoniacal silver nitrate. *B* when treated with an aqueous solution of $H_2NCONHNH_2 \cdot HCl$ and sodium acetate gives a product *C*. Identify the structure of *C*.

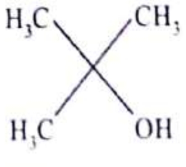
(a) $CH_3CH_2CH{=}NNHCONH_2$

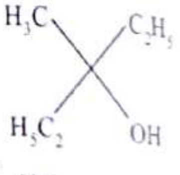
(b) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NNHCONH_2$

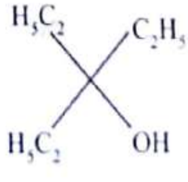
(c) 
$CH_3-\underset{\displaystyle CH_3}{\underset{|}{C}}{=}NCONHNH_2$

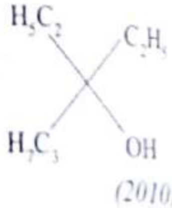
(d) $CH_3CH_2CH{=}NCONHNH_2$ *(2010)*

36. Ethyl ester $\xrightarrow[excess]{CH_3MgBr}$ *P*. The product *P* will be

(a) 

(b) 

(c) 

(d)  *(2010)*

37. Cyclohexene on ozonolysis followed by reaction with zinc dust and water gives compound *E*. Compound *E* on further treatment with aqueous KOH yields compound *F*. Compound *F* is

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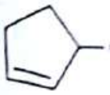
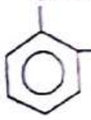
(a) 

(c) 

38. Maximum dec
(a) CH_3COO
(c) C_6H_5CH
(d) CH_3COC

39. If phthalic aci is first heatec product form

(a) 

(c) 

40. In a set o product S.

CH_3COOI

The struct

(a) 

(b) 

(c) 

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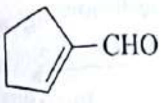
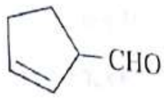
(a)


(b)


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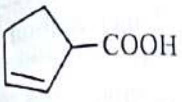

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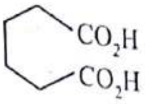
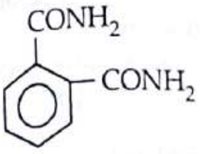
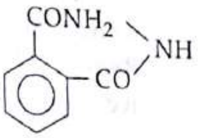


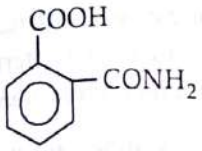
(2010)

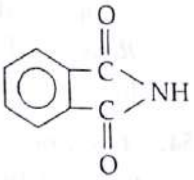
38. Maximum decarboxylation occurs in
(a) CH_3COOH (b) C_6H_5COOH
(c) $C_6H_5CH_2COOH$
(d) CH_3COCH_2COOH *(2011)*

39. If phthalic acid is treated with NH_3 and then it is first heated weakly then strongly, the final product formed is

(a)


(b)


(c)


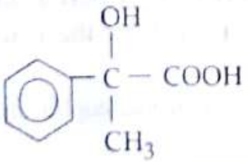
(d)


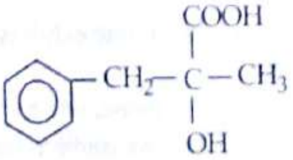
(2012)

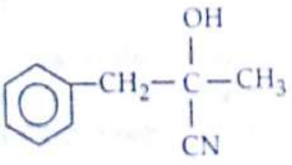
40. In a set of reactions, acetic acid yielded a product S.

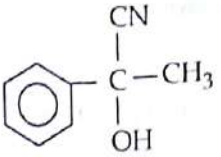
$$CH_3COOH \xrightarrow{SOCl_2} P \xrightarrow[\text{Anhy. } AlCl_3]{\text{Benzene}} Q \xrightarrow{HCN} R \xrightarrow{HOH} S$$

The structure of S would be

(a)


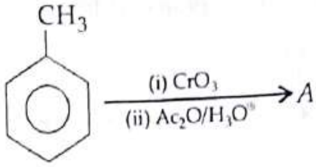
(b)


(c)


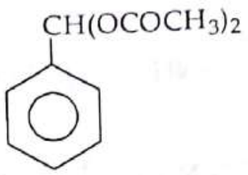
(d)


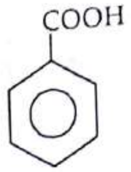
(2012,2017)

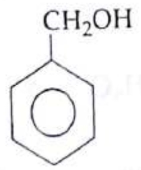
41. Arrange the following compounds in increasing order of reactivity towards nucleophilic addition reaction.
(I) $C_6H_5COCH_3$ (II) $CH_3CO—C_2H_5$
(III) C_6H_5CHO (IV) $Cl—CH_2—CHO$
(a) IV > III > II > I (b) IV > II > III > I
(c) I > II > III > IV (d) III > IV > II > I
(2013)

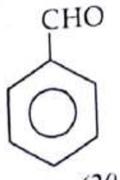
42.


A; Product A is

(a)


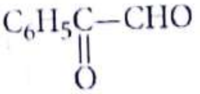
(b)


(c)


(d)


(2013)

43. Salicylic acid can be easily prepared by reaction between
(a) phenol and CO_2
(b) benzoic acid and H_2O_2
(c) benzene diazonium chloride and CO_2
(d) phenol and formic acid. *(2013)*

44. Which does not give Cannizzaro reaction?
(a) HCHO
(b)

$C_6H_5\underset{\underset{O}{\|}}{C}—CHO$
(c) Ph—CHO (d) Ph—CH_2—CHO
(2014)

45. In Clemmensen reduction, carbonyl compound is treated with
(a) zinc amalgam + HCl
(b) sodium amalgam + HCl
(c) zinc amalgam + HNO_3
(d) sodium amalgam + HNO_3 *(2014)*

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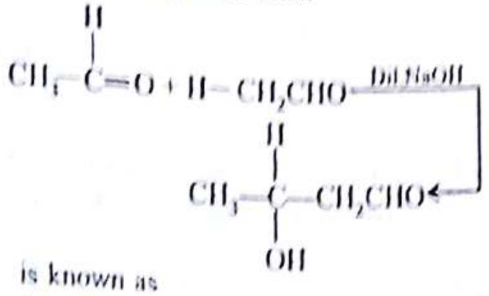
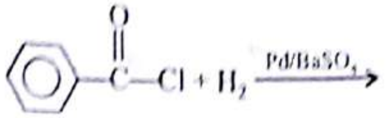
46. The following conversion

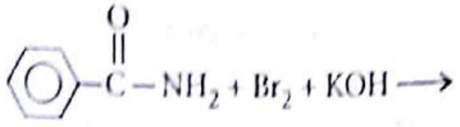


is known as

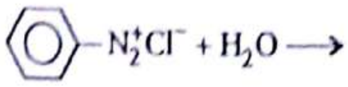
(a) Cannizzaro reaction
(b) aldol condensation
(c) polymerisation
(d) benzoin condensation. *(2015)*

47. Benzaldehyde can be prepared from

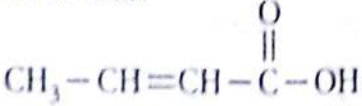
(a) 

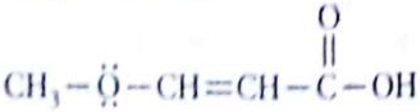
(b) 

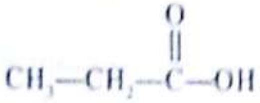
(c) 

(d)  *(2016)*

48. The acidic strength of the given compounds follows the order

I. 
$CH_3-CH=CH-C(=O)-OH$

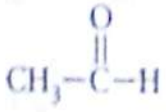
II. 
$CH_3-\ddot{O}-CH=CH-C(=O)-OH$

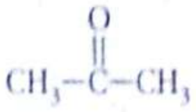
III. 
$CH_3-CH_2-C(=O)-OH$

(a) II > III > I
(b) III > II > I
(c) II > I > III
(d) I > II > III *(2016)*

49. Ease of nucleophilic addition in the given compounds is


I


II


III

(a) I > III > II
(b) II > III > I
(c) II > I > III
(d) III > I > II *(2016)*

50. What is the name of the following reaction?

$$PhCHO + (CH_3CO)_2O \xrightarrow{Na(OAc)_2} PhCH=CHCOOH$$

(a) Oxymercuration demercuration reaction
(b) Cannizzaro reaction
(c) Knoevenagel's reaction
(d) Perkin reaction *(2017)*

ASSERTION AND REASON

51. ***Assertion :*** Lower aldehydes and ketones are soluble in water but the solubility decreases as the molecular mass increases.

Reason : Distinction between aldehydes and ketones can be done by Tollens' test. *(1998)*

52. ***Assertion :*** Formic acid reduces mercuric chloride to mercurous chloride on heating, while acetic acid does not.

Reason : Formic acid is stronger acid than acetic acid. *(1995, 2000, 2016)*

53. ***Assertion :*** Boiling and melting points of amides are higher than corresponding acids.

Reason : It is due to strong intermolecular hydrogen bonding in their molecules. *(2002)*

54. ***Assertion :*** Hydroxyketones are not directly used in Grignard reaction.

Reason : Grignard reagents react with hydroxyl group. *(2003)*

55. ***Assertion :*** Acetamide has more polar $>C=O$ group than in ethyl acetoacetate.

Reason: $\ddot{N}H_2$ is more electron donating than $\ddot{O}C_2H_5$ *(2007)*

56. ***Assertion :*** $(CH_3)_3CCOC(CH_3)_3$ and acetone can be distinguished by the reaction with $NaHSO_3$.

Reason : HSO_3^- is the nucleophile in bisulphite addition. *(2008)*

57. ***Assertion :*** Cyclohexanone exhibits keto-enol tautomerism.

Reason : In cyclohexanone, one form contains the keto group while other contains enolic group $(-C=C-OH)$. *(2008)*

58. ***Assertion :*** Benzaldehyde is less reactive than ethanal towards nucleophilic attack.

Reason : The $+R$ effect of phenyl group decreases the electron density on the carbon atom of $>C=O$ group in benzaldehyde. *(2008)*

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59. ***Assertion :*** *p-N, N*-dimethylaminobenzaldehyde undergoes benzoin condensation.
Reason : The aldehydic (–CHO) group is *meta* directing. *(2009)*

60. ***Assertion :*** In sodium formate, both the C – O bonds have same value 1.27 Å.
Reason : Equal bond length is due to the phenomenon of resonance. *(2009)*

61. ***Assertion :*** Esters which contain α-hydrogens undergo Claisen condensation.
Reason : $LiAlH_4$ reduction of esters gives acids. *(2009)*

62. ***Assertion :*** Aldol condensation can be catalysed both by acids and bases.
Reason : β-Hydroxy aldehydes or ketones readily undergo acid catalysed dehydration. *(2010)*

63. ***Assertion :*** Toluene in presence of UV rays forms benzaldehyde.
Reason : Dichlorotoluene is formed as an intermediate. *(2011)*

64. ***Assertion :*** Acetamide on reaction with KOH and bromine gives acetic acid.
Reason : Bromine catalyses hydrolysis of acetamide. *(2013)*

65. ***Assertion :*** Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.
Reason : Benzaldehyde is strong electrophile than acetaldehyde. *(2013)*

66. ***Assertion :*** *cis*-3-Chloroprop-2-enoic acid is less stable than its *trans*-form.
Reason : Dipole moment of *cis*-form is greater than *trans*-form. *(2013)*

67. ***Assertion :*** $(CH_3)_3CCOOH$ does not give HVZ reaction.
Reason : $(CH_3)_3CCOOH$ does not have α-hydrogen atom. *(2014)*

68. ***Assertion :*** Aromatic aldehydes and formaldehyde undergo Cannizzaro reaction.
Reason : Aromatic aldehydes are almost as reactive as formaldehyde. *(2017)*

Answer Key

1.	(a)	**2.**	(b)	**3.**	(b)	**4.**	(c)	**5.**	(a)	**6.**	(d)	**7.**	(a)	**8.**	(c)
9.	(d)	**10.**	(d)	**11.**	(b)	**12.**	(c)	**13.**	(c)	**14.**	(a)	**15.**	(d)	**16.**	(b)
17.	(a)	**18.**	(d)	**19.**	(b)	**20.**	(c)	**21.**	(c)	**22.**	(b)	**23.**	(b)	**24.**	(b)
25.	(a)	**26.**	(c)	**27.**	(c)	**28.**	(c)	**29.**	(b)	**30.**	(c)	**31.**	(c)	**32.**	(a)
33.	(b)	**34.**	(a)	**35.**	(a)	**36.**	(a)	**37.**	(a)	**38.**	(d)	**39.**	(d)	**40.**	(a)
41.	(a)	**42**	(d)	**43.**	(a)	**44.**	(d)	**45.**	(a)	**46.**	(b)	**47.**	(a)	**48.**	(d)
49.	(b)	**50.**	(d)	**51.**	(b)	**52.**	(b)	**53.**	(a)	**54.**	(a)	**55.**	(a)	**56.**	(b)
57.	(a)	**58.**	(a)	**59.**	(b)	**60.**	(a)	**61.**	(c)	**62.**	(b)	**63.**	(d)	**64.**	(d)
65.	(a)	**66.**	(b)	**67.**	(a)	**68.**	(c)								

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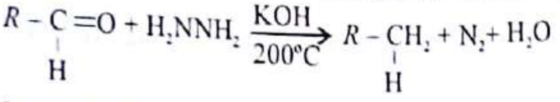
EXPLANATIONS

1. **(a) :** $\underset{\text{(Blue)}}{CH_3CHO + 2CuO} \rightarrow CH_3COOH + \underset{\text{(Red ppt)}}{Cu_2O}$

Thus in this reaction, precipitate of copper oxide (Cu_2O) is formed.

Fehling' solution is an alkaline solution of cupric ion complexed with sodium potassium tartarate.

2. **(b) :** Wolff – Kishner reduction : Aldehydes and ketones are reduced to hydrocarbons in the presence of excess of hydrazine and strong base on heating.



$$R-\underset{H}{C}=O + H_2NNH_2 \xrightarrow[200°C]{KOH} R-\underset{H}{CH_2} + N_2 + H_2O$$

3. **(b) :** Only HCHO does not have α-hydrogens which is the requirement of Cannizzaro's reaction.

$$2HCHO \xrightarrow{NaOH} CH_3OH + HCOONa$$

4. **(c) :** Formaldehyde does not contain α-hydrogen so will not undergo aldol condensation.

5. **(a) :** More is the no. of Cl atoms attached to α – carbon of – COOH group, greater is the acidity due to high electronegativity of Cl – atom (it pulls electrons towards itself).

6. **(d)**

7. **(a) :** $\underset{\text{Benzaldehyde}}{2C_6H_5CHO} \xrightarrow{\text{al. KCN}} \underset{\text{Benzoin}}{C_6H_5CH(OH)COC_6H_5}$

Thus in this reaction benzoin is formed. The reaction is known as benzoin condensation.

8. **(c) :** $RCH_2CH_2OH \xrightarrow{PBr_3} RCH_2CH_2Br \xrightarrow{KCN}$

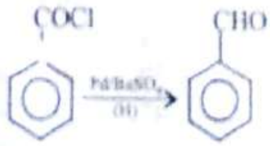
$$RCH_2CH_2CN \xrightarrow[H_2O]{H^+} RCH_2CH_2COOH$$

9. **(d) :** – Cl, – OH and – NH_2 groups are all o/p directing while – COOH group is a strong *m*-directing group (due to its electron withdrawing effect).

10. **(d) :** $CH_3CH_2C\equiv CH \xrightarrow[\text{alkaline } KMnO_4]{\text{Cold}}$

$$CH_3CH_2COOH + HCOOH$$

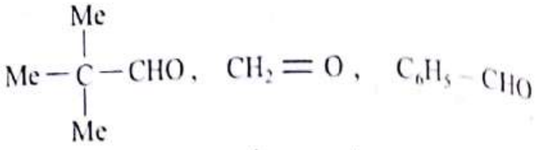
11. **(b) :**



Benzal chloride   Benzaldehyde

This reaction is called Rosenmund reaction.

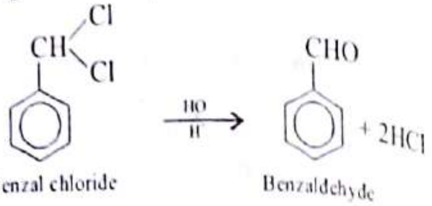
12. **(c) :** Cannizzaro's reaction is given by those aldehydes and ketones which do not contain any α-hydrogens.



$$Me-\overset{Me}{\underset{Me}{C}}-CHO,\quad CH_2=O,\quad C_6H_5-CHO$$

No α-hydrogen atom is present.

13. **(c) :**



Benzal chloride   Benzaldehyde

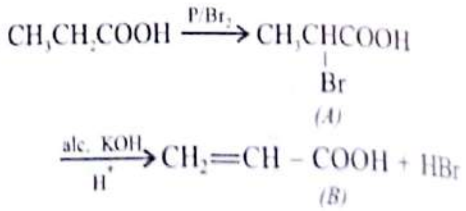
14. **(a) :** Phosphorus trichloride is a chlorinating agent which converts acid to its corresponding acid chloride.

15. **(d) :** Vinegar is 6–10% aqueous solution of acetic acid.

16. **(b) :** Carboxylic acids react with carbonates forming corresponding salts thus evolution of CO_2 must be from carbonates.

$$2RCOOH + Na_2CO_3 \rightarrow 2RCOONa + H_2O + CO_2\uparrow$$

17. **(a) :**



$$CH_3CH_2COOH \xrightarrow{P/Br_2} \underset{(A)}{CH_3\underset{Br}{C}HCOOH} \xrightarrow[H^+]{\text{alc. KOH}} \underset{(B)}{CH_2=CH-COOH} + HBr$$

P + Br_2 is brominating agent that brominates the α-position. The product then undergoes dehydrohalogenation in the presence of alcoholic potassium hydroxide.

18. **(d) :** Fluorine is a highly electronegative element, it withdraws electron from the neighbouring atoms. Therefore, more is the number of fluorine atoms attached, greater will be the acidity of the molecules e.g. FCH_2COOH is more acidic than CH_3COOH. Therefore, correct order of acidity is :

$$CF_3COOH > CF_2HCOOH > FCH_2COOH > CH_3COOH$$

19. **(b) :** Aldol condensation : When a carbonyl compound containing α-hydrogen is treated with a base, first of all carbanion is formed which acts as an intermediate.

e.g. $CH_3CHO \xrightarrow[NaOH]{OH} \overset{-}{C}H_2-CHO$

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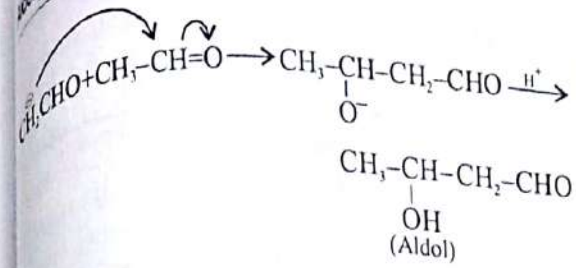
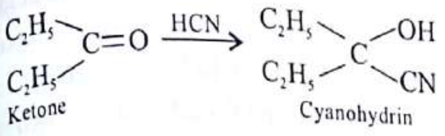


20. (c) : Cyanohydrin can be prepared easily by the reaction of HCN with carbonyl compounds (*i.e.* ketones).



21. (c)

22. (b) : In the given reaction aldehyde (C_6H_5CHO) reacts with aniline ($C_6H_5NH_2$), they form imine ($C_6H_5-N{=}CHC_6H_5$) which is known as Schiff's base.

23. (b)

24. (b) : Only $CH_3COOC_2H_5$ will give ethanol (C_2H_5OH) after hydrolysis (which can give positive iodoform test).

$CH_3COOCH_3 \rightarrow CH_3COOH + CH_3OH$

$CH_3COOC_2H_5 \rightarrow CH_3COOH + CH_3CH_2OH$

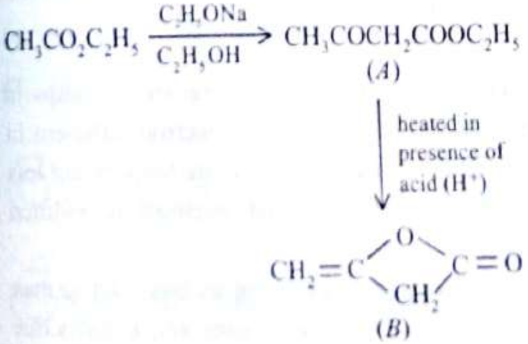
$C_6H_5COOCH_3 \rightarrow C_6H_5COOH + CH_3OH$

$CH_3COOC_6H_5 \rightarrow CH_3COOH + C_6H_5OH$

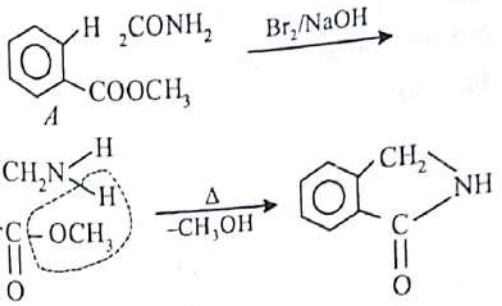
25. (a) : Acetophenone does not give addition reaction with $NaHSO_3$.

26. (c) : $-CH_3$ group is *o*- and *p*- directing group, however $-COOH$ group is *meta* directing, thus the new entering electrophile occupies the position which should be *m*- with respect to $-COOH$ group and *p*- with respect to $-CH_3$ group.

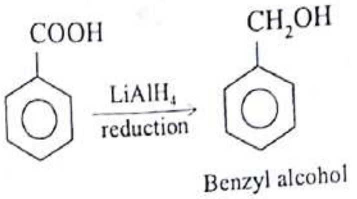
27. (c) : *Claisen condensation*



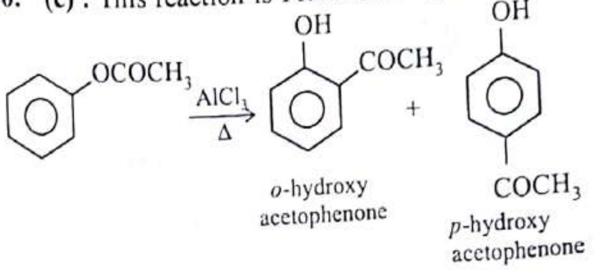
28. (c) :



29. (b) :

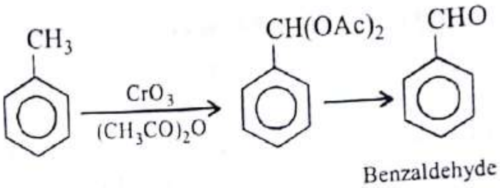


30. (c) : This reaction is Fries rearrangement

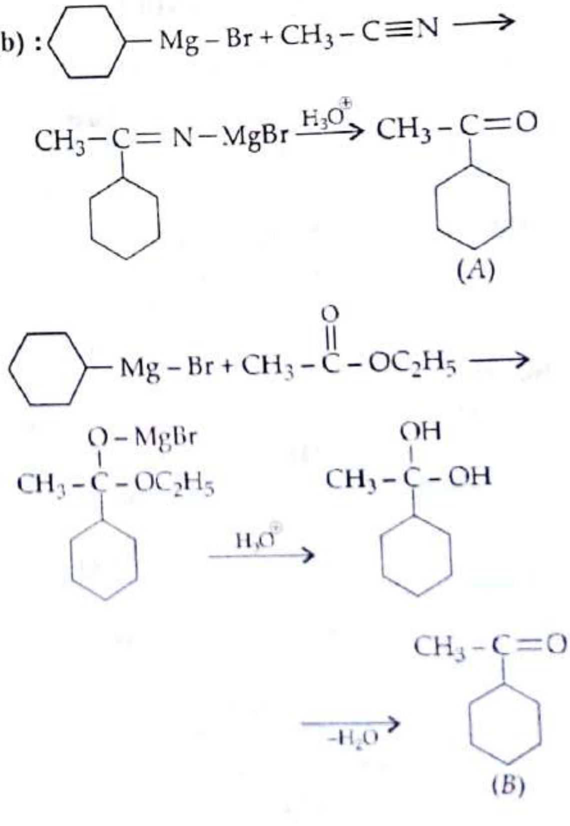


31. (c)

32. (a) :



33. (b) :



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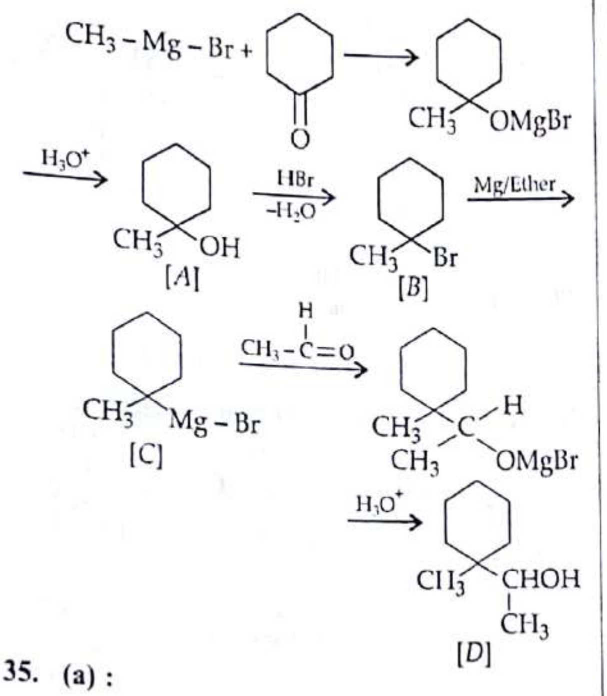
Thus in both cases, the same product, cyclohexyl methyl ketones is formed.

34. **(a) :**



35. **(a) :**

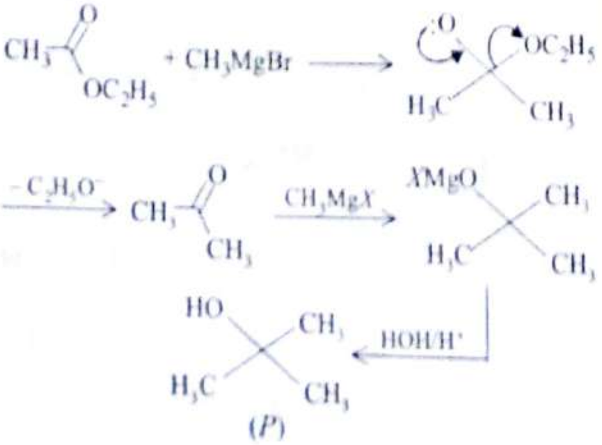
$$\begin{tikzcd} \underset{A}{C_3H_8O} \arrow[r, "K_2Cr_2O_7/H^+"] & \underset{B}{C_3H_6O} \arrow[r, "\text{amm. AgNO}_3"] \arrow[dr, "H_2NCONHNH_2\cdot HCl"'] & \text{Silver mirror} \\ & & C \end{tikzcd}$$

Reaction of *B* indicates that *B* is an aldehyde thus *B* should be C_2H_5CHO or CH_3CH_2CHO and therefore *C* should be $CH_3CH_2CH = NNHCONH_2$.

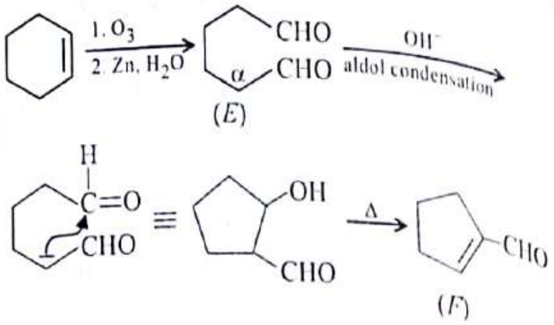
$$\begin{tikzcd} \underset{[A]}{CH_3CH_2CH_2OH} \arrow[r, "{[O]}"] & \underset{[B]}{CH_3CH_2CHO} \arrow[d, "\text{Silver mirror test}"] \\ & CH_3CH_2COOH + 2Ag\downarrow \end{tikzcd}$$

$$CH_3CH_2CHO + \underset{\text{semicarbazide}}{H_2NNHCONH_2} \longrightarrow \underset{\text{semicarbazone } [C]}{CH_3CH_2CH{=}NNHCONH_2}$$

36. **(a) :**

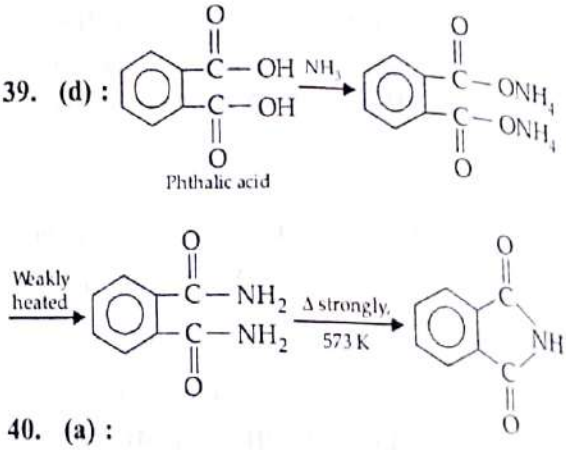


37. **(a) :**

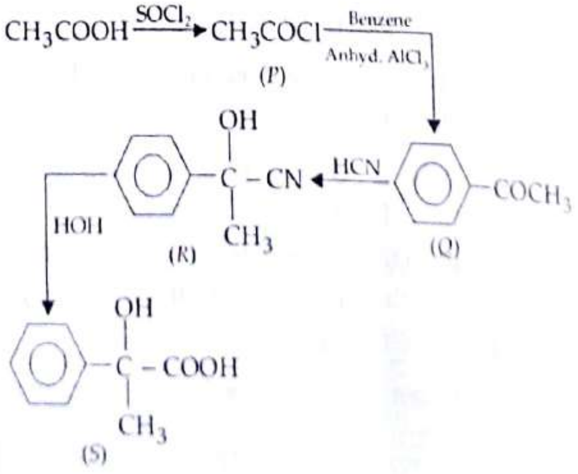


38. **(d) :** CH_3COCH_2COOH is a β-keto acid. Thus decarboxylation is maximum in a carboxylic acid containing an electron withdrawing group such as >CO or – COOH at the β-carbon atom with respect to the – COOH group.

39. **(d) :**



40. **(a) :**



41. **(a) :** Two electron releasing alkyl groups in ketones make the carbon less electron deficient in comparison to aldehydes. Therefore ketones are less reactive than aldehydes towards nucleophilic addition reactions.

Aromatic aldehydes and ketones are less reactive than corresponding aliphatic aldehydes and ketones due to +*R* effect of benzene ring.

Aromatic aldehy
ketones which i
ketones.
Since –Cl is m
increases the re
So, the order is
Cl – CH₂ – Cl
(IV)

42. (d) :

43. (a) :

44. (d

45. (a
group
group
concer

46. (

47. (

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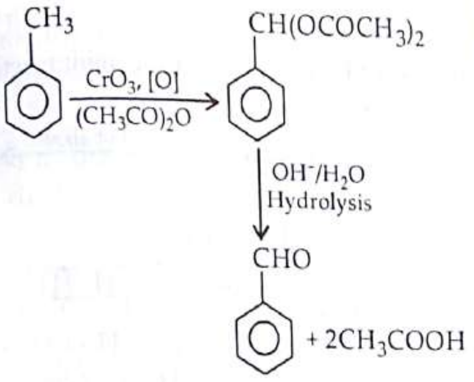
Aromatic aldehydes are more reactive than alkyl aryl ketones which in turn are more reactive than diaryl ketones.

Since –Cl is more electronegative than carbon, it increases the reactivity.

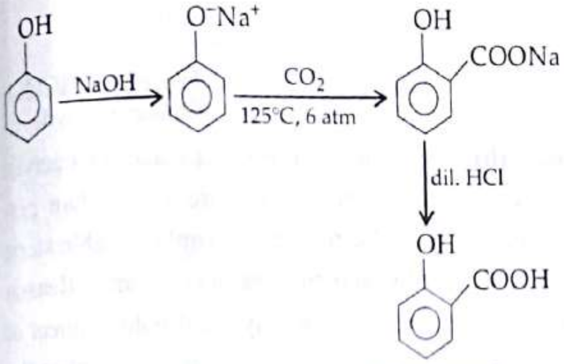
So, the order is

$$\underset{(IV)}{Cl-CH_2-CHO} > \underset{(III)}{C_6H_5CHO} > \underset{(II)}{CH_3COC_2H_5} > \underset{(I)}{C_6H_5COCH_3}$$

42. (d) :



43. (a) :



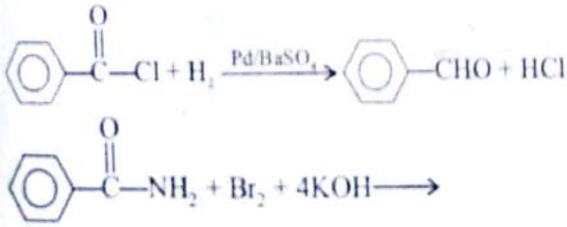
Salicylic acid

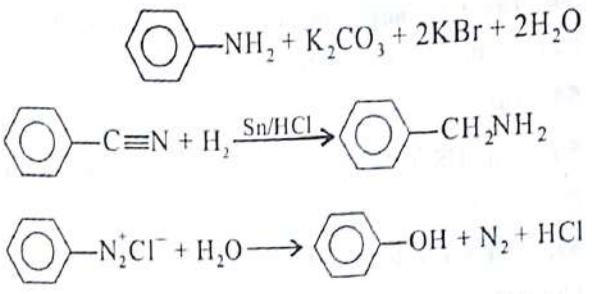
44. (d) :

45. (a) : In Clemmensen reduction, the carbonyl group of aldehydes and ketones is reduced to – CH_2 group on treatment with zinc amalgam and concentrated hydrochloric acid.

46. (b)

47. (a) :

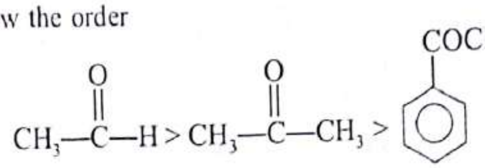




48. (d)

49. (b) : Aromatic aldehydes and ketones are less reactive than the corresponding aliphatic analogues towards nucleophilic addition reactions due to the +*R* effect of benzene ring. Further, aldehydes are more reactive than ketones due to +*I* effect and steric effect of alkyl group.

Therefore, the ease of nucleophilic addition will follow the order



50. (d)

51. (b) : Lower aldehydes and ketones are soluble in water due to polar effect of >C═O which makes hydrogen bonds with water molecules. As the size of the aldehydes and ketones increases the hydrophobic part *i.e.*, alkyl chain increases which weakens the H-bond formations with H_2O molecules and decreases the solubility.

52. (b) : Formic acid behaves as reducing agent as it is oxidised to an unstable acid, carbonic acid, which decomposes into CO_2 and H_2O.

$$HCOOH + 2HgCl_2 \xrightarrow{\Delta} Hg_2Cl_2 + CO_2 + 2HCl$$

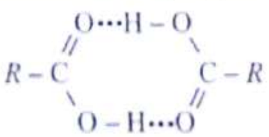
$$HCOOH + Hg_2Cl_2 \rightarrow CO_2 + 2HCl + 2Hg \text{ (Black)}$$

Acetic acid remains unaffected by mercuric chloride, as it does not show reducing properties.

53. (a) : Amides are $R-CONH_2$

Acids are $R-COOH$

Due to the presence of $-NH_2$ group in amides there is stronger hydrogen bonding between the amide molecules than that between the acid molecules. Some acids are rather present in dimer form due to the presence of intermolecular hydrogen bonding.



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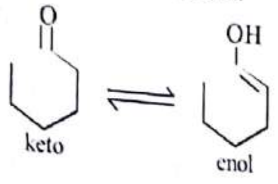
54. (a) : Grignard reagents are very reactive and can react with hydroxyl group.

55. (a)

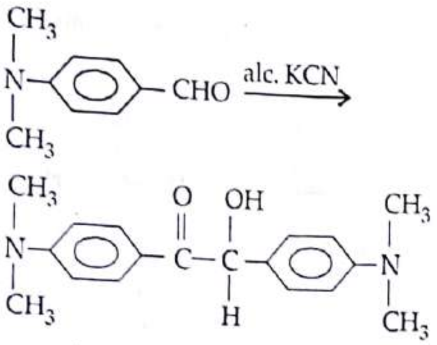
56. (b) : HSO_3^- is a bulky nucleophile, hence, cannot attack on sterically hindered ketones.

57. (a) : Cyclohexanone exists in two readily interconvertible different structures leading to dynamic equilibrium known as tautomerism.

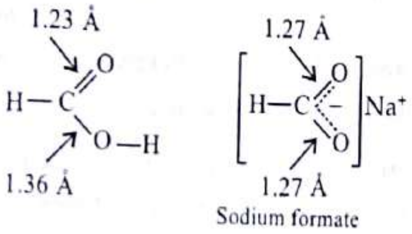


58. (a)

59. (b) :



60. (a) : Formate ion shows resonance and gives rise to identical bond lengths.

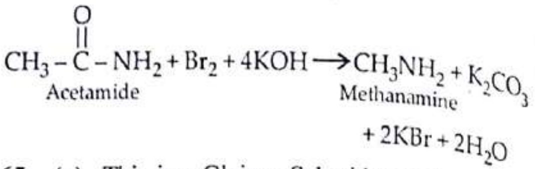


61. (c) : It is known that esters with α-hydrogens form carbanion when treated with base. It brings about nucleophilic substitution at the carbonyl group of the other molecule of the ester to yield β-keto ester. $LiAlH_4$ reduces esters to alcohols.

62. (b) : Both carbanions (formed in presence of base) and enol form (formed in presence of an acid) act as nucleophiles and hence add on the carbonyl group of aldehydes and ketones to give aldols.

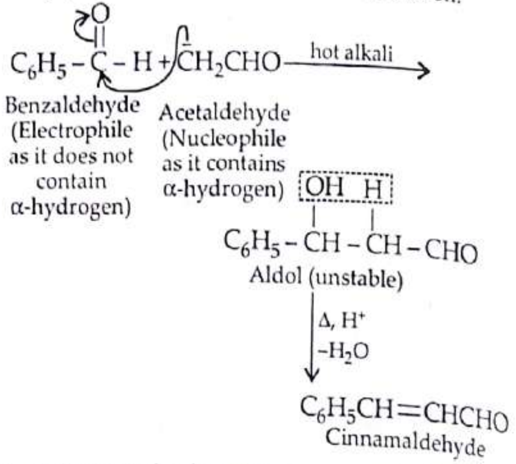
63. (d) : Oxidation of toluene using CrO_3 in acetic anhydride or CrO_2Cl_2 in CCl_4 or CS_2 and then hydrolysis gives benzaldehyde. No such intermediate is formed.

64. (d) :



$$\underset{\text{Acetamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methanamine}}{CH_3NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

65. (a) : This is a Claisen-Schmidt reaction.



66. (b) : Assertion is true because usually, for acrylic systems *trans*-isomers are more stable than *cis*-isomers. This is due to increased unfavourable steric interaction of the substituents in *cis*-isomer. Reason is also true because generally the dipole moment of *trans*-form is zero (or less) depending whether the substituents on both sides of double bond are same or not while *cis*-forms are polar in nature with certain value of dipole moment.

67. (a)

68. (c) : Aromatic aldehydes and formaldehyde do not contain α-hydrogen and thus undergo Cannizzaro reaction. Formaldehyde is more reactive than aromatic aldehydes.

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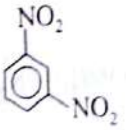
CHAPTER 27

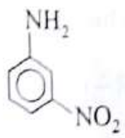
ORGANIC COMPOUNDS CONTAINING NITROGEN

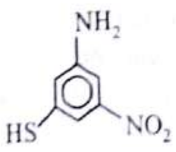
1. In the presence of an acid, hydrolysis of methyl cyanide produces
(a) methyl alcohol (b) acetic acid
(c) formic acid (d) methylamine.
(1995)

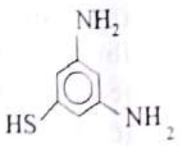
2. Which of the following is urotropine?
(a) Hexamethylenetetraamine
(b) Hexamethyldiamine
(c) Hexamethylenetriamine
(d) None of these. *(1996)*

3. The main product (70% to 80%) of the reaction between *m*-dinitrobenzene with NH_4HS is

(a) 

(b) 

(c) 

(d) 

(1997)

4. Reaction of nitrous acid with aliphatic primary amine will give
(a) dye (b) alcohol
(c) nitrite (d) diazonium salt.
(1997)

5. Nitrosoamines ($R_2N-N=O$) are soluble in water. On heating them with concentrated H_2SO_4, they give secondary amines. This reaction is called
(a) Sandmeyer's reaction
(b) Fittig's reaction
(c) Perkin reaction
(d) Liebermann's nitroso reaction
(1998)

6. Acetamide is treated separately with the following reagent. Which one of these would give methylamine?
(a) $HBr + NaOH$ (b) $NH_4OH + Br_2$
(c) $KOH + Br_2$ (d) None of these
(1998)

7. The reaction of primary amine with chloroform and ethanolic KOH, is called
(a) Reimer-Tiemann reaction
(b) Kolbe's reaction
(c) Carbylamine reaction
(d) None of these. *(1998)*

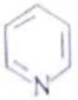
8. Acetamide and ethylamine can be distinguished by reacting with
(a) dilute HCl and heat
(b) NaOH solution and heat
(c) acidified $KMnO_4$
(d) Br_2 water. *(2000)*

9. Among the following the weakest base is
(a) $C_6H_5CH_2NH_2$ (b) $C_6H_5CH_2NHCH_3$
(c) $O_2NCH_2NH_2$ (d) CH_3NHCHO
(2003)

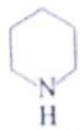
10. Nitrobenzene gives *N*-phenylhydroxylamine by
(a) Sn/HCl (b) H_2/Pd-C
(c) Zn/NaOH (d) Zn/NH_4Cl
(2003)

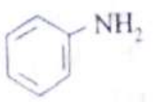
11. Among the following the dissociation constant is highest for
(a) C_6H_5OH (b) $C_6H_5CH_2OH$
(c) $CH_3C\equiv CH$ (d) $CH_3NH_3^+Cl^-$
(2004)

12. The strongest base among the following is

(a) 

(b) 

(c) 

(d) 

(2004)

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13. Aromatic nitriles (ArCN) are not prepared by reaction:
(a) $ArX + KCN$ (b) $ArN_2^+ + CuCN$
(c) $ArCONH_2 + P_2O_5$ (d) $ArCONH_2 + SOCl_2$
(2004)

14. Melting points are normally the highest for
(a) tertiary amides (b) secondary amides
(c) primary amides (d) amines.
(2004)

15. Which of the following chemicals are used to manufacture methyl isocyanate that caused "Bhopal Gas Tragedy"?
(i) Methylamine (ii) Phosgene
(iii) Phosphine (iv) Dimethylamine.
(a) (i) and (iii) (b) (iii) and (iv)
(c) (i) and (ii) (d) (ii) and (iv)
(2005)

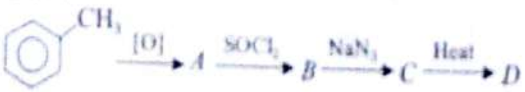
16. Among the following which one does not act as an intermediate in Hoffmann rearrangement?
(a) $RNCO$ (b) $RCO\ddot{N}$
(c) $RCO\ddot{N}HBr$ (d) RNC *(2005)*

17. Pyridine is less basic than triethylamine because
(a) pyridine has aromatic character
(b) nitrogen in pyridine is sp^2 hybridised
(c) pyridine is a cyclic system
(d) in pyridine, lone pair of nitrogen is delocalised. *(2005)*

18. $C_6H_5CONHCH_3$ can be converted into $C_6H_5CH_2NHCH_3$ by
(a) $NaBH_4$ (b) H_2-Pd/C
(c) $LiAlH_4$ (d) Zn-Hg/HCl
(2005)

19. Nitrobenzene on treatment with zinc dust and aqueous ammonium chloride gives
(a) $C_6H_5N{=}N{-}C_6H_5$ (b) $C_6H_5NH_2$
(c) C_6H_5NO (d) C_6H_5NHOH
(2006)

20. In the following sequence of the reactions, what is *D*?



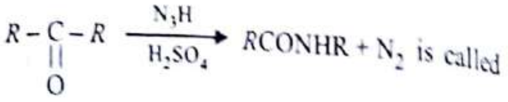
(a) Primary amine
(b) An amide
(c) Phenyl isocyanate
(d) A chain lengthed hydrocarbon
(2007)

21. Cyanogen gas is obtained in the reaction
(a) $CuSO_{4(aq)} + KCN \longrightarrow$
(b) $K_4[Fe(CN)_6] \xrightarrow{heat}$
(c) $CH_3CN + H_2O \xrightarrow{\Delta}$
(d) $CH_3CONH_2 + P_2O_5 \xrightarrow{\Delta}$
(2007)

22. Which of the following amines will not give N_2 gas on treatment with nitrous acid ($NaNO_2 + HCl$)?
(a) $C_2H_5NH_2$ (b) CH_3NH_2
(c) $(CH_3)_2CH-NH_2$ (d) All will give N_2
(2007)

23. Which of the following statement is true?
(a) Trimethyl amines form a soluble compound with Hinsberg reagent and KOH.
(b) Dimethylamines react with KOH and phenol to form an azo dye.
(c) Methylamine reacts with nitrous acid and liberates N_2 from aq. soln.
(d) None of these.
(2007)

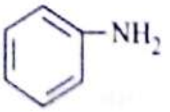
24. The reaction,

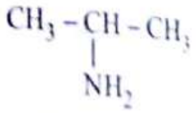


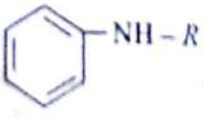
$$R-\underset{\underset{O}{\|}}{C}-R \xrightarrow[H_2SO_4]{N_3H} RCONHR + N_2$$ is called

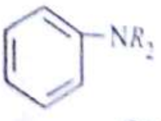
(a) Claisen-Schmidt reaction
(b) Kolbe-Schmidt reaction
(c) Schmidt reaction
(d) Kolbe's reaction. *(2008)*

25. Which of the following amines, can give *N*-nitrosoamine on treatment with HNO_2?

(a) 

(b) 
$CH_3-\underset{\underset{NH_2}{|}}{CH}-CH_3$

(c) 

(d) 

(2008)

26. Toluene is nitrated and the resulting product is reduced with tin and hydrochloric acid. The product so obtained is diazotised and then heated with cuprous bromide. The reaction mixture so formed contains
(a) mixture of *o*- and *m*-bromotoluenes
(b) mixture of *o*- and *p*-bromotoluenes
(c) mixture of *o*- and *p*-dibromobenzenes
(d) mixture of *o*- and *p*-bromo anilines.
(2008)

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27. The reaction of an organic compound with ammonia followed by nitration of the product gives a powerful explosive called RDX. The organic compound is

(a) phenol (b) toluene

(c) glycerine (d) formaldehyde.

(2008)

28. Which of the following reactions does not yield an amine?

(a) $R-X+NH_3 \longrightarrow$

(b) $R-CH{=}NOH+[H]\xrightarrow{Na/C_2H_5OH}$

(c) $R-CN+H_2O\xrightarrow{H^+}$

(d) $R-CONH_2\xrightarrow{LiAlH_4}$

(2010)

29. The compound which on reaction with aqueous nitrous acid at low temperature produces an oily nitrosoamine is

(a) methyl amine (b) ethyl amine

(c) diethyl amine (d) triethyl amine.

(2010)

30. Best method to form aromatic iodide is

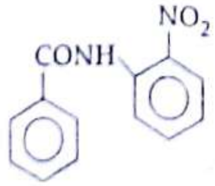
(a) $ArN_2^+ + HI \rightarrow$ (b) $RNH_2 + I_2 \rightarrow$

(c) $ArN_2^+ + KI \rightarrow$ (d) $ArN_2^+ + PI_3 \rightarrow$

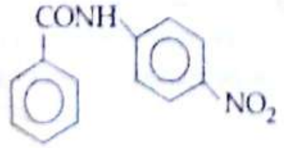
(2011)

31. Which is the major product formed when $C_6H_5CONHC_6H_5$ undergoes nitration?

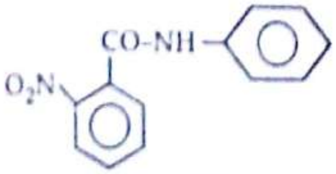
(a)



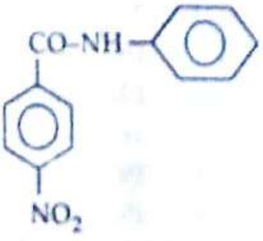
(b)



(c)



(d)



(2012)

32. Nitrobenzene $(PhNO_2)\xrightarrow{Zn+NH_4Cl}P$

P will be

(a) $C_6H_5NH_2$ (b) C_6H_5NHOH

(c) $C_6H_5-N{=}O$ (d) C_6H_6

(2012)

33. $PhCH_2Cl \xrightarrow{aq\ NaCN} ? \xrightarrow{Catalytic\ hydrogenation} (U)$

The final product (U) is :

(a) $C_6H_5CH_2CH_2NH_2$ (b) $C_6H_5CH_2CONH_2$

(c) $C_6H_5CH_2NH_2$ (d) $C_6H_5CH_2NHCH_3$

(2012)

34. Reaction of aniline with HNO_2 followed by treatment of dilute acid gives

(a) C_6H_5NHOH (b) C_6H_5OH

(c) $C_6H_5NHNH_2$ (d) C_6H_6 *(2013)*

35. Which of the following will give carbylamine test?

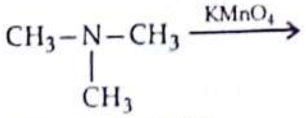
(a) CH_3NH_2 (b) CH_3NHCH_3

(c) $CH_3N(CH_3)CH_3$ (d) CH_3CONH_2

(2013)

36. Which of the following does not give nitroalkane?

(a)



$CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3 \xrightarrow{KMnO_4}$

(b) $C_2H_5I \xrightarrow{alc.\ AgNO_2}$

(c) $CH_3-CH_3 \xrightarrow{Fuming\ HNO_3}$

(d) Both (a) and (b) *(2013)*

37. Which one of the following forms propanenitrile as the major product?

(a) Propyl bromide + alcoholic KCN

(b) Ethyl bromide + alcoholic KCN

(c) Ethyl bromide + alcoholic AgCN

(d) Propyl bromide + alcoholic AgCN

(2014)

38. The reaction of a primary amine with chloroform and ethanolic solution of KOH is called

(a) Hoffmann's reaction

(b) Coupling reaction

(c) Carbylamine reaction

(d) Curtius reaction. *(2015)*

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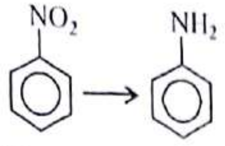
39. Which of the following reagents cannot be used for the given conversion?



(a) Sn-HCl
(b) Fe-HCl
(c) $LiAlH_4$
(d) Pd/C *(2016)*

40. Which amine amongst the following will answer positively the carbylamine test?

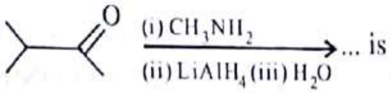
(a) $C_6H_5-NH-CH_3$

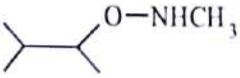
(b) 

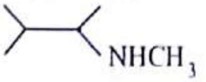
(c) $C_6H_5-NH-C_4H_9$

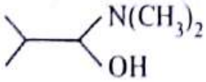
(d) $C_6H_5-N(C_2H_5)_2$ *(2016)*

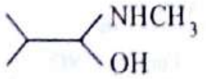
41. The major organic product formed in the following reaction



(a) 

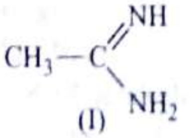
(b) 

(c) 

(d) 

(2016)

42. What is the correct order of basicity among the following compounds ?


$CH_3-C(=NH)NH_2$
(I)

$CH_3-CH_2-NH_2$
(II)

$(CH_3)_2NH$
(III)


$CH_3-\overset{O}{\overset{\|}{C}}-NH_2$
(IV)

(a) II > I > III > IV
(b) I > II > III > IV
(c) III > I > II > IV
(d) I > III > II > IV *(2017)*

ASSERTION AND REASON

43. ***Assertion*** : $p\text{-}O_2N-C_6H_4COCH_3$ is prepared by Friedel Crafts acylation of nitrobenzene.
Reason : Nitrobenzene easily undergoes electrophilic substitution reaction. *(2005)*

44. ***Assertion*** : Alkyl isocyanides in acidified water give alkyl formamides.
Reason : In isocyanides, carbon first acts as a nucleophile and then as an electrophile. *(2005)*

45. ***Assertion*** : Anilinium chloride is more acidic than ammonium chloride.
Reason : Anilinium ion is not resonance stabilised. *(2006, 2008)*

46. ***Assertion*** : Benzene diazonium salt on boiling with water forms phenol.
Reason : C – N bond is polar. *(2007)*

47. ***Assertion*** : C_2H_5Br reacts with alcoholic solution of $AgNO_2$ to form nitroethane as the major product.
Reason : NO_2^- is an ambidient ion. *(2009)*

48. ***Assertion*** : When acetamide reacts with NaOH and Br_2, methyl amine is formed.
Reason : The reaction occurs through intermediate formation of isocyanate. *(2016)*

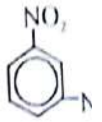
Answer Key

1.	(b)	**2.**	(a)	**3.**	(b)	**4.**	(b)	**5.**	(d)	**6.**	(c)	**7.**	(c)	**8.**	(b)
9.	(c)	**10.**	(d)	**11.**	(d)	**12.**	(c)	**13.**	(a)	**14.**	(c)	**15.**	(c)	**16.**	(d)
17.	(d)	**18.**	(d)	**19.**	(d)	**20.**	(c)	**21.**	(a)	**22.**	(d)	**23.**	(c)	**24.**	(c)
25.	(c)	**26.**	(b)	**27.**	(b)	**28.**	(c)	**29.**	(c)	**30.**	(c)	**31.**	(b)	**32.**	(b)
33.	(a)	**34.**	(b)	**35.**	(a)	**36.**	(a)	**37.**	(b)	**38.**	(c)	**39.**	(c)	**40.**	(b)
41.	(b)	**42.**	(d)	**43.**	(d)	**44.**	(a)	**45.**	(c)	**46.**	(b)	**47.**	(b)	**48.**	(a)

---

1. **(b)** : CH_3CN

2. **(a)** : When
ammonia, it forms
is known as urot
6HCHO +
Formaldehyde

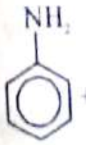
3. **(b)** : 

4. **(b)** : $R-NH$

5. **(d)** : Nitr
secondary amin
$HO-NO+H^+$
R_2NH+NO^+
Nitrosoamines a
by boiling with
$R_2N-NO+H_2$
The above rea
nitroso reactio
secondary ami

6. **(c)** : Th
Hoffmann's br
$RCONH_2 \xrightarrow{Br_2/KC}$

7. **(c)** : 1°
ethanoholic
carbylamine)
is known as
detection of



8. **(b)** : A
heat, change
not underg
CH_3CONH_2
Acetamide

9. **(c)** : In
exerts a str
which bas

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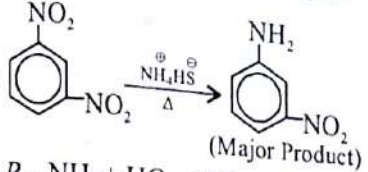
EXPLANATIONS

1. **(b) :** $CH_3CN \xrightarrow[H_2O]{H^+} CH_3-CO-NH_2$
$\xrightarrow[H_2O]{H^+} CH_3COOH + NH_3$
(Acetic acid)

2. **(a) :** When formaldehyde reacts with ammonia, it forms hexamethylenetetraamine, which is known as urotropine.

$$\underset{\text{Formaldehyde}}{6HCHO} + 4NH_3 \rightarrow \underset{\text{Urotropine}}{(CH_2)_6N_4} + 6H_2O$$

3. **(b) :** 

4. **(b) :** $R-NH_2 + \underset{\text{Nitrous acid}}{HO-NO} \rightarrow R-OH + N_2 + H_2O$

5. **(d) :** Nitrosoamines are prepared from secondary amines with nitrous acid.

$HO-NO + H^+ \rightleftharpoons H_2O + NO^+$

$R_2NH + NO^+ \rightleftharpoons R_2NH^+NO \rightarrow R_2N-NO + H^+$

Nitrosoamines are readily hydrolysed to the amines by boiling with concentrated H_2SO_4 (or dil.HCl).

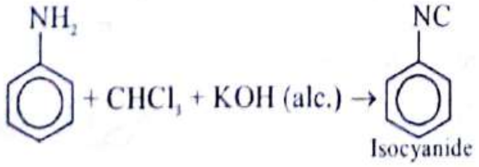
$R_2N-NO + H_2O \xrightarrow[\text{or } H_2SO_4]{HCl} R_2NH + HNO_2$

The above reaction is known as Liebermann's nitroso reaction and it is used for detection of secondary amine.

6. **(c) :** The reaction involved is called as Hoffmann's bromamide reaction.

$RCONH_2 \xrightarrow{Br_2/KOH} RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

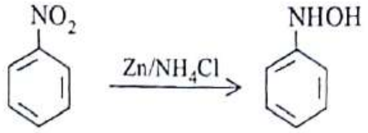
7. **(c) :** 1° amines on heating with $CHCl_3$ and ethanoholic KOH forms isocyanides (or carbylamine) which possess bad smell. This reaction is known as carbylamine reaction and used for detection of 1° amines.



8. **(b) :** Acetamide in the presence of NaOH and heat, changes to acetic acid while ethylamine does not undergo any such reaction.

$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow{NaOH/\Delta} CH_3COOH + NH_3\uparrow$

9. **(c) :** In compound, $O_2NCH_2NH_2$, $-NO_2$ group exerts a strong electron withdrawing effect due to which basicity at $-N$ atom decreases.

10. **(d) :** 

11. **(d) :** $CH_3\overset{+}{N}H_3\overset{-}{Cl}$ is a salt which can be completely ionized in aqueous solution and hence, have highest dissociation constant.

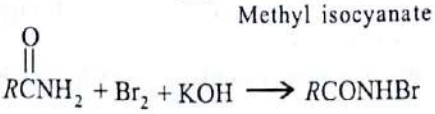
12. **(c) :** The basicity is a measure of a compound's ability to accept a proton (H^+). (b) and (d) are weaker bases as the lone pair are involved in resonance. In (a) carbon adjacent to N is sp^2 hybridised hence is more electronegative therefore, pulls the electron density from nitrogen.

13. **(a)**

14. **(c) :** Melting points are normally higher for primary amides due to presence of hydrogen bonding.

15. **(c) :** Methyl isocyanate is industrially prepared by the action of methyl amine with phosgene.

$CH_3NH_2 + COCl_2 \xrightarrow{-HCl} [CH_3NH-CO-Cl]$
$\xrightarrow[-HCl]{\Delta} \underset{\text{Methyl isocyanate}}{CH_3-N{=}C{=}O}$

16. **(d) :** (i) 
$R\overset{\overset{O}{\|}}{C}NH_2 + Br_2 + KOH \longrightarrow RCONHBr + KBr + H_2O$

(ii) $RCONHBr + KOH \rightarrow RNCO + KBr + H_2O$

(iii) $RNCO + 2KOH \rightarrow RNH_2 + K_2CO_3$

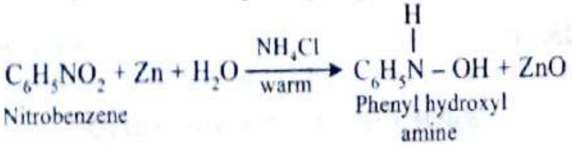
$RCONH_2 + Br_2 + 4KOH \rightarrow RNH_2 + 2KBr + K_2CO_3 + 2H_2O$

17. **(d) :** Basicity of amines is due to availability of an unshared pair (lone pair) of electrons on nitrogen. This lone pair of electrons is available for the formation of a new bond with a proton or Lewis acid. Pyridine is less basic than triethylamine because lone pair of nitrogen in pyridine is delocalised.

18 **(d):** $C_6H_5CONHCH_3 \xrightarrow[HCl]{Zn-Hg} C_6H_5CH_2NHCH_3$

This reaction is known as Clemmenson reduction.

19. **(d) :** When reduced with a neutral reducing agent like zinc dust and aqueous ammonium chloride, nitrobenzene gives phenyl hydroxyl amine.


$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + Zn + H_2O \xrightarrow[\text{warm}]{NH_4Cl} \underset{\text{Phenyl hydroxyl amine}}{C_6H_5\overset{\overset{H}{|}}{N}-OH} + ZnO$

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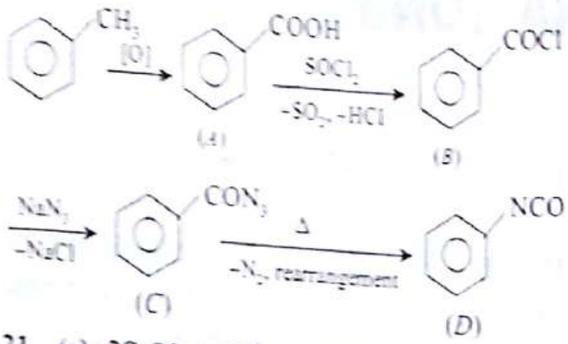
20. (c) :



21. (a) : $2CuSO_4 + 4KCN \rightarrow (CN)_2 + 2CuCN + 2K_2SO_4$
On combining solution of copper (II) salts and cyanides, an unstable copper (III) cyanide is formed which rapidly decomposes into copper (I) cyanide and cyanogen.

22. (d) : All aliphatic primary amines liberate N_2 gas on treatment with HNO_2.

$$R-NH_2 + HONO \xrightarrow{273-278\text{ K}} R-OH + N_2 + H_2O$$

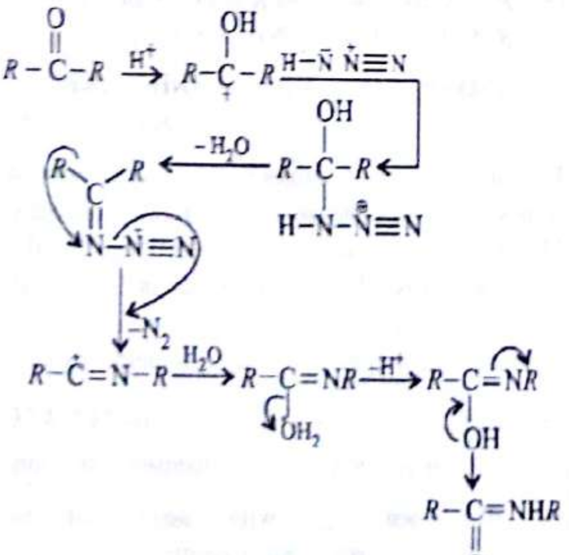
Since no other class of amines liberate N_2 gas on treatment with HNO_2, this reaction is used as a test for aliphatic primary amines.

23. (c) : Aliphatic 1° amines react with cold nitrous acid to give alcohols with quantitative evolution of N_2 gas.

$$\underset{\text{Methylamine}}{CH_3NH_2} + HONO \xrightarrow{273-278\text{K}} CH_3OH + N_2 + H_2O$$

This reaction is used as a test for aliphatic primary amines.

24. (c) :

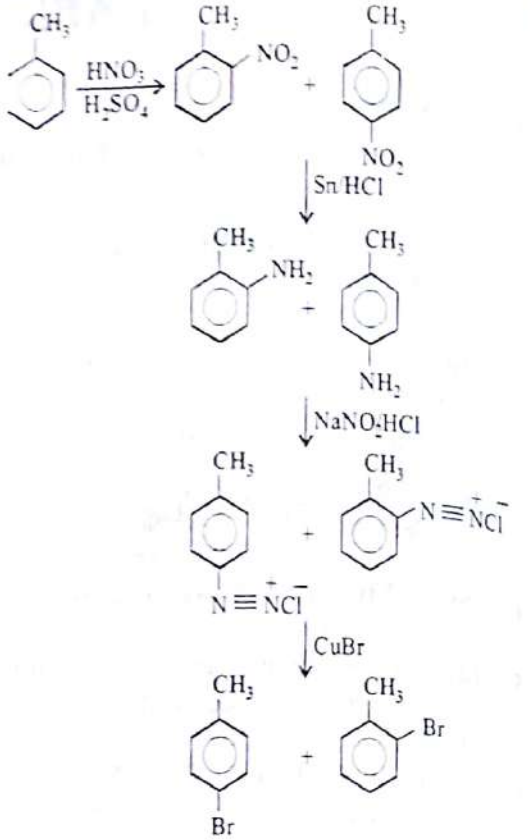


This is Schmidt reaction.

25. (c) : Secondary amines form nitrosoamines which are yellow oily liquids insoluble in water.

$$R_2NH + HONO \rightarrow \underset{\text{Dialkyl nitrosoamine}}{R_2NNO} + H_2O$$

26. (b) :



27. (b) : Trinitrotoluene (TNT) with ammonium nitrate is extensively employed as blasting explosive.

28. (c) : Cyanides, on hydrolysis, give acids

$$RCN + 2H_2O \xrightarrow{H^+} RCOOH + NH_3$$

while all other reactions give amines.

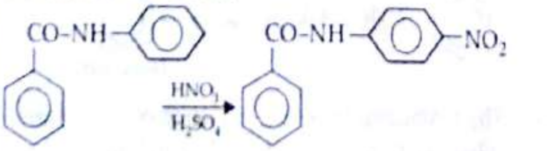
29. (c) : Secondary (2°) amines (aliphatic as well as aromatic) react with nitrous acid (HNO_2) to form *N*-nitrosoamines.

$$\underset{(2^\circ\text{amine})}{(C_2H_5)_2NH} + \underset{(\text{Nitrous acid})}{HONO} \longrightarrow \underset{(N\text{-nitrosodiethylamine})}{(C_2H_5)_2N-N=O} + H_2O$$

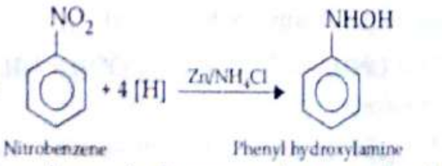
30. (c)

31. (b) : The ring attached to the nitrogen atom in benzanilide is strongly activated towards electrophilic substitution reaction.

∴ Nitration occurs at *p*-position to the ring attached to 'N' atom.



32. (b) :



In neutral medium, nitrobenzene reduces to phenyl hydroxylamine.

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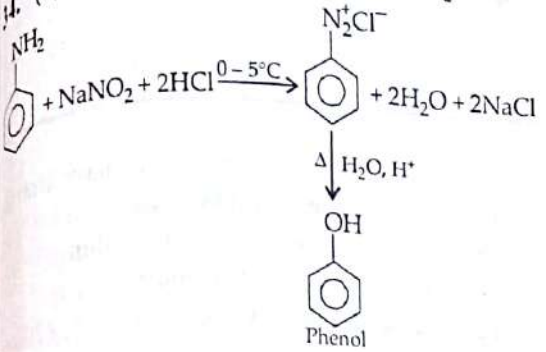
3. **(a) :** $PhCH_2Cl \xrightarrow{aq.\ NaCN} PhCH_2CN \xrightarrow[Cat.\ hydrogenation]{H_2,\ Pd} \underset{(U)}{PhCH_2CH_2NH_2}$

4. **(b) :** $NaNO_2 + HCl \rightarrow NaCl + HNO_2$



35. **(a) :** Only primary amines will give carbylamine test.

$$CH_3NH_2 + CHCl_3 + 3KOH \rightarrow \underset{(offensive\ smell)}{CH_3N \equiv C} + 3KCl + 3H_2O$$

36. **(a) :** Tertiary amines are not oxidised by $KMnO_4$.

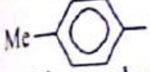
37. **(b) :** $\underset{Ethyl\ bromide}{C_2H_5Br} + KCN_{(alc.)} \xrightarrow{\Delta} \underset{\substack{Propanenitrile\\(Major\ product)}}{C_2H_5CN} + KBr$

38. **(c) :** In carbylamine reaction, aliphatic and aromatic primary amines on heating with chloroform and ethanolic KOH, form isocyanides or carbylamines which are foul smelling substances.

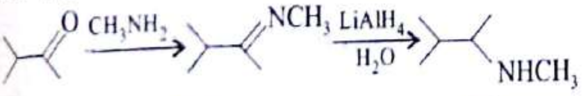
$$R\text{–}NH_2 + CHCl_3 + 3KOH_{(alc.)} \xrightarrow{\Delta} R\text{–}NC + 3KCl + 3H_2O$$

39. **(c) :** With $LiAlH_4$ nitroarenes give azo compounds.

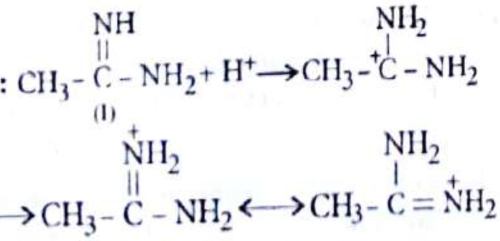
$$2C_6H_5NO_2 \xrightarrow{LiAlH_4} C_6H_5\text{—}N\text{=}N\text{—}C_6H_5$$

40. **(b) :** Only aliphatic and aromatic 1° amines (*i.e.*  NH$_2$ in the present case) give positive carbylamine test.

41. **(b) :**



42. **(d) :**



$$\underset{(I)}{CH_3\text{-}\overset{\overset{NH}{\|}}{C}\text{-}NH_2} + H^+ \rightarrow CH_3\text{-}\overset{\overset{NH_2}{|}}{\overset{+}{C}}\text{-}NH_2 \longleftrightarrow CH_3\text{-}\overset{\overset{\overset{+}{N}H_2}{\|}}{C}\text{-}NH_2 \longleftrightarrow CH_3\text{-}\overset{\overset{NH_2}{|}}{C}=\overset{+}{N}H_2$$

The conjugate acid formed by addition of a proton to I is stabilised by two equivalent resonance structures and hence, compound I is the most basic.

Further 2° amines (III) are more basic than 1° amines (II) while amides (IV) are least basic due to delocalisation of lone pair of electrons of N over the CO group. Thus, the order is : I > III > II > IV.

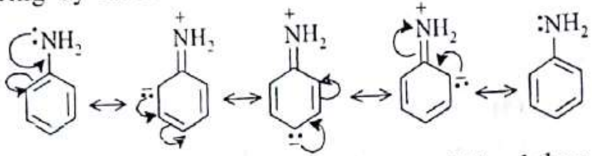
43. **(d) :** The nitro group strongly deactivates the benzene ring towards electrophilic substitution. Nitrobenzene does not undergo Friedel-Craft acylation reaction.

44. **(a) :** In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.

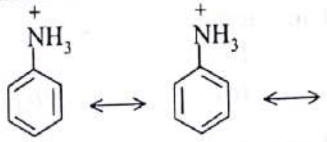
$$R\overset{+}{N} \equiv \overset{-}{C} + H_2O \longrightarrow RN{=}CHOH \longrightarrow \underset{Alkylformamide}{RNHCHO}$$

45. **(c) :** $\underset{\substack{Anilinium\ ion\\stronger\ acid}}{C_6H_5\overset{+}{N}H_3} \longrightarrow \underset{\substack{Aniline\\weaker\ conjugated\ base}}{C_6H_5NH_2} + H^+$

Aniline is weaker base than ammonium chloride. In NH_4Cl or aliphatic amines, the non-bonding electron pair of N is localized and is fully available for coordination with a proton. On the other hand, in aniline or other aromatic amines, the non-bonding electron pair is delocalised into benzene ring by resonance.

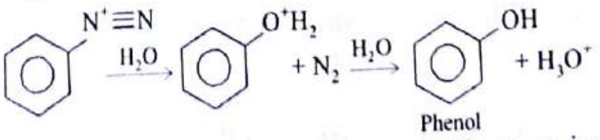


But anilinium ion is less resonance stabilised than aniline.



⟷ no other resonating structure possible

46. **(b) :** This is the substitution or replacement reaction of benzene diazonium salt, where nitrogen is lost as N_2 and different groups are introduced in its place.



47. **(b) :** The lone pair electrons on N^- atom in $AgNO_2$ attacks C_2H_5Br to form nitroethane as the major product.

48. **(a) :** $CH_3CONH_2 + Br_2 + 4NaOH \rightarrow CH_3NH_2 + Na_2CO_3 + 2NaBr + 2H_2O$

The reaction occurs through intermediate formation of alkyl isocyanate which on hydrolysis gives methylamine and sodium carbonate.

CHAPTER 28

BIOMOLECULES

1. Which of the following contains cobalt?
(a) Vitamin B_{12} (b) Haemoglobin
(c) Chlorophyll (d) Vitamin D
(1996)

2. The functional group, which is found in amino acid, is
(a) $-CH_3$ group (b) $-NH_2$ group
(c) $-COOH$ group (d) both (b) and (c).
(1998)

3. The common molecular formula for disaccharide is
(a) $C_{12}H_{22}O_{11}$ (b) $C_{10}H_{18}O_8$
(c) $C_{10}H_{20}O_{10}$ (d) $C_{18}H_{22}O_{11}$
(1999)

4. Enzymes with two sites are called
(a) apoenzyme (b) allosteric enzyme
(c) holoenzyme (d) conjugate enzyme.
(2002)

5. Subunits present in haemoglobin are
(a) 2 (b) 3
(c) 4 (d) 5 *(2003)*

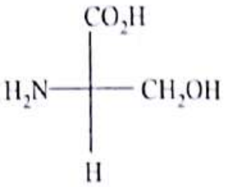
6. The nucleic acid base having two possible binding sites is
(a) thymine (b) cytosine
(c) guanine (d) adenine. *(2004)*

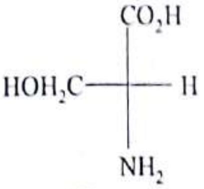
7. Which one of the following biomolecules is insoluble in water?
(a) α-Keratin (b) Haemoglobin
(c) Ribonuclease (d) Adenine *(2005)*

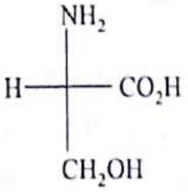
8. Which one of the following statements is true for protein synthesis (translation)?
(a) Amino acids are directly recognized by *m*-RNA.
(b) The third base of the codon is less specific.
(c) Only one codon codes for an amino acid.
(d) Every *t*-RNA molecule has more than one amino acid attachment. *(2005)*

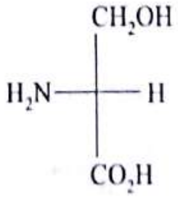
9. The pair in which both species have iron is
(a) nitrogenase, cytochromes
(b) carboxypeptidase, haemoglobin
(c) haemocyanin, nitrogenase
(d) haemoglobin, cytochromes. *(2006)*

10. Among the following L-serine is

(a)


(b)


(c)


(d)


(2006)

11. Thymine is
(a) 5-methyluracil (b) 4-methyluracil
(c) 3-methyluracil (d) 1-methyluracil.
(2006, 2015)

12. Lysine is least soluble in water in the pH range
(a) 3 to 4 (b) 5 to 6
(c) 6 to 7 (d) 8 to 9.
(2006, 2015)

13. Methyl-α-*D*-glucoside and methyl-β-*D*-glucoside are

(a) epimers
(b) anomers
(c) enantiomers
(d) conformational diastereomers. *(2006)*

14. Find the hydrolysis product when a phosphodiester bond of nucleotide breaks.
(a) 3-OH-deoxyribose-5-PO_4^{3-}
(b) 5-OH-deoxyribose-3-PO_4^{3-}
(c) 2-OH-deoxyribose-2-PO_4^{3-}
(d) 4-OH-deoxyribose-2-PO_4^{3-} *(2011)*

15. Find the hydrolysis product of maltose.
(a) α-*D*-glucose + α-*D*-glucose
(b) α-*D*-glucose + α-*D*-fructose
(c) α-*D*-glucose + α-*D*-galactose
(d) α-*D*-fructose + α-*D*-galactose *(2011)*

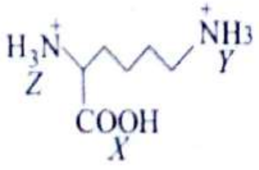
16. Which of the following is a non-reducing sugar?
(a) Sucrose (b) Maltose
(c) Lactose (d) Mannose *(2013)*

17. Maltose is made of the units
(a) α-*D* glucose and β-*D* glucose
(b) α-*D* glucose and β-*D* fructose
(c) α-*D* glucose and α-*D* glucose
(d) α-*D* glucose and β-*D* galactose. *(2014)*

18. 'Tocopherol' is the chemical name of
(a) vitamin K (b) vitamin E
(c) vitamin H (d) vitamin D *(2015)*

19. Glucose $\xrightarrow{HCN} (X) \xrightarrow{\text{Hydrolysis}} (Y) \xrightarrow[\Delta]{HI} (A)$
A is
(a) heptanoic acid
(b) 2-iodohexane
(c) heptane
(d) heptanol. *(2016)*

20.



Arrange *X*, *Y* and *Z* in order of increasing acidic strengths.
(a) $X > Z > Y$ (b) $Z < X > Y$
(c) $X > Y > Z$ (d) $Z > X > Y$ *(2017)*

ASSERTION AND REASON

21. ***Assertion:*** A solution of sucrose in water is dextrorotatory. But on hydrolysis in the presence of a little hydrochloric acid, it becomes laevorotatory.
Reason: Sucrose on hydrolysis gives unequal amounts of glucose and fructose. As a result of this, change in sign of rotation is observed. *(1998, 2016)*

22. ***Assertion*** : DNA molecules and RNA molecules are found only in the nucleus of a cell.
Reason : On heating, the enzymes do not lose their specific activity. *(2002)*

23. ***Assertion*** : Haemoglobin is an oxygen carrier.
Reason : Oxygen binds as O_2^- to Fe of haemoglobin. *(2003)*

24. ***Assertion*** : Glycosides are hydrolysed in acidic conditions.
Reason : Glycosides are acetals. *(2003)*

25. ***Assertion*** : Carboxypeptidase is an exopeptidase.
Reason : It cleaves the N-terminal bond. *(2004)*

26. ***Assertion*** : Sucrose is a non-reducing sugar.
Reason : It has glycosidic linkage. *(2004)*

27. ***Assertion*** : Maltose is a reducing sugar which gives two moles of *D*-glucose on hydrolysis.
Reason : Maltose has a 1,4-β-glycosidic linkage. *(2005)*

28. ***Assertion*** : In the iodometric titration, starch is used as an indicator.
Reason : Starch is a polysaccharide. *(2006)*

29. ***Assertion*** : Alpha (α)-amino acids exist as internal salt in solution as they have amino and carboxylic acid groups in near vicinity.
Reason : H^+ ion given by carboxylic group (–COOH) is captured by amino group (–NH_2) having lone pair of electrons. *(2007)*

30. ***Assertion*** : Millon's test is a test for identification of proteins.
Reason : Millon's reagent is a solution of mercurous nitrate and mercuric nitrate in nitric acid containing little nitrous acid. *(2009)*

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31. ***Assertion :*** β-pleated sheet structure of protein shows maximum extension.
Reason : Intermolecular hydrogen bonding is present in them. *(2011)*

32. ***Assertion :*** Fructose is a reducing sugar.
Reason : It has a ketonic group. *(2011)*

33. ***Assertion :*** All enzymes are made up of proteins and all proteins have three dimensional structures.
Reason : Secondary structures of protein are sequence of amino acids. *(2013)*

34. ***Assertion :*** Insulin is water soluble.
Reason : Insulin is a globular protein. *(2014)*

35. ***Assertion :*** Solubility of proteins is minimum at the isoelectric point.
Reason : At isoelectric point, protein molecule behaves as a zwitter ion. *(2015)*

36. ***Assertion :*** Nucleotides are phosphate esters of nucleosides.
Reason : The various nucleotides in nucleic acids are linked either through purine or pyrimidine bases. *(2017)*

Answer Key

1.	(a)	**2.**	(d)	**3.**	(a)	**4.**	(b)	**5.**	(c)	**6.**	(c)	**7.**	(a)	**8.**	(b)
9.	(d)	**10.**	(c)	**11.**	(a)	**12.**	(d)	**13.**	(b)	**14.**	(a)	**15.**	(a)	**16.**	(a)
17.	(c)	**18.**	(b)	**19.**	(a)	**20.**	(a)	**21.**	(c)	**22.**	(d)	**23.**	(c)	**24.**	(d)
25.	(c)	**26.**	(a)	**27.**	(c)	**28.**	(b)	**29.**	(a)	**30.**	(b)	**31.**	(b)	**32.**	(b)
33.	(d)	**34.**	(b)	**35.**	(a)	**36.**	(c)								

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EXPLANATIONS

1. **(a) :** Vitamin B_{12} contains cobalt, while haemoglobin contains iron and Chlorophyll contains magnesium.

2. **(d)**

3. **(a) :** Molecular formula for monosaccaride (*e.g.*, glucose, fructose) is given by : $C_6H_{12}O_6$. Therefore, molecular formula for disaccharide is $C_{12}H_{22}O_{11}$.

4. **(b) :** Enzymes with two active sites are called allosteric enzymes. One of these sites is the catalytic site for the concerned reaction. Other site may be the site for inhibition of catalysis by enzyme or to activate the enzyme further.

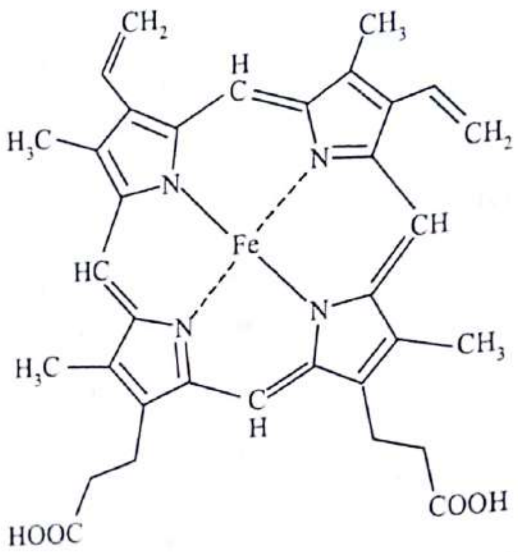
5. **(c) :** One molecule of haemoglobin has 4 haeme groups, and each of them is capable of taking up one molecule of O_2. Therefore, oxyhaemoglobin may be depicted as $Hb(O_2)_4$.

6. **(c)**

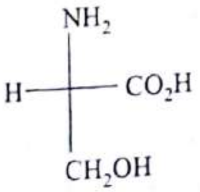
7. **(a) :** α-Keratin is a water insoluble fibrous protein which serves as the major constituent of hair, nails and skin.

8. **(b) :** Genetic code shows degeneracy *i.e.*, occurrence of more than 1 codon per amino acid. All the amino acids except methionine and tryptophan are coded by more than 1 codon.
For example, valine is specified by GUU, GUC, GUA, GUG.
This shows that first two bases are common in all the four codons coding for valine. But the third base can be changed.

9. **(d) :** Cytochromes are conjugated proteins consisting of an apoprotein and a prosthetic group (haeme). The haeme consists of a porphyrin with a central iron atom.
The name haemoglobin is the concatenation of haeme and globin, reflecting the fact that each subunit of haemoglobin is a globular protein with an embedded heme (or haem) group; each heme group contains an iron atom, and this is responsible for the binding of oxygen. The most common types of haemoglobin contains four such subunits, each with one heme group.

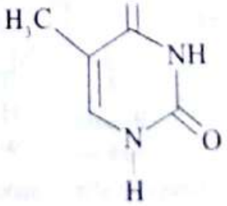


10. **(c) :**



L-serine
The laevorotatory isomer of 2-amino-3-hydroxypropanoic acid

11. **(a) :** Thymine, also known as 5-methyluracil, is a pyrimidine nucleobase. As the name implies, thymine may be derived by methylation of uracil at the 5th carbon.



12. **(d) :** Any amino acid has its lowest solubility at its isoelectric point and the isoelectric point is the pH at which the amino acid carries no charge.

13. **(b) :** Methyl-α-*D*-glucoside and methyl-β-*D* glucoside differ at C-1, hence are called anomers.

Methyl α-D-glucoside

Methyl β-D-glucoside

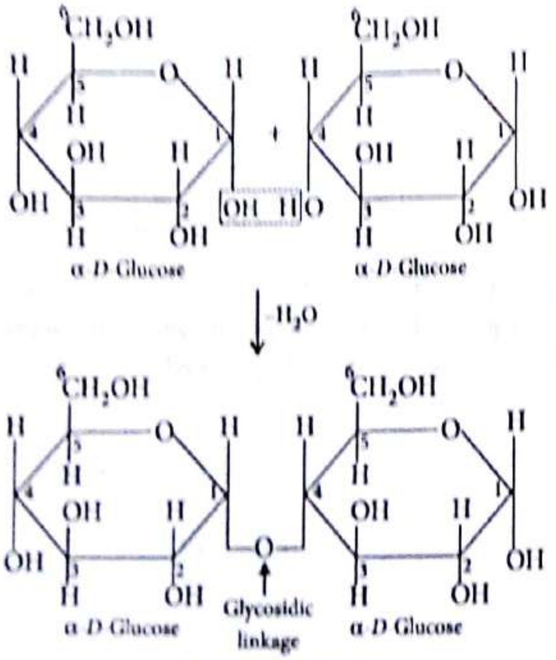
14. (a)

15. (a) : $C_{12}H_{22}O_{11} + H_2O \xrightarrow[\text{maltase}]{H^+ \text{ or}} C_6H_{12}O_6 + C_6H_{12}O_6$

Maltose Glucose Glucose

16. (a) : All the monosaccharides (aldoses and ketoses) and disaccharides except sucrose reduce Fehling's solution or Tollens' reagent and hence are reducing sugars.

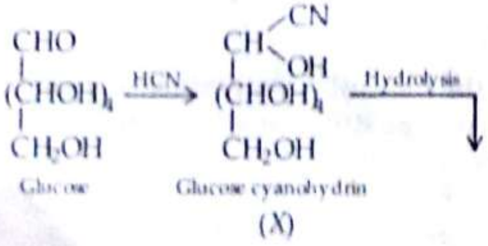
17. (c) : The disaccharide maltose (malt sugar) is formed by the condensation of two molecules of α-D-glycopyranose in which C_1 of one glucose unit is connected to C_4 of the other glucose unit.

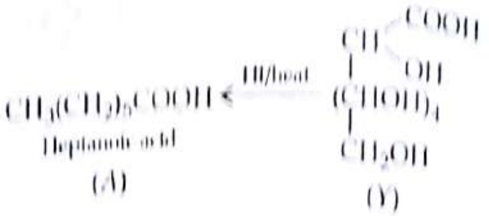


Structure of α D-maltose

18. (b)

19. (a) :





20. (a) : Carboxylic acid is stronger acid than $\overset{+}{N}H_3$, therefore, X is the strongest acid. Since –COOH has –I effect which decreases with distance, therefore, –I effect is more pronounced on Z than on Y. As a result, Z is more acidic than Y. Thus, overall order of decreasing acidic strength is X > Z > Y.

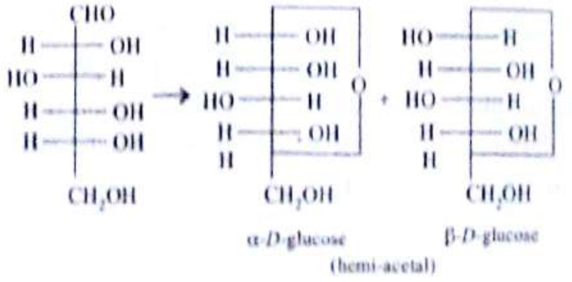
21. (c) : The hydrolysis of sucrose by boiling with a mineral acid (HCl), produces a mixture of equal molecules of D-glucose and D-fructose. Sucrose solution is dextrorotatory having specific rotation = +66.5°. But on hydrolysis, it becomes laevorotatory. The specific rotation of D-glucose is +52° and of D-fructose is –92°. Therefore, the net specific rotation of an equimolar mixture of both is :

$$\frac{+52°-92°}{2} = -20° \text{ (laevorotatory)}$$

22. (d) : In the cell, DNA molecules (*i.e.*, deoxyribose nucleic acid) are present predominantly in the nucleus, some DNA is also present in the mitochondria in Eukaryotes.
RNA molecules (*i.e.*, ribose nucleic acid) are present in cytoplasm of the eukaryotes and in nucleus in some prokaryotes and virus. Enzymes lose their specific activity on heating.

23. (c) : Haemoglobin is the oxygen carrier in the human blood. It consists of four subunits and one molecule of haemoglobin can carry 4 molecules of O_2. O_2 binds to Fe of heme part.

24. (d) : Glycosides are formed by treating glucose with CH_3OH in the presence of dry HCl gas and can be hydrolysed by strong reagents like HCN, NH_2OH and $C_6H_5NHNH_2$. Also, glycosides are known as hemi-acetals.



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25. (c) : Carboxypeptidase is an exopeptidase because it breaks the peptide chain at terminal ends. Carboxypeptidase cleaves carboxy-terminal amino acids that have aromatic or branched aliphatic side chains.

26. (a) : Sucrose is a non-reducing sugar as it does not reduce Tollens' or Fehling's reagent, due to absence of free aldehyde or ketone group. It contains stable acetal or ketal structure which cannot be opened into a free carboxyl group.

Sugar is composed of α-*D*-glucopyranose unit and β-*D*-fructofuranose unit. These units are joined by α, β-glycosidic linkage between C-1 of the glucose unit and C-2 of the fructose unit.

27. (c) : On hydrolysis one mole of maltose yields two moles of *D*-glucose. It is a reducing sugar. The two glucose units are linked through α-glycosidic linkage between C-1 of one unit and the C-4 of another.

28. (b) : Starch $(C_6H_{10}O_5)_n$ is a polysaccharide. It consists of two fractions - one is known as α-amylose and the other is β-amylose or amylopectin.

In iodimetric and iodometric titrations, starch solution is used as an indicator. It gives blue or violet colour with free iodine. At the end point, the blue or violet colour disappears when iodine is completely changed to iodide.

29. (a) : $NH_2—CH_2—COOH$ is a typical α-amino acid.

In solution it exists as, internal salt or Zwitter ion,

$({}^{+}NH_3—CH_2—COO^{-})$

because the proton (H^+) of COOH group is captured by $-NH_2$ group as NH_2 has a lone pair of electrons on N atom.

30. (b) : Millon's test is used for identification of proteins. When Millon's reagent is added to the aqueous solution of a protein, a white precipitate is formed.

31. (b) : In β-pleated sheet structure, the polypeptide chains are held together by intermolecular H-bonds. Extension and contraction of β-pleated sheet structure of protein depends on the size of *R*.

32. (b)

33. (d) : All enzymes are made up of proteins and all proteins do not have 3-dimensional structures. Structure of proteins are classified as primary, secondary, tertiary and quaternary structure and only tertiary structure is 3-dimensional. The sequence in which the amino acids are arranged in a protein is called primary structure of protein.

34. (b) : Insulin is a globular protein. This protein has three-dimensional folded structure. These are stabilised by internal hydrogen bonding, hence, they are water soluble.

35. (a) : At isoelectric point, protein molecules behave as zwitter ions and hence, do not move toward any electrode or act as neutral molecules. This reduces their solubility to minimum and thus, helps in their separation and purification.

36. (c) : The various nucleotides in nucleic acids are linked through phosphate ester groups.

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CHAPTER
29
POLYMERS

1. Nylon-6, 6 is made by using
(a) succinic acid (b) benzylchloride
(c) benzaldehyde (d) adipic acid.
(1997)

2. Which one of the following is used to make 'non-stick' cookware?
(a) Polyethylene
(b) Polytetrafluoroethylene
(c) Polystyrene
(d) None of these
(1998)

3. Teflon is a polymer of
(a) tetrafluoroethylene
(b) tetrabromoethylene
(c) tetraiodoethylene
(d) tetrachloroethylene.
(2002)

4. Which of the following is a biodegradable polymer?
(a) Cellulose (b) Polythene
(c) Polyvinyl chloride (d) Nylon-6
(2004)

5. The chemical name for melamine is
(a) 1,3,5-triamino-2,4,6-triazine
(b) 2,4,6-triamino-1,3,5-triazine
(c) 2-amino-1,3,5-triazine
(d) 2,4-diamino-1,3,5-triazine.
(2010)

6. Isoprene is
(a) 3-methyl-1,2-butadiene
(b) 2-methyl-1,3-butadiene
(c) 3-chloro-1,2-butadiene
(d) 2-chloro-1,3-butadiene.
(2011)

7. Which of the following is correct examples of condensation polymers?
(a) Nylon, buna-S
(b) Teflon, buna-N
(c) Nylon 6,6, dacron
(d) Neoprene, buna-S
(2012)

8. Non-stick cookwares generally have a coating of a polymer, whose monomer is
(a) $CH_2{=}CH_2$
(b) $CH_2{=}CHCN$
(c) $CH_2{=}CHCl$
(d) $CF_2{=}CF_2$
(2013)

9. Monomers of nylon-2-nylon-6 are
(a) glycine and amino caproic acid
(b) glycine and caproic acid
(c) hexamethylene diamine and adipic acid
(d) alanine and amino caproic acid.
(2014)

10. The polymer obtained by the interaction of ethylene glycol and terephthalic acid is
(a) nylon (b) dacron
(c) teflon (d) bakelite.
(2015)

11. Which is not classified as thermoplastics?
(a) Polyethylene (b) Polystyrene
(c) Bakelite (d) Neoprene
(2016)

12. Arrange the following monomers in order of decreasing ability to undergo cationic polymerisation.
I. $CH_2{=}CH-C_6H_4(NO_2)$
II. $CH_2{=}CH-C_6H_4(CH_3)$
III. $CH_2{=}CH-C_6H_4(OCH_3)$
(a) I > II > III (b) II > I > III
(c) III > II > I (d) I > III > II
(2017)

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ASSERTION AND REASON

13. ***Assertion*** **:** 1,3-butadiene is the monomer for natural rubber.

Reason **:** Natural rubber is formed through anionic addition polymerization.

(2006, 2016)

14. ***Assertion*** **:** Teflon has high thermal stability and chemical inertness.

Reason **:** Teflon is a thermoplastic.

(2008)

15. ***Assertion*** **:** Ebonite is highly vulcanised rubber.

Reason **:** Perlon is used in the manufacture of fibres.

(2009)

16. ***Assertion*** **:** Natural rubber is a polymer of isoprene.

Reason **:** Isoprene is another name of pentene.

(2014)

17. ***Assertion*** **:** Orlon is used as a synthetic fibre.

Reason **:** The monomer of orlon is vinyl chloride.

(2015)

18. ***Assertion*** **:** Teflon is chemically inert substance.

Reason **:** Chloroform when treated with antimony trifluoride gives teflon.

(2015)

Answer Key

1.	(d)	**2.**	(b)	**3.**	(a)	**4.**	(a)	**5.**	(b)	**6.**	(b)	**7.**	(c)	**8.**	(d)
9.	(a)	**10.**	(b)	**11.**	(c)	**12.**	(c)	**13.**	(d)	**14.**	(b)	**15.**	(b)	**16.**	(c)
17.	(c)	**18.**	(c)												

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EXPLANATIONS

1. **(d) :** Nylon-6, 6 is prepared from monomers, adipic acid and hexamethylene diamine by condensation process.

$$H_2N-(CH_2)_6-NH_2 + HOOC-(CH_2)_4-COOH \rightarrow \underset{\text{Nylon-6,6}}{\left[NH-(CH_2)_6-NH-CO-(CH_2)_4-CO\right]_n}$$

2. **(b)**

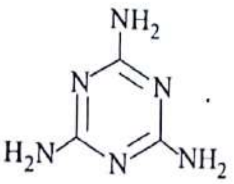
3. **(a) :** Teflon is polytetrafluoroethylene and it is prepared from tetrafluoro ethylene by heating under pressure in the presence of ammonium peroxydisulphate.

$$nCF_2{=}CF_2 \xrightarrow[\text{high pressure}]{(NH_4)_2{=}S_2O_8} \left(CF_2-CF_2\right)_n$$

It is chemically inert and heat resistant polymer.

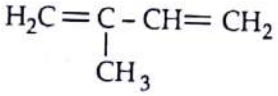
4. **(a) :** The substance which can be degraded by biological processes, as by bacterial or other enzymatic action is known as biodegradable substance.

5. **(b) :**



2,4,6-triamino-1,3,5-triazine

6. **(b) :** Isoprene is a monomer of natural rubber.



$$H_2C{=}\underset{\substack{|\\ CH_3}}{C}-CH{=}CH_2$$

2-Methyl-1,3-butadiene

7. **(c) :** Nylon 6, 6 and dacron are the examples of condensation polymers.

Condensation polymers are formed by condensation of two or more bifunctional monomers with the elimination of simple molecules like H_2O, NH_3, alcohol, etc.

Dacron is formed from ethylene glycol and terephthalic acid with the removal of H_2O.

Nylon 6, 6 is formed from hexamethylenediamine and adipic acid with the removal of H_2O.

8. **(d) :** $nCF_2{=}CF_2 \longrightarrow \underset{\text{Teflon}}{\left[CF_2-CF_2\right]_n}$

Teflon is used for non-stick cookwares.

9. **(a) :** Nylon-2-nylon-6 is an alternating polyamide copolymer of glycine (H_2N-CH_2-COOH)and amino caproic acid [$H_2N(CH_2)_5COOH$].

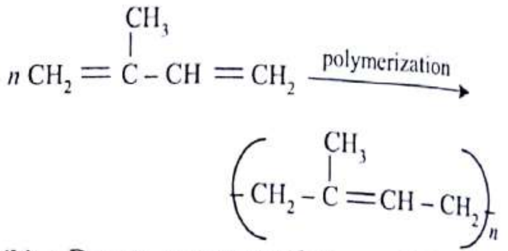
10. **(b)** 11. **(c)**

12. **(c) :** Electron releasing groups such as $-CH_3$, $-OCH_3$ activate the monomer towards cationic polymerisation because these groups provide stability to the carbocation formed. On the other hand, $-NO_2$ is a electron withdrawing group. So, it reduces the stability of carbocation formed. Thus, the correct order is

$$\underset{\text{(III)}}{CH_2{=}CH-C_6H_4(OCH_3)} > \underset{\text{(II)}}{CH_2{=}CH-C_6H_4(CH_3)} > \underset{\text{(I)}}{CH_2{=}CH-C_6H_4(NO_2)}$$

13. **(d) :** Isoprene (2-methyl-1,3-butadiene) is the monomer for natural rubber.

Natural rubber is formed through cationic addition polymerization. Cationic addition polymerization is catalysed by acids and Lewis acids. Alkenes containing electron-donating groups usually undergo cationic addition polymerization.



$$n\,CH_2{=}\overset{\substack{CH_3\\ |}}{C}-CH{=}CH_2 \xrightarrow{\text{polymerization}} \left(CH_2-\overset{\substack{CH_3\\ |}}{C}{=}CH-CH_2\right)_n$$

14. **(b) :** Due to presence of strong C-F bonds teflon has high thermal stability and chemical intertness. As, it softens on heating and can be remoulded so, it is a thermoplastic.

15. **(b) :** Ebonite is a very hard rubber which contains 30-40% sulphur.

16. **(c) :** Isoprene is 2-methyl-1, 3-butadiene.

17. **(c) :** The monomer of orlon is acrylonitrile.

18. **(c) :** When chloroform is treated with antimony trifluoride and hydrofluoric acid, tetrafluoroethylene is formed. On polymerisation, tetrafluoroethylene forms teflon.

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CHAPTER

30

CHEMISTRY IN EVERYDAY LIFE

1. Aspirin is an acetylation product of
   (a) *m*-hydroxybenzoic acid
   (b) *o*-hydroxybenzoic acid
   (c) *p*-dihydroxybenzene
   (d) *o*-dihydroxybenzene.
   (1994)

2. Glycerol is not used in
   (a) explosive (b) cosmetics
   (c) soaps (d) matches.
   (1996)

3. Which azide is explosive?
   (a) $Ba(N_3)_2$ (b) NaN_3
   (c) KN_3 (d) Mg_3N_2
   (2001)

4. Methyl orange is the example of which type of dye?
   (a) Acid dye (b) Mordant dye
   (c) Azo dye (d) Both (a) and (c).
   (2002)

5. The ligands in anti-cancer drug *cis*-platin are
   (a) NH_3, Cl (b) NH_3, H_2O
   (c) Cl, H_2O (d) NO, Cl
   (2005)

6. Chain transfer reagent is
   (a) CCl_4 (b) CH_4
   (c) O_2 (d) H_2
   (2007)

7. Which is a bactericidal antibiotics?
   (a) Penicillin
   (b) Erythromycin
   (c) Tetracycline
   (d) Chloramphenicol
   (2014)

8. Which one of the following is not employed as antihistamine?
   (a) Dimetane
   (b) Chloramphenicol
   (c) Seldane
   (d) Both (a) and (b)
   (2014)

9. Tincture of iodine is
   (a) aqueous solution of I_2
   (b) solution of I_2 in aqueous KI
   (c) alcohol-water solution of I_2
   (d) aqueous solution of KI.
   (2015)

10. Arsenic drugs are mainly used in the treatment of
    (a) Jaundice (b) Typhoid
    (c) Syphilis (d) Cholera.
    (2016)

ASSERTION AND REASON

11. ***Assertion :*** The micelle formed by sodium stearate in water has $-COO^-$ groups at the surface.
    Reason : Surface tension of water is reduced by the addition of stearate.
    (2003)

12. ***Assertion :*** Sulpha drugs contain sulphonamide group.
    Reason : Salvarsan is a sulpha drug.
    (2017)

Answer Key

1. (b) **2.** (d) **3.** (a) **4.** (d) **5.** (a) **6.** (a) **7.** (a) **8.** (b)
9. (c) **10.** (c) **11.** (b) **12.** (c)

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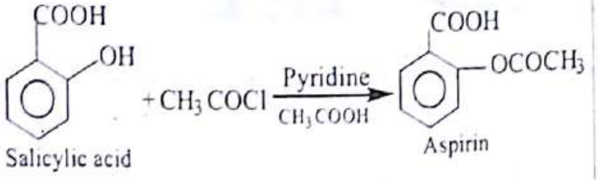
EXPLANATIONS

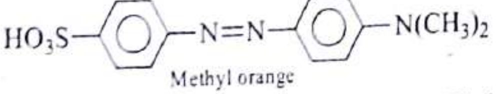
1. **(b) :** Aspirin (Acetyl salicylic acid) is obtained by heating salicylic acid (*o*-hydroxybenzoic acid) with acetyl chloride and glacial acetic acid.



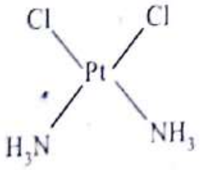
2. **(d)**

3. **(a) :** Ionic azides are usually much more stable *e.g.*, KN_3, NaN_3 and Mg_3N_2 than the covalent azides. Covalent azides are used as detonators and explosives *e.g.*, $Ba(N_3)_2$.

4. **(d) :** Methyl orange belongs to the group of azo dyes. It is also acidic in nature due to presence of sulphonic group.



5. **(a) :** *Cis*-diamminedichloroplatinum(II) (*cis*-platin) is a widely used anti-cancer drug. Ligands in *cis*-platin are NH_3 and Cl.



6. **(a) :** A substance that is able to cause a chain transfer in a chain polymerisation is called a chain transfer agent. It gives an atom to the radical at the growing end of a polymer chain and in doing so it results into a radical which can start the growth of a new chain. CCl_4 is a chain transfer reagent.

7. **(a) :** Penicillin is a bactericidal whereas erythromycin, tetracycline and chloramphenicol are bacteriostatic antibiotics.

8. **(b) :** Chloramphenicol is a bacteriostatic antibiotic drug.

9. **(c) :** Tincture of iodine is an alcohol-water solution containing 2-3% iodine.

10. **(c) :** Arsenic drugs such as salvarsan is used for treatment of syphilis.

11. **(b) :** Micelle is formed if molecules with polar and non-polar ends assemble in bulk to give non-polar interior and polar exterior.

12. **(c) :** Salvarsan is an antibacterial drug containing arsenic and it does not contain sulphonamide group.

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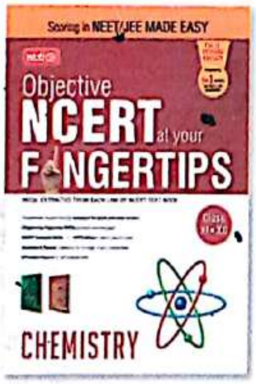

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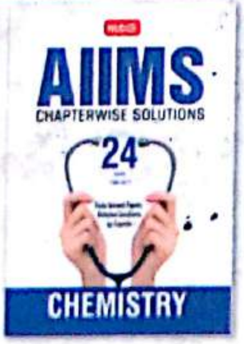

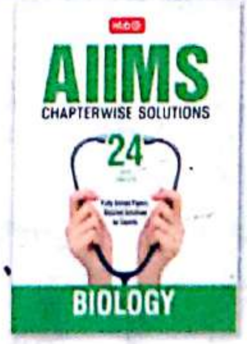

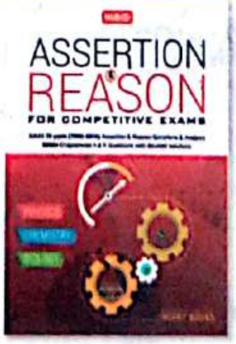

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