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OLYMPIAD PROBLEMS

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We Answer ✅

CHEMISTRY today

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TO OUR READERS

We are happy that intelligent students, teachers and other professionals continue to patronise Mathematics Today, Chemistry Today, Physics For You and Biology Today.

To them, we are addressing this open letter in view of increase in the cost of production and postage in the last five years. All round spiralling prices have pushed production costs so high, that many in out fraternity find it impossible to continue business. We are compelled to raise the price to ₹ 40 from July 2016 issue.

We understand the pressure of cost on the student-teacher community in general but, we are hoping our readers will understand our problems and that we have no option but to comply with this unavoidable move.

We on our part, will keep up our efforts to improve the magazines in all its aspects.

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CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / NEET / AIIMS / PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / NEET. The detailed solutions of these problems will be published in next issue of Chemistry Today.

The readers who have solved five or more problems may send their solutions. The names of those who send atleast five correct solutions will be published in the next issue.

We hope that our readers will enrich their problem solving skills through "Chemistry Musing" and stand in better stead while facing the competitive exams.

PROBLEM Set 35

JEE MAIN/NEET

1. A balloon filled with helium rises to a certain height at which it gets fully inflated to a volume of 1×10^5 litres. If at this altitude temperature and atmospheric pressure are 268 K and 2×10^{-3} atm respectively, what weight of helium will be required to fully inflate the balloon?
   - (a) 24.62 g
   - (b) 0.35 g
   - (c) 8.97 g
   - (d) 36.36 g

2. The enthalpy of neutralisation of a weak acid in 1 M solution with a strong base is –56.1 kJ mol^{-1}. If enthalpy of ionisation of the acid is 1.5 kJ mol^{-1} and enthalpy of neutralisation of the strong acid with a strong base is –57.3 kJ mol^{-1}, what is the % ionisation of the weak acid in molar solution (Assume the acid to be monobasic)?
   - (a) 10
   - (b) 15
   - (c) 20
   - (d) 25

3. Salicylic acid is treated with bromine under two different conditions as shown :
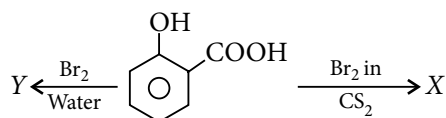
   Compounds X and Y in the given reactions are respectively

   (a)

   (b)

   (c)

   (d)
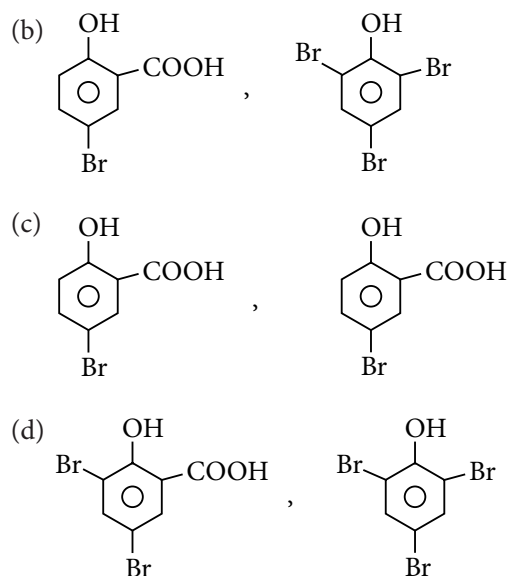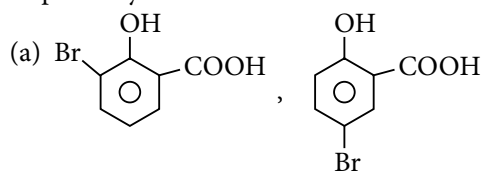
4. Which of the following does not react with AgCl?
   - (a) $Na_2S_2O_3$
   - (b) NH_4OH
   - (c) $NaNO_3$
   - (d) Na_2CO_3

5. Identify the number of optically active isomers of C_3H_4ClBr.
   - (a) 2
   - (b) 4
   - (c) 3
   - (d) 5

JEE ADVANCED

6. A 5.00 g sample of a natural gas, consisting of methane (CH_4) and ethylene (C_2H_4) was burnt in excess oxygen, yielding 14.5 g of CO_2 and some H_2O as products. What is the percentage of ethylene in the sample?
   - (a) 20.2%
   - (b) 40.4%
   - (c) 10.1%
   - (d) 38.8%

COMPREHENSION

When a quaternary ammonium halide is treated with moist silver oxide (a slurry of Ag_2O in water), a quaternary ammonium hydroxide is formed as the main product. Thermal decomposition of the quaternary ammonium hydroxide gives an alkene. This reaction is known as Hofmann elimination and has most of the characteristics of an E2 reaction.

$$CH_3CH_2\underset{\overset{|}{I^-N^+(CH_3)_3}}{C}HCH_3 \xrightarrow[(-AgI)]{Ag_2O/H_2O} CH_3CH_2\underset{\overset{|}{{^-}HON^+(CH_3)_3}}{C}HCH_3 \xrightarrow{Heat}$$

$$\underset{X}{CH_3CH{=}CHCH_3} + \underset{Y}{CH_3CH_2CH{=}CH_2}$$
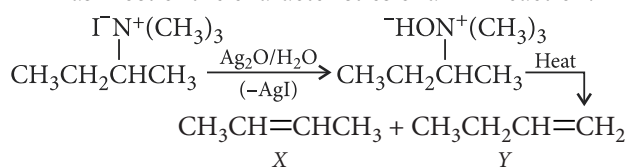
7. The Hofmann elimination reactions are
   (i) concerted
   (ii) stereoselective for *anti* elimination
   (iii) the reactions that occur in separate steps
   (iv) stereoselective for *syn* elimination.
   (a) (i) and (iv)   (b) (i) and (ii)
   (c) only (i)   (d) only (iii).

8. In the given reaction, which of the following is correct regarding yield of *X* and *Y*?

   (a) $X = Y$ (b) $X \approx Y$
   (c) $X > Y$ (d) $X < Y$

INTEGER VALUE

9. The number of moles of sodium acetate that should be dissolved to prepare one litre of 0.063 molar buffer solution of pH 4.5 is $x \times 10^{-2}$. The value of x is

10. Two 1.0 g carbon disks 1.00 cm apart have opposite charges of equal magnitude such that there is 1.00×10^{-5} N force between them. The ratio of excess electrons to total atoms on the negatively charged disk is nearly $x \times 10^{-14}$ electron/atom, The value of x is

◈ ◈

Solution Senders of Chemistry Musing	
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NEET

SOLVED PAPER 2016

Phase-I held on 1st May

Hurray!! We are happy to inform our readers that out of the 45 questions asked in NEET 2016, more than 60% questions were either exactly same or of similar type from the **MTG Books.** Hurray!!

Here, the references of few are given :

S. No.	MTG Books	Q. No.	Pg. No.
2	NCERT Fingertips	93	151
4	NEET Guide	138	550
5	NCERT Fingertips	97	125
7	NEET Guide	127	159
8	NEET Guide	72	621
20	NEET Guide	194	517
21	NCERT Fingertips	35	313
22	Objective Chemistry	164	766

S. No.	MTG Books	Q. No.	Pg. No.
23	Objective Chemistry	91	31
26	NEET Guide	90	594
30	NEET Guide	43	751
32	NCERT Fingertips	36	64
40	Objective Chemistry	82	203
41	NCERT Fingertips	80	149
43	NEET Guide	74	849
44	NEET Guide	35	8

and more such questions ……

1. Which of the following statements about the composition of the vapour over an ideal 1 : 1 molar mixture of benzene and toluene is correct? Assume that the temperature is constant at 25°C. (Given, vapour pressure data at 25°C, benzene = 12.8 kPa, toluene = 3.85 kPa)
   (a) The vapour will contain equal amounts of benzene and toluene.
   (b) Not enough information is given to make a prediction.
   (c) The vapour will contain a higher percentage of benzene.
   (d) The vapour will contain a higher percentage of toluene.

2. Match the compounds given in column I with the hybridisation and shape given in column II and mark the correct option.

	Column I		Column II
(A)	XeF_6	(i)	Distorted octahedral
(B)	XeO_3	(ii)	Square planar
(C)	$XeOF_4$	(iii)	Pyramidal
(D)	XeF_4	(iv)	Square pyramidal

Code :

	A	B	C	D
(a)	(iv)	(iii)	(i)	(ii)
(b)	(iv)	(i)	(ii)	(iii)
(c)	(i)	(iii)	(iv)	(ii)
(d)	(i)	(ii)	(iv)	(iii)

3. The correct statement regarding the comparison of staggered and eclipsed conformations of ethane, is
   (a) the eclipsed conformation of ethane is more stable than staggered conformation even though the eclipsed conformation has torsional strain
   (b) the staggered conformation of ethane is more stable than eclipsed conformation, because staggered conformation has no torsional strain
   (c) the staggered conformation of ethane is less stable than eclipsed conformation, because staggered conformation has torsional strain
   (d) the eclipsed conformation of ethane is more stable than staggered conformation, because eclipsed conformation has no torsional strain.

4. Fog is a colloidal solution of
   (a) solid in gas   (b) gas in gas
   (c) liquid in gas   (d) gas in liquid.

5. Match items of Column I with the items of Column II and assign the correct code :

|	Column I		Column II
(A)	Cyanide process	(i)	Ultrapure Ge
(B)	Froth floatation process	(ii)	Dressing of ZnS
(C)	Electrolytic reduction	(iii)	Extraction of Al
(D)	Zone refining	(iv)	Extraction of Au
		(v)	Purification of Ni

   Code :

	A	B	C	D
(a)	(i)	(ii)	(iii)	(iv)
(b)	(iii)	(iv)	(v)	(i)
(c)	(iv)	(ii)	(iii)	(i)
(d)	(ii)	(iii)	(i)	(v)

6. Which is the correct statement for the given acids?
   (a) Phosphinic acid is a monoprotic acid while phosphonic acid is a diprotic acid.
   (b) Phosphinic acid is a diprotic acid while phosphonic acid is a monoprotic acid.
   (c) Both are diprotic acids.
   (d) Both are triprotic acids.

7. The correct thermodynamic conditions for the spontaneous reaction at all temperatures is
   (a) $\Delta H < 0$ and $\Delta S > 0$ (b) $\Delta H < 0$ and $\Delta S < 0$
   (c) $\Delta H < 0$ and $\Delta S = 0$ (d) $\Delta H > 0$ and $\Delta S < 0$

8. Which one of the following statements is correct when SO_2 is passed through acidified $K_2Cr_2O_7$ solution?
   (a) SO_2 is reduced.
   (b) Green $Cr_2(SO_4)_3$ is formed.
   (c) The solution turns blue.
   (d) The solution is decolourised.

9. The correct statement regarding RNA and DNA, respectively is
   (a) the sugar component in RNA is a arabinose and the sugar component in DNA is ribose
   (b) the sugar component in RNA is 2′-deoxyribose and the sugar component in DNA is arabinose
   (c) the sugar component in RNA is arabinose and the sugar component in DNA is 2′-deoxyribose
   (d) the sugar component in RNA is ribose and the sugar component in DNA is 2′-deoxyribose.

10. Which of the following reagents would distinguish *cis*-cyclopenta-1-2-diol from the *trans*-isomer?
    (a) MnO_2 (b) Aluminium isopropoxide
    (c) Acetone   (d) Ozone

11. The correct statement regarding a carbonyl compound with a hydrogen atom on its alpha-carbon, is
    (a) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as carbonylation
    (b) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as keto-enol tautomerism
    (c) a carbonyl compound with a hydrogen atom on its alpha-carbon never equilibrates with its corresponding enol
    (d) a carbonyl compound with a hydrogen atom on its alpha-carbon rapidly equilibrates with its corresponding enol and this process is known as aldehyde-ketone equilibration.

12. At 100°C the vapour pressure of a solution of 6.5 g of a solute in 100 g water is 732 mm. If $K_b = 0.52$, the boiling point of this solution will be
    (a) 102°C   (b) 103°C
    (c) 101°C   (d) 100°C

13. Consider the nitration of benzene using mixed conc. H_2SO_4 and HNO_3. If a large amount of $KHSO_4$ is added to the mixture, the rate of nitration will be
    (a) unchanged   (b) doubled
    (c) faster   (d) slower.

14. The pressure of H_2 required to make the potential of H_2-electrode zero in pure water at 298 K is
    (a) 10^{-10} atm   (b) 10^{-4} atm
    (c) 10^{-14} atm   (d) 10^{-12} atm

15. The correct statement regarding the basicity of arylamines is
    (a) arylamines are generally more basic than alkylamines because of aryl group
    (b) arylamines are generally more basic than alkylamines, because the nitrogen atom in arylamines is *sp*-hybridised
    (c) arylamines are generally less basic than alkylamines because the nitrogen lone-pair electrons are delocalised by interaction with the aromatic ring π-electron system

(d) arylamines are generally more basic than alkylamines because the nitrogen lone-pair electrons are not delocalised by interaction with the aromatic ring π-electron system.

16. In a protein molecule various amino acids are linked together by
(a) peptide bond   (b) dative bond
(c) α-glycosidic bond   (d) β-glycosidic bond.

17. Consider the molecules CH_4, NH_3 and H_2O. Which of the given statements is false?
(a) The H—O—H bond angle in H_2O is smaller than the H—N—H bond angle in NH_3.
(b) The H—C—H bond angle in CH_4 is larger than the H—N—H bond angle in NH_3.
(c) The H—C—H bond angle in CH_4, the H—N—H bond angle in NH_3, and the H—O—H bond angle in H_2O are all greater than 90°.
(d) The H—O—H bond angle in H_2O is larger than the H—C—H bond angle in CH_4.

18. Which of the following statements is false?
(a) Ca^{2+} ions are not important in maintaining the regular beating of the heart.
(b) Mg^{2+} ions are important in the green parts of the plants.
(c) Mg^{2+} ions form a complex with ATP.
(d) Ca^{2+} ions are important in blood clotting.

19. Which one of the following orders is correct for the bond dissociation enthalpy of halogen molecules?
(a) $Br_2 > I_2 > F_2 > Cl_2$ (b) $F_2 > Cl_2 > Br_2 > I_2$
(c) $I_2 > Br_2 > Cl_2 > F_2$ (d) $Cl_2 > Br_2 > F_2 > I_2$

20. The rate of first-order reaction is 0.04 mol L^{-1} s^{-1} at 10 seconds and 0.03 mol L^{-1} s^{-1} at 20 seconds after initiation of the reaction. The half-life period of the reaction is
(a) 44.1 s   (b) 54.1 s
(c) 24.1 s   (d) 34.1 s

21. Which one given below is a non-reducing sugar?
(a) Glucose   (b) Sucrose
(c) Maltose   (d) Lactose

22. Which one of the following characteristics is associated with adsorption?
(a) ΔG and ΔH are negative but ΔS is positive.
(b) ΔG and ΔS are negative but ΔH is positive.
(c) ΔG is negative but ΔH and ΔS are positive.
(d) ΔG, ΔH and ΔS all are negative.

23. Two electrons occupying the same orbital are distinguished by
(a) azimuthal quantum number
(b) spin quantum number
(c) principal quantum number
(d) magnetic quantum number.

24. Lithium has a *bcc* structure. Its density is 530 kg m^{-3} and its atomic mass is 6.94 g mol^{-1}. Calculate the edge length of a unit cell of lithium metal. ($N_A = 6.02 \times 10^{23}$ mol^{-1})
(a) 527 pm   (b) 264 pm
(c) 154 pm   (d) 352 pm

25. The pair of electrons in the given carbanion, $CH_3C \equiv C^-$, is present in which of the following orbitals?
(a) sp^2 (b) sp
(c) $2p$ (d) sp^3

26. The product obtained as a result of a reaction of nitrogen with CaC_2 is
(a) $CaCN_3$ (b) Ca_2CN
(c) $Ca(CN)_2$ (d) $CaCN$

27. In the reaction
$$H—C \equiv CH \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2/\text{liq. } NH_3} X \xrightarrow[\text{(ii) } CH_3CH_2Br]{\text{(i) } NaNH_2/\text{liq. } NH_3} Y$$
X and Y are
(a) X = 2-butyne, Y = 2-hexyne
(b) X = 1-butyne, Y = 2-hexyne
(c) X = 1-butyne, Y = 3-hexyne
(d) X = 2-butyne, Y = 3-hexyne.

28. MY and NY_3, two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3?
(a) The salts MY and NY_3 are more soluble in 0.5 M KY than in pure water.
(b) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities.
(c) The molar solubilities of MY and NY_3 in water are identical.
(d) The molar solubility of MY in water is less than that of NY_3.

29. When copper is heated with conc. HNO_3 it produces
(a) $Cu(NO_3)_2$, NO and NO_2
(b) $Cu(NO_3)_2$ and N_2O
(c) $Cu(NO_3)_2$ and NO_2
(d) $Cu(NO_3)_2$ and NO

30. The product formed by the reaction of an aldehyde with a primary amine is
(a) carboxylic acid   (b) aromatic acid
(c) Schiff's base   (d) ketone.

31. The addition of a catalyst during a chemical reaction alters which of the following quantities?
(a) Enthalpy   (b) Activation energy
(c) Entropy   (d) Internal energy

32. Predict the correct order among the following :
(a) bond pair - bond pair > lone pair - bond pair
      > lone pair - lone pair
(b) lone pair - bond pair > bond pair - bond pair
      > lone pair - lone pair
(c) lone pair - lone pair > lone pair - bond pair
      > bond pair - bond pair
(d) lone pair - lone pair > bond pair - bond pair
      > lone pair - bond pair

33. Consider the following liquid-vapour equilibrium.

Liquid $\rightleftharpoons$ Vapour

Which of the following relations is correct?

(a) $\dfrac{d\ln P}{dT^2} = \dfrac{-\Delta H_v}{T^2}$ (b) $\dfrac{d\ln P}{dT} = \dfrac{\Delta H_v}{RT^2}$

(c) $\dfrac{d\ln G}{dT^2} = \dfrac{\Delta H_v}{RT^2}$ (d) $\dfrac{d\ln P}{dT} = \dfrac{-\Delta H_v}{RT}$

34. Which of the following biphenyls is optically active?

(a)

(b)

(c)

(d)
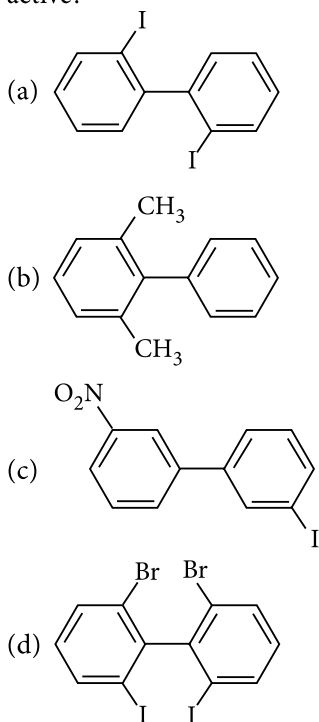
35. Which of the following statements about hydrogen is incorrect?
(a) Hydronium ion, H_3O^+ exists freely in solution.
(b) Dihydrogen does not act as a reducing agent.
(c) Hydrogen has three isotopes of which tritium is the most common.
(d) Hydrogen never acts as cation in ionic salts.

36. The electronic configurations of Eu (Atomic No. 63), Gd (Atomic No. 64) and Tb (Atomic No. 65) are
(a) $[Xe]4f^6\,5d^1\,6s^2$, $[Xe]4f^7\,5d^1\,6s^2$ and $[Xe]4f^8\,5d^1\,6s^2$
(b) $[Xe]4f^7\,6s^2$, $[Xe]4f^7\,5d^1\,6s^2$ and $[Xe]4f^9\,6s^2$
(c) $[Xe]4f^7\,6s^2$, $[Xe]4f^8\,6s^2$ and $[Xe]4f^8\,5d^1\,6s^2$
(d) $[Xe]4f^6\,5d^1\,6s^2$, $[Xe]4f^7\,5d^1\,6s^2$ and $[Xe]4f^9\,6s^2$

37. The reaction
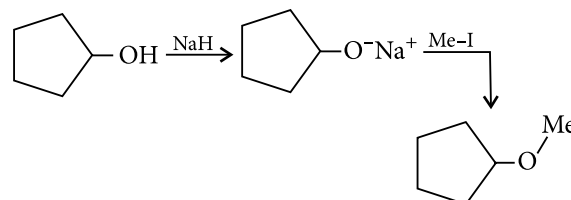
can be classified as
(a) dehydration reaction
(b) Williamson alcohol synthesis reaction
(c) Williamson ether synthesis reaction
(d) alcohol formation reaction.

38. For the following reactions :
(A) $CH_3CH_2CH_2Br + KOH \longrightarrow$
      $CH_3CH = CH_2 + KBr + H_2O$

(B)

(C)
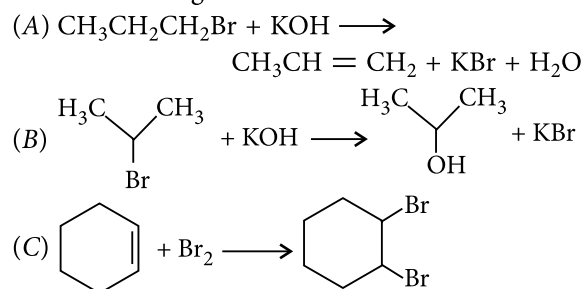
Which of the following statements is correct?
(a) (A) is elimination, (B) and (C) are substitution reactions.
(b) (A) is substitution, (B) and (C) are addition reactions.
(c) (A) and (B) are elimination reactions and (C) is addition reaction.
(d) (A) is elimination, (B) is substitution and (C) is addition reaction.

39. In which of the following options the order of arrangement does not agree with the variation of property indicated against it?
(a) I < Br < Cl < F (increasing electron gain enthalpy)
(b) Li < Na < K < Rb (increasing metallic radius)
(c) Al^{3+} < Mg^{2+} < Na^+ < F^- (increasing ionic size)
(d) B < C < N < O (increasing first ionisation enthalpy)

40. Equal moles of hydrogen and oxygen gases are placed in a container with a pin-hole through which both can escape. What fraction of the oxygen escapes in the time required for one-half of the hydrogen to escape?
(a) 3/8   (b) 1/2
(c) 1/8   (d) 1/4

41. Among the following, the correct order of acidity is
(a) $HClO_2$ < $HClO$ < $HClO_3$ < $HClO_4$
(b) $HClO_4$ < $HClO_2$ < $HClO$ < $HClO_3$
(c) $HClO_3$ < $HClO_4$ < $HClO_2$ < $HClO$
(d) $HClO$ < $HClO_2$ < $HClO_3$ < $HClO_4$

42. Which of the following is an analgesic?
(a) Streptomycin   (b) Chloromycetin
(c) Novalgin   (d) Penicillin

43. Natural rubber has
(a) alternate *cis-* and *trans*-configuration
(b) random *cis-* and *trans*-configuration
(c) all *cis*-configuration
(d) all *trans*-configuration.

44. The ionic radii of A^+ and B^- ions are 0.98×10^{-10} m and 1.81×10^{-10} m. The coordination number of each ion in AB is
(a) 8   (b) 2
(c) 6   (d) 4

45. Which of the following has longest C—O bond length? (Free C—O bond length in CO is 1.128 Å.)
(a) $[Fe(CO)_4]^{2-}$ (b) $[Mn(CO)_6]^+$
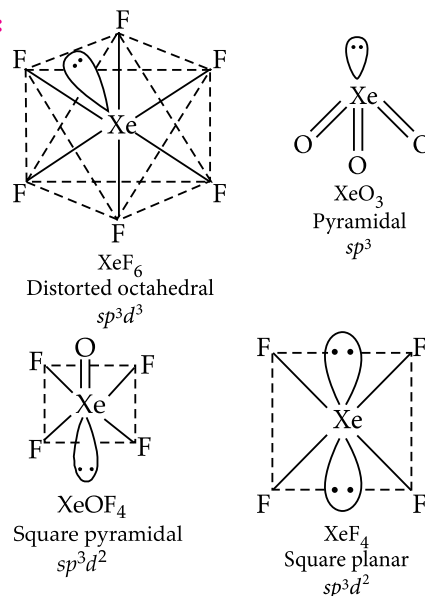(c) $Ni(CO)_4$ (d) $[Co(CO)_4]^-$

SOLUTIONS

1. **(c) :** $p_{Benzene} = x_{Benzene}\, p°_{Benzene}$
$p_{Toluene} = x_{Toluene}\, p°_{Toluene}$
For an ideal 1 : 1 molar mixture of benzene and toluene, $x_{Benzene} = \dfrac{1}{2}$ and $x_{Toluene} = \dfrac{1}{2}$

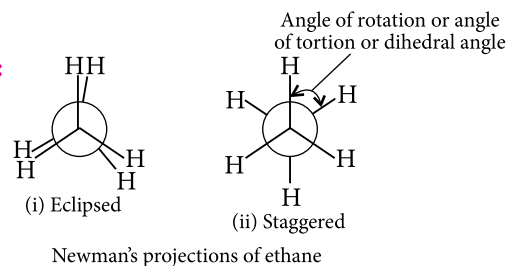$p_{Benzene} = \dfrac{1}{2} p°_{Benzene} = \dfrac{1}{2} \times 12.8\,\text{kPa} = 6.4\,\text{kPa}$

$p_{Toluene} = \dfrac{1}{2} p°_{Toluene} = \dfrac{1}{2} \times 3.85\,\text{kPa} = 1.925\,\text{kPa}$

Thus, the vapour will contain a high percentage of benzene as the partial vapour pressure of benzene is higher as compared to that of toluene.

2. **(c) :**

XeF$_6$
Distorted octahedral
sp^3d^3

XeO$_3$
Pyramidal
sp^3

XeOF$_4$
Square pyramidal
sp^3d^2

XeF$_4$
Square planar
sp^3d^2

3. **(b):**

Angle of rotation or angle of tortion or dihedral angle

(i) Eclipsed   (ii) Staggered
Newman's projections of ethane

Magnitude of torsional strain depends upon the angle of rotation about C—C bond. Staggered form has the least torsional strain and the eclipsed form has the maximum torsional strain so, the staggered conformation of ethane is more stable than the eclipsed conformation.

4. **(c) :** Fog is an example of aerosol in which dispersed phase is liquid and dispersion medium is gas.

5. **(c) :** Mac-Arthur Forest cyanide process is used for the extraction of gold and silver.
Froth floatation process is used for the concentration of sulphide ores *e.g.*, ZnS.
Electrolytic reduction is used for the extraction of highly electropositive metals like Na, K, Mg, Ca, Al, etc.
Zone refining method is used for producing semiconductor and other metals of very high purity *e.g.*, Ge, Si, B, Ga and In. Purification of Ni is done by vapour phase refining (Mond's process).

6. (a):

H_3PO_2	H_3PO_3
Hypophosphorous acid or Phosphinic acid (Monobasic)	Orthophosphorous acid or Phosphonic acid (Dibasic)
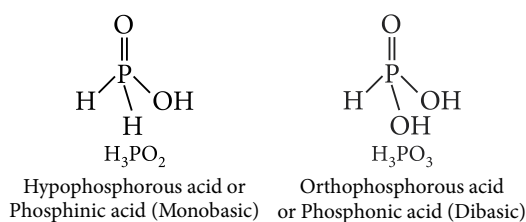
7. (a, c): $\Delta G = \Delta H - T\Delta S$
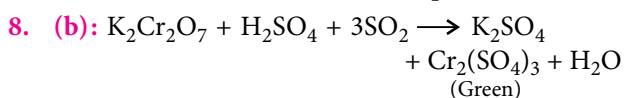
If $\Delta H < 0$ and $\Delta S > 0$

$\Delta G = (-ve) - T(+ve)$

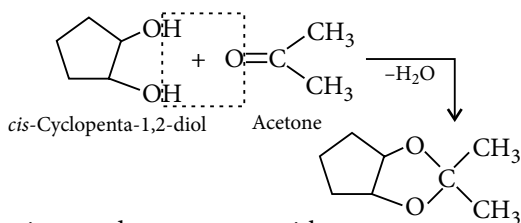then at all temperatures, $\Delta G = -ve$, spontaneous reaction.

If $\Delta H < 0$ and $\Delta S = 0$

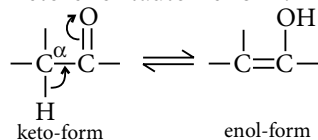$\Delta G = (-ve) - T(0) = -ve$ at all temperatures.

8. (b): $K_2Cr_2O_7 + H_2SO_4 + 3SO_2 \longrightarrow K_2SO_4$
$\qquad\qquad\qquad\qquad\qquad + Cr_2(SO_4)_3 + H_2O$
$\qquad\qquad\qquad\qquad\qquad\quad$ (Green)

9. (d)

10. (c):

cis-Cyclopenta-1,2-diol $\qquad$ Acetone

Trans-isomer does not react with acetone.

11. (b): Keto-enol tautomerism :

keto-form $\qquad\qquad$ enol-form

12. (c): Given : $W_B = 6.5$ g, $W_A = 100$ g, $p_s = 732$ mm, $K_b = 0.52$, $T_b^\circ = 100°C$, $p° = 760$ mm

$$\frac{p° - p_s}{p°} = \frac{n_2}{n_1} \Rightarrow \frac{760 - 732}{760} = \frac{n_2}{100/18}$$

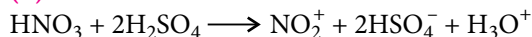$$\Rightarrow \quad n_2 = \frac{28 \times 100}{760 \times 18} = 0.2046 \text{ moles}$$

$$\Delta T_b = K_b \times m$$

$$T_b - T_b^\circ = K_b \times \frac{n_2 \times 1000}{W_A (\text{g})}$$

$$T_b - 100°C = \frac{0.52 \times 0.2046 \times 1000}{100} = 1.06$$
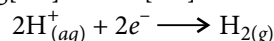
$$T_b = 100 + 1.06 = 101.06°C$$

13. (d): Mechanism of nitration is :

$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$

If a large amount of $KHSO_4$ is added then conc. of HSO_4^- ions increases and the reaction will be shifted in backward direction hence, the rate of nitration will be slower.

14. (c): pH = 7 for water.

$-\log[H^+] = 7 \Rightarrow [H^+] = 10^{-7}$

$2H^+_{(aq)} + 2e^- \longrightarrow H_{2(g)}$

$$E_{\text{cell}} = E°_{\text{cell}} - \frac{0.0591}{2} \log \frac{p_{H_2}}{[H^+]^2}$$

$$0 = 0 - \frac{0.0591}{2} \log \frac{p_{H_2}}{(10^{-7})^2}$$

$$\log \frac{p_{H_2}}{(10^{-7})^2} = 0 \Rightarrow \frac{p_{H_2}}{(10^{-7})^2} = 1 \quad [\because \log 1 = 0]$$

$$p_{H_2} = 10^{-14} \text{ atm}$$

15. (c):
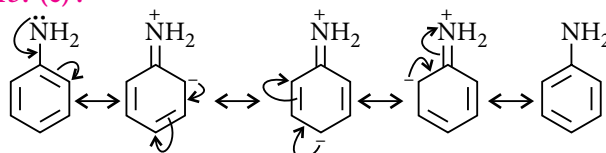
In arylamines, lone pair of electrons on nitrogen atom is delocalised over the benzene ring, thus, not available for donation. So, arylamines are less basic than alkylamines ($R-\ddot{N}H_2$).

16. (a)

17. (d):
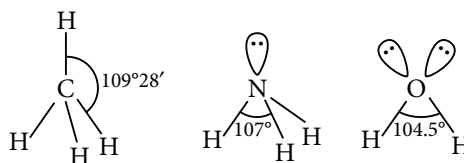
18. (a): Ca^{2+} ions are required to trigger the contraction of muscles and to maintain the regular beating of the heart.

19. (d): Enthalpy of dissociation decreases as the bond distance increases from F_2 to I_2 due to increase in size of the atom as we move down the group. Due to electron-electron repulsions between the lone pairs in small sized F atoms, the bond dissociation enthalpy of F_2 is, however, smaller than than of Cl_2 and even smaller than that of Br_2.

Thus, the order of bond dissociation enthalpy is :
$$Cl_2 > Br_2 > F_2 > I_2$$
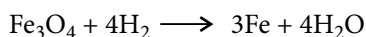
20. (c) : For a first order reaction, $A \rightarrow$ Products and for concentration of the reactant at two different times,

$$k = \frac{2.303}{t_2 - t_1} \log \frac{[A]_1}{[A]_2}$$

$$\therefore \quad k = \frac{2.303}{t_2 - t_1} \log \frac{(rate)_1}{(rate)_2} \qquad (\because rate \propto [A])$$

$$k = \frac{2.303}{(20-10)} \log\left(\frac{0.04}{0.03}\right) = 0.0287 \text{ sec}^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0287 \text{ sec}^{-1}} = 24.14 \text{ sec}$$

21. (b): All monosaccharides whether aldoses or ketoses are reducing sugars. Disaccharides such as sucrose in which the two monosaccharide units are linked through their reducing centres *i.e.*, aldehydic or ketonic groups are non-reducing.

22. (d): As the molecules of the adsorbate are held on the surface of the solid adsorbent, entropy decreases *i.e.*, $\Delta S = -ve$.

As $\Delta G = \Delta H - T\Delta S$

For the adsorption to occur, $\Delta G = -ve$ and it is possible only if $\Delta H = -ve$.

23. (b): For the two electrons occupying the same orbital values of n, l and m_l are same but m_s is different, $+\frac{1}{2}$ and $-\frac{1}{2}$.

24. (d): For *bcc*, $Z = 2$, $\rho = 530$ kg m^{-3}, at. mass of Li = 6.94 g mol^{-1}, $N_A = 6.02 \times 10^{23}$ mol^{-1}

$$\rho = 530 \text{ kg m}^{-3} = \frac{530 \times 1000 \text{ g}}{1 \times (100)^3 \text{ cm}^3} = 0.53 \text{ g cm}^{-3}$$

$$\rho = \frac{Z \times \text{At. mass}}{N_A \times a^3}$$

$$a^3 = \frac{Z \times \text{At. mass}}{N_A \times \rho} = \frac{2 \times 6.94}{6.02 \times 10^{23} \times 0.53}$$

$$a^3 = 4.35 \times 10^{-23} \text{ cm}^3 = 43.5 \times 10^{-24} \text{ cm}^3$$

$a = 3.52 \times 10^{-8}$ cm
$a = 352 \times 10^{-10}$ cm = 352 pm

25. (b): $CH_3 - \overset{sp}{C} \equiv \overset{sp}{C}^-$

Thus, pair of electrons is present in *sp*-hybridised orbital.

26. (c) : Read $Ca(CN)_2$ as $CaCN_2$.
$$CaC_2 + N_2 \longrightarrow \underset{\text{Nitrolim}}{CaCN_2} + C$$

27. (c) :

$$HC \equiv CH \xrightarrow{NaNH_2/liq.NH_3} HC \equiv CNa \xrightarrow{CH_3CH_2Br}$$

$$CH_3CH_2C \equiv CNa \xleftarrow{NaNH_2/liq. NH_3} \underset{\text{1-Butyne}(X)}{CH_3CH_2C \equiv CH}$$

$$\downarrow CH_3CH_2Br$$

$$\underset{\text{3-Hexyne}(Y)}{CH_3CH_2C \equiv CCH_2CH_3}$$

28. (d): For MY :
$$K_{sp} = s_1^2$$
$$\Rightarrow s_1 = \sqrt{K_{sp}} = \sqrt{6.2 \times 10^{-13}} = 7.87 \times 10^{-7} \text{ mol L}^{-1}$$

For NY_3 :
$$K_{sp} = 27 s_2^4 \Rightarrow s_2 = \sqrt[4]{\frac{6.2 \times 10^{-13}}{27}}$$
$$\Rightarrow s_2 = 3.89 \times 10^{-4} \text{ mol L}^{-1}$$

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

29. (c) : $Cu + 4HNO_3(\text{conc.}) \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

30. (c) : $\underset{}{\diagup}C = \boxed{O + H_2}NR \longrightarrow \underset{\text{Schiff's base}}{\diagup C = N - R}$

31. (b): A catalyst provides an alternate path to the reaction which has lower activation energy.

32. (c) : According to VSEPR theory, the repulsive forces between lone pair and lone pair are greater than between lone pair and bond pair which are further greater than bond pair and bond pair.

33. (b): This is Clausius—Clapeyron equation.

34. (d): *o*-Substituted biphenyls are optically active as both the rings are not in one plane and their mirror images are non-superimposable.

35. (b, c) : Dihydrogen acts as a powerful reducing agent and reduces metal oxides such as CuO, ZnO, PbO and Fe_3O_4 to their respective metals.

$$CuO + H_2 \longrightarrow Cu + H_2O$$
$$ZnO + H_2 \longrightarrow Zn + H_2O$$

$$Fe_3O_4 + 4H_2 \longrightarrow 3Fe + 4H_2O$$

Hydrogen has three isotopes of which protium is the most common and tritium is radioactive.

36. (b)

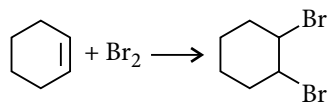**37. (c) :** Williamson's ether synthesis reaction involves the treatment of sodium alkoxide with a suitable alkyl halide to form an ether.

38. (d): $CH_3CH_2CH_2Br + KOH \longrightarrow CH_3CH=CH_2$
$+ KBr + H_2O$
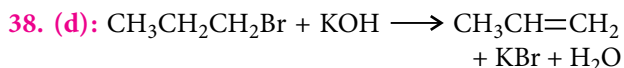
Saturated compound is converted into unsaturated compound by removal of group of atoms hence, it is an elimination reaction.
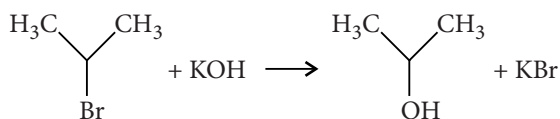
—Br group is replaced by —OH group hence, it is a substitution reaction.

Addition of Br_2 converts an unsaturated compound into a saturated compound hence, it is an addition reaction.

39. (a, d) : The correct order of increasing negative electron gain enthalpy is : I < Br < F < Cl
and the correct order of increasing first ionisation enthalpy is B < C < O < N.

40. (c) : Let the number of moles of each gas = x

Fraction of hydrogen escaped $= \dfrac{1}{2}x$

$$\frac{r_{O_2}}{r_{H_2}} = \sqrt{\frac{M_{H_2}}{M_{O_2}}}$$

$$\Rightarrow \frac{n_{O_2}/t}{\dfrac{x}{2}/t} = \sqrt{\frac{2}{32}} = \sqrt{\frac{1}{16}} = \frac{1}{4}$$

$$\Rightarrow \frac{n_{O_2}/t}{\dfrac{x}{2}/t} = \frac{1}{4} \Rightarrow n_{O_2} = \frac{1}{8}x$$

Hence, fraction of oxygen escaped $= \dfrac{1}{8}$

41. (d): The acidic character of the oxoacids increases with increase in oxidation number of the halogen atom *i.e.*,

$$HClO < HClO_2 < HClO_3 < HClO_4$$
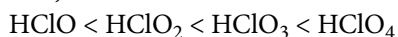
This can be explained on the basis of relative stability of the anions left after removal of a proton. Since

the stability of the anion decreases in the order : $ClO_4^- > ClO_3^- > ClO_2^- > ClO^-$, acid strength also decreases in the same order.

42. (c) : Streptomycin, chloromycetin and penicillin are antibiotics while novalgin is an analgesic.

43. (c) : Natural rubber is *cis*-polyisoprene.

44. (c) : Radius ratio, $\dfrac{r_+}{r_-} = \dfrac{0.98 \times 10^{-10}}{1.81 \times 10^{-10}} = 0.541$

It lies in the range of 0.414 to 0.732 hence, coordination number of each ion will be 6 as the compound will have NaCl type structure *i.e.*, octahedral arrangement.

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

◈ ◈

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Practice paper for phase II

1. On combustion in excess of air, lithium forms mainly the oxide, sodium forms peroxide while potassium or rubidium or caesium forms superoxides. It suggests that as cationic size increases the
   (a) anionic polarisability increases, thus stability decreases
   (b) anionic size increases, polarisability increases, covalency increases, thus stability increases
   (c) anionic size increases, coordination number increases, lattice energy increases, thus stability increases
   (d) anionic size decreases, stability increases.

2. The reaction of $KMnO_4$ and HCl results in
   (a) oxidation of Mn in $KMnO_4$ and production of Cl_2
   (b) reduction of Mn in $KMnO_4$ and production of H_2
   (c) oxidation of Mn in $KMnO_4$ and production of H_2
   (d) reduction of Mn in $KMnO_4$ and production of Cl_2.

3. The ether that undergoes electrophilic substitution reaction is
   (a) $CH_3OC_2H_5$ (b) $C_6H_5OCH_3$
   (c) CH_3OCH_3 (d) $C_2H_5OC_2H_5$

4. The boiling point of methanol is greater than methyl thiol because
   (a) there is intramolecular hydrogen bonding in methanol and intermolecular hydrogen bonding in methyl thiol
   (b) there is intermolecular hydrogen bonding in methanol and no hydrogen bonding in methyl thiol
   (c) there is no hydrogen bonding in methanol and intermolecular hydrogen bonding in methyl thiol

   (d) there is no hydrogen bonding in methanol and intramolecular hydrogen bonding in methyl thiol.

5. For a reaction $2N_2O_5 \rightarrow 4NO_2 + O_2$, rate and rate constant are 1.02×10^{-4} mol L^{-1} s^{-1} and 3.4×10^{-5} s^{-1}. The concentration of N_2O_5 at that time will be
   (a) 1.732 mol L^{-1} (b) 3 mol L^{-1}
   (c) 1.02×10^{-4} mol L^{-1} (d) 3.2×10^{5} mol L^{-1}

6. With respect to benzyl carbocation and benzyl carbanion, the correct statement is
   (a) $C_6H_5\overset{+}{C}H_2$ ion is more stable than $\overset{+}{C}H_3$ ion and $C_6H_5\overset{-}{C}H_2$ ion is also more stable than $\overset{-}{C}H_3$ ion
   (b) $C_6H_5\overset{+}{C}H_2$ ion is less stable than $\overset{+}{C}H_3$ ion and $C_6H_5\overset{-}{C}H_2$ ion is more stable than $\overset{-}{C}H_3$ ion
   (c) $C_6H_5\overset{+}{C}H_2$ ion is more stable than $\overset{+}{C}H_3$ ion and $C_6H_5\overset{-}{C}H_2$ ion is less stable than $\overset{-}{C}H_3$ ion
   (d) $C_6H_5\overset{+}{C}H_2$ ion is less stable than $\overset{+}{C}H_3$ ion and $C_6H_5\overset{-}{C}H_2$ ion is also less stable than $\overset{-}{C}H_3$ ion.

7. A cylinder contains 100 g of an ideal gas (mol. wt. 40 g mol^{-1}) at 27°C and 2 atm pressure. In transference process, the cylinder fell and a dent was created, *i.e.*, there was a decrease in the volume of cylinder. But valve attached to the cylinder cannot keep the pressure greater than 2 atm, so 10 g of gas leaked out. Calculate the volume of the cylinder after dent.
   (a) 3.08 L   (b) 30.8 L
   (c) 2.770 L   (d) 27.71 L

8. A clathrate may be defined as a
   (a) cage compound   (b) liquid crystal
   (c) mixture   (d) solid solution.

9. For the reaction,
   $H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$

if the initial pressure of $H_2 = CO_2$ and x moles/litre of hydrogen is consumed at equilibrium, the correct expression of K_p is

(a) $\dfrac{x^2}{1-x^2}$ (b) $\dfrac{(1+x)^2}{(1-x)^2}$
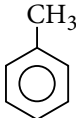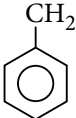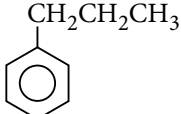
(c) $\dfrac{x^2}{(1-x)^2}$ (d) $\dfrac{x^2}{(2+x)^2}$

10. Which of the following sets contains only addition polymers?
(a) Polyethylene, polypropylene, terylene
(b) Polyethylene, PVC, acrilan
(c) Buna-S, nylon, polybutadiene
(d) Bakelite, PVC, polyethylene

11. The wave number of first line of Balmer series of hydrogen is 15200 cm^{-1}. The wave number of the first Balmer line of Li^{2+} ion is
(a) 15200 cm^{-1} (b) 60800 cm^{-1}
(c) 76000 cm^{-1} (d) 136800 cm^{-1}

12. Compound X on oxidation with alkaline $KMnO_4$ gives benzoic acid. X may be

(a) [benzene ring with CH$_3$] (b) [benzene ring with CH$_2$CH$_3$]

(c) [benzene ring with CH$_2$CH$_2$CH$_3$] (d) all of these.

13. Match list I with list II and select the correct answer using the codes given below the lists.

List I (Compound)	List II (Oxidation state of nitrogen)
(P) N_2O_5	(i) −2
(Q) NaN_3	(ii) +5
(R) NO	(iii) −1/3
(S) N_2H_4	(iv) +2

	P	Q	R	S
(a)	(ii)	(iii)	(iv)	(i)
(b)	(i)	(ii)	(iii)	(iv)
(c)	(iv)	(i)	(ii)	(iii)
(d)	(iii)	(i)	(iv)	(ii)

14. Aldehydes and ketones cannot be distinguished by
(a) Molisch's test (b) Tollens' test
(c) Benedict's test (d) Schiff's test.

15. The correct order of increasing ionic character of the given compounds is
(a) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$
(b) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$
(c) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$
(d) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$

16. Which of the following is incorrect?
(a) Molecular weight of NaCl found by osmotic pressure measurements is half of the theoretical value.
(b) Molecular weight of CH_3COOH in benzene found by cryoscopic methods is double of the theoretical value.
(c) Osmotic pressure of 0.1 M glucose solution is half of that of 0.1 M NaCl solution.
(d) Molecular weight of HCl found by any colligative property will be same in the aqueous solution and benzene solution.

17. Match list I (reagents used with ethyne) with list II (products) and select the correct answer using the codes given below the lists.

List I	List II
P. Hydrogen in presence of catalyst	(i) Benzene
Q. Heat at 600°C	(ii) Acetaldehyde
R. Hydrogen in presence of Pd and $CaCO_3$ at 473 K	(iii) Ethene
S. Water in presence of H_2SO_4 and $HgSO_4$	(iv) Ethane

|	P	Q	R	S
(a)	(ii)	(iii)	(iv)	(i)
(b)	(i)	(iv)	(iii)	(ii)
(c)	(i)	(iv)	(ii)	(iii)
(d)	(iv)	(i)	(iii)	(ii)

18. The sequence in which different reagents are used to separate each component in a mixture of PbS, ZnS and FeS from froth floatation process is
(a) potassium ethyl xanthate, KCN
(b) potassium ethyl xanthate, KCN, NaOH, $CuSO_4$, acid
(c) KCN, $CuSO_4$, acid
(d) none of these.

19. Correct statement about carbonyl group is
(a) it is non-planar
(b) carbon atom is sp^2 hybridised
(c) oxygen has five non-bonding electrons
(d) carbon oxygen bond is non-polar.

20. Which of the following will produce hard water?
(a) Saturation of water with $CaSO_4$
(b) Addition of Na_2SO_4 to water
(c) Saturation of water with $CaCO_3$
(d) Saturation of water with $MgCO_3$

21. Which of the following sets consists only essential amino acids?
(a) Leucine, Proline, glycine
(b) Leucine, Histidine, Lysine
(c) Valine, Glycine, Proline
(d) Tyrosine, Arginine, Serine.

**22.** Consider the graph between compressibility factor Z and pressure P
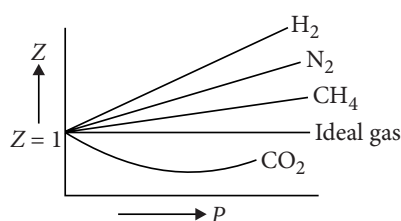
The correct increasing order of ease of liquefaction of the gases shown in the above graph is
(a) $H_2 < N_2 < CH_4 < CO_2$
(b) $CO_2 < CH_4 < N_2 < H_2$
(c) $H_2 < CH_4 < N_2 < CO_2$
(d) $CH_4 < H_2 < N_2 < CO_2$

23. Under identical conditions of temperature and pressure, the ratio of the rates of effusion of O_2 and CO_2 gases is given by
(a) $\dfrac{\text{rate of effusion of oxygen}}{\text{rate of effusion of carbon dioxide}} = 0.87$
(b) $\dfrac{\text{rate of effusion of oxygen}}{\text{rate of effusion of carbon dioxide}} = 1.17$
(c) $\dfrac{\text{rate of effusion of oxygen}}{\text{rate of effusion of carbon dioxide}} = 8.7$
(d) $\dfrac{\text{rate of effusion of oxygen}}{\text{rate of effusion of carbon dioxide}} = 11.7$

24. Which of the following statements is false?
(a) Lower the concentration of D.O., more polluted is the water sample.
(b) The tolerable limit of lead in drinking water is 50 ppb.
(c) Water is considered pure if it has BOD less than 5 ppm.
(d) In COD determination, the pollutants resistant to microbial oxidation are not oxidised by oxidising agent like $K_2Cr_2O_7$.

25. The number of electrons involved in the reaction when one Faraday of electricity is passed through an electrolyte in solution is
(a) 12×10^{46} (b) 96540
(c) 8×10^{16} (d) 6×10^{23}

26. The reaction,
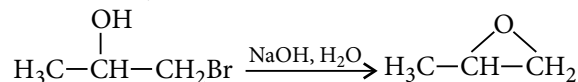
can be described as
(a) acid-base reaction followed by an intramolecular S_N1 reaction
(b) acid-base reaction followed by an intramolecular Williamson's ether synthesis
(c) E2 reaction followed by an addition reaction to a double bond
(d) S_N2 reaction following an intramolecular Williamson's ether synthesis.

27. The two complexes given below are
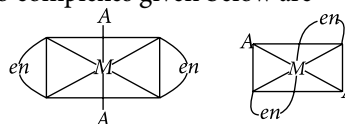
(a) geometrical isomers   (b) position isomers
(c) optical isomers   (d) identical.

28. Tertiary nitro compounds do not tautomerise because
(a) there is no double bond
(b) there is no α-hydrogen
(c) oxygen is more electronegative than hydrogen
(d) all of the above.

29. The prefixes *syn* and *anti* are used to denote
(a) structural isomers
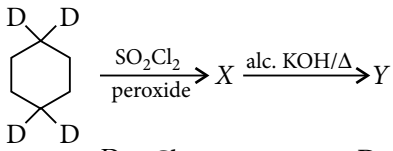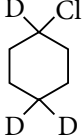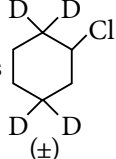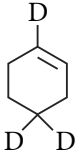(b) conformational isomers
(c) geometrical isomers
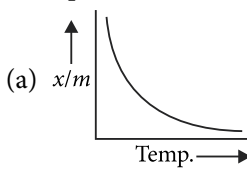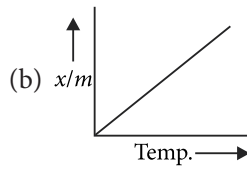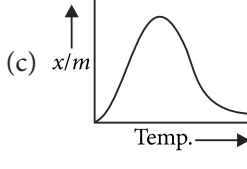(d) optical isomers.
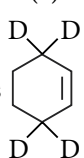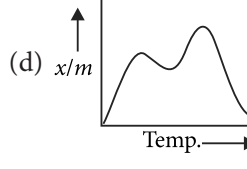
30. Which of the following has correct increasing basic strength?
(a) $MgO < BeO < CaO < BaO$
(b) $BeO < MgO < CaO < BaO$
(c) $BaO < CaO < MgO < BeO$
(d) $CaO < BaO < BeO < MgO$

31. In a ferromagnetic material
(a) all the magnetic moment vectors are aligned in one direction
(b) half of the magnetic moment vectors point in one direction and rest in the opposite direction
(c) all the magnetic moment vectors are randomly oriented
(d) it is characterised by small magnetic moment.

32. The heats of neutralization of CH_3COOH, $HCOOH$, HCN and H_2S are –13.2, –13.4, –2.9 and –3.8 kcal per equivalent respectively. The correct increasing order of acid strength is
(a) $HCOOH < CH_3COOH < H_2S < HCN$
(b) $HCN < H_2S < CH_3COOH < HCOOH$
(c) $HCOOH < CH_3COOH < HCN < H_2S$
(d) $CH_3COOH < H_2S < HCN < HCOOH$

33. If the bond enthalpy of $HCl_{(g)}$, $H_{2(g)}$ and $Cl_{2(g)}$ is 103, 104 and 58 kcal mol^{-1}, then the enthalpy change at constant volume for the following reaction at 300 K will be
$$\frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)} \longrightarrow HCl_{(g)}$$
(a) -44 kcal mol^{-1} (b) -66 kcal mol^{-1}
(c) -11 kcal mol^{-1} (d) -22 kcal mol^{-1}

34. In context with the transition elements, which of the following statements is incorrect?
(a) In addition to the normal oxidation states, the zero oxidation state is also shown by these elements in complexes.
(b) In the highest oxidation states, transition metals show basic character and form cationic complexes.
(c) In the highest oxidation states of the first five transition elements (Sc to Mn), all the $4s$ and $3d$ electrons are used for bonding.
(d) Once the d^5 configuration is exceeded, the tendency to involve all the $3d$ electrons in bonding decreases.

35. Which of the following observations are correct about the major products X and Y of the following reaction?

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

36. Which of the following is most basic?
(a) $Ce(OH)_3$ (b) $Lu(OH)_3$
(c) $Yb(OH)_3$ (d) $Tb(OH)_3$

37. The correct statement about orthoboric acid is
(a) it is a strong monobasic acid
(b) it is not a proton donor, but a weak Lewis acid
(c) it is a tribasic acid
(d) it is harmful for eyes.

38. When phenol is treated with Br_2 water, the product is
(a) *o*- and *p*-bromophenol
(b) 2,3,4-tribromophenol
(c) 2,4,6-tribromophenol
(d) none of these.

39. Arsenic drugs are mainly used in the treatment of
(a) jaundice   (b) typhoid
(c) syphilis   (d) cholera.

40. In the standardization of $Na_2S_2O_3$ using $K_2Cr_2O_7$ by iodometry, the equivalent weight of $K_2Cr_2O_7$ is
(a) (molecular weight)/2
(b) (molecular weight)/6
(c) (molecular weight)/3
(d) same as the molecular weight.

41. Which of the following represents physical adsorption?

42. Secondary amine with Hinsberg's reagent forms
(a) *N*-alkyl sulphonamide soluble in KOH solution.
(b) *N*-alkyl sulphonamide insoluble in KOH solution.
(c) *N,N*-dialkyl sulphonamide soluble in KOH solution.
(d) *N,N*-dialkyl sulphonamide insoluble in KOH solution.

43. Primary alcohols can be prepared by the reaction of *R*Mg*X* with
(a) C_2H_5CHO (b) CH_3CHO
(c) $HCHO$ (d) C_3H_7CHO

44. Which one of the following statements is not true?
(a) The conjugate base of $H_2PO_4^-$ is HPO_4^{2-}.
(b) pH + pOH = 14 for all aqueous solutions.
(c) The pH of 1×10^{-8} M HCl is 8.
(d) pH decreases with rise in temperature.

45. Which is not the correct statement for ionic solids in which positive and negative ions are held by strong electrostatic attractive forces?
(a) The radius ratio r_+/r_- increases as coordination number increases.
(b) As the difference in size of ions increases, coordination number increases.
(c) When coordination number is eight, r_+/r_- ratio lies between 0.225 to 0.414.
(d) In ZnS type structure, anions have *ccp* arrangement and cations occupy alternate tetrahedral voids. the coordination number of Zn^{2+} and S^{2-} respectively are 4 and 4.

SOLUTIONS

1. **(c) :** The stability of the peroxides and superoxides increases as the metal ions become larger. Basically, larger cations are stabilised by larger anions because if both ions are similar in size, the coordination number will be high and this gives a high lattice energy.

2. **(d):** $2KMnO_4 + 16HCl \longrightarrow 2KCl + 2MnCl_2 + 8H_2O + 5Cl_2$
In the reaction, manganese is reduced and changes from Mn^{+7} to Mn^{2+} while Cl^- is oxidised to Cl_2.

3. **(b):** Alkyl aryl ethers undergo electrophilic substitution reactions.

4. **(b):** Intermolecular H-bonding is present in methanol while there is no H-bonding in methyl thiol, CH_3SH.

$$\cdots\text{H}-\text{O}\cdots\text{H}-\text{O}\cdots\text{H}-\text{O}\cdots\text{H}-\text{O}\cdots$$
$$\quad\;\;|\qquad\quad|\qquad\quad|\qquad\quad|$$
$$\quad\text{CH}_3\quad\;\text{CH}_3\quad\;\text{CH}_3\quad\;\text{CH}_3$$

Methanol

5. **(b):** Unit of rate constant shows that it is a first order reaction.
∴ Rate = Rate constant $[N_2O_5]$
$$\Rightarrow [N_2O_5] = \frac{\text{Rate}}{\text{Rate constant}} = \frac{1.02 \times 10^{-4}}{3.4 \times 10^{-5}} = 3\,M$$

6. **(a) :** Both +ve and –ve charge are delocalised on the benzene ring hence, $C_6H_5\overset{+}{C}H_2$ and $C_6H_5\overset{-}{C}H_2$, both are stable.

7. **(d):** As 10 g of gas leaked out after the dent, 90 g of the gas must occupy the volume of the cylinder at 2 atm and 27°C.
$$PV = \frac{w}{M}RT,$$
$$2 \times V = \frac{90}{40} \times 0.0821 \times 300 \implies V = 27.7\,L$$

8. **(a) :** Clathrates are defined as cage compounds in which gaseous atoms are entrapped in cavities of crystal lattices of other compounds.
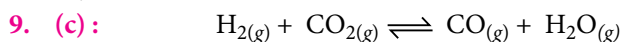
9. **(c) :**
$$H_{2(g)} + CO_{2(g)} \rightleftharpoons CO_{(g)} + H_2O_{(g)}$$
Initial pressure   1   1   0   0
At equilibrium $(1-x)$ $(1-x)$ x x
$$K_p = \frac{p_{CO} \times p_{H_2O}}{p_{H_2} \times p_{CO_2}} = \frac{(x)(x)}{(1-x)(1-x)} = \frac{x^2}{(1-x)^2}$$

10. **(b)**

11. **(d):** Applying $\bar{\upsilon} = R\left[\dfrac{1}{n_1^2} - \dfrac{1}{n_2^2}\right]Z^2$
$$\bar{\upsilon}_{Li^{2+}} = \bar{\upsilon}_H \times 3^2 = 15200 \times 9 = 136800\,cm^{-1}$$

12. **(d):** The alkyl side chain on benzene, irrespective of its size or nature, is completely oxidised to carboxylic group on oxidation with alkaline $KMnO_4$.

13. **(a)**

14. **(a) :** Aldehydes and ketones cannot be distinguished by Molisch's test.

15. **(a) :** Ionic character of compounds of metals increases down the group.

16. **(d):** In aqueous solution, HCl dissociates but in benzene it does not.

17. **(d)**

18. **(b):** Potassium ethyl xanthate acts as a collector, KCN and NaOH depress the froth floatation property of ZnS and FeS particles. Thus, only PbS go into froth. Then copper sulphate is added to the tank (mixture) which activates floating character of ZnS and only ZnS comes along with froth. The remaining slurry is acidified and FeS floats along with froth.

19. **(b)**

20. **(a) :** $CaSO_4$ is soluble in water and provides Ca^{2+} ions to develop hardness. $CaCO_3$ and $MgCO_3$ are insoluble in water.
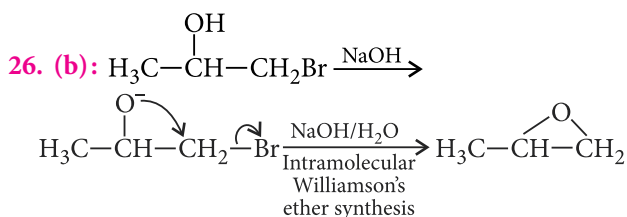
21. (b)

22. (a): Z is less than 1 means more compressible gases while $Z > 1$ means less compressible gases.

23. (b): $\dfrac{r_{O_2}}{r_{CO_2}} = \sqrt{\dfrac{M_{CO_2}}{M_{O_2}}} = \sqrt{\dfrac{44}{32}} = 1.17$

24. (d): In COD determination, the pollutants resistant to microbial oxidation are also oxidised by oxidising agent like $K_2Cr_2O_7$.

25. (d): One Faraday of electricity means one mole of electrons *i.e*, 6×10^{23} electrons.

26. (b):
$$\underset{\overset{|}{OH}}{H_3C-CH-CH_2Br} \xrightarrow{NaOH}$$

$$\underset{\overset{|}{O^-}}{H_3C-CH-CH_2 \curvearrowright Br} \xrightarrow[\substack{Intramolecular \\ Williamson's \\ ether\ synthesis}]{NaOH/H_2O} H_3C-\overset{O}{\overbrace{CH-CH_2}}$$
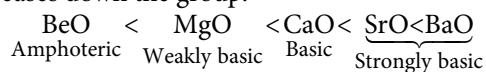
27. (d): Both represent only one molecule and no isomerism is seen.

28. (b): Tertiary nitro compounds do not have any α-hydrogen atom hence, do not show tautomerism.

29. (c): *Syn* and *anti* prefixes are used to denote geometrical isomers involving either C=N or N=N bond, *e.g.*,


Syn-Benzaldoxime   *anti*-Benzaldoxime
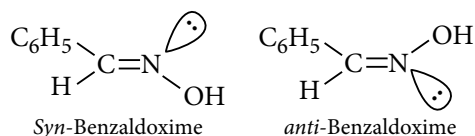
30. (b): The basic strength of the oxides increases gradually as the ionization enthalpy of metal decreases down the group.
$$\underset{Amphoteric}{BeO} < \underset{Weakly\ basic}{MgO} < \underset{Basic}{CaO} < \underset{Strongly\ basic}{SrO < BaO}$$

31. (a): In ferromagnetic materials, all the magnetic moment vectors are aligned in one direction and these substances show magnetic properties even in the absence of external magnetic field.

32. (b): Stronger the acid, more will be the heat of neutralization. Negative sign signifies evolution of heat.
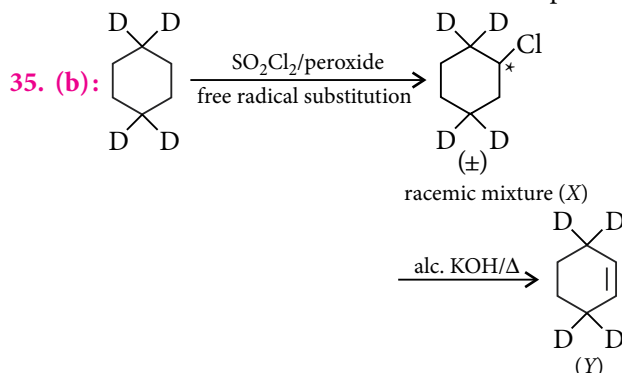
33. (d): $\dfrac{1}{2}H_{2(g)} + \dfrac{1}{2}Cl_{2(g)} \longrightarrow HCl_{(g)}$
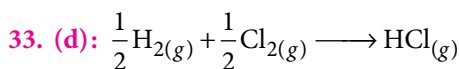
$\Delta H_{reaction} = \Sigma(B.E.)_{reactants} - \Sigma(B.E.)_{products}$

$= \dfrac{1}{2}\Big[(B.E.)_{H-H} + (B.E.)_{Cl-Cl}\Big] - (B.E.)_{HCl}$

$= \dfrac{1}{2}[104 + 58] - 103 = -22$ kcal mol^{-1}

34. (b): When the transition metals are in their highest oxidation states, they no longer have tendency to give away electrons, thus they are not basic but show acidic character and form anionic complexes.

35. (b):

36. (a): As the size of the lanthanide ions decreases from Ce^{3+} to Lu^{3+}, the covalent character of $M-OH$ bond increases and hence, the basic strength decreases.

Thus, $Ce(OH)_3$ is most basic while $Lu(OH)_3$ is least basic.
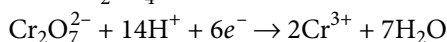
37. (b) : Orthoboric acid is a weak monobasic acid with $K_a = 5.6 \times 10^{-10}$. It does not act as protonic acid (*i.e.*, proton donor) but behaves as Lewis acid by accepting a pair of electrons from OH^- ion.
$$B(OH)_3 + 2H-O-H \rightarrow [B(OH)_4]^- + H_3O^+$$

38. (c) : When bromine water is added to phenol at room temperature, direct bromination gives white precipitate of 2,4,6-tribromophenol.

Phenol $\xrightarrow[-3HBr]{3\ Br_2/water}$ 2,4,6-Tribromophenol
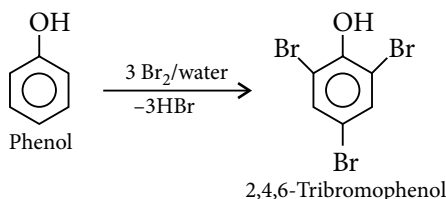
39. (c) : Arsenic drugs (salvarsan) are mainly used in treatment of syphilis.

40. (b) : $K_2Cr_2O_7$ acts as an oxidising agent in presence of dil. H_2SO_4.
$$Cr_2O_7^{2-} + 14H^+ + 6e^- \rightarrow 2Cr^{3+} + 7H_2O$$
Equivalent weight of $K_2Cr_2O_7$
$$= \frac{\text{Molecular weight}}{\text{Number of electrons gained}} = \frac{M}{6}$$

41. (a) : The physical adsorption isobar shows a decrease in x/m throughout with rise in temperature.

42. (d) : $PhSO_2Cl + RR'NH \rightarrow PhSO_2NRR'$
N, N-dialkyl sulphonamide
(Insoluble in KOH)
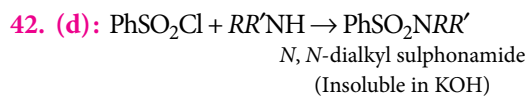
43. (c) : All aldehydes except formaldehyde (HCHO) give secondary alcohols with Grignard reagent ($RMgX$).
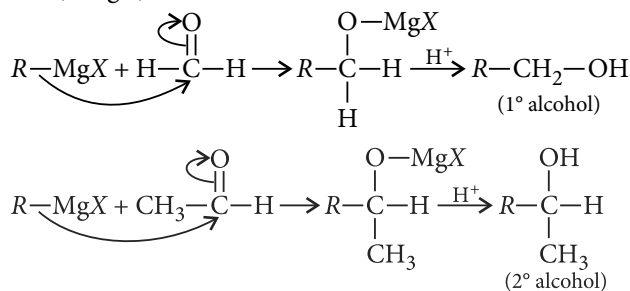
44. (c) : In case of dilute solutions of acids, $[H^+]$ of water cannot be neglected.
10^{-8} M HCl $= 10^{-8}$ M H^+
Also from H_2O, $[H^+] = 10^{-7}$ M
Total $[H^+] = 10^{-7} + 10^{-8} = 10^{-7}(1 + 0.1)$
$$= 10^{-7}(1.1)$$
Hence, pH $= 7 - 0.0414 = 6.96$

45. (c) : When coordination number is 8, r_+/r_- ratio lies between 0.732 – 1.

◈ ◈

CONCEPT
BOOSTER
BEWARE OF BASES

Hello students!! When there was a discussion about ACIDS in the last article, how can it be possible that BASES will not come this month!! I am really thankful to all my avid readers. I believe you will like this article same as before. Thanks for the support. Stay healthy.. ☺☺

*Arunava Sarkar

BASICITY CORNER

○ **Concept 1 :** Basicity is a thermodynamic term. Basicity is better defined with the overall stability of the process during proton abstraction *e.g.*,

$$>C-H + B: \rightleftharpoons \ddot{C} + \overset{+}{B}H$$
(Base) (Conjugate acid of the base)
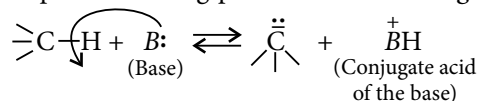
Now, if $\overset{+}{B}H$ is stable enough, then the overall equilibrium will be shifted towards the right and base B: is considered to be a good base. If $\overset{+}{B}H$ is not well stabilized then the equilibrium will be towards left and B: is not considered to be a good bas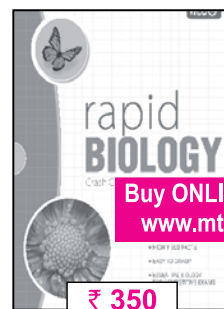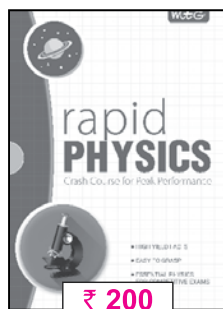e. The stability of $\overset{+}{B}H$ is determined by the polarisability of $\overset{+}{B}H$ bond. Greater the polarisability, lesser will be the $\Delta H°$ for bond dissociation (*i.e.* bond dissociation energy) and abstracted H^+ will be released which will in turn decrease the basicity. The fact is :

$$A—O—H$$

Highly electronegative so, can withdraw the bond pair with hydrogen atom
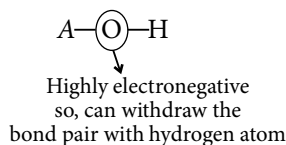
Now, if A^- is electron donating then it will decrease acidity (antagonistic to the attraction force of oxygen towards the bonding electrons with hydrogen) but if A^- is electron withdrawing then it will increase acidity (reinforcing the attraction force of oxygen towards the bonding electrons with hydrogen). So, with the increase in the bond polarisability of $\overset{+}{B}—H$ bond, basicity decreases.

As per this, the basicity order of period 2 elements is :

$$R_3\ddot{C} > R_2\ddot{N} > R\ddot{O}: > :\ddot{F}: \text{ or}$$
$$\ddot{C}H_3 > \ddot{N}H_2 > \ddot{O}H > \ddot{F}$$
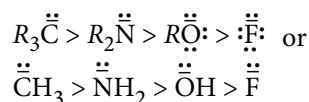
For the similar reason, along the group, polarisability increases and basicity decreases, so, $R\ddot{O}: > R\ddot{S}:$.

As per the electron donating or electron withdrawing tendency of the attached group(s), basicity alters, *e.g.*,

$$CH_3—NH_2 > H—NH_2 > H_2N←NH_2 > HO—\ddot{N}H_2$$
+*I* effect   Does almost nothing   –*I* effect   Stronger –*I* effect
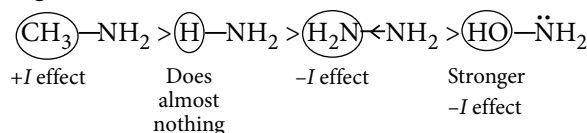
○ **Concept 2 :** In general, with increase in the number of alkyl groups attached with electron donating atom, basicity increases, *e.g.*,

$$R_3\ddot{N} > R_2\ddot{N}H > R\ddot{N}H_2 > \ddot{N}H_3$$
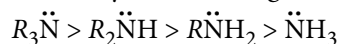
But a few exceptions are there which are given in the following table :

Table 1 :

Compound	pK_b
$:NH_3$	4.5
$CH_3\ddot{N}H_2$	3.36
$\begin{matrix}CH_3\\CH_3\end{matrix}>\ddot{N}H$	3.23 ⎫
$\begin{matrix}H_3C\\H_3C—N:\\H_3C\end{matrix}$	4.2 ⎭ surprising

---

* Institute of Chemistry (IOC)- Asansol, Durgapur, Dhanbad, Burdwan, Kolkata, Jamshedpur, Bokaro, Patna

Table 2 :

Compound	pK_b	
Et$\ddot{N}H_2$	3.33	
$\begin{array}{c}Et \\ Et\end{array}\!\!\ddot{N}H$	3.07	⎫
$\begin{array}{c}Et \\ Et - N\!: \\ Et\end{array}$	3.12	⎬ surprising

This only happens in water or a solvent with proton (H$^+$). But in gaseous phase normal order *i.e.*, 3° > 2° > 1° amine is observed.

○ **Concept 3** : 3° > 2° > 1°

$$R_3N\!: \xrightarrow{RI} R_4\overset{+}{\ddot{N}}I \xrightarrow{\text{Moist Ag}_2O} R_4\overset{+}{\ddot{N}}OH$$

Tertiary   Tetraalkyl ammonium
amine   hydroxide
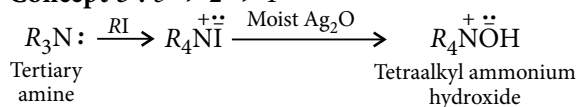
$R_4\overset{+}{\ddot{N}}OH$ is reported to be completely ionized and it has basicity comparable with mineral alkalies.

○ **Concept 4 :** Guanidine is an extremely strong base with pK_b = 0.4. Guanidine has the following structure :
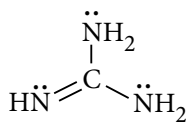
and this is expected to show the following resonating structures :
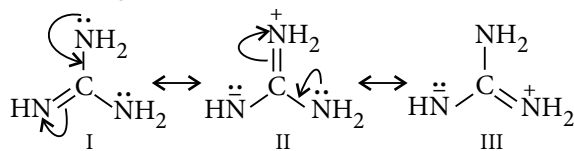
When guanidine accepts a proton (*i.e.* it acts as a base),
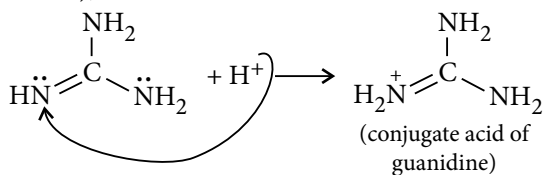
The conjugate acid formed has the following resonating structures :
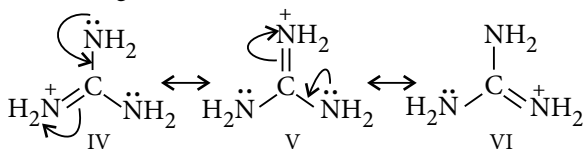
Now, a few points which are to be considered are :

1. Structures II and III are having charge separation and this is not good as per the overall stability of the resonating structures is considered whereas in structures IV, V and VI there is no charge separation, only the +ve charge is distributed here which is a good sign as per the stability of resonating structures is considered. So, I is not as resonance stabilised as IV.

2. I is not equivalent with II and III. IV is equivalent with V and VI. Equivalent structures give better stability.

3. For protonation of guanidine, a very small amount of energy is required. So, energy difference is not of much importance.
   Guanidine is definitely a strong base. Structures are said to be equivalent on the basis of the energy content and symmetry.
   Guanidine has pK_b value of 0.4 but a similar structure of amidine *i.e.*, $R\overset{\displaystyle C}{\underset{\displaystyle NH}{\|}}\!\!-NH_2$ has pK_b = 1.6

   with $R = -CH_3$

This is due to the lesser stability of the corresponding conjugate acid of amidine in comparison with the conjugate acid of guanidine.

Which nitrogen will be protonated in case of multiple presence of nitrogen atoms?

Suppose, the following base is given :

Protonation of sp^2 nitrogen :

Protonation of sp^3 nitrogen :

    No resonance!!

Therefore, sp^2 hybridised nitrogen will be protonated.

○ **Concept 5 :** Which one is more basic?

 pyridine or imidazoline

Protonate both of them.

As per the resonance, both are more or less looking fine. So, here comes a next concept.

As imidazoline contains two nitrogen atoms whereas pyridine contains only one hence, imidazoline is a better base. The following table confirms it :

Table 3 :

Compound	pK_b
Imidazoline	3
Pyridine	7.8

○ **Concept 6 :** Aromatic amine *i.e.*, aniline is less basic than ammonia because the lone pair over nitrogen

atom takes part in resonance with the benzene ring. This can be understood from the pK_b values given in the following table :

Table 4 :

Compound	pK_b	
NH_3	4.75	basicity decreases a lot
$C_6H_5NH_2$	9.38	
C_6H_5NHMe	9.16	
$C_6H_5NMe_2$	8.85	

In case of $C_6H_5NMe_2$, there is a steric repulsion between the *ortho* hydrogen and the bulky —NMe_2 group.

Due to this steric repulsion, lone pair of nitrogen can show basicity.

◈ ◈

SOLUTIONS OF MAY 2016 CROSSWORD

Winners of April 2016 Crossword

- Hrishikesh Sarmah, Assam
- Samrat Gupta, Kolkata

NCERT CORNER

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry. Papers of JEE(Main & Advanced)/ NEET/AIIMS/other PMTs are drawn heavily from NCERT books. Practice Hard! All the best!!

CLASS XI-XII

1. 1 g of Mg is burnt in a closed vessel containing 0.5 g of O_2. Which of the following statements is correct?
   (a) O_2 is the limiting reagent and Mg is in excess by 0.25 g.
   (b) Mg is the limiting reagent and is in excess by 0.5 g.
   (c) O_2 is the limiting reagent and is in excess by 0.25 g.
   (d) O_2 is the limiting reagent and Mg is in excess by 0.75 g.

2. Hydrogen bonds are formed in many compounds like H_2O, HF and NH_3. The correct decreasing order of boiling points of these compounds is
   (a) $HF > H_2O > NH_3$ (b) $H_2O > HF > NH_3$
   (c) $NH_3 > HF > H_2O$ (d) $NH_3 > H_2O > HF$

3. Brine is electrolysed by using inert electrodes. The reaction at anode is
   (a) $Cl^-_{(aq)} \longrightarrow \frac{1}{2} Cl_{2(g)} + e^-$; $E^\circ_{cell} = 1.36$ V
   (b) $2H_2O_{(l)} \longrightarrow O_{2(g)} + 4H^+ + 4e^-$; $E^\circ_{cell} = 1.23$ V
   (c) $Na^+_{(aq)} + e^- \longrightarrow Na_{(s)}$; $E^\circ_{cell} = -2.71$ V
   (d) $H^+_{(aq)} + e^- \longrightarrow \frac{1}{2} H_{2(g)}$; $E^\circ_{cell} = 0.00$ V

4. An organic compound 'A' having molecular formula C_3H_6 on treatment with aqueous H_2SO_4 gives 'B' which on treatment with $HCl/ZnCl_2$ gives 'C'. The compound 'C' on treatment with ethanolic KOH gives back the compound 'A'. Identify the compound 'C'.
   (a) $CH_3CH_2CH_2Cl$ (b) $CH_3 — CH{=}CH_2$
   (c) $CH_3\underset{|}{\overset{}{C}}HCH_3$ with Cl   (d) $CH_3CH_2CH_3$

5. Considering the elements F, Cl, O and N, the correct order of their chemical reactivity in terms of oxidising property is
   (a) $F > Cl > O > N$ (b) $F > O > Cl > N$
   (c) $Cl > F > O > N$ (d) $O > F > N > Cl$

6. The pollutants which come directly in the air from sources are called primary pollutants. Primary pollutants are sometimes converted into secondary pollutants. Which of the following belongs to secondary air pollutants?
   (a) CO   (b) Hydrocarbon
   (c) Peroxyacetyl nitrate   (d) NO

7. Which of the following is homopolymer?
   (a) PMMA   (b) Bakelite
   (c) Glyptal   (d) Nylon-6,6

8. Which of the following reactions increases the production of dihydrogen from synthesis gas?
   (a) $CH_{4(g)} + H_2O_{(g)} \xrightarrow[\text{Ni}]{1270\text{ K}} CO_{(g)} + 3H_{2(g)}$
   (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) $C_2H_{6(g)} + 2H_2O_{(g)} \xrightarrow[\text{Ni}]{1270\text{ K}} 2CO_{(g)} + 5H_{2(g)}$

9. If q_1 is the specific charge (e/m) of cathode rays and q_2 is that of positive rays then
   (a) $q_1 = q_2$ (b) $q_1 < q_2$
   (c) $q_1 > q_2$ (d) none of these.

10. Alum is added to water containing suspended impurities
    (a) to make a colloidal solution
    (b) to coagulate the suspended impurities
    (c) to remove impurities of calcium and magnesium
    (d) to protect the colloidal solution from getting precipitated.

11. Which of the following reactions will not yield phenol?
    (a) $\xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) Fusion with NaOH at 300 atm}}$

(b) [benzene ring with NH$_2$] $\xrightarrow[\text{(ii) H}_2\text{O (warming)}]{\text{(i) NaNO}_2\text{/HCl}}$

(c) [benzene ring] $\xrightarrow[\substack{\text{(ii) NaOH, (heating)} \\ \text{(iii) H}^+}]{\text{(i) Oleum}}$

(d) [benzene ring with Cl] $\xrightarrow[\text{(ii) HCl}]{\text{(i) NaOH}_{(aq.)}, \text{298 K/1 atm}}$
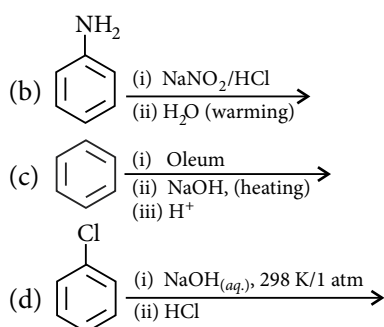
12. How many years would it take to spend Avogadro number of rupees at the rate of 10 lac rupees per second?
(a) 1.90×10^{10} years   (b) 6.02×10^3 years
(c) 1.90×10^6 years   (d) 4.01×10^4 years

13. Which product(s) is/are formed when the compound [benzene ring]—CHO is treated with concentrated aqueous KOH solution?

(a) K^+O^-—[benzene ring]—CHO

(b) [benzene ring]—$\overset{\overset{O}{\|}}{C}$—$O^-K^+$ and [benzene ring]—CH_2OH

(c) K^+O^-—[benzene ring]—$\overset{\overset{O}{\|}}{C}$—$O^-K^+$ and

K^+O^-—[benzene ring]—O^-K^+

(d) [benzene ring]—$\overset{\overset{O}{\|}}{C}$—$O^-K^+$ and [benzene ring]—O^-K^+
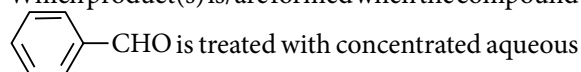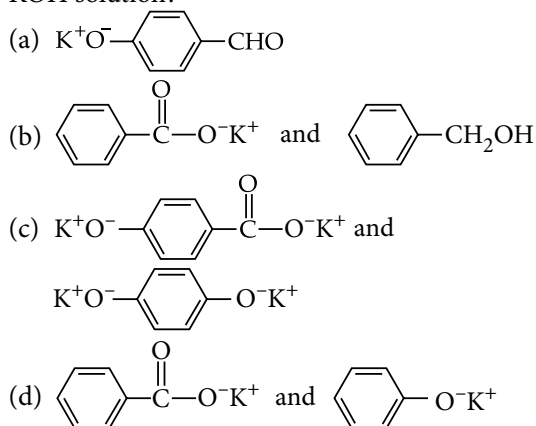
14. Predict the structure of the product in the given reaction.

[Fischer projection: top Br; H—Ph; MeO—H; bottom Ph] $\xrightarrow[\text{acetone}]{\text{NaI}}$

(a) [Fischer: top I; H—Ph; MeO—H; bottom Ph]
(b) [Fischer: top I; I—Ph; NaO—I; bottom Ph]
(c) [Fischer: top I; Ph—H; MeO—H; bottom Ph]
(d) [Fischer: top Br; I—Ph; NaO—I; bottom Ph]
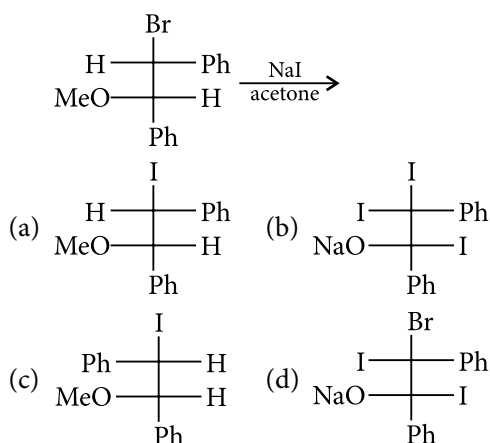
15. Which is the correct decreasing order of reactivity towards S_N2 displacement of the following compounds?

(a) 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane > 1-Bromo-3-methylbutane > 1-Bromobutane

(b) 1-Bromo-2,2-dimethylpropane > 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-3-methylbutane

(c) 1-Bromobutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane > 1-Bromo-3-methylbutane

(d) 1-Bromobutane > 1-Bromo-3-methylbutane > 1-Bromo-2-methylbutane > 1-Bromo-2,2-dimethylpropane

16. Corrosion of iron is essentially an electrochemical phenomenon where the cell reactions are
(a) Fe is oxidised to Fe^{2+} and dissolved oxygen in water is reduced to OH^-
(b) Fe is oxidised to Fe^{3+} and H_2O is reduced to O_2^{2-}
(c) Fe is oxidised to Fe^{2+} and H_2O is reduced to O_2^-
(d) Fe is oxidised to Fe^{2+} and H_2O is reduced to O_2.

17. For the given reactions (i) and (ii) which of the algebric relations is correct?
(i) $C_{(g)} + 4H_{(g)} \rightarrow CH_{4(g)}$; $\Delta_r H = x$ kJ mol^{-1}
(ii) $C_{(s)}$ (graphite) $+ 2H_{2(g)} \rightarrow CH_{4(g)}$;
$$\Delta_r H = y \text{ kJ mol}^{-1}$$
(a) $x = y$ (b) $x = 2y$ (c) $x > y$ (d) $x < y$

18. Which of the following is a broad spectrum antibiotic?
(a) Ampicillin   (b) Penicillin
(c) Chloramphenicol (d) Terpineol

19. When a substance 'A' reacts with water it produces a combustible gas 'B' and a solution of substance 'C' in water. When another substance 'D' reacts with this solution of 'C', it also produces the same gas 'B'. 'A' imparts a deep golden yellow colour to smokeless flame of Bunsen burner. A, B, C and D are respectively
(a) Na, H_2, NaOH and Zn
(b) K, H_2, KOH and Al
(c) Ca, H_2, Ca(OH)$_2$ and Sn
(d) CaC$_2$, C$_2$H$_2$, Ca(OH)$_2$ and Fe

20. Identify the correct order of acidic strengths of CO_2, CuO, CaO and H_2O.
(a) CaO < CuO < H_2O < CO_2
(b) H_2O < CuO < CaO < CO_2
(c) CaO < H_2O < CuO < CO_2
(d) H_2O < CO_2 < CaO < CuO

21. Consider a first order gas phase decomposition reaction given below :
$$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$$
The initial pressure of the system before decomposition of A was P_i. After lapse of time 't', total pressure of the system increased by x units and became 'P_t'. The rate constant k for the reaction is given as
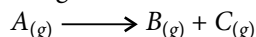
(a) $k = \dfrac{2.303}{t} \log \dfrac{P_i}{P_i - x}$

(b) $k = \dfrac{2.303}{t} \log \dfrac{P_i}{2P_i - P_t}$

(c) $k = \dfrac{2.303}{t} \log \dfrac{P_i}{2P_i + P_t}$

(d) $k = \dfrac{2.303}{t} \log \dfrac{P_i}{P_i + x}$

22. Which of the following represents the product formed in the given reaction?
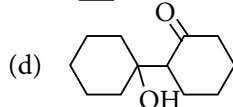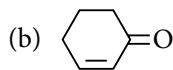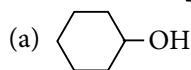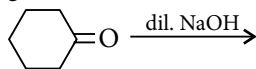
23. The critical temperature of water is higher than that of O_2 because the H_2O molecule has
 (a) fewer electrons than O_2
 (b) two covalent bonds
 (c) V-shape
 (d) dipole moment.

24. The standard electrode potentials of few metals are given below :
$K^+/K = -2.93$ V, $Ag^+/Ag = 0.80$ V, $Hg^{2+}/Hg = 0.79$ V, $Mg^{2+}/Mg = -2.37$ V, $Cr^{3+}/Cr = -0.74$ V.
Arrange these metals in increasing order of their reducing power.
 (a) $Hg < Cr < Ag < Mg < K$
 (b) $Hg < K < Mg < Cr < Ag$
 (c) $Ag < K < Mg < Hg < Cr$
 (d) $Ag < Hg < Cr < Mg < K$

25. For the equilibrium,
$$CuSO_4 . 5H_2O_{(s)} \longrightarrow CuSO_4 . 4H_2O_{(s)} + H_2O_{(g)}$$
which of the given plots should be useful to determine the enthalpy change of the reaction (ΔH)?
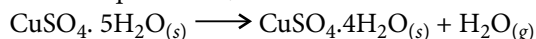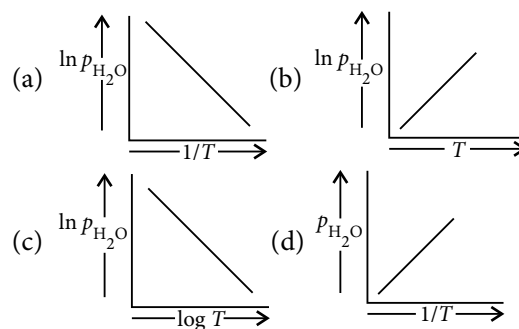
26. When aqueous solution of potassium fluoride is added to the blue coloured aqueous $CuSO_4$ solution, a green precipitate is formed. This is because
 (a) on adding KF, H_2O being weak field ligand is replaced by F^- ions forming $[CuF_4]^{2-}$ which is green in colour
 (b) potassium is coordinated to $[Cu(H_2O)_4]^{2+}$ ion present in $CuSO_4$ and gives green colour
 (c) on adding KF, Cu^{2+} are replaced by K^+ forming a green complex
 (d) blue colour of $CuSO_4$ and yellow colour of KI form green colour on mixing.

27. Which of the following statements is incorrect?
 (a) In equilibrium mixture of ice and water kept in perfectly insulated flask, mass of ice and water does not change with time.
 (b) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.
 (c) On addition of catalyst the equilibrium constant value is not affected.
 (d) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases.

28. P_4O_6 reacts with water according to the equation $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$. Calculate the volume of 0.1 M NaOH solution required to neutralise the acid formed by dissolving 1.1 g of P_4O_6 in H_2O.
 (a) 0.004 L   (b) 0.4 L
 (c) 4.4 L   (d) 1.2 L

29. Negative electronic energy (negative sign for all values of energy) for hydrogen atom means
 (a) the energy of an electron in the atom is lower than the energy of a free electron at rest which is taken as zero
 (b) when the electron is free from the influence of nucleus it has a negative value which becomes more negative
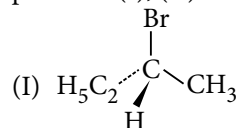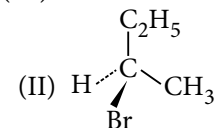
(c) when the electron is attracted by the nucleus the energy is absorbed which means a negative value

(d) energy is released by hydrogen atom in ground state.

30. White metallic tin gets converted to grey powder at low temperature. This transformation is related to
   (a) an interaction with nitrogen of the air at very low temperatures
   (b) a change in the crystalline structure of tin
   (c) an interaction with water vapour contained in the humid air
   (d) a change in the partial pressure of oxygen in the air.

31. In the Lassaigne's test for nitrogen in an organic compound, the prussian blue colour is obtained due to the formation of
   (a) $Na_4[Fe(CN)_6]$
   (b) $Fe_4[Fe(CN)_6]_3$
   (c) $Fe_2[Fe(CN)_6]$
   (d) $Fe_3[Fe(CN)_6]_4$

32. Magnetic moment of Cr^{2+} is nearest to
   (a) Fe^{2+} (b) Mn^{2+} (c) Co^{2+} (d) Ni^{2+}

33. A graph of adsorption isobar of chemisorption shows that adsorption
   (a) first decreases with temperature and then increases
   (b) first increases with temperature and then decreases
   (c) increases with temperature
   (d) decreases with temperature.

34. An aqueous solution contains equimolar quantities of $Zn(NO_3)_2$, $AgNO_3$, $Cu(NO_3)_2$.
   $E°$ values of
   $Zn^{2+}/Zn = -0.76$ V; $Ag^+/Ag = +0.80$ V, $Cu^{2+}/Cu = +0.34$.
   As the voltage is increased, the sequence in which metals are expected to be deposited is
   (a) Cu, Ag   (b) Ag, Cu
   (c) Cu, Zn   (d) Zn, Cu, Ag

35. Most common types of secondary structures of proteins are
   (a) α-helix and β-helix structures
   (b) α-helix and β-pleated sheet structures
   (c) right and left hand twisted structures
   (d) globular and fibrous structures.

36. For a gaseous reaction
   $2A + B_2 \longrightarrow 2AB$,

The following rate data were obtained at 300 K.

Expt.	Concentration		Rate of disappearance of B_2 (mol L^{-1} min^{-1})
	$[A]$	$[B_2]$	
1.	0.015	0.15	1.8×10^{-3}
2.	0.09	0.15	1.08×10^{-2}
3.	0.015	0.45	5.4×10^{-3}

What is the rate law?
(a) $r = k[A][B_2]$
(b) $r = [A]^2 [B_2]^1$
(c) $r = k[A][B_2]^2$
(d) $r = k[B_2]$

37. The drain cleaner, Drainex contains small bits of aluminium which react with caustic soda to produce dihydrogen. What volume of dihydrogen at 20°C and one bar will be released when 0.15 g of aluminium reacts?
   (a) 204 mL   (b) 200 mL
   (c) 203 mL   (d) 400 mL

38. The molecular shapes of SF_4, CF_4 and XeF_4 are
   (a) the same with 2, 0 and 1 lone pairs of electrons on the central atom, respectively
   (b) the same with 1, 1 and 1 lone pair of electrons on the central atom, respectively
   (c) different with 0, 1 and 2 lone pairs of electrons on the central atom, respectively
   (d) different with 1, 0 and 2 lone pairs of electrons on the central atom, respectively.

39. Which of the following is a correct statement?
   (a) $(SiH_3)_3N$ is a stronger base than $(CH_3)_3N$.
   (b) $(CH_3)_3N$ has a pyramidal structure.
   (c) $(SiH_3)_3N$ has a pyramidal structure.
   (d) SiO_4^{4-} units are not tetrahedral.

40. The addition of HBr to 1-butene gives a mixture of products (I), (II) and (III).

(I)   (II)

(III) $CH_3 — CH_2 — CH_2 — CH_2 — Br$
The mixture consists of
   (a) (I) and (II) as major and (III) as minor products
   (b) (II) as major, (I) and (III) as minor products
   (c) (II) as minor, (I) and (III) as major products
   (d) (I) and (II) as minor and (III) as major products.

41. Of the following reaction,

$$CH_3COOH \xrightarrow{(X)} CH_3COONa \xrightarrow[\Delta]{(Y)}$$
$$CH_4 \xrightarrow{Cl_2/h\nu} Z$$
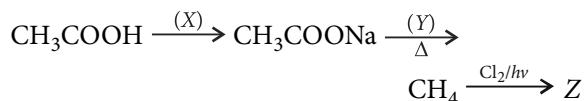
X, Y and Z are respectively
(a) sodalime, $NaOH_{(aq)}$, CH_3Cl
(b) $NaOH_{(aq)}$, sodalime, CH_3Cl
(c) CH_3Cl, $NaOH_{(aq)}$, sodalime
(d) sodalime, CH_3Cl, $NaOH_{(aq)}$.

42. The edge length of unit cell of a metal having molecular weight 75 g/mol is 5 Å which crystallizes in body centred cubic lattice. If the density is 2 g/cc then find the radius in pm of metal atom. ($N_A = 6 \times 10^{23}$).
(a) 116.5 pm   (b) 316.5 pm
(c) 216.5 pm   (d) 416.5 pm

43. X-ray diffraction studies show that copper crystallises in *fcc* unit cell with cell edge of 3.608×10^{-8} cm. In a separate experiment, copper is determined to have a density of 8.92 g/cm^3. The atomic mass of copper is
(a) 160 u   (b) 35 u
(c) 63 u   (d) 25 u

44. In the reaction,

Acetanilide
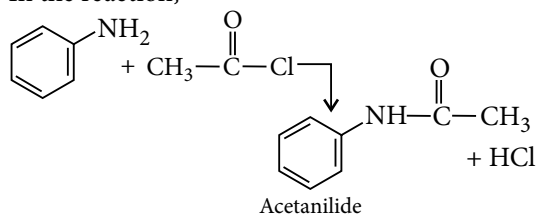
What is not true about the $-NH-\overset{O}{\overset{\|}{C}}-CH_3$ group?
(a) It reduces the activating influence of $-NH_2$ group.
(b) The group is *ortho-para* directing.
(c) The group can be converted into $-NH_2$ by adding a dilute acid.
(d) When this group is present on the benzene ring, it becomes very easy to carry on nucleophilic substitution.

45. In Duma's method 0.52 g of an organic compound on combustion gave 68.6 mL N_2 at 27°C and 756 mm pressure. What is the percentage of nitrogen in the compound?
(a) 12.22%   (b) 14.93%
(c) 15.84%   (d) 16.23%

46. Amongst the given set of reactants, the most appropriate for preparing 2° amine is
(a) 2° R—Br + NH_3
(b) 2° R—Br + NaCN followed by H_2/Pt
(c) 1° R—NH_2 + RCHO followed by H_2/Pt
(d) 1° R—Br (2 mol) + potassium phthalimide followed by H_3O^+/heat.

47. Which of the following statements is not correct?
(a) 5% aqueous solutions of NaCl and KCl are said to be isomolar.
(b) 1 M sucrose solution and 1 M glucose solution are isotonic.
(c) Molecular mass of acetic acid or benzoic acid is higher than normal mass in cryoscopic methods.
(d) For the same solution, $\dfrac{\Delta T_b}{\Delta T_f} = \dfrac{K_b}{K_f}$.

48. The correct order of stability is
(a) $SnF_2 > PbF_2 > GeF_2$
(b) $GeF_2 > SnF_2 > PbF_2$
(c) $GeF_2 > PbF_2 > SnF_2$
(d) $PbF_2 > SnF_2 > GeF_2$

49. The correct energy level diagram for $[Co(CN)_6]^{3-}$ is
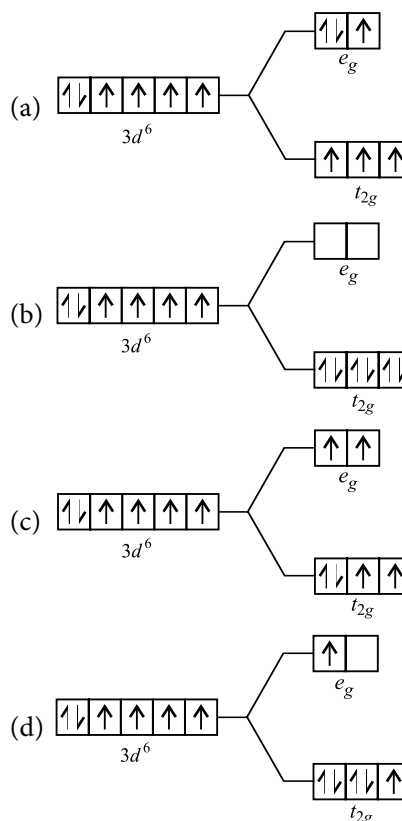
50. 1.0 mol of a monoatomic ideal gas is expanded from state (1) to (2) as shown in figure. Calculate the work done for the expansion of gas from state (1) to (2) at 298 K.
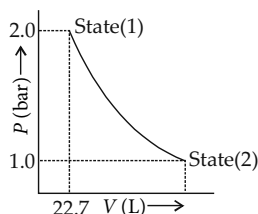
(a) – 1717.63 J   (b) – 5705.8 J

(c) + 1717.63 J   (d) + 5705.8 J

SOLUTIONS

1. (a) : $2Mg + O_2 \rightarrow 2MgO$

           2×24 2×16 $2(24 + 16)$
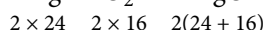
48 g of Mg requires 32 g of O_2

1 g of Mg requires $\frac{32}{48} = 0.66$ g of O_2

Oxygen available = 0.5 g

Hence, O_2 is the limiting reagent.

32 g of O_2 reacts with 48 g of Mg

0.5 g of O_2 will react with $\frac{48}{32} \times 0.5 = 0.75$ g of Mg

Excess of Mg = 1.0 – 0.75 = 0.25 g

2. (b) : Strength of H-bond is in the order :

H----F > H----O > H----N
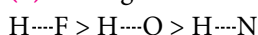
But each H_2O molecule is linked to 4 other H_2O molecules through H-bonds whereas each HF molecule is linked only to two other HF molecules. Hence, boiling point of H_2O > boiling point of HF.

3. (a) : For oxidation at anode, two possible reactions are oxidation of chlorine and of oxygen. Out of these two, oxidation of chlorine ion is preferred because oxidation of oxygen requires overvoltage.

Chlorine is obtained by electrolysis giving out hydrogen and aqueous NaOH as by-products.

4. (c) :

$$CH_3-CH=CH_2 \xrightarrow[aq.\ H_2SO_4]{(Hydration)} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3$$

Propene (A)   Propan-2-ol (B)

Ethanolic KOH

$$CH_3-\underset{\underset{Cl}{|}}{CH}-CH_3 \xleftarrow{HCl/ZnCl_2}$$

(C)

$$CH_3-CH=CH_2$$

Propene (A)
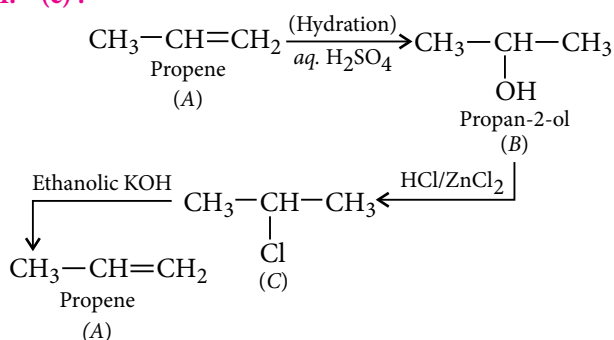
5. (b): Within a period, the oxidising character increases from left to right. Therefore, among F, O and N, oxidising power decreases in the order : F > O > N. However, within a group, oxidising power decreases from top to bottom. Thus, F is a stronger oxidising agent than Cl. Further because O is more electronegative than Cl, therefore, O is a stronger oxidising agent than Cl. Thus, overall decreasing order of oxidising power is : F > O > Cl > N.

6. (c) : Peroxyacetyl nitrate (PAN) formed from the primary pollutants NO_2, O_3 and hydrocarbons is the secondary pollutant.

7. (a) : PMMA is homopolymer *i.e.,* polymethyl-methacrylate.

8. (c) : $CO + H_2O \xrightarrow[catalyst]{673\ K} CO_2 + H_2$

The production of dihydrogen can be increased by reacting CO of syngas mixture with steam in presence of iron chromate as a catalyst. This is called water-gas shift reaction.

9. (c) : Mass of positively charged ions in positive rays is more than the mass of electrons.

10. (b): Water obtained from natural sources often contains suspended impurities. Alum is added to such water to coagulate the suspended impurities and make water fit for drinking purposes.

11. (d): Chlorobenzene does not undergo hydrolysis on treatment with aqueous NaOH at 298 K.

12. (a) : Avogadro number = 6.023×10^{23}

Total rupees = 6.023×10^{23}

Rate of spending = 10 lac rupees/sec = 10^6 rupees/sec

Total amount spent in one year

$= 10^6 \times 60 \times 60 \times 24 \times 365$ rupees

∴ Number of years to spend all the rupees

$= \dfrac{6.023 \times 10^{23}\ \text{rupees}}{10^6 \times 60 \times 60 \times 24 \times 365\ \text{rupees/year}}$

$= 1.90988 \times 10^{10}$ years

13. (b): Benzaldehyde when treated with conc. KOH solution undergoes Cannizzaro reaction. One molecule of aldehyde is reduced and other is oxidised.

14. (c) :

NaI/acetone
(Finkelstein reaction)
S_N2 reaction
(inversion of configuration)

15. (d) : $CH_3CH_2CH_2CH_2Br$

1-Bromobutane
(1° with no branching)

$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-\overset{\alpha}{CH_2Br}$

1-Bromo-2,2-dimethylpropane
(1° with two β-methyl groups)

$CH_3CH_2-\overset{\overset{\beta CH_3}{|}}{CH}-\overset{\alpha}{CH_2Br}$

1-Bromo-2-methylbutane
(1° with one β -methyl group)

$CH_3-\overset{\overset{\gamma CH_3}{|}}{CH}-\overset{\beta}{CH_2}-\overset{\alpha}{CH_2}-Br$

1-Bromo-3-methylbutane
(1° with one methyl group at γ-position)

Since in case of 1° alkyl halides, steric hindrance increases in the order : *n*-alkyl halides, alkyl halide with a substituent at any position other than the β-position, one substituent at the β-position, two substituents at the β-position, therefore, the reactivity decreases in the same order. Thus, the reactivity of the given alkyl bromides decreases in the order :

1-Bromobutane > 1-Bromo-3-methylbutane >

1-Bromo-2-methylbutane >1-Bromo-2,
2-dimethylpropane

16. (a) : At anode : $Fe \longrightarrow Fe^{2+} + 2e^-$

At cathode : $O_2 + 2H_2O + 4e^- \longrightarrow 4OH^-$

The overall reaction is

$2Fe + O_2 + 2H_2O \longrightarrow 2Fe(OH)_2$

$Fe(OH)_2$ may be dehydrated to iron oxide FeO, or further oxidised to $Fe(OH)_3$ and then dehydrated to iron rust, Fe_2O_3.

17. (c) : $x > y$ because same bonds are formed in reactions (i) and (ii) but bonds between reactant molecules are broken only in reaction (ii). As energy is absorbed when bonds are broken, energy released in reaction (i) is greater than that in reaction (ii).

18. (c) : Chloramphenicol is a broad spectrum drug and can be used in treatment of typhoid, dysentery, meningitis, etc.

19. (a) : $\underset{(A)}{2Na} + 2H_2O \longrightarrow \underset{(C)}{2NaOH}_{(aq.)} + \underset{(B)}{H_2}$

$\underset{(C)}{2NaOH} + \underset{(D)}{Zn} \longrightarrow Na_2ZnO_2 + \underset{(B)}{H_2}$

Na (*A*) imparts golden yellow colour to the flame.

20. (a) : CaO is basic while CO_2 is most acidic of these. The increasing acidic strength order is

$CaO < CuO < H_2O < CO_2$.

21. (b) : Consider a first order gas phase decomposition reaction :

$$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$$

The initial pressure of the system before decomposition of *A* was P_i.

After lapse of time (*t*), total pressure of the system increased by *x* units and became 'P_t'.

In other words, the pressure of *A* decreased by *x*.

$$A_{(g)} \longrightarrow B_{(g)} + C_{(g)}$$

Initial pressure : $\quad P_i \qquad 0 \quad 0$

Pressure after time, $t : (P_i - x) \qquad x \quad x$

$P_t = (P_i - x) + x + x = P_i + x$

$x = P_t - P_i$

Pressure of *A* after time t, $P_A = P_i - x$

$\qquad\qquad\qquad = P_i - P_t + P_i = 2P_i - P_t$

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{t} \log \frac{P_i}{2P_i - P_t}$$

22. (d) :

dil. NaOH
(Aldol condensation)

2-(1-Hydroxy-1-cyclohexyl)
cyclohexan-1-one

23. (d) : More the dipole moment more is the critical temperature.

24. (d) : Lower the electrode potential, better is the reducing power. Since the electrode potentials increase in the order : K^+/K(–2.93 V), Mg^{2+}/Mg (–2.37 V), Cr^{3+}/Cr (–0.74 V), Hg^{2+}/Hg(0.79 V), Ag^+/Ag (0.80 V), therefore, reducing power of metals increases in the order :

$Ag < Hg < Cr < Mg < K$.

25. (a) : In this case, $K_p = p_{H_2O}$; we know

$$\ln K_p = \ln A - \frac{\Delta H}{RT}$$

∴ Slope will give the value of ΔH.

26. (a) : Aqueous $CuSO_4$ solution contains $[Cu(H_2O)_4]^{2+}$ ions which are blue in colour. When aqueous solution of KF is added, H_2O being weak field ligand can be replaced by F^- ions forming $[CuF_4]^{2-}$ which is green in colour.

$[Cu(H_2O)_4]^{2+} + \underset{(from\ KF)}{4F^-} \longrightarrow \underset{Green}{[CuF_4]^{2-}} + 4H_2O$

27. (b): When oxalic acid is added to a solution containing iron nitrate and potassium thiocyanate, oxalic acid reacts with Fe^{3+} ions to form a stable complex ion $[Fe(C_2O_4)_3]^{3-}$ thus, decreasing the concentration of free Fe^{3+} ions which in turn decreases the intensity of red colour.

$$Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{(Red)}}{[Fe(SCN)]^{2+}}$$

28. (b): $P_4O_6 + 6H_2O \rightarrow 4H_3PO_3$

$[H_3PO_3 + 2NaOH \rightarrow Na_2HPO_3 + 2H_2O] \times 4$
       (Neutralisation reaction)

$P_4O_6 + 8NaOH \rightarrow 4Na_2HPO_3 + 2H_2O$
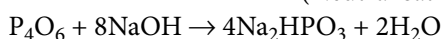
Product formed by 1 mol of P_4O_6 is neutralised by 8 moles of NaOH.

$\therefore$ Product formed by $\dfrac{1.1}{220}$ mol of P_4O_6 will be

neutralised by $\dfrac{1.1}{220} \times 8$ moles of NaOH.

Molarity of NaOH solution is 0.1 M.

$\Rightarrow$ 0.1 mol NaOH is present in 1 L solution.

$\therefore$ $\dfrac{1.1}{220} \times 8$ moles NaOH will be present in

$$\frac{1.1 \times 8}{220 \times 0.1} = \frac{88}{220} = \frac{4}{10} = 0.4 \text{ L}$$

29. (a): The negative sign means that the energy of an electron in an atom is lower than the energy of a free electron at rest. When electron is free from the influence of nucleus, the energy is taken as zero. When the electron is attracted by the nucleus, the energy is emitted and lowered.

30. (b): As temperature decreases, white tin (β-form) changes to grey tin (α-form).

$$\underset{\text{white}}{\beta\text{-Sn}} \xrightarrow{13.2°C} \underset{\text{grey}}{\alpha\text{-Sn}}$$

During conversion of white tin to grey tin volume increases. Grey tin is very brittle and easily crumbles down to powder.

31. (b): The prussian blue colour in the Lassaigne's test is due to the formation of ferric ferrocyanide, $Fe_4[Fe(CN)_6]_3$.

32. (a): $Cr^{2+} = 3d^4$, No. of unpaired electrons (n) = 4
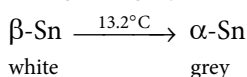
Magnetic moment $= \sqrt{n(n+2)}$ BM
$= \sqrt{4(4+2)} = \sqrt{24} = 4.89$ BM

$Fe^{2+} = 3d^6$, No. of unpaired electrons (n) = 4

Magnetic moment $= \sqrt{4(4+2)}$ BM
$= \sqrt{24} = 4.89$ BM

$Mn^{2+} = 3d^5$, No. of unpaired electrons (n) = 5

Magnetic moment $= \sqrt{5(5+2)}$ BM
$= \sqrt{35} = 5.91$ BM

$Co^{2+} = 3d^7$, No. of unpaired electrons (n) = 3

Magnetic moment $= \sqrt{3(3+2)}$ BM
$= \sqrt{15} = 3.87$ BM

$Ni^{2+} = 3d^8$, No. of unpaired electrons (n) = 2

Magnetic moment $= \sqrt{2(2+2)}$ BM

$= \sqrt{8} = 2.82$ BM

33. (b): A graph of adsorption isobar of chemisorption shows that the adsorption first increases with temperature and then decreases. The initial increase is due to heat supplied, which acts as activation energy required in chemisorption. Later, it decreases due to the exothermic nature of adsorption at equilibrium.

34. (b): Higher the reduction potential of a metal more easily it is deposited at cathode. In an aqueous solution Zn will not be deposited.

35. (b): Due to regular folding of backbone of the peptide chain, two most common secondary structures of proteins are α-helix and β-pleated sheet structures. In α-helix, all H-bonds are formed by twisting the chain into a right handed helix. In β-pleated, all peptide chains are stretched to maximum extension and then laid side by side and connected by hydrogen bonds.

36. (a): From expt. (1) and (2), it is clear that when $[B_2]$ is kept constant and $[A]$ is made 6 times, the rate also becomes 6 times, thus $r \propto [A]^1$. Further from expt (1) and (3) when $[A]$ is kept constant and $[B_2]$ is tripled, rate also becomes three times,

Thus, $r \propto [B_2]^1$

Hence, $r = k [A]^1 [B_2]^1$

37. (c): The reaction between aluminium and caustic soda is

$$\underset{2 \times 27 = 54 \text{ g}}{2Al} + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + \underset{3 \times 22.4 \text{ L}}{3H_2}$$
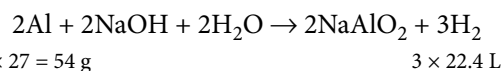
$\therefore$ 54 g of Al produces 3×22.4 L of H_2 at STP

0.15 g of Al will produce $\dfrac{3 \times 22.4}{54} \times 0.15 = 0.187$ L of H_2 at STP

At STP   Given conditions

$P_1 = 1$ atm $P_2 = 1$ bar $= 0.987$ atm

$V_1 = 0.187$ L $V_2 = ?$

$T_1 = 273$ K $T_2 = 273 + 20 = 293$ K

Applying ideal gas equation, $\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

$\dfrac{1 \times 0.187}{273} = \dfrac{0.987 \times V_2}{293}$

$V_2 = \dfrac{293}{0.987} \times \dfrac{1 \times 0.187}{273} = 0.203\,\text{L} = 203\,\text{mL}$

38. (d): SF_4 (sp^3d, trigonal bipyramidal with one equatorial position occupied by one lone pair), CF_4 (sp^3, tetrahedral, no lone pair), XeF_4 (sp^3d^2, square planar, two lone pairs).

39. (b): $(SiH_3)_3N$ is planar, while $(CH_3)_3N$ is pyramidal.

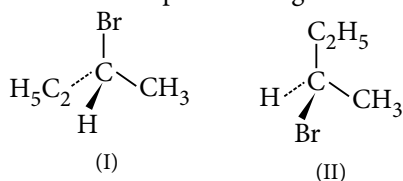**40. (a):** $CH_3CH_2CH{=}CH_2 + HBr \longrightarrow$
 1-Butene

$CH_3CH_2CH_2CH_2Br + CH_3CH_2{-}\overset{*}{C}H{-}CH_3$
(III) Minor $\qquad\qquad$ | Br
$\qquad\qquad\qquad$ A (exists in 2 enantiomers
$\qquad\qquad\qquad$ I and II) Major

(A) can have two spatial arrangements :

Br $\qquad\qquad$ C_2H_5
| $\qquad\qquad\qquad$ |
$H_5C_2{-}C{-}CH_3$ $\qquad$ $H{-}C{-}CH_3$
| $\qquad\qquad\qquad$ |
H $\qquad\qquad\qquad$ Br
(I) $\qquad\qquad\qquad$ (II)

41. (b): $CH_3COOH \xrightarrow{\ NaOH_{(aq)}(X)\ } CH_3COONa \xrightarrow[\Delta]{\text{sodalime }(Y)}$

$CH_3Cl \xleftarrow{\ Cl_2/h\nu\ } CH_4$
$\qquad (Z)$

42. (c): For bcc, $r = \dfrac{\sqrt{3}}{4}a = \dfrac{\sqrt{3}}{4} \times 5 = 2.165\,\text{Å} = 216.5\,\text{pm}$

43. (c): In case of fcc lattice, number of atoms per unit cell, $Z = 4$ atoms

Therefore, $M = \dfrac{dN_A a^3}{Z}$

$= \dfrac{8.92 \times 6.022 \times 10^{23} \times (3.608 \times 10^{-8})^3}{4} = 63.1\,\text{g mol}^{-1}$

Atomic mass of copper = 63.1 u

44. (d): This method is adopted to protect $-NH_2$ group and to reduce its activating influence.

45. (b): $V_1 = 68.6\,\text{mL}$, $P_1 = 756\,\text{mm}$, $T_1 = 300\,\text{K}$
$V_2 = ?$, $P_2 = 760\,\text{mm}$, $T_2 = 273\,\text{K}$

$\dfrac{P_1V_1}{T_1} = \dfrac{P_2V_2}{T_2}$

At NTP, vol. of N_2, $V_2 = \dfrac{P_1V_1}{T_1} \cdot \dfrac{T_2}{P_2} = \dfrac{756 \times 68.6}{300} \times \dfrac{273}{760}$
$\qquad\qquad\qquad = 62.09\,\text{mL}$

Percentage of nitrogen in organic compound

$= \dfrac{28}{22400} \times \dfrac{V_2}{w} \times 100 = \dfrac{28}{22400} \times \dfrac{62.09}{0.52} \times 100 = 14.93\%$

46. (c): $1° R-NH_2 + R$CHO followed by reduction.

$\underset{H}{\overset{R}{{>}}}C{=}O + RNH_2 \xrightarrow[-H_2O]{\Delta} R-\overset{\overset{H}{|}}{C}{=}N{-}R$
$\qquad\qquad\qquad\qquad\qquad\quad H_2 \big\downarrow Ni$
$\qquad\qquad\qquad R-CH_2-NH-R$
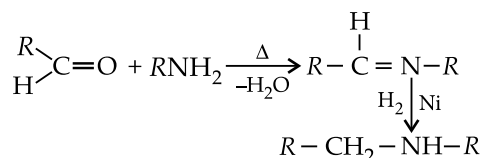
47. (a): Both NaCl and KCl have different molecular masses.

48. (d): The stability of fluorides increases as the size of central atom increases. Thus, the correct order is $PbF_2 > SnF_2 > GeF_2$.

49. (b): In $[Co(CN)_6]^{3-}$, oxidation state of Co = +3
As CN^- is a strong field ligand, it results in pairing of electrons hence,
$Co^{3+} : 3d^6$ configuration $= t_{2g}^6 e_g^0$
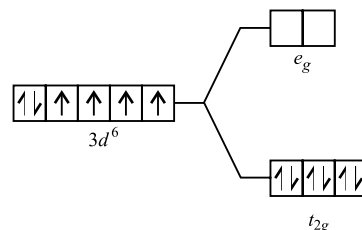
50. (a): It is clear from the figure that the process has been carried out in infinite steps hence, it is an isothermal reversible expansion.

$w = -2.303\,nRT \log \dfrac{V_2}{V_1}$

But, $P_1V_1 = P_2V_2 \Rightarrow \dfrac{V_2}{V_1} = \dfrac{P_1}{P_2} = \dfrac{2}{1} = 2$

$\therefore \quad w = -2.303\,nRT \log \dfrac{P_1}{P_2}$
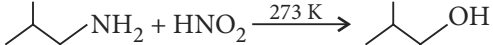
$= -2.303 \times 1\,\text{mol} \times 8.314\,\text{J mol}^{-1}\,\text{K}^{-1} \times 298\,\text{K} \times \log 2$
$= -2.303 \times 8.314 \times 298 \times 0.3010\,\text{J}$
$= -1717.63\,\text{J}$

◈ ◈

50 MCQs PMTs PETs
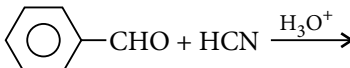
EXAM PREP

Questions for Practice

1. A flask contains H_2 gas and a few drops of water. Pressure in the flask is 755 mm Hg at certain temperature T K. If the temperature is increased by 1%, the pressure inside the flask will be (Given, aqueous tension at two temperatures are 25 mm Hg and 30 mm Hg)
   (a) 762.1 (b) 767.3 (c) 770.4 (d) 775.6

2. Consider the following reactions of alcohols :
   I. $CH_2{=}CHCH_2OH \xrightarrow{A} CH_2{=}CHCHO$
   II. $(CH_3)_3COH \xrightarrow{B} CH_3{-}\underset{CH_3}{C}{=}CH_2$
   III. $CH_3CH_2OH \xrightarrow{C} CH_3CO_2H$
   IV. $CH_3CH{=}CHCH_3 \xrightarrow{D} CH_3CO_2H$
   A, B, C and D are respectively
   (a) MnO_2, Cu/Δ, H_2CrO_4, $KMnO_4/\Delta$
   (b) Cu/Δ, MnO_2, H_2CrO_4, $KMnO_4/\Delta$
   (c) MnO_2, Cu/Δ, $KMnO_4/\Delta$, H_2CrO_4
   (d) MnO_2, H_2CrO_4, Cu/Δ, $KMnO_4$

3. Which of the following statements is correct?
   (a) Diamond is unaffected by conc. acids but graphite reacts with hot conc. HNO_3 forming graphitic acid, $C_6(COOH)_6$.
   (b) CO is toxic because it forms a complex with haemoglobin in the blood.
   (c) C_3O_2, carbon suboxide, is a foul-smelling gas.
   (d) All of these

4. In a cell that utilises the reaction,
   $Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$, addition of H_2SO_4 to cathode compartment will
   (a) lower the value of E_{cell} and shift equilibrium to the right
   (b) lower the value of E_{cell} and shift equilibrium to the left
   (c) increase the value of E_{cell} and shift equilibrium to the right
   (d) increase the value of E_{cell} and shift equilibrium to the left.

5. Which is not the correct reaction?
   (a) ⬡—Cl + NH_3 ⟶ ⬡ + NH_4Cl
   (b) >—Cl + $2NH_3$ ⟶ >—NH_2 + NH_4Cl
   (c) >—Cl + NH_3 ⟶ —< + NH_4Cl
   (d) $\diagdown\diagup NH_2$ + HNO_2 $\xrightarrow{273\ K}$ $\diagdown\diagup OH$

6. Which of the following reactions should be most favoured thermodynamically?
   (a) $Na_2O + Cl_2O_7 \longrightarrow 2NaClO_4$
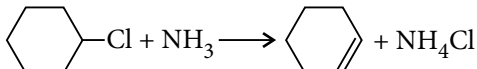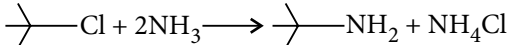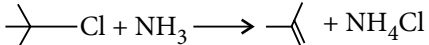   (b) $Na_2O + SO_3 \longrightarrow Na_2SO_4$
   (c) $3Na_2O + P_2O_5 \longrightarrow 2Na_3PO_4$
   (d) $Na_2O + SiO_2 \longrightarrow Na_2SiO_3$

7. The enthalpy changes for the following processes are listed below :
   $$Cl_{2(g)} \longrightarrow 2Cl_{(g)}; \qquad 242.3\ \text{kJ mol}^{-1}$$
   $$I_{2(g)} \longrightarrow 2I_{(g)}; \qquad 151.0\ \text{kJ mol}^{-1}$$
   $$I_{2(s)} \longrightarrow I_{2(g)}; \qquad 62.76\ \text{kJ mol}^{-1}$$
   $$ICl_{(g)} \longrightarrow I_{(g)} + Cl_{(g)}; \quad 211.3\ \text{kJ mol}^{-1}$$
   Given that the standard states for iodine and chlorine are $I_{2(s)}$ and $Cl_{2(g)}$, standard enthalpy of formation of $ICl_{(g)}$ is
   (a) -16.8 kJ mol^{-1} (b) $+16.8$ kJ mol^{-1}
   (c) $+244.8$ kJ mol^{-1} (d) -14.6 kJ mol^{-1}

8. In which case, chiral carbon is not generated?
   (a) $CH_3COCH_3 + HCN \xrightarrow{H_3O^+}$
   (b) $CH_3CHO + HCN \xrightarrow{H_3O^+}$
   (c) $CH_3COCOOH + HCN \xrightarrow{H_3O^+}$
   (d) ⬡—CHO + HCN $\xrightarrow{H_3O^+}$

9. What may be expected to happen when phosphine gas is mixed with chlorine gas?
   (a) $PH_3{\cdot}Cl_2$ is formed with warming up.
   (b) The mixture only cools down.

(c) PCl_3 and HCl are formed and the mixture warms up.

(d) PCl_5 and HCl are formed and the mixture cools down.

10. The hydrolysis of ethyl acetate was carried out separately with 0.05 M HCl and 0.05 M H_2SO_4. The rate constants were found to be k_1 and k_2 respectively then
   (a) $k_1 < k_2$ (b) $k_1 > k_2$
   (c) $k_1 = k_2$ (d) $k_2 = 2k_1$

11. The nodal plane in the π-bond of ethene is located in
   (a) the molecular plane
   (b) a plane parallel to the molecular plane
   (c) a plane perpendicular to the molecular plane which bisects the carbon-carbon sigma bond at right angle
   (d) a plane perpendicular to the molecular plane which contains the carbon-carbon sigma bond.

12. The water pollutants mainly responsible for eutrophication are
   (a) Cd, Pb and Hg present in industrial waste
   (b) heavy metals present in mining waste
   (c) detergents and fertilizers containing phosphate anion
   (d) polychlorinated biphenyls.

13. If λ_0 is the threshold wavelength of a metal and λ is the wavelength of the incident radiation the maximum velocity of the ejected electrons from the metal would be
   (a) $\left[\dfrac{hc}{m}\left(\dfrac{\lambda - \lambda_0}{\lambda\lambda_0}\right)\right]^{1/2}$ (b) $\left[\dfrac{2hc}{m}\left(\dfrac{\lambda_0 - \lambda}{\lambda_0\lambda}\right)\right]^{1/2}$
   (c) $\left[\dfrac{h}{m}(\lambda_0 - \lambda)\right]^{1/2}$ (d) $\left[\dfrac{2h}{m}(\lambda - \lambda_0)\right]^{1/2}$

14. A new carbon-carbon bond formation is possible in
   (a) Cannizzaro reaction
   (b) Reimer-Tiemann reaction
   (c) Clemmensen reduction
   (d) none of the above.

15. The electronic spectrum of $[Ti(H_2O)_6]^{3+}$ gives a single broad peak with a maxima at 20300 cm^{-1}. The crystal field stabilization energy is equal to (1 kJ $mol^{-1} \equiv$ 83.7 cm^{-1})
   (a) 97 kJ mol^{-1} (b) 243 kJ mol^{-1}
   (c) 297 kJ mol^{-1} (d) none of these.

16. Which of the following is correct, if for the same element three separate radii 105 nm, 100 nm and 90 nm are reported?
   (a) These are van der Waals', metallic and covalent radii.
   (b) These are metallic, covalent and van der Waals' radii respectively.
   (c) These are covalent, metallic and van der Waals' radii respectively.
   (d) These are metallic, van der Waals' and covalent radii respectively.

17. The compound which is not isomeric to cyclobutanol is
   (a)   (b) butanone
   (c) but-3-ene-1-ol   (d) diethyl ether.

18. Pb_3O_4 reacts with HNO_3 forming nitrate and oxide which are
   (a) $Pb(NO_3)_2$ from PbO, and PbO_2 remains unreacted
   (b) $Pb(NO_3)_2$ from PbO_2 and PbO remains unreacted
   (c) $Pb(NO_3)_2$ from $Pb(NO_3)_4$ and PbO remains unreacted
   (d) Pb_3O_4 remains insoluble in HNO_3.

19. In a particular solution of sulphur dissolved in carbon disulphide, 80% of the sulphur atoms exist as S_8 while remaining as S_2. What should be the value of van't Hoff factor 'i' for the calculation of colligative properties?
   (a) 1   (b) $\dfrac{1}{2}$
   (c) $\dfrac{1}{5}$ (d) $\dfrac{1}{8}$

20. How many chirality centers are present in 1-chloro-2-methylcyclohexane?
   (a) 2   (b) 4   (c) 1   (d) 3

21. Cerium ($Z = 58$) is an important member of the lanthanides. Which of the following statements about cerium is incorrect?
   (a) The common oxidation states of cerium are +3 and +4.
   (b) Cerium (IV) acts as an oxidising agent.
   (c) The +4 oxidation state of cerium is not known in solutions.
   (d) The +3 oxidation state of cerium is more stable than the +4 oxidation state.

22. ZSM-5 is one of the zeolite with formula
    (a) $H_x[(AlO_2)_x . (SiO_2)_{96-x}] . 16H_2O$
    (b) $Na_{56}[(AlO_2)_{56} . (SiO_2)_{36}] . 250H_2O$
    (c) $Na_2Ca(AlO_2)_2 (SiO_2)_4 . 6H_2O$
    (d) none of the above is correct.

23. Which of the following hydrocarbons has the lowest dipole moment?
    (a) $\begin{matrix} H_3C \\ H \end{matrix} C = C \begin{matrix} CH_3 \\ H \end{matrix}$ (b) $CH_3C \equiv CCH_3$
    (c) $CH_3CH_2C \equiv CH$ (d) $CH_2 = CH - C \equiv CH$

24. Which of the following are peroxy acids?
    (a) $H_2S_2O_3$ and $H_2S_2O_6$ (b) $H_2S_2O_6$ and H_2SO_5
    (c) H_2SO_5 and $H_2S_2O_8$ (d) $H_2S_2O_3$ and $H_2S_2O_8$

25. Assuming complete dissociation which of the following aqueous solutions will have the same pH value?
    (i) 100 mL of 0.01 M HCl
    (ii) 100 mL of 0.01 M H_2SO_4
    (iii) 50 mL of 0.01 M HCl
    (iv) Mixture of 50 mL of 0.02 M H_2SO_4 and 50 mL of 0.02 M NaOH
    (a) (i), (ii)   (b) (i), (iii)
    (c) (ii), (iv)   (d) (i), (iv)

26. Which of the following will require maximum volume of x M H_2SO_4 for complete reaction?
    (a) 65 mg of Zn
    (b) 20 mL of 0.15 M KOH
    (c) 15 mL of 0.2 M Na_2CO_3
    (d) 25 mL of 0.1 M $Ba(OH)_2$

27. The acidic character of H_2O, H_2O_2 and CO_2 in increasing order is
    (a) $H_2O < H_2O_2 < CO_2$ (b) $H_2O < CO_2 < H_2O_2$
    (c) $H_2O_2 < H_2O < CO_2$ (d) $CO_2 < H_2O < H_2O_2$

28. Molecular weight of H_3PO_4 is 98. Its equivalent weight in the reaction given below is
    $H_3PO_4 + NaOH \longrightarrow H_2O + NaH_2PO_4$
    (a) 98   (b) 49
    (c) 294   (d) 32.67

29. Which one of the following statements about protein structure is correct?
    (a) Proteins consisting of one polypeptide can have quarternary structure.
    (b) The formation of a disulphide bond in a protein requires that the two participating cysteine residues be adjacent to each other in the primary sequence of the protein.

(c) The stability of quaternary structure in proteins is mainly due to covalent bonds among the sub-units.
(d) The information required for the correct folding of a protein is contained in the specific sequence of amino acids along the polypeptide chain.

30. BeF_2 is soluble in water whereas fluorides of other alkaline earth metals are insoluble because of
    (a) ionic nature of BeF_2
    (b) covalent nature of BeF_2
    (c) greater hydration energy of Be^{2+} ion as compared to its lattice energy
    (d) none of these.

31. Consider the following equilibria at 300 K and 400 K with their equilibrium constants :

		300 K	400 K
I.	$A_{(g)} \rightleftharpoons 2B_{(g)}$	$K_{eq} = 10$	$K_{eq} = 5$
II.	$C_{(g)} \rightleftharpoons D_{(g)}$	$K_{eq} = 2$	$K_{eq} = 5$

    The data shows that
    (a) I is endothermic, II is exothermic
    (b) I is exothermic, II is endothermic
    (c) I and II both are endothermic
    (d) I and II both are exothermic.

32. Which of the following detergents acts as a germicide?
    (a) Cetyltrimethylammonium chloride
    (b) Sodium laurylsulphate
    (c) Sodium-4-(1-dodecyl)benzenesulphonate
    (d) All of the above

33. Select the incorrect statement.
    (a) H^+ can exist as $H_9O_4^+$ in water.
    (b) H_2 is thermally stable.
    (c) Ionisation of CH_3COOH is slower than that of CH_3COOD.
    (d) Kinetic isotopic effect is observed when there is retardation in the rate of a reaction when H_2O is replaced by D_2O.

34. The pyknometric density of sodium chloride crystal is 2.165×10^3 kg m^{-3}, while its X-rays density is 2.178×10^3 kg m^{-3}. The fraction of unoccupied sites in sodium chloride crystal is
    (a) 5.96   (b) 5.96×10^{-1}
    (c) 5.96×10^{-2} (d) 5.96×10^{-3}

35. The major organic products A and B in the given reactions are respectively

(a) and (b) and

(c) and (d) and
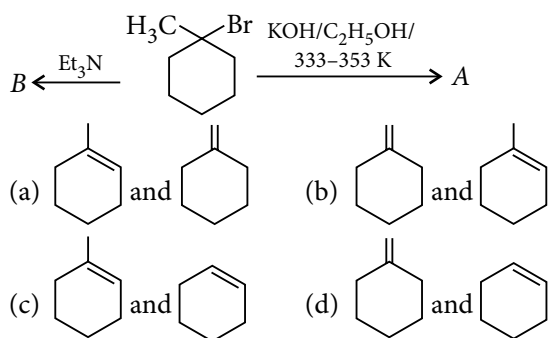
36. Which of the following is not correct?
- (a) Chromyl bromide test is conducted for Br^- ion.
- (b) Borax bead test is for coloured salts.
- (c) Dimethylglyoxime is a test reagent for Ni^{2+}.
- (d) Ring test is performed for NO_3^-.

37. Which among the following statements is false?
- (a) Adsorption may be monolayered or multilayered.
- (b) Particle size of adsorbent will not affect the amount of adsorption.
- (c) Increase of pressure increases the amount of adsorption.
- (d) Increase of temperature may decrease the amount of adsorption.

38. Which of the following does not exhibit tautomerism?

(a) (b)

(c) (d) All exhibit tautomerism.
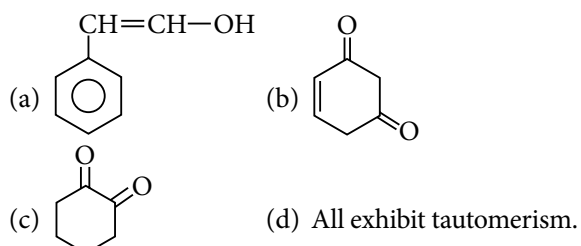
39. Which one of the following sequences represents the increasing order of the polarizing power of the cationic species, K^+, Ca^{2+}, Mg^{2+}, Be^{2+}?
- (a) Mg^{2+}, Be^{2+}, K^+, Ca^{2+}
- (b) Be^{2+}, K^+, Ca^{2+}, Mg^{2+}
- (c) K^+, Ca^{2+}, Mg^{2+}, Be^{2+}
- (d) Ca^{2+}, Mg^{2+}, Be^{2+}, K^+

40. 1 g H_2 gas at STP is expanded so that volume is doubled. Hence, work done is
- (a) 22.4 L atm
- (b) 5.6 L atm
- (c) 11.2 L atm
- (d) 44.8 L atm

41.

(a) (b)

(c) (d)
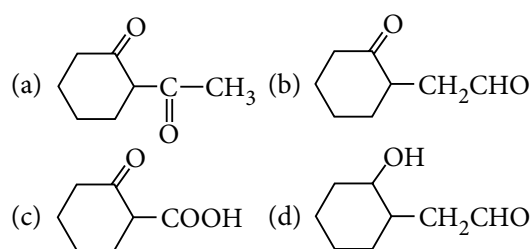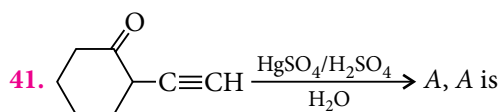
42. HNO_3 is changing to N_2O, NO, NO_2 and N_2O_5. The changes involved in number of electrons per N-atom are respectively
- (a) 0, 1, 2, 4
- (b) 4, 3, 1, 0
- (c) 1, 2, 4, 5
- (d) 3, 1, 4, 0

43. NH_3 gas is liquefied more easily than N_2. Hence,
- (a) values of van der Waals' constants a and b of NH_3 are greater than that of N_2
- (b) values of van der Waals' constant a and b of NH_3 are less than that of N_2
- (c) $a(NH_3) > a(N_2)$ but $b(NH_3) < b(N_2)$
- (d) $a(NH_3) < a(N_2)$ but $b(NH_3) > b(N_2)$

44. Which of the following statements is correct w.r.t. the reactions of aqueous solution of methanamine?
- (a) It converts aqueous $CuSO_4$ to blue
- (b) It dissolves AgCl in it
- (c) Fe^{3+} gives brown precipitate of $Fe(OH)_3$
- (d) All of the above

45. The correct order of crystal field stabilisation energies for the given ions is
- (a) $V^{2+} < Mn^{2+} < Fe^{2+} < Co^{2+} < Ni^{2+}$
- (b) $Ni^{2+} < Co^{2+} < Fe^{2+} < Mn^{2+} < V^{2+}$
- (c) $Mn^{2+} < V^{2+} < Co^{2+} < Fe^{2+} < Ni^{2+}$
- (d) $V^{2+} \approx Mn^{2+} \approx Fe^{2+} \approx Co^{2+} \approx Ni^{2+}$

46. Butanone can be best obtained by the ozonolysis of

(a) (b)

(c) (d)

47.
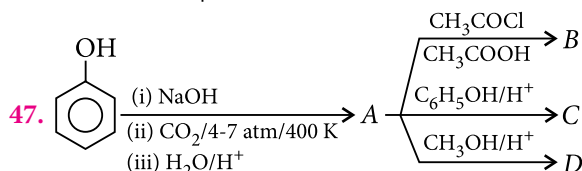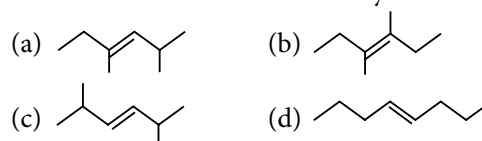
B, C and D respectively are
- (a) aspirin, salol, oil of wintergreen
- (b) salol, aspirin, oil of wintergreen
- (c) oil of wintergreen, aspirin, salol
- (d) oil of wintergreen, salol, aspirin.

48. The colourless species is

    (a) VCl_3 (b) $VOSO_4$

    (c) Na_3VO_4 (d) $[V(H_2O)_6]SO_4 . H_2O$

49. In the reaction,

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

    (a) 6 L $HCl_{(aq)}$ is consumed for every 3 L $H_{2(g)}$ produced

    (b) 33.6 L $H_{2(g)}$ is produced regardless of temperature and pressure for every mole of Al reacted

    (c) 67.2 L $H_{2(g)}$ at STP is produced for every mole of Al reacted

    (d) 11.2 L $H_{2(g)}$ at STP is produced for every mole of $HCl_{(aq)}$ consumed.

50. Assume that a particular amino acid has an isoelectric point of 6.0. In a solution of pH 1.0, which of the following species will predominate?

    (a) $\overset{R}{\underset{|}{H_3\overset{+}{N}CHCO_2H}}$ (b) $\overset{R}{\underset{|}{H_2NCHCO_2H}}$

    (c) $\overset{R}{\underset{|}{H_3\overset{+}{N}CHCO_2^-}}$ (d) $\overset{R}{\underset{|}{H_2NCHCO_2^-}}$

SOLUTIONS

1. (b): Pressure of dry H_2 at T K = 755 – 25 = 730 mm Hg

New temperature = $T + \dfrac{1}{100}T = 1.01\,T$

New pressure of dry $H_2 = \dfrac{P_1}{T_1} \times T_2 = \dfrac{730}{T} \times 1.01\,T$

$\qquad\qquad\qquad\qquad = 737.3$ mm Hg

New pressure of moist H_2 in flask = 737.3 + 30

$\qquad\qquad\qquad\qquad\qquad\qquad = 767.3$ mm Hg

2. (a): MnO_2 is very selective and can oxidise only allylic, benzylic or propargylic alcohols.

3. (d)

4. (c): $Zn_{(s)} + 2H^+_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + H_{2(g)}$

$$E_{cell} = E°_{cell} - \frac{0.059}{2} \log \frac{[Zn^{2+}]}{[H^+]^2}$$

When H_2SO_4 is added to cathode compartment then, $[H^+]$ will increase therefore, E_{cell} will also increase and equilibrium will shift towards right.
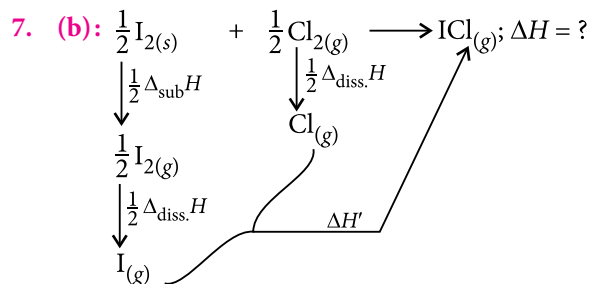
5. (b): NH_3 (a strong nucleophile) causes elimination from 3° alkyl halide.

6. (a): Na_2O is basic in nature and Cl_2O_7 is most acidic among the given oxides.

Greater the acidic nature, greater is the tendency of the reaction to occur thus, reaction of Na_2O with Cl_2O_7 is most favourable.

7. (b):

$$\Delta H = \left(\frac{1}{2}\Delta_{sub}H + \frac{1}{2}\Delta_{diss.}H\right)_{I_2} + \frac{1}{2}(\Delta_{diss.}H)_{Cl_2} + \Delta H'$$

$$= \frac{1}{2} \times 151 + \frac{1}{2} \times 62.76 + \frac{1}{2} \times 242.3 - 211.3$$

$$= 75.5 + 31.38 + 121.15 - 211.3$$

$$= 228.03 - 211.3 = 16.73 \text{ kJ mol}^{-1}$$

8. (a)

9. (d): $PH_3 + 4Cl_2 \longrightarrow PCl_5 + 3HCl$

Cl_2 oxidises P^{3-} to P^{5+}. The reaction is endothermic thus, the mixture cools down.

10. (a): In the presence of an acid, hydrolysis of ethyl acetate is a pseudo-unimolecular reaction but the actual value of k depends upon the concentration of H^+ ions. As H_2SO_4 is a stronger acid than HCl and moreover H^+ ions produced from 0.05 M H_2SO_4 is double than 0.05 M HCl therefore, $k_2 > k_1$.

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

13. (b): $E = K.E. + E_{threshold}$

$$\frac{hc}{\lambda} = \frac{1}{2}mv^2 + \frac{hc}{\lambda_0}$$

$$\frac{1}{2}mv^2 = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}$$

$$v^2 = \frac{2hc}{m}\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$

$$v = \left[\frac{2hc}{m}\left(\frac{\lambda_0 - \lambda}{\lambda_0 \lambda}\right)\right]^{1/2}$$

14. (b): In the Reimer-Tiemann reaction, new C—C bond is formed between the carbon of benzene ring and —CHO group.

CONCEPT MAP

ALDEHYDES, KETONES AND CARBOXYLIC ACIDS

Being important constituents of fabrics, flavourings, plastics and drugs, carbonyl compounds are of utmost importance to organic chemistry while carboxylic acids are amongst the earliest organic compounds to be isolated from nature and are still known by their common names.

ALDEHYDES AND KETONES

Structure and Nomenclature

Aldehydes

- $R—\overset{\overset{O}{\|}}{C}—H$ where, $R = H$, alkyl or aryl group.
- In IUPAC system, aldehydes are named as *alkanals*.

Ketones

- $R—\overset{\overset{O}{\|}}{C}—R'$ where R and R' both can be same or different groups.
- In IUPAC system, they are named as *alkanones*.

Physical Properties

- Solubility in water $\propto \dfrac{1}{\text{Molecular mass}}$
- Compounds having upto four carbon atoms are soluble in water due to hydrogen bonding.
- Due to dipole-dipole interactions their b.pts. are higher than the corresponding hydrocarbons or ethers but lesser than alcohols or carboxylic acids which have intermolecular H-bonding.
- Due to two electron donating alkyl groups, ketones have higher b.pts. than the corresponding aldehydes.

Distinction Tests

Test	Aldehydes	Ketones
Schiff's reagent	Pink colour	No colour
Fehling's solution	Red ppt.	No ppt.
Tollens' reagent	Silver mirror	No ppt.
Sodium hydroxide	Brown resinous mass (except HCHO)	No reaction
Alkaline sodium nitroprusside	A deep red colour (except HCHO)	Red colour which changes to orange

Structure and Nomenclature

Carboxylic acids

- $R—\overset{\overset{O}{\|}}{C}—OH$ where, $R = H$, alkyl or aryl group.
- In IUPAC system, they are named as *alkanoic acids*.

Physical Properties
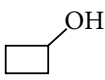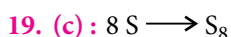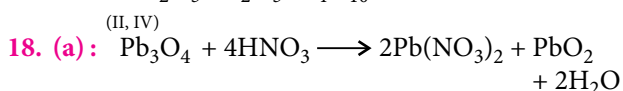
- Solubility in water $\propto \dfrac{1}{\text{Molecular mass}}$
- High b.pt. due to intermolecular hydrogen bonding.
- M.pts. and b.pts of aromatic acids are usually higher than those of aliphatic acids.

CARBOXYLIC ACIDS

Chemical Properties

- *Acidity order :* Carboxylic acids>Phenols>Alcohols
- *EDG* decreases the acidity and *EWG* increases the acidity.
- More the electronegativity of the atom attached to the carboxyl group, more will be the acidity.

Distinction Tests

Test	Carboxylic acids	Phenols	Alcohols
$NaHCO_3$	Brisk effervescence of CO_2 gas	No reaction	No reaction
$FeCl_3$	Buff coloured ppt.	Violet, blue or red colour	No reaction

Preparation

- **Oxidation of alcohols :**

$$RCH_2OH + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4(dil.)} RCHO + H_2O$$
(1° alcohol)

$$RCH(OH)R' + [O] \xrightarrow{K_2Cr_2O_7/H_2SO_4(dil.)} RCOR' + H_2O$$
(2° alcohol)

- **Catalytic decomposition of carboxylic acids :**

$$RCOOH + HOOCH \xrightarrow{MnO, 573 K} RCHO + CO_2 + H_2O$$

$$RCOOH + HOOCR' \xrightarrow{MnO, 573 K} RCOR' + CO_2 + H_2O$$

- **Hydroboration-oxidation of alkynes :**

$$R—C \equiv C—H \xrightarrow{\underset{\text{THF}}{B_2H_6}} \left[\begin{array}{c} R—C=C—H \\ \quad | \quad | \\ \quad H \quad BH_2 \end{array}\right] \xrightarrow{\underset{OH^-}{H_2O_2}}$$

$$R—C=C—H \rightleftharpoons RCH_2\overset{\overset{O}{\|}}{C}—H$$
$$\quad | \quad | $$
$$\quad H \quad OH$$

Terminal alkyne

$$R—C \equiv C—R' \xrightarrow{\underset{\text{THF}}{B_2H_6}} \left[\begin{array}{c} R—C=C—R' \\ \quad | \quad | \\ \quad H \quad BH_2 \end{array}\right] \xrightarrow{\underset{OH^-}{H_2O_2}}$$

$$R—C=C—R' \rightleftharpoons RCH_2\overset{\overset{O}{\|}}{C}—R'$$
$$\quad | \quad | $$
$$\quad H \quad OH$$

- **Ozonolysis of alkenes :**

$$RCH=\underset{\underset{R'}{|}}{C}—R'' \xrightarrow{\underset{H_2O, Zn}{O_3}} RCHO + \overset{R'}{\underset{R''}{>}}C=O$$

- **From gem-dihalides :**

$$R—\overset{\overset{R'}{|}}{\underset{\underset{Cl}{|}}{C}}—Cl \xrightarrow{\underset{\text{or } Ba(OH)_2}{aq. \text{ KOH}}} R—\overset{\overset{R'}{|}}{C}=O$$

$\left(\begin{array}{l}\text{Aldehyde when } R' = H \\ \text{Ketone when } R' = \text{alkyl group}\end{array}\right)$

Chemical Properties

- *Nucleophilic addition reactions :*

$$\overset{|}{\underset{|}{C}}=O + :Nu^- \xrightarrow{\text{slow}} \overset{|}{\underset{|}{C}}\overset{O^-}{\underset{Nu}{}} \xrightarrow{H^+, \text{ fast}} \overset{|}{\underset{|}{C}}\overset{OH}{\underset{Nu}{}}$$

- *Reactivity order :*

Aldehydes > Ketones (steric and electronic reasons)

HCHO > $RCHO$ > PhCHO > $RCOR$ > $RCOPh$ > PhCOPh

- *Nucleophilic addition-elimination reactions :*

$$\overset{|}{\underset{|}{>}}C=O \xrightarrow[\underset{(ii) \Delta}{(i) NH_3}]{} >C=NH + H_2O \quad \text{Imine}$$

$$\xrightarrow[\underset{(ii) \Delta}{(i) NH_2—Z}]{} >C=N—Z + H_2O$$

$\left(Z = \text{alkyl, aryl,} —OH, —NH_2, —NHC_6H_5,\right.$

$$—NH—\overset{NO_2}{\underset{}{\bigcirc}}—NO_2, —NH—\overset{\overset{O}{\|}}{C}—NH_2\left.\right)$$

- *Reduction and oxidation :*

$$\left.\begin{array}{l} RCHO \xrightarrow{\text{Reduction}} RCH_2OH \\ RCOR' \xrightarrow{\text{Reduction}} RCH(OH)R' \end{array}\right\} \begin{array}{l}(H_2/Ni \text{ or Pt or Pd,} \\ LiAlH_4 \text{ or } NaBH_4)\end{array}$$

$$\left.\begin{array}{l} RCHO \xrightarrow{\text{Reduction}} RCH_3 \\ RCOR' \xrightarrow{\text{Reduction}} RCH_2R' \end{array}\right\} \begin{array}{l}(Zn\text{-}Hg/HCl, NH_2NH_2/KOH, \\ HI/\text{Red P})\end{array}$$

$$RCHO \xrightarrow{\text{Oxidation}} RCOOH \begin{array}{l}(\text{Even with mild oxidising agents)} \\ (\text{same no. of C atoms})\end{array}$$

$$RCOR' \xrightarrow{\text{Oxidation}} RCOOH \begin{array}{l}(\text{With strong oxidising agents)} \\ (\text{lesser no. of C atoms})\end{array}$$

- *Haloform reaction :*

Given by compounds having $CH_3CO—$ group or $CH_3CH(OH)—$ group

$$RCOCH_3 \xrightarrow{NaOX} RCOONa + CHX_3$$
Haloform

- *Aldol condensation :*

$$CH_3—\overset{\overset{O}{\|}}{C}+H—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}—\overset{\overset{H}{|}}{C}=O \xrightarrow{\text{dil.NaOH}} CH_3—\overset{\overset{OH}{|}}{\underset{\underset{H}{|}}{C}}—\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}—\overset{\overset{H}{|}}{C}=O$$
(Aldehyde or ketone having α-hydrogen) ⟶ Aldol

- *Cannizzaro reaction :*

$$HCHO + HCHO \xrightarrow{\text{KOH (conc.)}} CH_3OH + HCOO^- K^+$$
(Aldehyde or ketone having no α-hydrogen)

Preparation

- **Oxidation of 1° alcohols :**

$$RCH_2OH \xrightarrow[\underset{[O]}{\text{alk. } KMnO_4}]{} RCHO \xrightarrow[\text{acid}]{[O]} RCOOH$$

- **Hydrolysis of nitriles and amides :**

$$RCN + 2H_2O \xrightarrow[\underset{OH^-}{H^+ or}]{} RCOOH + NH_3$$

$$RCONH_2 \xrightarrow[\text{heat}]{H_2O} RCOOH + NH_3$$

- **From Grignard reagents :**

$$CO_2 + CH_3MgBr \xrightarrow[\underset{H^+, H_2O}{\text{Dry ether}}]{} CH_3COOH + Mg(OH)Br$$

- **Hydrolysis of esters :**

$$RCOOR' + H_2O \xrightarrow{H^+ \text{ or } OH^-} RCOOH + R'OH$$

- **Carbonylation (Koch reaction) of alkenes :**

$$CH_2=CH_2 + CO + H_2O \xrightarrow[\underset{\text{(steam)}}{H_3PO_4, 573-673 K}]{\text{Under pressure}} CH_3CH_2COOH$$

- **From methyl ketones :**

$$CH_3CH_2—\overset{\overset{O}{\|}}{C}—CH_3 + 3NaOI \xrightarrow[-NaCl]{HCl} CH_3CH_2COOH$$
$$+ CHI_3 + 2NaOH$$

Chemical Reactions

- *Reactions involving cleavage of —OH group :*

$$R—\overset{\overset{O}{\|}}{C}\dashv OH$$

$$\xrightarrow[\underset{P_2O_5, \Delta}{RCOOH/H^+, \Delta}]{} (RCO)_2O \text{ Anhydride}$$

$$\xrightarrow{R'OH/H^+} RCOOR' \text{ Ester}$$

$$\xrightarrow[\underset{\text{or } SOCl_2 \text{ in pyridine}}{PCl_3 \text{ or } PCl_5}]{} RCOCl \text{ Acid chloride}$$

$$\xrightarrow{NH_3, \Delta} RCONH_2 \text{ Amide}$$

- *Reactions involving proton of —OH group :*

$$R—\overset{\overset{O}{\|}}{C}—O\dashv H$$

$$\xrightarrow{Na} 2RCOONa + H_2$$

$$\xrightarrow{NaOH} RCOONa + H_2O$$

$$\xrightarrow{Na_2CO_3} 2RCOONa + CO_2 + H_2O$$

$$\xrightarrow{NaHCO_3} RCOONa + CO_2 + H_2O$$

- *Reactions involving $>C=O$ group :*

$$R—\overset{\overset{O}{\|}}{C}—OH \xrightarrow[\underset{(ii) H_3O^+ \text{ (Reduction)}}{(i) LiAlH_4/\text{ether or } B_2H_6/\text{ether}}]{} RCH_2OH$$

- *Ring substitution in aromatic acids :*

—COOH group is deactivating and *meta* directing.

$$\overset{COOH}{\underset{}{\bigcirc}} \xrightarrow[FeBr_3, \Delta]{Br_2} \overset{COOH}{\underset{Br}{\bigcirc}}$$

$$\xrightarrow[\underset{\text{Conc. } H_2SO_4, \Delta}{\text{Conc. } HNO_3}]{} \overset{COOH}{\underset{NO_2}{\bigcirc}}$$

- *Reactions involving —COOH group :*

$$R\dashv\overset{\overset{O}{\|}}{C}—OH \xrightarrow[\underset{\Delta \text{ (Decarboxylation)}}{NaOH \text{ and } CaO}]{} RH + Na_2CO_3$$

- *Reactions involving —R group :*

$$RCH_2—\overset{\overset{O}{\|}}{C}—OH \xrightarrow[\underset{(ii) H_2O}{(i) X_2/\text{Red P}}]{} R—\overset{\underset{\underset{X}{|}}{}}{CH}—COOH$$
α-Halocarboxylic acid (Hell-Volhard Zelinsky reaction)

Phenol + Chloroform → Salicylaldehyde + 3NaCl + 2H$_2$O

$$\text{Phenol} + CHCl_3 + 3NaOH \longrightarrow \text{Salicylaldehyde} + 3NaCl + 2H_2O$$
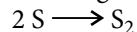
15. (b): 1 kJ mol^{-1} = 83.7 cm^{-1}

$$\Delta_o = \frac{20300}{83.7} = 243 \text{ kJ mol}^{-1}$$

16. (a): van der Waals' radius > metallic radius > covalent radius.

17. (d): Cyclobutanol is [structure] (C$_4$H$_8$O), diethyl ether is C$_2$H$_5$OC$_2$H$_5$ (C$_4$H$_{10}$O).

18. (a):
$$Pb_3O_4 + 4HNO_3 \xrightarrow{\text{(II, IV)}} 2Pb(NO_3)_2 + PbO_2 + 2H_2O$$

19. (c): 8 S $\longrightarrow$ S$_8$
0.8 mol of S gives 0.1 mol of S$_8$
   2 S $\longrightarrow$ S$_2$
0.2 mol of S gives 0.1 mol of S$_2$
      Total moles = 0.1 + 0.1 = 0.2
∴   1 mole of sulphur atoms behave as 0.2 moles.
So, i = 0.2

20. (a): A carbon bonded with four different types of groups or atoms is known as chiral carbon.

This compound has two chiral carbon atoms.
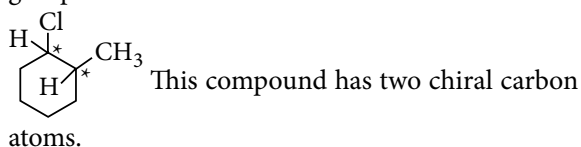
21. (c): +4 oxidation state of cerium is also known in solutions.

22. (a)

23. (b): CH$_3$—C≡C—CH$_3$. It is because symmetrical individual dipoles get cancelled leading to least dipole moment. Others are unsymmetrical, therefore, dipoles do not get cancelled.

24. (c):

(H$_2$SO$_5$)   (H$_2$S$_2$O$_8$)
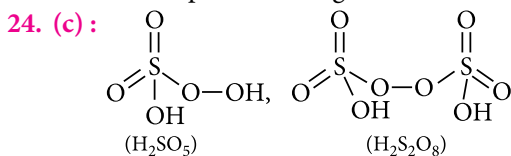
25. (d): Number of eq. of 0.01 M HCl = $\dfrac{0.01 \times 100}{1000}$

$$= 1 \times 10^{-3}$$

pH = –log[1 × 10^{-3}] = 3
Number of eq. of 0.02 M H$_2$SO$_4$ = $\dfrac{0.04 \times 50}{1000}$

$$= 2 \times 10^{-3}$$

Number of eq. of 0.02 M NaOH = $\dfrac{0.02 \times 50}{1000}$

$$= 1 \times 10^{-3}$$

[H$^+$] left = 2 × 10^{-3} – 1 × 10^{-3} = 1 × 10^{-3} : pH = 3

26. (c): Millimoles of H$_2$SO$_4$ required for different reagents are as follows :

For Zn = $\dfrac{65}{65} = 1$

For KOH = $\dfrac{20 \times 0.15}{2} = 1.5$

For Na$_2$CO$_3$ = 15 × 0.2 = 3
For Ba(OH)$_2$ = 25 × 0.1 = 2.5

27. (a)

28. (a): Only one H of H$_3$PO$_4$ has been replaced. Hence,

Eq. wt. of H$_3$PO$_4$ = $\dfrac{\text{Mol wt.}}{\text{Basicity in the reaction}}$

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

29. (d): Quaternary structure is observed in proteins which exists as assemblies of two or more polypeptide chains called sub-units which are held together by non-covalent forces such as hydrogen bonds, electrostatic interactions and van der Waals' interactions. The correct folding of a protein is guided by specific interactions among the side chains of the amino acid residues of a polypeptide chain. The two cysteine residues that react to form the disulphide bond may be a great distance apart in the primary structure (or on separate polypeptides) but are brought into close proximity by the three dimensional folding of the polypeptide chain.

30. (c)

31. (b): For exothermic reactions on increasing temperature, equilibrium constant gets decreased and inverse is true for endothermic reactions.

32. (a): Quaternary ammonium halides made from long chain aliphatic amines are called invert soaps because their positive ion acts as surfactant. These are used as germicides.

33. (c): Deuterium bond is stronger than the proton bond hence, ionisation of CH$_3$COOD is slower than CH$_3$COOH.

34. (d): Difference = 2.178 × 10^3 – 2.165 × 10^3
= 0.013 × 10^3

Fraction unoccupied $= \dfrac{0.013 \times 10^3}{2.178 \times 10^3} = 5.96 \times 10^{-3}$

35. (a) : Dehydrohalogenation using KOH/C_2H_5OH produces Saytzeff product as the major product while the strong bases like Et_3N or $(CH_3)_3COH/KOH$ produce Hofmann product as the major product.
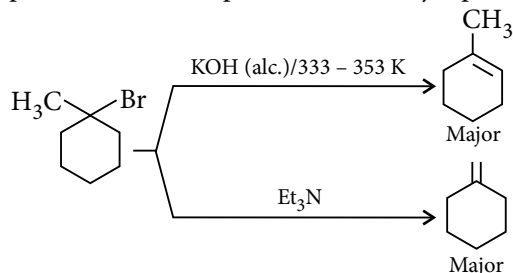
36. (a) : There is no test named as chromyl bromide test. Chromyl bromide is not stable at all.

37. (b) : Adsorption increases with increase in surface area.

38. (d) :
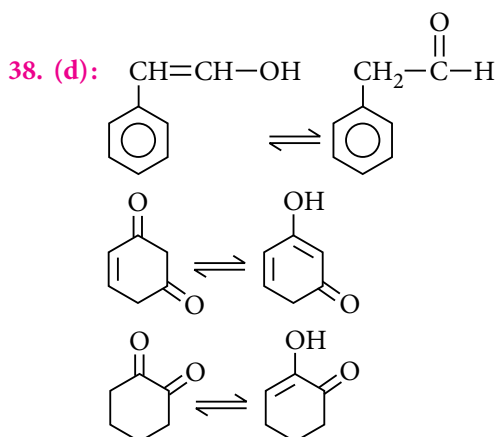
39. (c) : Smaller the size of cation, higher will be its polarizing power.

40. (c) : 1 g H_2 at STP $= 0.5$ mol $= 11.2$ L $= V_1$

$W = p(V_2 - V_1) = p(2V_1 - V_1)$

$= pV_1 = 1 \times 11.2$ L atm

41. (b) :

($C=O$) is electron withdrawing group hence π-electrons are migrated as shown. H_2O

42. (b) :
$$\overset{+5}{HNO_3}, \ \overset{+1}{N_2O}, \ \overset{+2}{NO}, \ \overset{+4}{NO_2} \ \overset{+5}{N_2O_5}$$

$4e^-$
$3e^-$
$1e^-$
$0e^-$
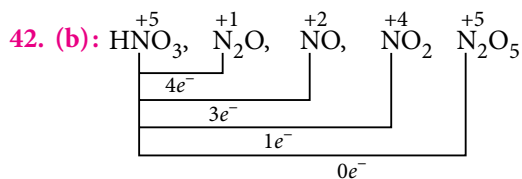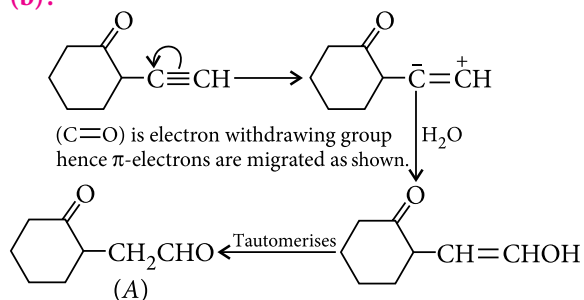
43. (a) : If a gas is liquefied, it means volume is decreased and attractive forces exist. a is a measure of attractive forces and b is the measure of excluded volume hence,

$a(NH_3) > a(N_2)$ and $b(NH_3) > b(N_2)$

44. (c)

45. (b) : CFSE $\propto \dfrac{1}{\text{Number of } d\text{-electrons}}$

(For metal ions having same charge)

46. (b) :

Butanone

47. (a) :
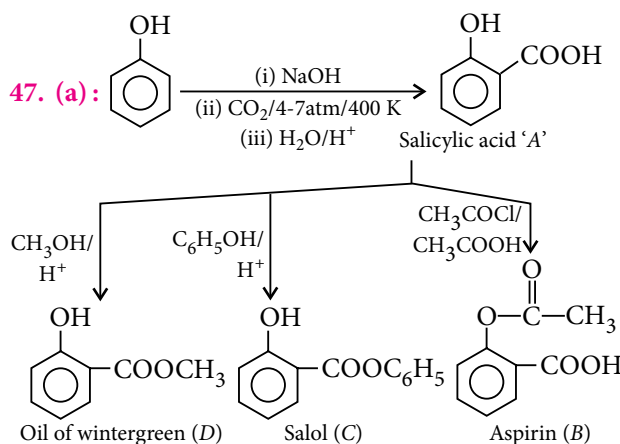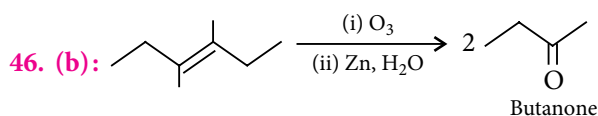
48. (c) : In Na_3VO_4, oxidation state of V is +5, *i.e.*, $3d^0 4s^0$ electronic configuration. Hence, no *d-d* transition takes place due to which it is colourless.

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

6 mol $\qquad\qquad\qquad\qquad$ 3×22.4 L

3×22.4 L $H_{2(g)}$ at STP are produced from 6 moles HCl. Hence, 11.2 L $H_{2(g)}$ at STP are produced from 1 mole HCl.
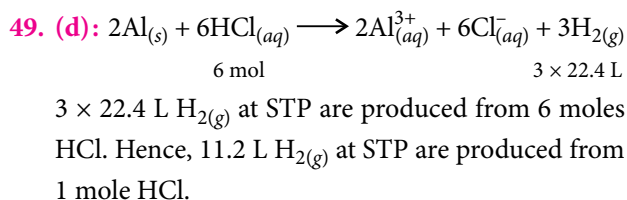
50. (a) : In acidic medium $-COO^-$ group acts as a base and accepts a proton.

◈◈

OLYMPIAD PROBLEMS

1. Which molecule will give following dicarboxylic acid upon treatment with acidic solution of $KMnO_4$?

(a)   (b)

(c)   (d)
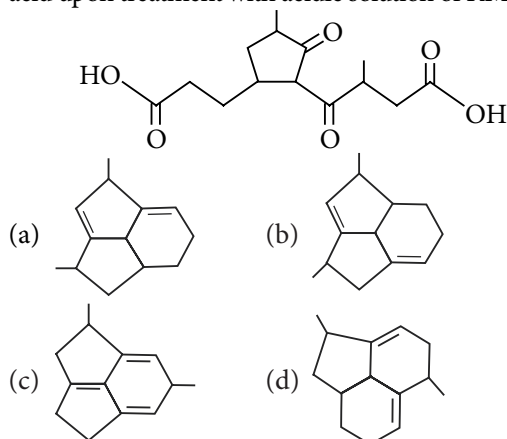
2. At what temperature will hydrogen molecules have the same kinetic energy as nitrogen molecules have at 35° C?

   (a) $\left(\dfrac{28 \times 35}{2}\right)°C$ (b) $\left(\dfrac{2 \times 35}{28}\right)°C$

   (c) $\left(\dfrac{2 \times 28}{35}\right)°C$ (d) 35°C
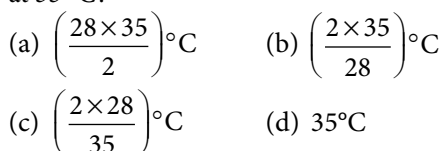
3. Which of the following pairs of molecules have the identical bond dissociation energies?
   (a) F_2 and H_2 (b) N_2 and CO
   (c) F_2 and I_2 (d) HF and O_2

4. If the dispersed phase in colloidal iron (III) hydroxide and colloidal gold is positively and negatively charged respectively then which of the following statements is not correct?
   (a) Magnesium chloride solution coagulates gold sol readily than iron (III) hydroxide sol.
   (b) Sodium sulphate solution causes coagulation in both sol.
   (c) Mixing of the two sols has no effect.
   (d) Coagulation in both sols can be brought about by electrophoresis.
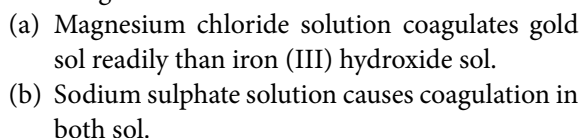
5. Consider a p_y-orbital of an atom and identify the correct statement.
   (a) s-orbital of another atom produces π-bond when y is the bond formation axis.
   (b) p_y-orbital of another atom produces σ-bond when x is the bond formation axis.
   (c) p_z-orbital of another atom produces π-bond when x is the bond formation axis.
   (d) d_{xy}-orbital of another atom produces π-bond when x is the bond formation axis.
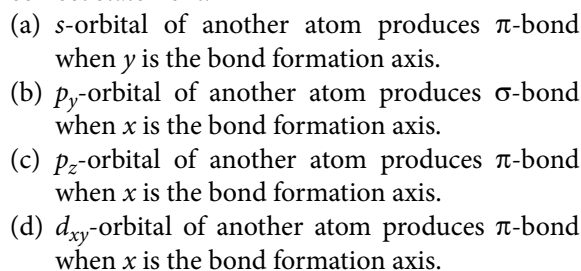
6. Calculate the % of free SO_3 in an oleum (considered as a solution of SO_3 in H_2SO_4) that is labelled '109% H_2SO_4'.
   (a) 30%   (b) 40%
   (c) 35%   (d) 20%
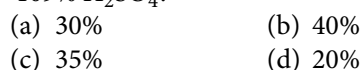
7. Among the following, which intermediate is the best hydride donor in a Cannizzaro reaction?

(a) $C_6H_5-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle OH}{|}}{C}}-O^-$ (b) $C_6H_5-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle O^-}{|}}{C}}-O^-$

(c)   (d)
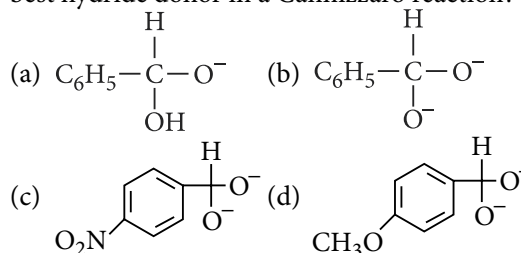
8. A pale green crystalline metal salt of 'M' dissolves freely in water. On standing, it gives a brown ppt. on addition of aqueous NaOH. The metal salt solution also gives a black ppt. on bubbling H_2S in basic medium. An aqueous solution of the metal salt decolourises the pink colour of the permanganate solution. The metal 'M' in the metal salt solution is

(a) copper   (b) aluminium
(c) lead   (d) iron.

9. For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, $K_p = \dfrac{\alpha^2}{(1-\alpha)V}$; temperature remaining constant,

(a) K_p will increase with the increase in volume
(b) K_p will increase with the decrease in volume
(c) K_p will not change with the change in volume
(d) K_p may increase or decrease with the change in volume.

10. The product of the following reaction is
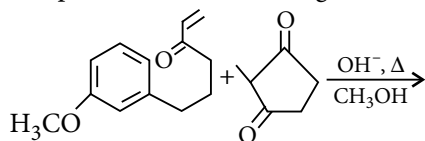
(d) none of these.

11. Acetone exhibits keto-enol tautomerism as shown below :

$$(CH_3)_2C{=}O \rightleftharpoons CH_3-\overset{\overset{\textstyle OH}{|}}{C}{=}CH_2$$
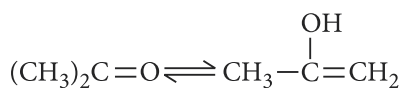
Which of the following products is obtained when acetone is treated with an excess of D_2O for a sufficient time in the presence of a small amount of a dilute NaOH solution?

(a) $CH_3-\overset{\overset{\textstyle OD}{|}}{C}{=}CH_2$ (b) $CH_2D-\overset{\overset{\textstyle OH}{|}}{C}{=}CH_2$

(c) $CD_3-\overset{\overset{\textstyle O}{||}}{C}-CD_3$ (d) $CH_3-\overset{\overset{\textstyle OD}{|}}{C}{=}CHD$

12. A fuel oil contains significant quantity of sulphur. When the oil is burnt, the sulphur is oxidised to

SO_2 as; $S + O_2 \rightarrow SO_2$. In a city, 465 tonnes of SO_2 are emitted by power plants each day. If 50% of SO_2 comes from the combustion of fuel oil that contains 3% S by weight, how many tonnes of oil is burnt per day?

(a) 3875 tonnes   (b) 7750 tonnes
(c) 1938 tonnes   (d) 1140 tonnes

13. Which is the major product formed in the following reaction?

$$C_6H_6 + (CH_3)_2CHCH_2OH \xrightarrow{H_2SO_4}$$
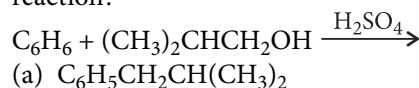
(a) $C_6H_5CH_2CH(CH_3)_2$

(b) $C_6H_5-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-CH_3$

(c) $C_6H_5-\overset{\overset{\textstyle CH_3}{|}}{\underset{\underset{\textstyle CH_3}{|}}{C}}-C_6H_5$

(d) A mixture of all of these.

14. Which of the following represents the crystal field splitting energy diagram in a linear field (assuming that the ligands lie on the z-axis)?

(a) $\begin{array}{c} \overline{d_{z^2}}\ \overline{d_{xz}}\ \overline{d_{yz}} \\ \overline{d_{xy}}\ \overline{d_{x^2-y^2}} \end{array}$ (b) $\begin{array}{c} \overline{d_{xz}}\ \ \overline{d_{yz}} \\ \overline{d_{z^2}} \\ \overline{d_{xy}}\ \ \overline{d_{x^2-y^2}} \end{array}$

(c) $\begin{array}{c} \overline{d_{z^2}} \\ \overline{d_{xz}}\ \ \overline{d_{yz}} \\ \overline{d_{xy}}\ \ \overline{d_{x^2-y^2}} \end{array}$

(d) No splitting in linear field is possible.

15. When pressure on 10 g of hydrogen is reduced from 20 to 1 atm at a constant temperature of 273 K. The gas behaves ideally. Calculate heat 'q' absorbed by the system.

(a) 4140 cal   (b) 8180 cal
(c) 2140 cal   (d) 5490 cal

16. The vapours of Hg absorb some electrons accelerated by a potential difference of 4.5 volts as a result of which light is emitted. If the full energy of single incident electron is supposed to be converted into light emitted by single Hg atom, find the wave number of the light.

(a) $7.209 \times 10^{-19}\ m^{-1}$ (b) $3.63 \times 10^{6}\ m^{-1}$
(c) $4.20 \times 10^{4}\ m^{-1}$ (d) $5.65 \times 10^{6}\ m^{-1}$

17. Ammonia reacts with Nessler's reagent to give a brown precipitate known as iodide of Millon's base.

This base is believed to have the structure

(a) $\left[O \left\langle \begin{array}{c} Hg \\ Hg \end{array} \right\rangle NH_2 \right] I \cdot H_2O$

(b) $O \left\langle \begin{array}{c} HgI_2 \\ NH_2 \end{array} \right.$

(c) $-O \left\langle \begin{array}{c} \overset{+}{N}H_3 \\ OHgI_2 \end{array} \right.$

(d) $O \left\langle \begin{array}{c} NHNH_2 \\ HgI \end{array} \right.$
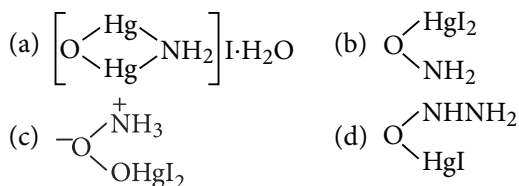
18. The nitrogen atom in each of the following tertiary amines may be removed as trimethyl amine by repeated Hofmann elimination. Which of the following amines requires the greater number of Hofmann sequence to accomplish this?
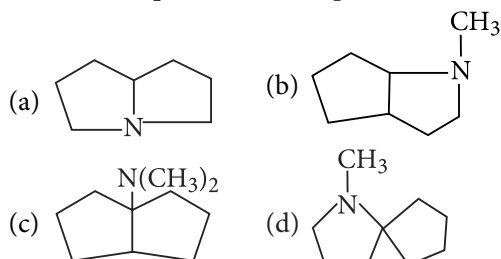
19. Cyclopentadiene is unusually acidic for a hydrocarbon. This is because
    (a) the carbon atoms of cyclopentadiene are sp-hybridised
    (b) cyclopentadiene is aromatic
    (c) the removal of a proton from it yields an aromatic anion
    (d) cyclopentadiene yields a highly stable free radical.

20. The kinetics of decomposition of N_2O_5 in CCl_4 solution is studied by measuring the evolved oxygen. If 24 mL of the gas was evolved in one hour while 35 mL of the gas was evolved when no more oxygen was coming out, calculate the fraction of N_2O_5 decomposed in one hour.
    (a) 0.486   (b) 1.642
    (c) 0.686   (d) 0.721

21. Which of the following does not have dangling bond?
    (a) Graphite   (b) Silica
    (c) Fullerene (C_{60})   (d) None of these

22. 36.4 g of 1, 1, 2, 2-tetrachloropropane was heated with zinc dust and the product was bubbled through ammoniacal $AgNO_3$. What is the weight of precipitate obtained?
    (a) 25.3 g   (b) 42.6 g
    (c) 8.0 g   (d) 29.4 g

23. Gold and platinum dissolve in aqua regia to produce respectively

(a) $H[AuCl_4]$ and $H[PtCl_3]$
(b) $H[AuCl_4]$ and $H_2[PtCl_6]$
(c) $H_2[AuCl_6]$ and $H[PtCl_4]$
(d) $H_2[AuCl_6]$ and $[PtCl_6]$

24. Find the pH of a solution prepared by mixing 25 mL of a 0.5 M solution of HCl, 10 mL of a 0.5 M solution of NaOH and 15 mL of water.
    (a) 0.623   (b) 0.824
    (c) 0.912   (d) 0.412

25. The osmotic pressure of an aqueous solution of sucrose is 2.47 atm at 303 K and the molar volume of the water present is 18.10 cm^3. Calculate the elevation in boiling point of the solution. Given $\Delta H_{vap.}$ = 540 cal/g. (Assume volume of solvent equal to volume of solution.)
    (a) 9.93×10^{-2} (b) 4.93×10^{-2}
    (c) 5.14×10^{-2} (d) 9.98×10^{-2}

26. 2, 6-Dimethylphenyl allyl ether, in which the carbon atom next to the oxygen in allyl group is ^{14}C, on being heated to 200°C, gives
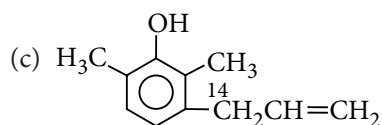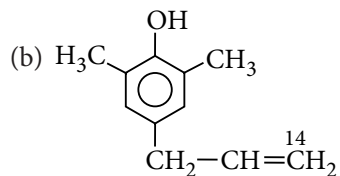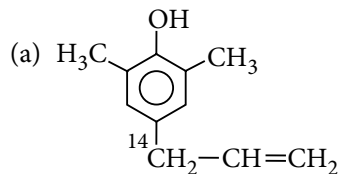
(d) none of these.

27. Which systematic diagram represents the correct chemical relations between calcium and its compounds?

(a)

(b)

(c)

(d)
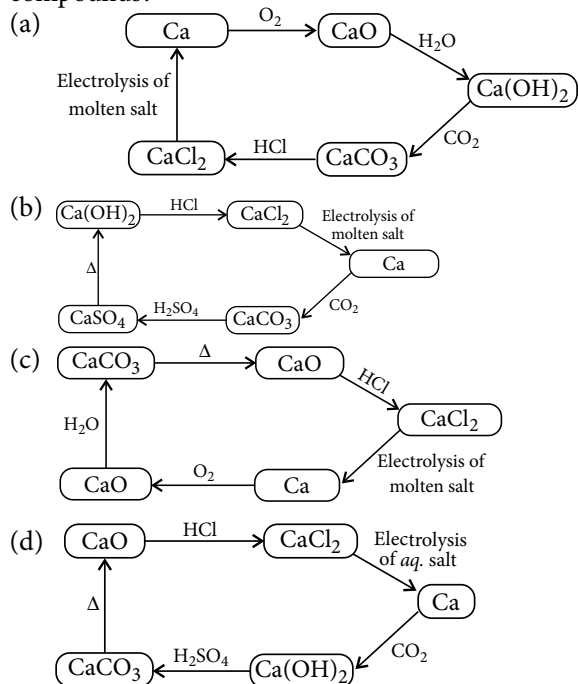
28. Which of the following statements is incorrect in the context of silicones?
(a) They are more stable to heat than other polymers.
(b) They are strongly water-repellent, good electrical insulators, and have non-sticking and antifoaming properties.

(c) The Si—O bond energy is higher than C—C bond energy.
(d) The Si—O bond energy is lower than C—C bond energy.

29. A galvanic cell is composed of two hydrogen electrodes, one of which is a standard one. In which of the following solutions should the other electrode be immersed to get maximum e.m.f?
(a) 0.1 M HCl
(b) 0.1 M CH_3COOH
(c) 0.1 M H_3PO_4
(d) 0.1 M H_2SO_4

30. The correct decreasing order of relative reactivity of the following chlorides toward aqueous KOH solution is
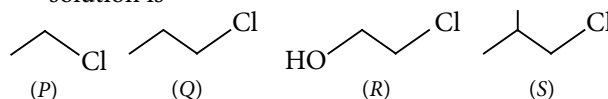
(a) $P > Q > R > S$
(b) $R > P > Q > S$
(c) $S > R > Q > P$
(d) $R > S > Q > P$

ANSWER KEYS

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

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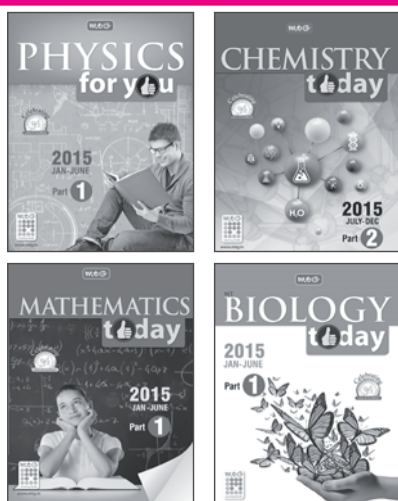
ACE YOUR WAY CBSE XII

Series 1

CHAPTERWISE PRACTICE PAPER : THE SOLID STATE | SOLUTIONS

Time Allowed : 3 hours

Maximum Marks : 70

GENERAL INSTRUCTIONS

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

1. What are pseudo solids?

2. What is a de-icing agent? How does it function?

3. Give the significance of a 'lattice point'.

4. Why is Fe_3O_4 ferrimagnetic at room temperature but becomes paramagnetic at 850 K?

5. Solid *A* is a very hard electrical insulator in solid as well as in molten state and melts at extremely high temperature. What type of solid is it?

6. Inspite of long range order in the arrangement of particles, why are the crystals usually not perfect?

7. Explain with suitable examples in each case why the molar masses of some substances determined with the help of colligative properties are
   (i) higher
   (ii) lower than the actual values.

8. An element crystallises in a *fcc* lattice having edge length 400 pm. Calculate the maximum diameter of atom which can be placed in interstitial site without distorting the structure.

   OR

   (i) What type of semiconductor is obtained when silicon is doped with boron?
   (ii) What type of magnetism is shown in the following alignment of magnetic moments?

   ↑ ↑ ↑ ↑ ↑ ↑

9. H_2S, a toxic gas with rotten egg like smell, is used for qualitative analysis. If the solubility of H_2S in water at STP is 0.195 m, calculate Henry's law constant.

10. Schottky defects generate an equal number of cation and anion vacancies while doping produces only cation vacancies and not anion vacancies. Why?

11. **(i)** Niobium crystallises in body-centred cubic structure. If density is 8.55 g cm^{-3}, calculate atomic radius of niobium using its atomic mass 93 u.
    (ii) Name the parameters that characterise a unit cell.

12. Henry's law constant for CO_2 in water is 1.67×10^8 Pa at 298 K. Calculate the quantity of CO_2 in 500 mL of soda water when packed under 2.5 atm CO_2 pressure at 298 K.

13. (i) Zinc oxide is white but it turns yellow on heating. Explain.

(ii) A sample of drinking water was found to be severely contaminated with chloroform, $CHCl_3$ which is supposed to be a carcinogen. The level of contamination was 15 ppm (by mass).

(a) Express this in percent by mass.

(b) Determine the molality of chloroform in the water sample.

14. At 25°C, the vapour pressures of benzene (C_6H_6) and toluene (C_7H_8) are 93.4 torr and 26.9 torr, respectively. A solution is made by mixing 35.0 g of benzene and 65.0 g of toluene. At what applied pressure, in torr, will this solution boil at 25°C?

15. (i) Why glasspanes fixed to windows and doors of old buildings are found to be slightly thicker at the bottom part?

(ii) Why the defects of crystalline solids are called thermodynamic defects?

(iii) What structural changes are observed when sodium chloride crystals are subjected to high pressure?

OR

Metallic gold crystallises in a face-centred cubic lattice. The length of the cubic unit cell is $a = 4.070$ Å. (atomic mass of gold = 197 u)

(i) What is the closest distance between gold atoms?

(ii) How many "nearest neighbours" does each gold atom have?

(iii) What is the density of gold?

16. (i) Osmotic pressure of a solution containing 7 g of dissolved protein per 100 cm^3 of solution is 25 mm Hg at body temperature (310 K). Calculate the molecular mass of protein ($R = 0.08205$ L atm mol^{-1} deg^{-1}).

(ii) Calculate the boiling point of a solution containing 0.456 g of camphor (molar mass = 152 g mol^{-1}) dissolved in 31.4 g of acetone (b.p. = 56.30°C), if the molal elevation constant of acetone is 1.72°C kg mol^{-1}.

17. Calculate the molarity of a solution of $CaCl_2$, if it is found that 200 cm^3 of $CaCl_2$ solution contains 3.01×10^{22} chloride ions. Assume that $CaCl_2$ is completely ionised in solution.

18. (i) Graphite is a conductor of electricity. Give reasons.

(ii) How will you differentiate between *hcp* and *ccp* lattice?

19. What will be the osmotic pressure of a 0.1 M monobasic acid, if its pH is 2.0 at 25°C?

20. How many mL of 0.1 M HCl are required to react completely with 1 g mixture of Na_2CO_3 and $NaHCO_3$ containing equimolar amounts of the two?

21. Aluminium crystallises in a cubic close packed structure. Radius of the atom in the metal is 125 pm.

(i) What is the length of the unit cell?

(ii) How many unit cells are there in 1 cm^3 of aluminium?

22. (i) Based on solute-solvent interactions arrange the following in order of increasing solubility in *n*-octane and explain.
Cyclohexane, KCl, CH_3OH, CH_3CN

(ii) Two elements *A* and *B* form compounds having molecular formula AB_2 and AB_4. When dissolved in 20 g of benzene (C_6H_6), 1 g of AB_2 lowers the freezing point by 2.3 K whereas 1 g of AB_4 lowers it by 1.3 K. The molal depression constant for benzene is 5.1 K kg mol^{-1}. Calculate atomic masses of *A* and *B*.

23. Aamir, a science student dismantled an old electronic gadget to know about its components. He found that the gadget is composed of various chips, wires and other small components fitted on a circuit plate. To further explore, he searched about these chips and other components on internet and found that majority of these components are made up of a specific class of solids.

(i) What are the values shown by Aamir?

(ii) What is this class of solids called?

(iii) Explain why this class of solids is used to prepare components of electric devices?

(iv) What is the conductivity range of this class of solids?

24. (i) Heating crystals of KCl in potassium vapours makes crystals violet, why?

(ii) The density of KBr is 2.75 g cm^{-3}. The length of edge of the unit cell is 654 pm. Predict the type of cubic lattice to which unit cell of KBr belongs. ($N_A = 6.023 \times 10^{23}$ mol^{-1},

Atomic mass : K = 39, Br = 80)

(iii) Sodium has a *bcc* structure with nearest neighbour distance 365.9 pm. Calculate its density (Atomic mass of sodium = 23).

OR

(i) Refractive index of a solid is observed to have the same value along all directions. Comment on the nature of this solid. Would it show cleavage property?

(ii) (a) Sodium chloride is insulator in solid state but conductor in aqueous solution. Explain why?

    (b) What kind of magnetic properties are exhibited by ions of NaCl?

    (c) What type of defects are generally observed in sodium chloride?

25. (i) Why is camphor preferred as a solvent in determination of depression in freezing point (ΔT_f)?

(ii) Aquatic species are more comfortable in cold water rather than in warm water. Why?

(iii) The vapour pressures of pure liquids *A* and *B* are 450 and 700 mm Hg at 350 K respectively. Find out the composition of the liquid mixture, if total vapour pressure is 600 mm Hg. Also, find the composition of the vapour phase.

OR

(i) When kept in water, raisins swell in size. Name and explain the phenomenon involved with the help of a diagram. Give three applications of the phenomenon.

(ii) Explain why on addition of 1 mol of NaCl to 1 litre of water, the boiling point of water increases, while addition of 1 mol of methyl alcohol to one litre of water decreases its boiling point.

26. (i) Frenkel defects are not found in alkali metals. Explain.

(ii) Br^- ions form close packed structure. If the radius of Br^- ion is 195 pm, calculate the radius of the cation that just fits in the tetrahedral hole. Can a cation A^+ having a radius of 82 pm be slipped into the octahedral hole of the crystal A^+B^-.

(iii) (a) Name the non-stoichiometric point defect responsible for colour in alkali metal halides.

    (b) What is Piezoelectric effect? Explain with suitable example.

OR

(i) In terms of band theory, what is the difference
(a) between a conductor and an insulator
(b) between a conductor and a semiconductor?

(ii) Non-stoichiometric cuprous oxide, Cu_2O can be prepared in the laboratory. In this oxide, copper to oxygen ratio is slightly less than 2:1. Can you account for the fact that this substance is a *p*-type semiconductor?

SOLUTIONS

1. Amorphous solids which have tendency to flow slowly and resemble liquids in many respects are called pseudo solids or super cooled liquids. *e.g.*, glass.

2. De-icing agent is a substance which prevents the formation of ice by lowering the freezing point of water to such an extent that it does not freeze to form ice.

3. Each lattice point represents one constituent particle of the solid which may be an atom, an ion, or a molecule.

4. Fe_3O_4 is ferrimagnetic at room temperature because in its crystals magnetic domains of Fe (II) and Fe (III) ions are unequal in magnitude and aligned in parallel and antiparallel directions but when heated at 850 K, the arrangement is randomised and substance becomes paramagnetic.

5. Covalent or network solid.

6. An ideal crystal is one which has the same unit cell containing the same lattice points across the whole crystal. But when crystallisation of solids takes place specially at fast or moderate rate some deviations from ideal arrangement may be introduced which are called defects. Thus, crystals are usually imperfect.

7. (i) When a solute undergoes association in the solution then the number of solute particles decreases. Hence, the colligative property will be lower and the molar mass will be higher *e.g.*, $2CH_3COOH \longrightarrow (CH_3COOH)_2$.

(ii) When a solute undergoes dissociation in solution then the number of solute particles increases. Hence, colligative property will be higher and the molar mass will be lower *e.g.*, $NaCl \longrightarrow Na^+ + Cl^-$.

8. In a cubic crystal system, there are two types of voids known as octahederal and tetrahederal voids. If *r* is the radius of void and *R* is the radius of atom creating these voids then

$\left(\dfrac{r}{R}\right)_{\text{octa}} = 0.414$ and $\left(\dfrac{r}{R}\right)_{\text{tetra}} = 0.225$

The above radius ratio values indicate that octahedral void has larger radius hence, for maximum diameter of atom to be present in interstitial space.

$$r = 0.414\,R$$

Also, in *fcc*, $4R = \sqrt{2}a$

Diameter required $(2r) = (2R) \times 0.414$

$$= \dfrac{a}{\sqrt{2}} \times 0.414 = \dfrac{400 \times 0.414}{\sqrt{2}} = 117 \text{ pm}$$

OR

(i) When silicon is doped with boron which contains only three valence electrons, a hole is created at the place where the fourth valence electron is missing. This hole increases the conductivity and this type of semiconductors are called *p*-type semiconductors.

(ii) As all the magnetic moments are aligned in one direction hence, the substance will show ferromagnetism.

9. Solubility of H_2S = 0.195 m = 0.195 mol in 1000 g of the solvent (water)

$$n_{H_2O} = \dfrac{1000 \text{ g}}{18 \text{ g mol}^{-1}} = 55.55 \text{ moles}$$

$$\therefore \quad x_{H_2S} = \dfrac{n_{H_2S}}{n_{H_2S} + n_{H_2O}} = \dfrac{0.195}{0.195 + 55.55}$$

$$= \dfrac{0.195}{55.745} = 0.0035$$

Pressure at STP = 0.987 bar

Applying Henry's law, $p_{H_2S} = K_H \times x_{H_2S}$

or $\quad K_H = \dfrac{p_{H_2S}}{x_{H_2S}} = \dfrac{0.987 \text{ bar}}{0.0035} = 282 \text{ bar.}$

10. Schottky defects exist in pairs to maintain electrical neutrality. So, equal number of cation and anion vacancies are generated.

Ionic solids are doped with metal ions of higher valency and some cations of lower valency are displaced to maintain electrical neutrality. Hence, only cation vacancies are produced not anion vacancies.

11. (i) Given $d = 8.55 \text{ g cm}^{-3}$, $M = 93 \text{ g mol}^{-1}$, $Z = 2$ (for *bcc*), $N_A = 6.022 \times 10^{23}$, $r = ?$
Using formula,

$$a^3 = \dfrac{M \times Z}{d \times N_A} = \dfrac{93 \times 2}{8.55 \times 6.022 \times 10^{23}}$$

or, $a^3 = 3.61 \times 10^{-23} = 36.1 \times 10^{-24} \text{ cm}^3$

$\therefore \quad a = 3.304 \times 10^{-8} \text{ cm} = 330.4 \times 10^{-12} \text{ m}$
$= 330.4 \text{ pm}$

For body-centred cubic,

$$r = \dfrac{\sqrt{3}}{4}a = 0.433\,a = 0.433 \times 330.4 \text{ pm}$$
$$= 143.1 \text{ pm}$$

(ii) The size and shape of a unit cell is determined by the lengths of the edges of the unit cell (*a*, *b* and *c*) which may or may not be mutually perpendicular and by the angles α, β and γ between the edges *b* and *c*, *c* and *a* and *a* and *b* respectively.

12. Since, 1 atm = 1.01325×10^5 pascal
Hence, 2.5 atm = $2.5 \times 1.01325 \times 10^5$ pascal
$= 2.533125 \times 10^5$ pascal
By Henry's law $p_{CO_2} = K_H\, x_{CO_2}$

$$x_{CO_2} = \dfrac{p_{CO_2}}{K_H} = \dfrac{2.533125 \times 10^5 \text{ Pa}}{1.67 \times 10^8 \text{ Pa}}$$
$$= 1.52 \times 10^{-3}$$

Also, 500 mL soda water (water containing CO_2)
$= 500$ g (assuming density of water = 1 g mL^{-1})

$$n_{H_2O} = \dfrac{500}{18} = 27.77 \text{ mol}$$

Let $n_{CO_2} = n$ mol

$\therefore$ Total moles $= 27.77 + n$

$$\therefore \quad x_{CO_2} = \dfrac{n}{27.77 + n} = 1.52 \times 10^{-3}$$

$$\therefore \quad \dfrac{n}{27.77} = 1.52 \times 10^{-3} \qquad (\because n <<< 27.77)$$

$$\therefore \quad n_{CO_2} = 1.52 \times 10^{-3} \times 27.77 \text{ mol}$$
$$= 0.0422 \text{ mol} = 0.0422 \text{ mol} \times 44 \text{ g mol}^{-1}$$
$$= 1.8568 \text{ g}$$

13. (i) On heating ZnO loses oxygen according to the following reaction :
$$\text{ZnO} \longrightarrow \text{Zn}^{2+} + \dfrac{1}{2} O_2 + 2e^-$$
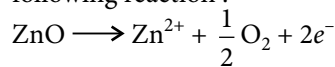
Zn^{2+} ions are entrapped in the interstitial voids and electrons are entrapped in the neighbouring interstitial voids to maintain electrical neutrality. These electrons absorb visible light and radiate yellow colour.

(ii) (a) 15 ppm means 15 parts per million, *i.e.*, 15 parts of $CHCl_3$ in 10^6 parts by mass of the solution.

$$\therefore \% \text{ by mass} = \dfrac{15}{10^6} \times 100 = 15 \times 10^{-4} \%$$

(b) Taking 15 g chloroform in 10^6 g of the solution so, mass of solvent = 10^6 g

Molar mass of $CHCl_3 = 12 + 1 + 3 \times 35.5$
$$= 119.5 \text{ g mol}^{-1}$$

$\therefore n_{CHCl_3} = \dfrac{15}{119.5}$

$\therefore$ Molality $= \dfrac{n_{CHCl_3}}{w_{H_2O}(\text{in g})} \times 1000$

$$= \dfrac{15/119.5}{10^6} \times 1000 = 1.25 \times 10^{-4} \text{ m}$$

14. This solution of benzene and toluene will boil at 25°C when the pressure above the solution is equal to the sum of the vapour pressures of benzene and toluene in the solution.

$p^{\circ}_{C_6H_6} = 93.4$ torr, $p^{\circ}_{C_6H_5CH_3} = 26.9$ torr
$w_{C_6H_6} = 35$ g, $w_{C_6H_5CH_3} = 65$ g
Molar mass of $C_6H_6 = 12 \times 6 + 1 \times 6$
$$= 72 + 6 = 78 \text{ g mol}^{-1}$$

Therefore, $n_{C_6H_6} = \dfrac{35}{78} = 0.449$

Molar mass of $C_6H_5CH_3 = 12 \times 7 + 8 \times 1 = 92$ g mol^{-1}

Therefore, $n_{C_6H_5CH_3} = \dfrac{65}{92} = 0.707$

Now, the mole fractions of C_6H_6 and $C_6H_5CH_3$ are

$x_{C_6H_6} = \dfrac{n_{C_6H_6}}{n_{C_6H_6} + n_{C_6H_5CH_3}}$

$$= \dfrac{0.449}{0.449 + 0.707} = \dfrac{0.449}{1.156} = 0.388$$

$x_{C_6H_5CH_3} = \dfrac{n_{C_6H_5CH_3}}{n_{C_6H_5CH_3} + n_{C_6H_6}}$

$$= \dfrac{0.707}{0.707 + 0.449} = \dfrac{0.707}{1.156} = 0.612$$

Therefore, vapour pressures of C_6H_6 and $C_6H_5CH_3$ are

$p_{C_6H_6} = p^{\circ}_{C_6H_6} \times x_{C_6H_6} = 93.4 \times 0.388 = 36.24$ torr
$p_{C_6H_5CH_3} = p^{\circ}_{C_6H_5CH_3} \times x_{C_6H_5CH_3}$
$$= 26.9 \times 0.612 = 16.46 \text{ torr}$$

$\therefore$ Total vapour pressure of the solution,

$P_{\text{total}} = p_{C_6H_6} + p_{C_6H_5CH_3} = 36.24 + 16.46 = 52.7$ torr

15. (i) This is because glass is a supercooled liquid (amorphous solid) and it flows down very slowly making the bottom portion slightly thicker.

(ii) There is perfect arrangement of the constituent particles only at absolute zero (0 K). This arrangement corresponds to lowest energy. As temperature increases, deviation from perfectly ordered arrangement starts and number of defects increases with temperature. Hence, the defects are called thermodynamic defects.

(iii) On applying high pressure, NaCl acquires the CsCl structure *i.e.,* the coordination number changes from 6 : 6 to 8 : 8.

OR

(i) Given, edge length $= a = 4.070$ Å
Closest distance between two gold atoms in *fcc* lattice $(d) = 2r = \dfrac{2 \times a}{2\sqrt{2}}$

$\Rightarrow d = \dfrac{a}{\sqrt{2}} = \dfrac{4.070}{\sqrt{2}} = 2.878$ Å

(ii) Coordination number of each ion in *fcc* lattice is 12 hence, the number of nearest neighbours = 12

(iii) $d = \dfrac{ZM}{N_A a^3} = \dfrac{4 \times 197}{6.02 \times 10^{23} \times (4.07 \times 10^{-8})^3}$
$$= 19.4 \text{ g/cm}^3$$

16. (i) We know that
$\pi V = n_2 RT$

$\pi V = \dfrac{w_2}{M_2} RT$ or $M_2 = \dfrac{w_2 RT}{\pi V}$

Here, $w_2 = 7$ g, $\pi = 25$ mm Hg $= \dfrac{25}{760}$ atm

$R = 0.08205$ L atm mol^{-1} deg^{-1} and

$$V = \dfrac{100}{1000} = 0.1 \text{ litre}$$

$T = 310$ K

$\therefore M_2 = \dfrac{7 \times 0.08205 \times 310 \times 760}{25 \times 0.1}$
$$= 54126.7 \text{ g mol}^{-1}$$

(ii) We know that,

$\Delta T_b = \dfrac{1000 K_b w_2}{M_2 w_1 (\text{in g})} = \dfrac{1000 \times 1.72 \times 0.456}{152 \times 31.4} = 0.16$

$\therefore \Delta T_b =$ Boiling point of solution –
boiling point of solvent

$\therefore 0.16 =$ Boiling point of solution – 56.30

$\Rightarrow$ Boiling point of solution $= 0.16 + 56.30$
$$= 56.46°C$$

17. Calcium chloride ionises as follows :
$CaCl_2 \longrightarrow Ca^{2+} + 2Cl^-$
$\Rightarrow$ 1 mole of $CaCl_2$ gives 2 moles of Cl^- ions.
i.e., $2 \times 6.02 \times 10^{23}$ Cl^- ions are obtained from 1 mole of $CaCl_2$.
$\therefore 3.01 \times 10^{22}$ Cl^- ions will be obtained from
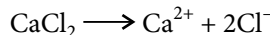
$$= \dfrac{3.01 \times 10^{22}}{2 \times 6.02 \times 10^{23}} = \dfrac{1}{40} \text{ mole of } CaCl_2$$

Thus, 200 mL solution contains $\dfrac{1}{40}$ mole of $CaCl_2$.

∴ 1000 mL solution will contain

$$= \frac{1}{40} \times \frac{1000}{200} = 0.125 \text{ mol of } CaCl_2$$

Therefore, molarity of solution is 0.125 M.

18. (i) In graphite, three electrons of each carbon atom are covalently bonded to three other C-atoms of its own layer. The fourth valence electron of each atom forms a delocalised layer of mobile electrons. This is why graphite is a conductor of electricity.

(ii) In *hcp* lattice, each third layer is parallel to first layer *i.e., ABAB*.......... type arrangement.

In *ccp* lattice, each fourth layer is parallel to the first layer *i.e., ABCABC*......... type arrangement.

19.

$$\text{H}A \rightleftharpoons \text{H}^+ + A^-$$

Initial C mol L^{-1} 0   0
At equilibrium $(C - C\alpha)$ $C\alpha$ $C\alpha$

(α = degree of dissociation)
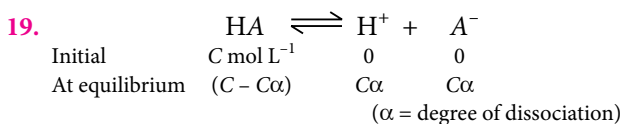
$\Rightarrow \quad [\text{H}^+] = C\alpha$
But $[\text{H}^+] = 10^{-2}$ M $[\because$ pH = 2$]$
$\therefore \quad C\alpha = 10^{-2}$

or $\alpha = \dfrac{10^{-2}}{C} = \dfrac{10^{-2}}{0.1} = 0.1$

Total number of particles after dissociation

$= C - C\alpha + C\alpha + C\alpha = C(1 + \alpha)$

$\therefore$ van't Hoff factor, $(i) = \dfrac{C(1 + \alpha)}{C}$

$= 1 + \alpha = 1 + 0.1 = 1.1$

$\therefore$ Osmotic pressure (π) of the monobasic acid

$= iCRT = 1.1 \times 0.1 \times 0.0821 \times 298$
$= 2.69$ atm

20. Let 1 g mixture contains x g of Na_2CO_3.

$\therefore$ Number of moles of $Na_2CO_3 = \dfrac{x}{106}$ mol

[$\because$ molar mass of $Na_2CO_3 = 106$ g mol^{-1}]

and number of moles of $NaHCO_3 = \dfrac{1-x}{84}$

[$\because$ molar mass of $NaHCO_3 = 84$ g mol^{-1}]

As the mixture contains equimolar amounts of the two therefore,

$\dfrac{x}{106} = \dfrac{1-x}{84} \quad \Rightarrow \quad x = 0.558$ g

$\therefore$ No. of moles of $Na_2CO_3 = \dfrac{0.558}{106} = 0.00526$

and no. of moles of $NaHCO_3 = \dfrac{1-0.558}{84}$

$= 0.00526$ mol

Reactions of HCl with Na_2CO_3 and $NaHCO_3$ take place as follows :

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + H_2O + CO_2$$
$$NaHCO_3 + HCl \longrightarrow NaCl + H_2O + CO_2$$
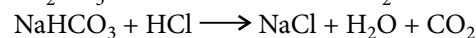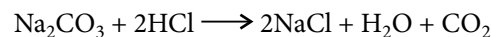
From the reaction, 1 mol of Na_2CO_3 requires

2 moles of HCl

$\therefore$ 0.00526 mol of Na_2CO_3 will require 2×0.00526

$= 0.01052$ mole of HCl

Similarly, 1 mol of $NaHCO_3$ requires 1 mole of HCl

$\therefore$ 0.00526 mol of $NaHCO_3$ will require 0.00526×1

$= 0.00526$ mole of HCl

$\therefore$ Total moles of HCl required $= 0.01052 + 0.00526$

$= 0.01578$ mol

0.1 M solution of HCl means that

0.1 mol of HCl is present in 1000 mL of solution

$\therefore$ 0.01578 mol of HCl will be present in

$$= \frac{1000 \times 0.01578}{0.1} = 157.8 \text{ mL of HCl solution.}$$

21. (i) For cubic closed packed structure,

edge length, $a = \dfrac{4r}{\sqrt{2}} = 2\sqrt{2}r$

$= 2\sqrt{2} \times 125$ pm $= 250\sqrt{2}$ pm $= 353.55$ pm

$= 353.55 \times 10^{-12}$ m $= 353.55 \times 10^{-10}$ cm

(ii) Volume of 1 unit cell $= (353.55 \times 10^{-10})^3$ cm^3

$= 4.4193 \times 10^{-23}$ cm^3

4.4193×10^{-23} cm^3 = 1 unit cell

$\therefore \quad 1$ cm$^3 = \dfrac{1 \text{ unit cell}}{4.4193 \times 10^{-23}}$

$= 2.263 \times 10^{22}$ unit cells

22. (i) Solubility in *n*-octane :

$KCl < CH_3CN < CH_3OH <$ Cyclohexane.

The order can be explained on the basis of 'like dissolves like'. *n*-Octane is a non polar solvent hence, non polar compounds will be highly soluble in *n*-octane. KCl is an ionic compound, CH_3CN is more polar than CH_3OH and cyclohexane is non polar.

Therefore, solubility increases with decreasing polarity.

(ii) Applying the formula,

$$M_2 = \frac{1000 \times K_f \times w_2}{w_1 \times \Delta T_f}$$

$$M_{AB_2} = \frac{1000 \times 5.1 \times 1}{20 \times 2.3} = 110.87 \text{ g mol}^{-1}$$

$$M_{AB_4} = \frac{1000 \times 5.1 \times 1}{20 \times 1.3} = 196.15 \text{ g mol}^{-1}$$

Suppose atomic masses of A and B are 'a' and 'b' respectively. Then

Molar mass of $AB_2 = a + 2b = 110.87$ g mol^{-1}
Molar mass of $AB_4 = a + 4b = 196.15$ g mol^{-1}
Eqn. (ii) - Eqn. (i) gives $2b = 85.28$ or $b = 42.64$
Substituting in eqn. (i) we get,
$a + 2 \times 42.64 = 110.87$ or $a = 25.59$
Thus, atomic mass of $A = 25.59$ u
atomic mass of $B = 42.64$ u

23. **(i)** Curiosity to learn or discover new things and appropriate usage of resources are the values shown by Aamir.

(ii) Semiconductors is the class of solids used in the components of electric devices.

(iii) In electronic devices, there is need to control the current flow in the circuit which is possible only in semiconductors by appropriate doping. However, if conductors are used then such control is not possible and they conduct the whole amount of current from the power source.

(iv) Conductivity range of semiconductors is 10^{-6} to 10^4 ohm^{-1} m^{-1}.

24. **(i)** KCl becomes violet coloured when heated in potassium vapours as there are excess of K$^+$ ions which attract Cl$^-$ ions and electrons are trapped at the site of anion forming F-centres. These electrons absorb energy from visible light and radiate complimentary violet colour.

(ii) For cubic crystals,

$$d = \frac{Z \times M}{a^3 \times N_A} \quad \text{or,} \quad Z = \frac{d \times a^3 \times N_A}{M}$$

$$\therefore Z = \frac{(2.75 \text{ g cm}^{-3})(654 \times 10^{-10} \text{ cm})^3 \times (6.023 \times 10^{23})}{(39 + 80) \text{ g mol}^{-1}}$$

$= 3.89 = 4$

So, there are four formula units of KBr present per unit cell. Hence, it has face-centred cubic lattice.

(iii) For the *bcc* structure, nearest neighbour distance (*d*) is related to the edge length (*a*) as

$$d = \frac{\sqrt{3}}{2}a$$

or, $a = \dfrac{2}{\sqrt{3}}d = \dfrac{2}{1.732} \times 365.9 = 422.5$ pm

For *bcc* structure, $Z = 2$
For sodium, $M = 23$

Density, $\rho = \dfrac{Z \times M}{a^3 \times N_A}$

$$\rho = \frac{2 \times 23 \text{ g mol}^{-1}}{(422.5 \times 10^{-10} \text{ cm})^3 \times (6.02 \times 10^{23} \text{ mol}^{-1})}$$
$$= 1.013 \text{ g/cm}^3$$

OR

(i) As the solid has same value of refractive index along all directions, it is isotropic in nature. It is because there is no long range order and the arrangement is irregular along all the directions and hence, amorphous. Being an amorphous solid, it would not show a clean cleavage when cut with a knife. Instead, it would break into pieces with irregular surfaces.

(ii) (a) In solid state of sodium chloride (NaCl), cations (Na$^+$) and anions (Cl$^-$) are held together by strong electrostatic (coulombic) forces hence, it does not carry electrical charges.

But in the presence of water, sodium chloride gets hydrolysed and splits in cations (Na$^+$) and anions (Cl$^-$) which are free to move and carry electrical charges through the aqueous medium.

$$\text{NaCl}_{(s)} \xrightarrow{H_2O} \text{Na}^+_{(aq)} + \text{Cl}^-_{(aq)}$$
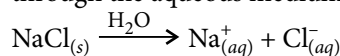
Hence, sodium chloride which is insulator in solid state, carries charges in aqueous solution and becomes a good conductor.

(b) The electronic configuration of Na$^+$ is $1s^2 2s^2 2p^6$ and that of Cl$^-$ is $1s^2 2s^2 2p^6 3s^2 3p^6$. As no unpaired electron is present in both the ions hence, both will exhibit diamagnetic properties.

(c) Schottky defect and metal excess defect are generally observed in sodium chloride.

25. **(i)** Camphor has very high molal depression constant ($K_f = 39.70$ K kg mol^{-1}) therefore, depression in freezing point will be large even when small quantity of a solute is added. This would be easily measurable even by an ordinary thermometer.

(ii) Aquatic species need dissolved oxygen for breathing. As the solubility of gas, *e.g.,* O$_2$ decreases with rise in temperature, less oxygen is available in warm water. Hence, they feel more comfortable in cold water when rather more dissolved oxygen is available.

(iii) Given, $p_A^\circ = 450$ mm, $p_B^\circ = 700$ mm,
$P_{\text{total}} = 600$ mm

According to Raoult's law, $p_A = x_A \times p_A^\circ$

$p_B = x_B \times p_B^\circ = (1 - x_A) p_B^\circ$

$P_{\text{total}} = p_A + p_B = x_A p_A^\circ + (1 - x_A) p_B^\circ$
$= p_B^\circ + (p_A^\circ - p_B^\circ) x_A$

On substituting the values, we get

$600 = 700 + (450 - 700) x_A$

or $250 x_A = 100$

or $x_A = \dfrac{100}{250} = 0.40$

Thus, composition of the liquid mixture will be

mole fraction of $A(x_A) = 0.40$,
mole fraction of $B(x_B) = 1 - 0.40 = 0.60$

$\therefore$ $p_A = x_A \times p_A^\circ = 0.40 \times 450$ mm $= 180$ mm
$p_B = x_B \times p_B^\circ = 0.60 \times 700$ mm $= 420$ mm

Thus, mole fraction of A in vapour phase

$$= \frac{p_A}{p_A + p_B} = \frac{180}{180 + 420} = 0.30$$

Mole fraction of B in vapour phase $= 1 - 0.30$
$= 0.70$

OR

(i) This phenomenon is called endosmosis, *i.e.,* movement of water inside the raisin which can be shown with the help of diagram as :
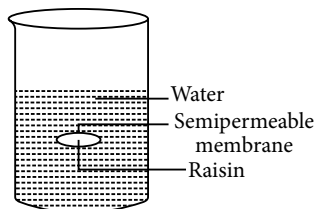
The process of osmosis is of immense biological as well as industrial importance. It is evident from the following examples :

(a) Movement of water from soil into plant roots and subsequently into upper portion of the plant is partly due to osmosis.

(b) Preservation of meat against bacterial action by addition of salt.

(c) Preservation of fruits against bacterial action by adding sugar. Bacteria in canned fruits lose water through the process of osmosis and become inactive.

(ii) NaCl is a non-volatile solute hence, it lowers the vapour pressure of water and boiling point of water increases. Methyl alcohol is a volatile solute hence, it increases the vapour pressure and results in decrease in boiling point of water.

26. (i) Alkali metal ions have large size and cannot fit into interstitial sites. Hence, Frenkel defect is not found in alkali metals.

(ii) Radius of cation that just fits in the tetrahedral hole,

$r = 0.225\,R$

or, $r = 0.225 \times 195 = 43.875$ pm

For octahedral void, $\dfrac{r}{R} = 0.414$ to 0.732

Radius ratio of given ions, $\dfrac{r_+}{r_-} = \dfrac{82}{195} = 0.4205$

As the ratio lies in the range of radius of octahedral void hence, cation A^+ can be slipped into the octahedral void of A^+B^- crystal.

(iii) (a) Metal excess defects due to anionic vacancies result in the formation of F-centres. These F-centres produce colour in alkali metal halides.

(b) When the electricity is produced by applying mechanical stress on some polar crystals, it is known as piezoelectric effect. Quartz shows this property.

OR

(i) (a) According to band theory the energy gap between valence band and conduction band (Forbidden band) in insulator is very large whereas in a conductor valence band and conduction band overlap with each other, it has no forbidden band.

(b) Conductors have no forbidden band whereas semiconductors have small forbidden band.
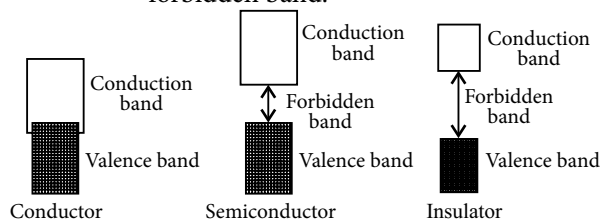
(ii) Copper to oxygen ratio in Cu_2O is less than 2:1. Thus, the solid has Cu^+ ions less than required. This solid has cation vacancies which are produced when some of Cu^+ ions are replaced by Cu^{2+} ions and holes are produced. Thus, this substance is a p-type semiconductor.

SOLVED PAPER **2016**

Kerala PET

1. Choose the wrong statement in the following.
   (a) TiO_2 is used in the pigment industry.
   (b) MnO_2 is used in dry battery cells.
   (c) V_2O_5 catalyses the oxidation of SO_2 in the manufacture of sulphuric acid.
   (d) Ziegler catalyst is used in the manufacture of high density polyethylene.
   (e) The 'silver' UK coins are made of Ag/Ni alloy.

2. In aqueous solution, Cr^{2+} is stronger reducing agent than Fe^{2+}. This is because
   (a) Cr^{2+} ion is more stable than Fe^{2+}
   (b) Cr^{3+} ion with d^3 configuration has favourable crystal field stabilisation energy
   (c) Cr^{3+} has half-filled configuration and hence more stable
   (d) Fe^{3+} in aqueous solution is more stable than Cr^{3+}
   (e) Fe^{2+} ion with d^6 configuration has favourable crystal field stabilisation energy.

3. Choose the correct matching of transition metal ion and magnetic moment from the codes given below :
   (At. No : Ti = 22, V = 23, Fe = 26)

Transition element	Magnetic moment (B.M.)
(A) Titanium (III)	(1) 4.9
(B) Vanadium (II)	(2) 1.73
(C) Iron (II)	(3) 3.87

   (a) (A) - (2), (B) - (3), (C) - (1)
   (b) (A) - (2), (B) - (1), (C) - (3)
   (c) (A) - (1), (B) - (2), (C) - (3)
   (d) (A) - (1), (B) - (3), (C) - (2)
   (e) (A) - (3), (B) - (2), (C) - (1)

4. The standard enthalpy of formation of $H_2O_{(l)}$ and $Fe_2O_{3(s)}$ are respectively –286 kJ mol^{-1} and – 824 kJ mol^{-1}. What is the standard enthalpy change for the following reaction?
   $$Fe_2O_{3(s)} + 3H_{2(g)} \longrightarrow 3H_2O_{(l)} + 2Fe_{(s)}$$

   (a) – 538 kJ mol^{-1}
   (b) + 538 kJ mol^{-1}
   (c) – 102 kJ mol^{-1}
   (d) + 34 kJ mol^{-1}
   (e) – 34 kJ mol^{-1}

5. The correct descending order of the heat liberated (in kJ) during the neutralisation of the acids CH_3COOH (W), HF (X), HCOOH (Y) and HCN (Z) under identical conditions (K_a of $CH_3COOH = 1.8 \times 10^{-5}$, $HCOOH = 1.8 \times 10^{-4}$, $HCN = 4.9 \times 10^{-10}$ and $HF = 3.2 \times 10^{-4}$) is
   (a) $Y > X > Z > W$
   (b) $X > Y > W > Z$
   (c) $W > X > Y > Z$
   (d) $Z > W > Y > X$
   (e) $Z > Y > X > W$

6. How many times a 0.1 M strong monobasic acid solution should be diluted so that pH of the resulting solution is tripled?
   (a) 50 (b) 10 (c) 25 (d) 100 (e) 1000

7. The equilibrium pressure for the reaction $MSO_4 . 2H_2O_{(s)} \rightleftharpoons MSO_{4(s)} + 2H_2O_{(g)}$ is $\pi/4$ atm at 400 K. The K_p for the given reaction (in atm^2) is
   (a) $\pi^2/4$
   (b) $\pi/6$
   (c) $\pi^2/16$
   (d) $\pi/16$
   (e) $16/\pi$

8. Calculate the molality of a solution that contains 51.2 g of naphthalene, ($C_{10}H_8$), in 500 mL of carbon tetrachloride. The density of CCl_4 is 1.60 g/mL.
   (a) 0.250 m
   (b) 0.500 m
   (c) 0.750 m
   (d) 0.840 m
   (e) 1.69 m

9. 31 g of ethylene glycol ($C_2H_6O_2$) is mixed with 500 g of solvent (K_f of the solvent is 2 K kg mol^{-1}). What is the freezing point of the solution in K? (freezing point of solvent = 273 K)
   (a) 272
   (b) 271
   (c) 270
   (d) 274
   (e) 275

10. The standard reduction potential for Zn^{2+}/Zn, Ni^{2+}/Ni and Fe^{2+}/Fe are –0.76, –0.23 and –0.44 V respectively. The reaction
$X + Y^{2+} \longrightarrow X^{2+} + Y$ will have more negative ΔG value when X and Y are
(a) $X = Ni; Y = Fe$ (b) $X = Ni; Y = Zn$
(c) $X = Fe; Y = Zn$ (d) $X = Zn; Y = Ni$
(e) $X = Fe; Y = Ni$

11. Thermal decomposition of ammonium dichromate gives
(a) N_2, H_2O and Cr_2O_3 (b) N_2, NH_3 and CrO
(c) $(NH_4)_2CrO_4$ and H_2O (d) N_2, H_2O and CrO_3
(e) N_2, H_2O and CrO

12. An element crystallising in body centred cubic lattice has an edge length of 500 pm. If its density is 4 g cm^{-3}, the atomic mass of the element (in g mol^{-1}) is (consider $N_A = 6 \times 10^{23}$)
(a) 100   (b) 250
(c) 125   (d) 150
(e) 50

13. The rate constant of the reaction,
$2N_2O_5 \longrightarrow 4NO_2 + O_2$ at 300 K is 3×10^{-5} s^{-1}. If the rate of the reaction at the same temperature is 2.4×10^{-5} mol dm^{-3} s^{-1}, then the molar concentration of N_2O_5 is
(a) 0.4 M   (b) 0.8 M
(c) 0.04 M   (d) 0.08 M
(e) 0.6 M

14. In the reaction $A \rightarrow$ Products, when the concentration of A was reduced from 2.4×10^{-2} M to 1.2×10^{-2} M the rate decreased 8 times at the same temperature. The order of the reaction is
(a) 0   (b) 1
(c) 2   (d) 3
(e) 0.5

15. Enzymatic reactions are given in Column I and enzymes in Column II

Column I		Column II
(A) Maltose → Glucose	(i)	Zymase
(B) Sucrose → Glucose + Fructose	(ii)	Pepsin
(C) Glucose → Ethyl alcohol + CO_2	(iii)	Maltase
(D) Starch → Maltose	(iv)	Invertase
(E) Proteins → Amino acids	(v)	Diastase

Choose the correct matching of enzymatic reaction and enzyme that catalyses the correct reaction from the codes given below :
(a) (A) - (ii), (B) - (iv), (C) - (v), (D) - (iii), (E) - (i)
(b) (A) - (iii), (B) - (iv), (C) - (i), (D) - (v), (E) - (ii)
(c) (A) - (v), (B) - (iv), (C) - (ii), (D) - (i), (E) - (iii)
(d) (A) - (v), (B) - (iii), (C) - (iv), (D) - (ii), (E) - (i)
(e) (A) - (ii), (B) - (iii), (C) - (i), (D) - (v), (E) - (iv)

16. In which one of the following properties, physisorption and chemisorption resemble each other?
(a) Force of attraction
(b) Enthalpy of adsorption
(c) Temperature effect
(d) Effect of surface area
(e) Number of adsorption layers

17. Consider the following two complex ions : $[CoF_6]^{3-}$ and $[Co(C_2O_4)_3]^{3-}$. Which of the following statement(s) is/are false?
I. Both are octahedral.
II. $[Co(C_2O_4)_3]^{3-}$ is diamagnetic while $[CoF_6]^{3-}$ is paramagnetic.
III. Both are outer orbital complexes.
IV. In both the complexes the central metal is in the same oxidation state.
(a) II and III   (b) II, III and IV
(c) III only   (d) III and IV
(e) I, II and IV

18. Chlorophyll is a coordination compound of
(a) iron   (b) magnesium
(c) manganese   (d) chromium
(e) zinc.

19. Which one of the following is a benzenoid aromatic compound?
(a) Furan   (b) Thiophene
(c) Pyridine   (d) Aniline
(e) Cyclopentadienyl anion

20. The major product obtained by the addition reaction of HBr to 4-methylpent-1-ene in the presence of peroxide is
(a) 1-bromo-4-methylpentane
(b) 4-bromo-2-methylpentane
(c) 2-bromo-4-methylpentane
(d) 3-bromo-2-methylpentane
(e) 2-bromo-2-methylpentane.

21. Which one of the following involves nucleophilic addition?
    (a) Kolbe's reaction of phenol
    (b) Williamson's synthesis of ethers
    (c) Reimer-Tiemann's reaction of phenol
    (d) Kolbe's electrolytic synthesis of ethane from sodium acetate
    (e) Aldol formation from ethanal

22. The number of possible stereoisomers of the compound $CH_3—CH=CH—CH_3$ is
    (a) 2   (b) 4   (c) 3   (d) 5   (e) 6

23. Some organic compounds are given in List I and their uses in List II. Choose the correct matching.

List I		List II
(A) Triiodomethane	(i)	solvent for alkaloids
(B) p, p'-Dichlorodiph-enyltrichloroethane	(ii)	propellant in aerosols
(C) Trichloromethane	(iii)	antiseptic
(D) Dichloromethane	(iv)	insecticide

    (a) (A) - (ii), (B) - (iv), (C) - (i), (D) - (iii)
    (b) (A) - (iii), (B) - (iv), (C) - (i), (D) - (ii)
    (c) (A) - (ii), (B) - (i), (C) - (iv), (D) - (iii)
    (d) (A) - (iii), (B) - (i), (C) - (iv), (D) - (ii)
    (e) (A) - (i), (B) - (iii), (C) - (ii), (D) - (iv)

24. The total number of monohalogenated products formed by halogenation of 2,4,4-trimethylhexane is
    (a) 5   (b) 7
    (c) 6   (d) 8
    (e) 0

25. Number of acyclic structural isomers of the compound having the molecular formula $C_4H_{10}O$ is
    (a) 4   (b) 5
    (c) 6   (d) 7
    (e) 3

26. 375 mg of an alcohol reacts with required amount of methyl magnesium bromide and releases 140 mL of methane gas at STP. The alcohol is
    (a) ethanol   (b) n-butanol
    (c) methanol   (d) n-propanol
    (e) phenol.

27. Predict the product (B) in the following sequence of reactions :
    Ethylbenzene $\xrightarrow{KMnO_4 – KOH}$ A $\xrightarrow{H_3O^+}$ B

    (a) Benzaldehyde   (b) Benzophenone
    (c) Benzene   (d) Acetophenone
    (e) Benzoic acid

28. Freon 12 is manufactured from CCl_4 by
    (a) Wurtz reaction   (b) Swarts reaction
    (c) Fittig reaction   (d) Wurtz-Fittig reaction
    (e) Sandmeyer reaction.

29. Which one of the following can be prepared by Gabriel phthalimide synthesis?
    (a) Aniline   (b) o-Toluidine
    (c) Benzylamine   (d) N-Methylethanamine
    (e) 4-Bromoaniline

30. 4-Nitrotoluene is treated with bromine to get compound 'P'. 'P' is reduced with Sn and HCl to get compound 'Q'. 'Q' is diazotised and the product is treated with phosphinic acid to get compound 'R'. 'R' is oxidized with alkaline $KMnO_4$ to get compound 'S'. Compound 'S' is
    (a) 2-bromo-4-hydroxybenzoic acid
    (b) benzoic acid
    (c) 4-bromobenzoic acid
    (d) 3-bromobenzoic acid
    (e) 2-bromobenzoic acid.

31. Narcotic analgesic is
    (a) aspirin   (b) paracetamol
    (c) codeine   (d) zantac
    (e) cimetidine.

32. In double strand helix structure of DNA, heterocyclic base cytosine forms hydrogen bond with
    (a) adenine   (b) guanine
    (c) purine   (d) thyamine
    (e) uracil.

33. The amino acid containing mercaptan unit is
    (a) leucine   (b) glutamine
    (c) cysteine   (d) lysine
    (e) isoleucine.

34. Which one of the following is a non-reducing sugar?
    (a) Maltose   (b) Lactose
    (c) Sucrose   (d) Glucose
    (e) Fructose

35. In the hydrogen atomic spectrum, the emission of the least energetic photon takes place during the transition from $n = 6$ energy level to $n = $ .... energy level.
    (a) 1   (b) 3   (c) 5   (d) 4   (e) 2

36. If 27 g of water is formed during complete combustion of pure propene (C_3H_6), the mass of propene burnt is
(a) 42 g (b) 21 g (c) 14 g (d) 56 g (e) 40 g

37. When 2.46 g of a hydrated salt ($MSO_4 \cdot xH_2O$) is completely dehydrated, 1.20 g of anhydrous salt is obtained. If the molecular weight of anhydrous salt is 120 g mol^{-1} what is the value of x?
(a) 2 (b) 4 (c) 5 (d) 6 (e) 7

38. Identify the T-shaped molecule in the following :
(a) BF_3 (b) NH_3 (c) NF_3 (d) ClF_3 (e) PCl_3

39. Which one of the following molecules has the least dipole moment?
(a) H_2O (b) BeF_2
(c) NH_3 (d) NF_3
(e) BF_3

40. Dipole-dipole interaction energy between polar molecules in solids depends on the radius of the molecule (r) and it is directly proportional to
(a) $(1/r^2)$ (b) $(1/r^6)$
(c) $(1/r)$ (d) $(1/r^5)$
(e) $(1/r^3)$

41. Critical density of a gas having molecular weight 39 g mol^{-1} is 0.1 g cm^{-3}. Its critical volume in L mol^{-1} is
(a) 0.390 (b) 3.90
(c) 0.039 (d) 39.0
(e) 390

42. The various types of hydrides and examples of each type are given below :

Hydride type	Compound
(A) Electron deficient	(i) LiH
(B) Saline	(ii) CH_4
(C) Electron-precise	(iii) NH_3
(D) Interstitial	(iv) B_2H_6
(E) Electron rich	(v) CrH

Choose the correct matching from the codes given below :
(a) (A) - (ii), (B) - (iv), (C) - (v), (D) - (iii), (E) - (i)
(b) (A) - (iv), (B) - (i), (C) - (ii), (D) - (v), (E) - (iii)
(c) (A) - (iv), (B) - (iii), (C) - (v), (D) - (ii), (E) - (i)
(d) (A) - (v), (B) - (iii), (C) - (iv), (D) - (ii), (E) - (i)
(e) (A) - (iv), (B) - (v), (C) - (i), (D) - (ii), (E) - (iii)

43. One mole of hydrazine (N_2H_4) loses 10 moles of electrons in a reaction to form a new compound X. Assuming that all the nitrogen atoms in hydrazine appear in the new compound, what is the oxidation state of nitrogen in X?
(Note : There is no change in the oxidation state of hydrogen in the reaction.)
(a) –1 (b) –3 (c) +3 (d) +5 (e) +1

44. The low solubility of LiF and that of CsI in water are respectively due to which of the properties of the alkali metal ions?
(a) Higher hydration enthalpy of Li^+, higher lattice enthalpy of Cs^+.
(b) Smaller hydration enthalpy of Li^+, higher lattice enthalpy of Cs^+.
(c) Smaller lattice enthalpy of Li^+, higher hydration enthalpy of Cs^+.
(d) Smaller hydration enthalpy of Li^+, smaller lattice enthalpy of Cs^+.
(e) Higher lattice enthalpy of Li^+, smaller hydration enthalpy of Cs^+.

45. The second ionization enthalpy of which of the following alkaline earth metals is the highest?
(a) Ba (b) Mg (c) Ca (d) Sr (e) Be

46. Which one of the following group 16 elements does not exist in –2 oxidation state?
(a) S (b) Se (c) O (d) Po (e) Te

47. In which one of the following compounds of xenon, highest number of lone pair of electrons is present on xenon?
(a) XeF_6 (b) XeF_4
(c) $XeOF_4$ (d) XeO_3
(e) XeF_2

48. The hybridized state of Al^{3+} in the complex ion formed when $AlCl_3$ is treated with aqueous acid is
(a) sp^3 (b) dsp^2 (c) sp^3d^2 (d) sp^2d (e) sp^2

SOLUTIONS

1. (e) : The silver UK coins are made of Cu–Ni alloy.

2. (b): Cr^{3+} ion with d^3 (t_{2g}^3) configuration has favourable crystal field stabilisation energy.

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

Ion	Electronic Configuration	Number of unpaired electrons	μ
Ti^{3+}	d^1	1	1.73
V^{2+}	d^3	3	3.87
Fe^{2+}	d^6	4	4.90

4. (e) : $Fe_2O_{3(s)} + 3H_{2(g)} \longrightarrow 3H_2O_{(l)} + 2Fe_{(s)}$

$\Delta_r H° = \Sigma\Delta_f H°_{(Products)} - \Sigma\Delta_f H°_{(Reactants)}$

$\Rightarrow \quad \Delta_r H° = 3(-286) - (-824)$

$[\because \Delta_f H° \text{ for } Fe_{(s)}, H_{2(g)} = 0]$

$= -858 + 824 = -34 \text{ kJ mol}^{-1}$

5. (b) : From the K_a values, strength of acids is in the order :

HF > HCOOH > CH_3COOH > HCN

Stronger the acid, higher is the heat liberated during the neutralisation as lesser energy is used for ionisation.

$\therefore$ The correct order of heat liberated is

X > Y > W > Z

6. (d) : $pH = -\log[H^+]$

pH of 0.1 M strong monobasic acidic solution = 1

pH of the resulting solution = 3

$\therefore \quad [H^+] = 10^{-3} = \dfrac{0.1}{100}$

So, the original solution is diluted 100 times.

7. (c) : The given reaction is :

$MSO_4 \cdot 2H_2O_{(s)} \rightleftharpoons MSO_{4(s)} + 2H_2O_{(g)}$

As the pressure is due to $H_2O_{(g)}$ only hence,

$K_p = (p_{H_2O})^2 = \left(\dfrac{\pi}{4}\right)^2 = \dfrac{\pi^2}{16} \text{ atm}^2$

8. (b) : Volume of CCl_4 = 500 mL

Density of CCl_4 = 1.60 g/mL

$\therefore$ Mass of CCl_4 (w_1) = 500 × 1.60 = 800 g

Mass of Naphthalene (w_2) = 51.2 g

Now, $m = \dfrac{w_2 \times 1000}{M_2 \times w_1 (\text{in g})} = \dfrac{51.2 \times 1000}{128 \times 800} = 0.500 \text{ m}$

9. (b) : $\Delta T_f = K_f \times m$

$= K_f \times \dfrac{w_2 \times 1000}{M_2 \times w_1(\text{in g})} = 2 \times \dfrac{31 \times 1000}{62 \times 500} = 2$

$\therefore$ Freezing point of solution = 273 – 2 = 271 K

10. (d) : $X + Y^{2+} \longrightarrow X^{2+} + Y$

$\Delta G = -nFE_{cell}$

Greater the value of E_{cell}, more negative will be the value of ΔG and greater the difference between standard reduction potentials of X^{2+} and Y^{2+}, greater will be the value of E_{cell}.

Hence, X = Zn and Y = Ni

11. (a) : $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O$

12. (d) : For bcc, Z = 2

$d = \dfrac{Z \times M}{N_A \times a^3}$

$\Rightarrow \quad M = \dfrac{d \times N_A \times a^3}{Z}$

$\therefore \quad M = \dfrac{4 \times 6 \times 10^{23} \times (500 \times 10^{-10})^3}{2}$

$= \dfrac{4 \times 6 \times 10^{23} \times 125 \times 10^{-24}}{2} = 150 \text{ g mol}^{-1}$

13. (b) : Rate constant, $k = 3 \times 10^{-5} \text{ s}^{-1}$

From the unit of k it is clear that the reaction is of first order.

$\Rightarrow$ Rate = $k[N_2O_5]$

$\Rightarrow [N_2O_5] = \dfrac{\text{Rate}}{k} = \dfrac{2.4 \times 10^{-5}}{3 \times 10^{-5}} \text{ mol dm}^{-3}$

$= 0.8 \text{ mol dm}^{-3}$

14. (d) : $\dfrac{r_1}{r_2} = \left[\dfrac{2.4 \times 10^{-2}}{1.2 \times 10^{-2}}\right]^x$

$8 = (2)^x \quad \Rightarrow \quad (2)^3 = (2)^x$

$\therefore \quad x = 3$

Hence, the order of reaction is 3.

15. (b) : Maltose $\xrightarrow{\text{Maltase}}$ Glucose

Sucrose $\xrightarrow{\text{Invertase}}$ Glucose + Fructose

Glucose $\xrightarrow{\text{Zymase}}$ Ethyl alcohol + CO_2

Starch $\xrightarrow{\text{Diastase}}$ Maltose

Proteins $\xrightarrow{\text{Pepsin}}$ Amino acids

16. (d) : Physisorption and chemisorption both increase with increase in surface area.

17. (c) : $[CoF_6]^{3-}$,

Co^{3+} :

$[CoF_6]^{3-}$:

sp^3d^2 hybridisation, $\quad 6e^-$ pairs from $6F^-$ ligands

Hence, due to presence of 4 unpaired electrons $[CoF_6]^{3-}$ is paramagnetic and F^- being a weak field ligand forms an outer orbital complex.

$[Co(C_2O_4)_3]^{3-}$,

Co^{3+} :

$[Co(C_2O_4)_3]^{3-}$:

d^2sp^3 hybridisation

Hence, $[Co(C_2O_4)_3]^{3-}$ is diamagnetic and $C_2O_4^{2-}$ causes pairing of electrons and forms an inner orbital complex.

18. (b)

19. (d):

Furan   Thiophene   Pyridine   Aniline

Cyclopentadienyl anion
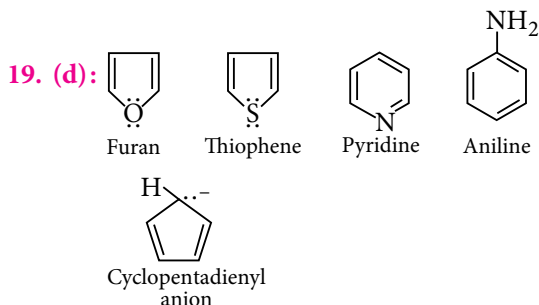
Benzenoid aromatic compounds have a benzene ring intact.

20. (a):

4-Methylpent-1-ene

1-Bromo-4-methylpentane
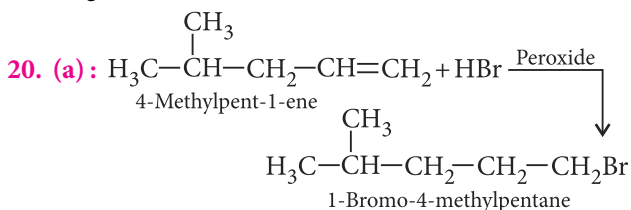
21. (e): Kolbe's reaction of phenol : It is an electrophilic substitution reaction.

Williamson's synthesis of ethers : It occurs by S_N2 mechanism.

Reimer-Tiemann's reaction of phenol : It is an example of electrophilic substitution reaction involving dichlorocarbene as the electrophile.

Kolbe's electrolytic synthesis of ethane from sodium acetate : It involves free radical mechanism.

Aldol formation from ethanal : It is nucleophilic addition reaction.

22. (a): $CH_3-CH=CH-CH_3$ will show geometrical isomerism.

cis–form   *trans*–form
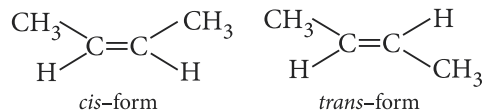
23. (b): Triiodomethane – antiseptic

p, p'-Dichlorodiphenyltrichloroethane – insecticide

Trichloromethane – solvent for alkaloids

Dichloromethane – propellant in aerosols.

24. (c):
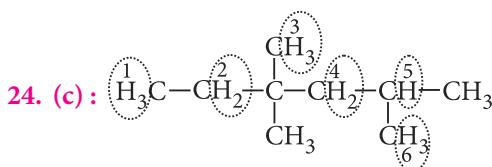
Six structural isomers corresponding to the substitution of 6 types of H atoms are possible.

25. (d): Four alcohols are possible :
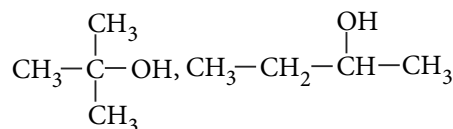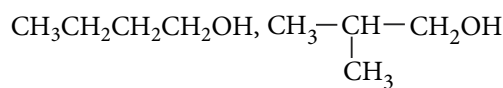
$CH_3CH_2CH_2CH_2OH$,

and three ethers are possible :

$CH_3OCH_2CH_2CH_3$, $CH_3CH_2OCH_2CH_3$,

26. (d): $ROH + CH_3MgBr \longrightarrow CH_4$

1 mol (ROH) ; 1 mol CH_4 = 22400 mL

22400 mL of $CH_4 \equiv$ 1 mol of alcohol
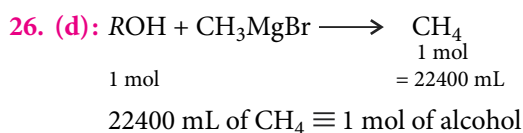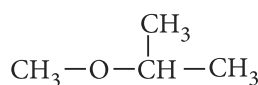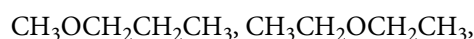
$\therefore$ 140 mL of $CH_4 \equiv \dfrac{1}{22400} \times 140$

$= 6.25 \times 10^{-3}$ mol of alcohol

Now, $n = \dfrac{w}{M}$

$\Rightarrow$ Molecular mass of alcohol $= \dfrac{w}{n} = \dfrac{375 \times 10^{-3}}{6.25 \times 10^{-3}}$

$= 60$ g mol^{-1}

Hence, the alcohol is *n*-propanol ($CH_3CH_2CH_2OH$).

27. (e):

A
Potassium benzoate

B
Benzoic acid
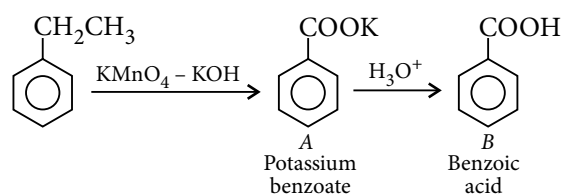
28. (b): Freon 12 is manufactured from CCl_4 by Swarts reaction.

$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} 3CCl_2F_2 + 2SbCl_3$

Freon 12
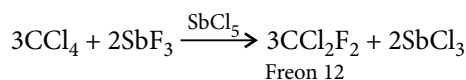
29. (c): Only primary aliphatic amines can be prepared by Gabriel phthalimide synthesis.

Hence, benzylamine can be prepared from Gabriel phthalimide synthesis.

30. (e) :

4-Nitrotoluene → (P) → (Q) → (R) → 2-Bromobenzoic acid
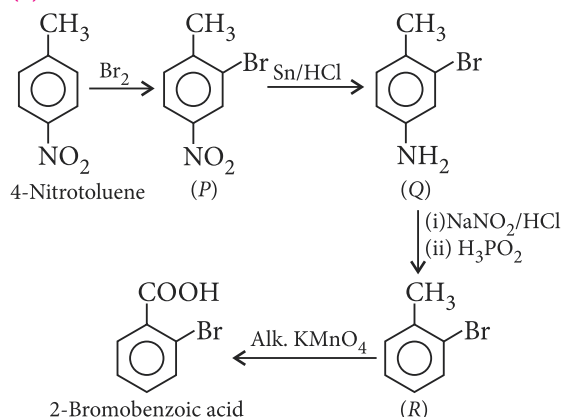
31. (c)

32. (b) : Cytosine forms three hydrogen bonds with guanine.

33. (c) : Side chain in cysteine is —CH_2SH.

34. (c) : Sucrose is a disaccharide in which the two monosaccharide units are linked through their reducing centres.

35. (c) : As we move towards outer shells, the energy increases but the difference between the successive shells decreases *i.e.,*

$E_2 — E_1 > E_3 — E_2 > E_4 — E_3$ ......

Hence, the emission of least energetic photon takes place during the transition from $n = 6$ energy level to $n = 5$ energy level.

36. (b) : $CH_3CH{=}CH_2 + 9/2O_2 \longrightarrow 3CO_2 + 3H_2O$

42 g 3×18

= 54 g
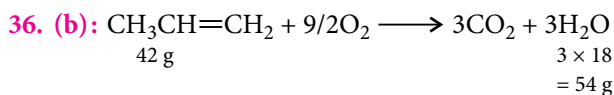
54 g of $H_2O \equiv 42$ g of propene

∴   27 g of $H_2O = \dfrac{42}{54} \times 27 = 21$ g

37. (e) : $MSO_4 . xH_2O \longrightarrow MSO_4 + xH_2O$

2.46 g   1.20 g
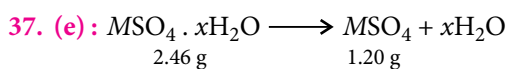
Mass of water = 2.46 – 1.20 = 1.26 g

∴   No. of moles of $H_2O = \dfrac{1.26}{18} = 0.07$

No. of moles of $MSO_4 = \dfrac{1.20}{120} = 0.01$

∴   0.07 moles of water associated with 0.01 mole of salt.

Thus, there are 7 moles of water per mole of anhydrous salt.

38. (d) : BF_3 — sp^2 hybridisation, trigonal planar

NH_3 — sp^3 hybridisation, pyramidal

NF_3 — sp^3 hybridisation, pyramidal

ClF_3 — sp^3d hybridisation, T-shaped

PCl_3 — sp^3 hybridisation, pyramidal

39. (b, e) : BeF_2 has linear shape and BF_3 is symmetrical hence, both have zero dipole moment.

40. (e) : Dipole-dipole interaction energy between stationary polar molecules (as present in the solids) is proportional to $1/r^3$.

41. (a) : Critical density = 0.1 g cm^{-3} = 100 g L^{-1}

Critical volume = $\dfrac{\text{Molecular weight}}{\text{Critical density}}$

$= \dfrac{39}{100} = 0.39$ L mol^{-1}

42. (b) : Electron deficient – B_2H_6

Saline – LiH

Electron precise – CH_4

Interstitial – CrH

Electron rich – NH_3

43. (c) : $N_2H_4 \longrightarrow X$

No. of electrons lost per N-atom = 5

Oxidation state of N in new compound = –2 + 5 = +3

44. (e)

45. (e) : On moving down the group, ionization energy decreases. This is due to the fact that the electrons in lower shells experience higher force of attraction from the nucleus. Thus, it is difficult for them to ionise.

46. (d)

47. (e) : XeF_2 : 3 lone pairs and 2 bond pairs.

48. (c) : $AlCl_3$ forms $[Al(H_2O)_6]^{3+}$ complex when treated with aqueous acid and hybridisation of Al is sp^3d^2 in this complex.

◈ ◈
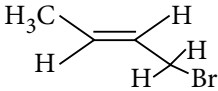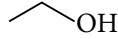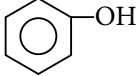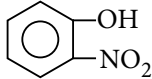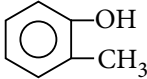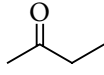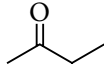
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KARNATAKA CET

1. The half-life period of a I order reaction is 60 minutes. What percentage will be left over after 240 minutes?
   (a) 6.25%   (b) 4.25%
   (c) 5%   (d) 6%

2. Which of the following is not a colligative property?
   (a) Osmotic pressure
   (b) Optical activity
   (c) Depression in freezing point
   (d) Elevation in boiling point

3. The contribution of particle at the edge centre of a particular unit cell is,
   (a) $\dfrac{1}{2}$ (b) $\dfrac{1}{4}$
   (c) 1   (d) $\dfrac{1}{8}$

4. When an electrolyte is dissociated in solution, the van't Hoff factor (i) is
   (a) > 1 (b) < 1 (c) $= 0$ (d) $= 1$

5. Which of the following is incorrect in a galvanic cell?
   (a) Oxidation occurs at anode.
   (b) Reduction occurs at cathode.
   (c) The electrode at which electrons are gained is called cathode.
   (d) The electrode at which electrons are lost is called cathode.

6. A secondary cell is one which
   (a) can be recharged
   (b) can be recharged by passing current through it in the same direction
   (c) can be recharged by passing current through it in the opposite direction
   (d) cannot be recharged.

7. Osmotic pressure of the solution can be increased by
   (a) increasing the temperature of the solution
   (b) decreasing the temperature of the solution
   (c) increasing the volume of the vessel
   (d) diluting the solution.

8. The amount of current in faraday required for the reduction of 1 mol of $Cr_2O_7^{2-}$ ions to Cr^{3+} is
   (a) 1 F   (b) 2 F   (c) 6 F   (d) 4 F

9. For a chemical reaction,
   $mA \rightarrow xB$, the rate law is $r = k[A]^2$.
   If the concentration of A is doubled, the reaction rate will be
   (a) doubled   (b) quadrupled
   (c) increased by 8 times   (d) unchanged.

10. Schottky defect in a crystal 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) no ion is missing from its lattice site.

11. $3A \longrightarrow 2B$, rate of reaction, $+\dfrac{d[B]}{dt}$ is equal to
    (a) $-\dfrac{3}{2}\dfrac{d[A]}{dt}$ (b) $-\dfrac{2}{3}\dfrac{d[A]}{dt}$
    (c) $+2\dfrac{d[A]}{dt}$ (d) $-\dfrac{1}{3}\dfrac{d[A]}{dt}$

12. The activation energy of a chemical reaction can be determined by
    (a) evaluating rate constants at two different temperatures
    (b) changing the concentration of reactants

(c) evaluating the concentration of reactants at two different temperatures

(d) evaluating rate constant at standard temperature.

13. Which of the following statements is incorrect *w.r.t.* physisorption?

(a) The forces involved are van der Waals' forces.

(b) More easily liquifiable gases are adsorbed easily.

(c) Under high pressure it results into multi-molecular layer on adsorbent surface.

(d) $\Delta H_{adsorption}$ is low and +ve.

14. Sulphur sol contains

(a) discrete S-atoms

(b) discrete S-molecules

(c) large aggregates of S-molecules

(d) water dispersed in solid sulphur.

15. Reactions in zeolite catalyst depend on

(a) pores   (b) apertures

(c) size of cavity   (d) all of these.

16. IUPAC name of the compound

is

(a) 1-bromobut-2-ene   (b) 2-bromo-2-butene

(c) bromobutene   (d) 1-bromobut-3-ene.

17. Replacement of Cl of Chlorobenzene to give phenol requires drastic conditions, but Cl of 2,4-dinitrochlorobenzene is readily replaced. This is because

(a) $-NO_2$ group makes the ring electron rich at *ortho* and *para* positions

(b) $-NO_2$ group withdraws electrons from *meta* position

(c) $-NO_2$ donates electrons at *meta* position

(d) $-NO_2$ withdraws electrons from *ortho* and *para* positions.

18. In the reaction :

Ethanol $\xrightarrow{PCl_5} X \xrightarrow{alc.\ KOH} Y \xrightarrow[H_2O,\ \Delta]{H_2SO_4,\ Room\ temp.} Z$,

the product Z is

(a) C_2H_4 (b) $CH_3CH_2OCH_2CH_3$

(c) $CH_3CH_2OSO_3H$ (d)

19. Which of the following compounds is most acidic?

(a) $Cl-CH_2-CH_2-OH$ (b)

(c)   (d)

20. Benzene carbaldehyde is reacted with concentrated NaOH solution to give the products *A* and *B*. The product *A* can be used as food preservative and the product *B* is an aromatic hydroxy compound where OH group is linked to sp^3 hybridised carbon atom next to benzene ring. The products *A* and *B* are respectively,

(a) sodium benzoate and phenol

(b) sodium benzoate and phenyl methanol

(c) sodium benzoate and cresol

(d) sodium benzoate and picric acid.

21. The reaction which involves dichlorocarbene as an electrophile is

(a) Reimer-Tiemann reaction

(b) Kolbe's reaction

(c) Friedel-Crafts' acylation

(d) Fittig's reaction.

22. Ethanol is converted into ethoxyethane

(a) by heating excess of ethanol with conc. H_2SO_4 at 140°C

(b) by heating ethanol with excess of conc. H_2SO_4 at 443 K

(c) by treating with conc. H_2SO_4 at room temperature

(d) by treating with conc. H_2SO_4 at 273 K.

23. An organic compound *X* is oxidised by using acidified $K_2Cr_2O_7$ solution. The product obtained reacts with phenyl hydrazine but does not answer silver mirror test. The compound *X* is

(a) 2-propanol   (b) ethanal

(c) ethanol   (d) $CH_3CH_2CH_3$

24. Predict the product '*C*' in the following series of reactions :

$CH_3-COOH \xrightarrow{PCl_5} A \xrightarrow[Anhyd.\ AlCl_3]{C_6H_6} B \xrightarrow{CH_3MgBr} C$

(a)   (b) $CH_3CH(OH)C_6H_5$

(c) $CH_3CH(OH)C_2H_5$ (d) $(CH_3)_2C(OH)C_6H_5$

25. The number of oxygen atoms in 4.4 g of CO_2 is

(a) 1.2×10^{23} (b) 6×10^{22}

(c) 6×10^{23} (d) 12×10^{23}

26. If the bond energies of H—H, Br—Br and H—Br are 433, 192 and 364 kJ mol^{-1} respectively, then $\Delta H°$ for the reaction :
$H_{2(g)} + Br_{2(g)} \longrightarrow 2HBr_{(g)}$ is
(a) – 261 kJ   (b) + 103 kJ
(c) + 261 kJ   (d) – 103 kJ

27. In the reaction; $Fe(OH)_{3(s)} \rightleftharpoons Fe^{3+}_{(aq)} + 3OH^-_{(aq)}$, if the concentration of OH^- ions is decreased by $\frac{1}{4}$ times, then the equilibrium concentration of Fe^{3+} will increase by
(a) 8 times   (b) 16 times
(c) 64 times   (d) 4 times.

28. The correct statement regarding entropy is
(a) at absolute zero temperature, entropy of a perfectly crystalline solid is zero
(b) at absolute zero temperature, the entropy of a perfectly crystalline substance is +ve
(c) at absolute zero temperature, the entropy of all crystalline substances is zero
(d) at 0°C, the entropy of a perfect crystalline solid is zero.

29. Equilibrium constants K_1 and K_2 for the following equilibria
(1) $NO_{(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}$
(2) $2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}$
are related as :
(a) $K_1 = \sqrt{K_2}$ (b) $K_2 = \dfrac{1}{K_1}$
(c) $K_1 = 2K_2$ (d) $K_2 = \dfrac{1}{K_1^2}$

30. van-Arkel method of refining zirconium involves
(a) removing all oxygen and nitrogen impurities
(b) removing CO impurity
(c) removing hydrogen impurity
(d) removing silica impurity.

31. The composition of 'copper matte' is
(a) $Cu_2S + FeS$ (b) $Cu_2S + Cu_2O$
(c) $Cu_2S + FeO$ (d) $Cu_2O + FeS$

32. The complex formed when Al_2O_3 is leached from bauxite using concentrated NaOH solution is
(a) $Na[Al(OH)_4]$ (b) $NaAl_2O_4$
(c) $Na_2[Al(OH)_3]$ (d) Na_2AlO_2

33. The property which is not true about fluorine is
(a) most of its reactions are exothermic
(b) it forms only one oxo acid
(c) highest electronegativity
(d) high F-F bond dissociation enthalpy.

34. Which is true regarding nitrogen?
(a) Less electronegative
(b) Has low ionisation enthalpy
(c) d-orbitals are available
(d) Ability to form $p\pi$-$p\pi$ bonds with itself

35. The shape of XeF_6 is
(a) square planar   (b) distorted octahedral
(c) square pyramidal   (d) pyramidal.

36. The number of isomers possible for the octahedral complex $[CoCl_2(en)(NH_3)_2]^+$ is
(a) two   (b) three
(c) no isomer   (d) four isomers.

37. CO is a stronger ligand than Cl^-, because
(a) CO is a neutral molecule.
(b) CO has π-bonds.
(c) CO is poisonous.
(d) CO is more reactive.

38. The bivalent metal ion having maximum paramagnetic behaviour among the first transition series elements is
(a) Mn^{2+} (b) Cu^{2+}
(c) Sc^{2+} (d) Cu^+

39. When a brown compound of Mn (A) is treated with HCl, it gives a gas (B). The gas (B) taken in excess reacts with NH_3 to give an explosive compound (C).
The compounds A, B and C are
(a) $A = MnO_2$, $B = Cl_2$, $C = NCl_3$
(b) $A = MnO$, $B = Cl_2$, $C = NH_3Cl$
(c) $A = Mn_3O_4$, $B = Cl_2$, $C = NCl_3$
(d) $A = MnO_3$, $B = Cl_2$, $C = NCl_2$

40. Mn^{2+} compounds are more stable than Fe^{2+} compounds towards oxidation to their +3 state, because
(a) Mn^{2+} is more stable with high 3rd ionisation energy
(b) Mn^{2+} is bigger in size
(c) Mn^{2+} has completely filled d-orbitals
(d) Mn^{2+} does not exist.

41. Which of the following sequence is correct regarding field strength of ligands as per spectrochemical series?
(a) $SCN^- < F^- < CN^- < CO$
(b) $F^- < SCN^- < CN^- < CO$
(c) $CN^- < F^- < CO < SCN^-$
(d) $SCN^- < CO < F^- < CN^-$

42. As per IUPAC norms, the name of the complex $[Co(en)_2(ONO)Cl]Cl$ is
(a) Chlorido*bis*(ethane-1,2-diamine)nitro-O-cobalt (III) chloride.
(b) Chloro*bis*(ethylenediamine)nitro-O-cobalt (III) chloride.
(c) Chloridodi(ethylene diamine)nitrocobalt (III) chloride.
(d) Chloroethylenediaminenitro-O-cobalt (III) chloride.

43. In the following sequence of reactions;

$$A \xrightarrow{\text{Reduction}} B \xrightarrow{\text{HNO}_2} CH_3CH_2OH$$

The compound A is
(a) propane nitrile   (b) ethane nitrile
(c) nitromethane   (d) methyl isocyanate.

44. An organic compound A on reduction gives compound B, which on reaction with trichloro methane and caustic potash forms C. The compound 'C' on catalytic reduction gives N-methyl benzenamine, the compound 'A' is
(a) nitrobenzene   (b) nitromethane
(c) methanamine   (d) benzenamine.

45. Which of the following gives positive Fehling's solution test?
(a) Sucrose   (b) Glucose
(c) Fats   (d) Protein

46. A liquid can exist only
(a) between triple point and critical point
(b) at any temperature above melting point
(c) between melting point and critical point
(d) between boiling and melting points.

47. The energy of electron in the nth Bohr orbit of H-atom is
(a) $\dfrac{-13.6}{n^2}\,eV$ (b) $\dfrac{-13.6}{n}\,eV$
(c) $\dfrac{-13.6}{n^4}\,eV$ (d) $\dfrac{-13.6}{n^3}\,eV$

48. Consider the following sets of quantum numbers : Which of the below setting is not permissible arrangement of electrons in an atom?

n	l	m	s
(a) 4	0	0	$-\dfrac{1}{2}$
(b) 5	3	0	$+\dfrac{1}{2}$
(c) 3	2	-2	$-\dfrac{1}{2}$
(d) 3	2	-3	$+\dfrac{1}{2}$

49. The increasing order of bond orders of O_2, O_2^+, O_2^- and O_2^{--} is
(a) $O_2^+, O_2, O_2^-, O_2^{--}$ (b) $O_2^{--}, O_2^-, O_2^+, O_2$
(c) $O_2, O_2^+, O_2^-, O_2^{--}$ (d) $O_2^{2-}, O_2^-, O_2, O_2^+$

50. HCl gas is covalent and NaCl is an ionic compound. This is because
(a) sodium is highly electropositive
(b) hydrogen is a non-metal
(c) HCl is a gas
(d) electronegativity difference between H and Cl is less than 2.1.

51. Which of the following is not true?
(a) In vulcanisation the rubber becomes harder and stronger.
(b) Natural rubber has '*trans*' configuration at every double bond.
(c) Buna-S is a co-polymer of butene and styrene.
(d) Natural rubber is 1,4-polymer of isoprene.

52. Which of the following is a polyamide?
(a) Nylon-6, 6   (b) Terylene
(c) Polythene   (d) Buna-S

53. Which of the following is correct about H-bonding in DNA?
(a) A — T, G — C   (b) A — G, T — G
(c) G — T, A — C   (d) A — A, T — T

54. Which of the following is employed as tranquilizer?
(a) Equanil   (b) Naproxen
(c) Tetracyclin   (d) Dettol

55. Reactivity order of halides for dehydrohalogenation is
(a) $R — F > R — Cl > R — Br > R — I$
(b) $R — I > R — Br > R — Cl > R — F$
(c) $R — I > R — Cl > R — Br > R — F$
(d) $R — F > R — I > R — Br > R — Cl$

56. Main axis of diatomic molecule is z. The orbitals p_x and p_y overlap to form
(a) π-molecular orbital   (b) σ-molecular orbital
(c) δ-molecular orbital   (d) no bond is formed.

57. The hybridisation of C in diamond, graphite and ethyne is in the order
(a) sp^3, sp, sp^2 (b) sp^3, sp^2, sp
(c) sp, sp^2, sp^3 (d) sp^2, sp^3, sp

58. A miscible mixture of C_6H_6 + $CHCl_3$ can be separated by
(a) sublimation   (b) distillation
(c) filtration   (d) crystallisation.

59. An organic compound contains C = 40%, H = 13.33% and N = 46.67%. Its emperical formula is
(a) C_2H_2N (b) C_3H_7N
(c) CH_4N (d) CHN

60. Electrophile that participates in nitration of benzene is
(a) NO^+ (b) NO_2^+ (c) NO   (d) NO_3^-

<div align="center">

SOLUTIONS

</div>

1. **(a) :** $t_{1/2} = \dfrac{0.693}{k} \Rightarrow \dfrac{0.693}{t_{1/2}} = k \Rightarrow \dfrac{0.693}{60} = k$

$k = 0.01155\ \text{min}^{-1}$

$k = \dfrac{2.303}{t} \log\left(\dfrac{a}{a-x}\right)$

Let the initial amount (a) be 100.

$0.01155\ \text{min}^{-1} = \dfrac{2.303}{240\,\text{min}} \log\left(\dfrac{100}{a-x}\right)$

$\dfrac{0.01155\,\text{min}^{-1} \times 240\,\text{min}}{2.303} = \log\left(\dfrac{100}{a-x}\right)$

$1.204 = \log 100 - \log(a-x)$
$1.204 = 2 - \log(a-x)$
$\log(a-x) = 2 - 1.204$
$\log(a-x) = 0.796$
$(a-x) = 6.25\%$

2. **(b):** Colligative property depends on the concentration of solution and not on the type of particles, while optical activity depends on the type of particles.

3. **(b):** Each particle at edge centre is surrounded by four unit cells thus, its contribution to each unit cell is 1/4.

4. **(a) :** van't Hoff factor (i) depends on the number of particles of solute. On dissociation of an electrolyte, number of particles of solute increases, therefore $i > 1$.

5. **(d):** The electrode at which electrons are lost is called anode.

6. **(c)**

7. **(a) :** $\pi = CRT = \dfrac{n}{V}RT$

$\pi \propto T$

8. **(c) :** $Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$
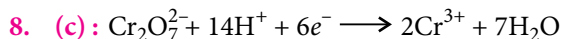
9. **(b):** $r = k[A]^2$
When concentration of A is doubled,
$r = k[2A]^2$
$r = 4k[A]^2$

10. **(b)**

11. **(b):** $-\dfrac{1}{3}\dfrac{d[A]}{dt} = +\dfrac{1}{2}\dfrac{d[B]}{dt}$

$-\dfrac{2}{3}\dfrac{d[A]}{dt} = +\dfrac{d[B]}{dt}$

12. **(a) :** $\log\dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left(\dfrac{T_2 - T_1}{T_1 T_2}\right)$

13. **(d):** $\Delta H_{adsorption}$ is always negative.

14. **(c) :** Sulphur sol consists of particles containing a thousand or more of S_8 sulphur molecules.

15. **(d)**   **16.** **(a)**

17. **(d):** NO_2 withdraws electrons from the carbon bearing chlorine group making the C—Cl bond weak.

18. **(d):** $CH_3CH_2OH \xrightarrow{PCl_5} \underset{X}{CH_3CH_2Cl} \xrightarrow{\text{alc. KOH}}$

$\overset{}{\triangle}\text{OH or } \underset{Z}{CH_3CH_2OH} \xleftarrow[H_2O,\ \Delta]{H_2SO_4,\ \text{room temp.}} \underset{Y}{CH_2\!\!=\!\!CH_2}$
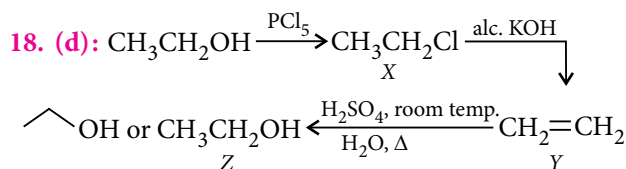
19. **(c) :** Due to electron withdrawing nature of $-NO_2$ group, o-nitrophenol is most acidic among all the given compounds.

20. **(b):**
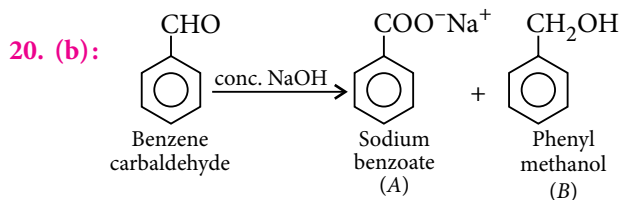
This is Cannizzaro reaction where one molecule gets reduced to alcohol and other gets oxidised to sodium salt of carboxylic acid. Sodium benzoate is used as a food preservative.

21. (a):

2-Hydroxy benzaldehyde
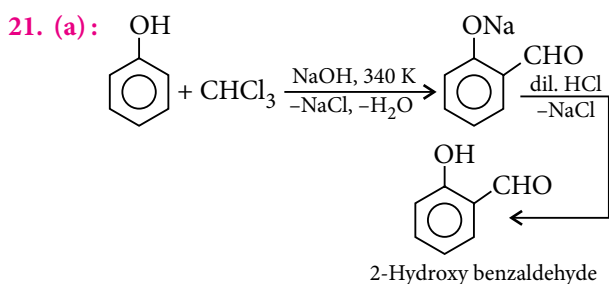
Mechanism :
(i) Generation of electrophile

$$HO^- + CHCl_3 \rightleftharpoons H_2O + CCl_3^- \longrightarrow :CCl_2 + Cl^-$$

Dichloro carbene (E^+)

(ii) Electrophilic substitution

22. (a):

$$CH_3CH_2OH \xrightarrow[140°C]{conc.\ H_2SO_4}$$

Ethanol (excess)

$$CH_3CH_2-O-CH_2CH_3 + H_2O$$

Ethoxyethane

23. (a):
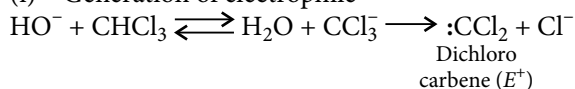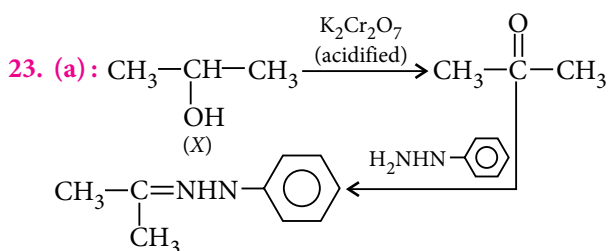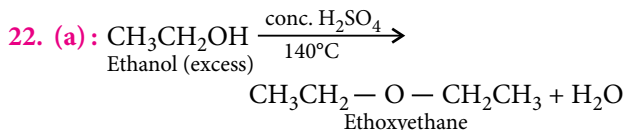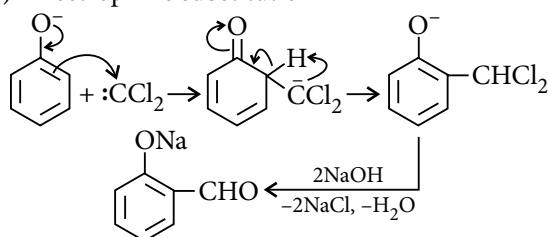
Ketones do not reduce Tollens' solution therefore, *X* is 2-propanol.

24. (d): $CH_3COOH \xrightarrow{PCl_5} CH_3COCl \xrightarrow[Anhyd.\ AlCl_3]{Benzene}$
(A)

25. (a): 44 g of CO_2 contain = 6.023×10^{23} molecules of CO_2
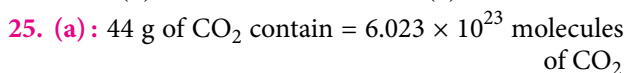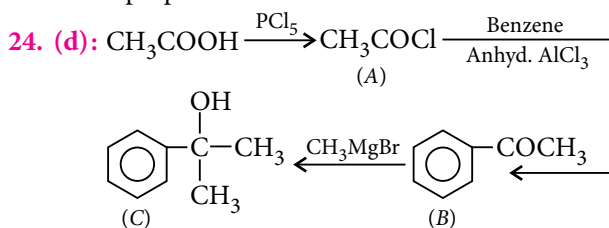
4.4 g of CO_2 will contain = $\dfrac{6.023 \times 10^{23}}{44} \times 4.4$

$= 6.023 \times 10^{22}$ molecules of CO_2

1 molecule of CO_2 contains two oxygen atoms.
6.023×10^{22} molecules of CO_2 will contain
$2 \times 6.023 \times 10^{22} = 1.2 \times 10^{23}$ oxygen atoms

26. (d): $\Delta_r H = \Sigma B.E._{(Reactants)} - \Sigma B.E._{(Products)}$

$= [B.E._{(H_2)} + B.E._{(Br_2)}] - [2B.E._{(HBr)}]$

$= [433 + 192 - 2 \times 364]$ kJ $= -103$ kJ

27. (c): $K_c = [x][3x]^3$ ...(i)

When concentration of OH^- ions is decreased by

$\dfrac{1}{4}$ times, $K_c = [x']\left[\dfrac{3x}{4}\right]^3$ ...(ii)

Equating eq. (i) and (ii)

$x \times (3x)^3 = x'\left(\dfrac{3x}{4}\right)^3$

$64x = x'$

28. (a)

29. (d): $NO_{(g)} + \dfrac{1}{2}O_{2(g)} \rightleftharpoons NO_{2(g)}; K_1$ ...(i)

$2NO_{2(g)} \rightleftharpoons 2NO_{(g)} + O_{2(g)}; K_2$ ...(ii)
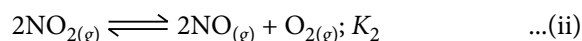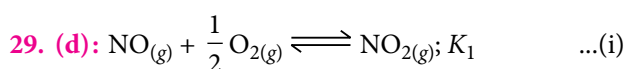
Equation (ii) can be obtained by multiplying equation (i) by 2 and reversing it. Therefore, K_1 and K_2 are related as $K_2 = \dfrac{1}{K_1^2}$.

30. (a)

31. (a): Cu_2S containing little FeS is copper matte.

32. (a): $Al_2O_3 + 2NaOH + 3H_2O \longrightarrow 2Na[Al(OH)_4]$
Sodium metaaluminate
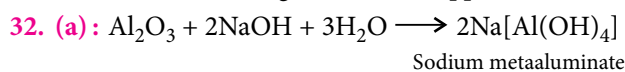
33. (d): Due to small size of fluorine atoms, electrons repel each other and hence, bond dissociation enthalpy of F_2 is low.

34. (d): Because of its small size, nitrogen has a strong tendency to form $p\pi$-$p\pi$ bonds. It has high electronegativity and does not have any *d*-orbital. Also, it has high ionisation enthalpy due to its stable half-filled electronic configuration.

35. (b):

Distorted octahedral

36. (d):

trans w.r.t. Cl

trans w.r.t. NH_3

cis w.r.t. Cl and NH_3 both
(optically active)
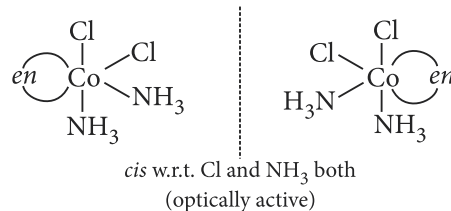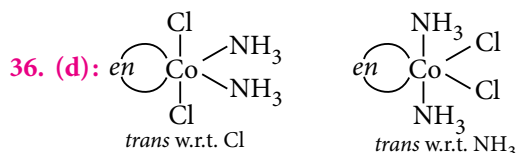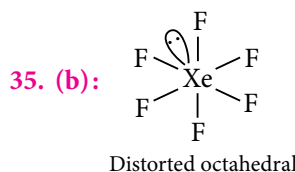
37. (b): CO is a π-donor ligand which acts as a stronger ligand.

38. (a): Mn^{2+} $(3d^5 4s^0) \longrightarrow$ 5 unpaired electrons
Cu^{2+} $(3d^9 4s^0) \longrightarrow$ 1 unpaired electron
Sc^{2+} $(3d^1 4s^0) \longrightarrow$ 1 unpaired electron
Cu^+ $(3d^{10} 4s^0) \longrightarrow$ 0 unpaired electron
Hence, Mn^{2+} has maximum number of unpaired electrons thus, it shows maximum paramagnetic behaviour.

39. (a): $\underset{(A)}{MnO_2} + 4HCl \longrightarrow \underset{(B)}{Cl_2} + MnCl_2 + 2H_2O$
$\underset{(excess)}{3Cl_2} + NH_3 \longrightarrow \underset{(C)}{NCl_3} + 3HCl$

40. (a): Mn^{2+} has stable half-filled electronic configuration thus, it has high third ionisation energy while Fe^{2+} on losing one more electron will acquire this stable electronic configuration. Thus, Fe^{2+} is more prone to get oxidised to +3 oxidation state.

41. (a)   **42. (a)**

43. (b): $\underset{\substack{Ethanenitrile \\ (A)}}{CH_3CN} \xrightarrow{Reduction} \underset{(B)}{CH_3CH_2NH_2} \xrightarrow{HNO_2}$
$H_2O + N_2 + CH_3CH_2OH$

44. (a):
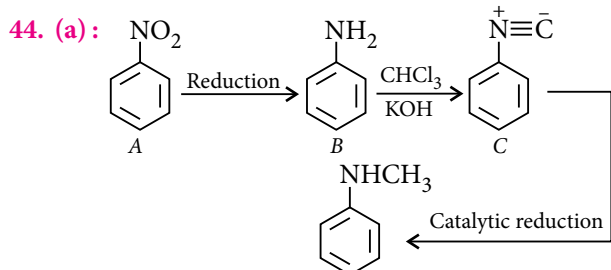
45. (b): Fehling's test is for aldehydes. In sucrose, there is no free aldehyde group but glucose in its open chain structure has free aldehyde group.

46. (d)   **47. (a)**

48. (d): For a given value of 'l' the permissible values of 'm' are $-l, -(l-1)....0....(l-1), l$
Thus, for $l = 2$, m cannot have a value of -3.

49. (d): In O_2^{2-} and O_2^-, the added extra electron enters the antibonding orbital which decreases the bond order. In O_2^+, the electron is removed from antibonding orbital which increases the bond order.

50. (d)

51. (b): Natural rubber has '*cis*' configuration at every double bond.

52. (a): Hexamethylenediamine and adipic acid polymerise to form polyamide linkages in nylon-6, 6.

Nylon-6, 6
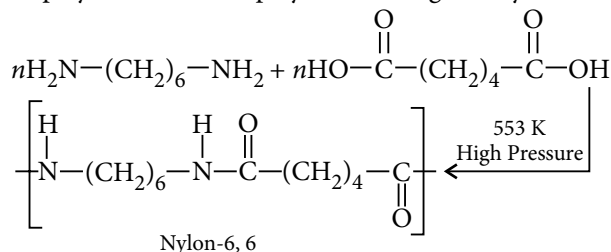
53. (a): In DNA, adenine (*A*) forms two hydrogen bonds with thymine (*T*) and guanine (*G*) forms three hydrogen bonds with cytosine (*C*).

54. (a): Equanil is a tranquilizer used in depression and hypertension.

55. (b): As the size of halide ion increases the $R—X$ bond strength decreases and the halide ion will be a good leaving group. Thus, the reactivity order is $R—I > R—Br > R—Cl > R—F$.

56. (d): The p_x and p_y orbitals do not overlap thus, no bond is formed.

57. (b)

58. (b): Two miscible liquids with different boiling points can be separated by distillation through selective evaporation and condensation.

59. (c):

Element	%	No. of moles	Molar ratio	Simplest ratio
C	40	40/12 = 3.33	$\dfrac{3.33}{3.33} = 1$	1
H	13.33	13.33/1 = 13.33	$\dfrac{13.33}{3.33} = 4$	4
N	46.67	46.67/14 = 3.33	$\dfrac{3.33}{3.33} = 1$	1

Thus, the empirical formula is CH_4N.

60. (b): $HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$
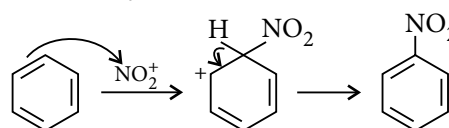
ADVANCED CHEMISTRY BLOC

(GEOMETRICAL ISOMERS)

Mukul C. Ray, Odisha

FOR ALKENES, OXIMES AND AZO COMPOUNDS

The primary requirement for an open chain compound to show geometrical isomerism is that, the double bonded carbon must have two different substituents. This is not required for double bonded nitrogen as nitrogen is trivalent. A few examples are :
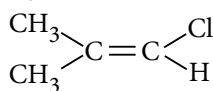
$$\begin{array}{c}CH_3 \\ CH_3\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}Cl \\ H\end{array}$$

(No geometrical isomers)

$$\begin{array}{c}CH_3 \\ CH_3CH_2\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}Cl \\ Br\end{array}$$

(Two geometrical isomers)

$$\begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=N-OH$$

(Two geometrical isomers)

$$Ph-N=N-Ph$$
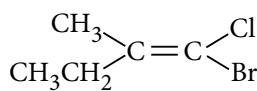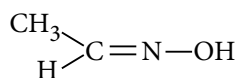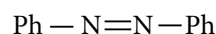
(Two geometrical isomers)

Physical properties

○ If the geometrical isomers do not differ much in polarity, the one that has higher enthalpy has the higher boiling point, higher density and higher refractive index. This is the *Auwers-Skita rule*. For example,

$$\begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}CH_3 \\ H\end{array}$$
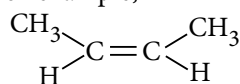
(Higher enthalpy, higher b.pt., higher density and higher refractive index)

$$\begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}H \\ CH_3\end{array}$$
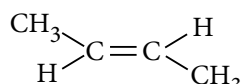
○ If the isomers differ much in polarity, the more polar one has the higher boiling point, higher density and higher refractive index. For example,

$$\begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}H \\ Cl\end{array}$$

$$\begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}Cl \\ H\end{array}$$
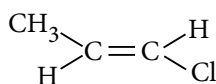
(More polar, higher boiling point, higher density and higher refractive index)
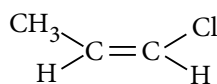
Stability

○ In general *trans*-isomer is more stable than *cis*-isomer. The stability of isomers of butene determined from their heats of combustion is as follows :

$$\begin{array}{c}CH_3 \\ CH_3\end{array}\!\!>\!\!C=CH_2 \;>\; \begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}H \\ CH_3\end{array}$$

$$>\; \begin{array}{c}CH_3 \\ H\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}CH_3 \\ H\end{array}$$
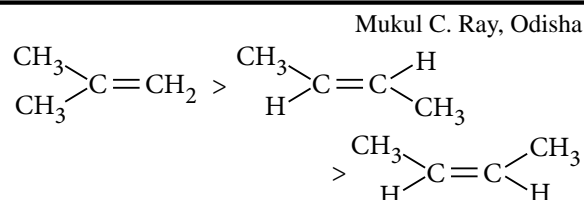
General, stability order is :

$R_2C=CR_2 > R_2C=CHR > RCH=CHR$ (*trans > cis*)
$\approx R_2C=CH_2 > RCH=CH_2 > CH_2=CH_2$
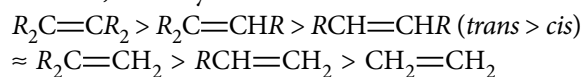
○ For dihalo-ethylenes, the *cis*-form is more stable than *trans* due to forces of attraction coming from the partial charges.

$$\begin{array}{c}\ddot{C}l \\ H\end{array}\!\!>\!\!C=C\!\!<\!\!\begin{array}{c}\overset{\delta-}{Cl} \\ \overset{\delta+}{H}\end{array} \;\longleftrightarrow\; \begin{array}{c}\overset{+}{Cl} \cdots\cdots \overset{\delta-}{\ddot{C}l} \\ \| \qquad\quad \\ H\;C - \bar{C}\; H\end{array}$$
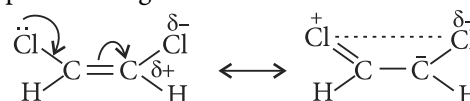
○ Exceptions are only di-iodo and bromo-iodo compounds, where the *trans*-form is more stable than *cis* due to steric factors.

FOR CONJUGATED DIENES

Number of geometrical isomers for a conjugated diene depends on the number of double bonds and whether the end groups are different or identical.

○ When the end groups are different :
e.g., $CH_3-CH=CH-CH=CH-C_2H_5$ has four geometrical isomers.

trans ... *trans* (A)

trans ... *cis* (B)

cis ... *cis* (C)

cis ... *trans* (D)
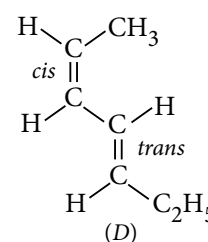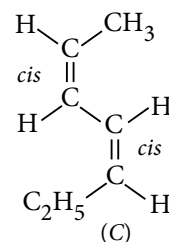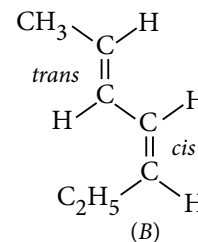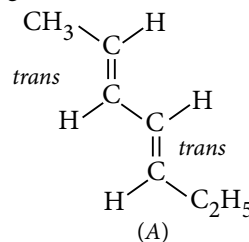
○ When the end groups are identical :

e.g., $CH_3-CH=CH-CH=CH-CH_3$ has three geometrical isomers.

If the pattern similar to the previous example is followed then (*B*) and (*D*) become equal.

○ The number of geometrical isomers can be calculated using mathematical rules :

- When the end groups are different, and *n* is the number of conjugated double bonds :

No. of geometrical isomers = 2^n

- When the end groups are identical and *n* is the number of conjugated double bonds :

No. of geometrical isomers = $2^{n-1} + 2^{p-1}$

$p = \dfrac{n}{2}$ when *n* is even and

$p = \dfrac{(n+1)}{2}$ when *n* is odd.

FOR CUMULATED DIENES

Geometrical isomers are observed when the number of double bonds is odd. For example,

No geometrical isomers

Two geometrical isomers
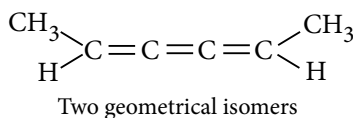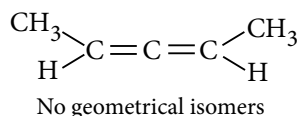
Rings can replace such double bonds as well.

Two geometrical isomers

No geometrical isomers
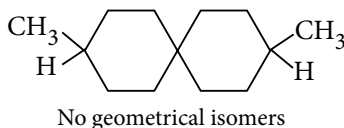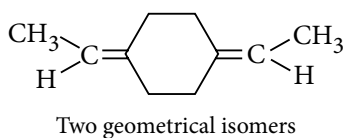
For even number of double bonds, geometrical isomers are not possible as the groups are equidistant in space.
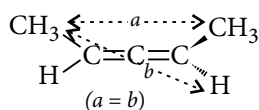
FOR CYCLOALKENES

Cis-isomers are possible for all ring sizes. Both *cis*-form and *trans*-form exist from ring size eight and onwards.

only *cis*   *cis* (more stable)   *trans*
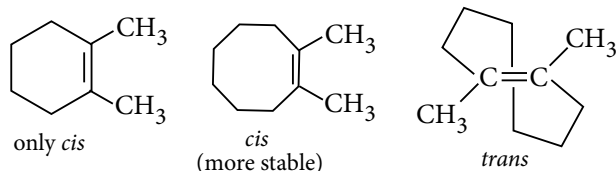
For cyclooctene, *cis*-form is more stable than *trans*.

FOR RING COMPOUNDS CARRYING SUBSTITUENTS
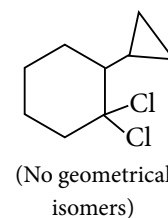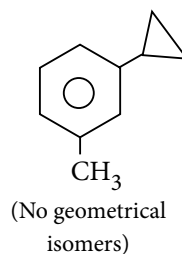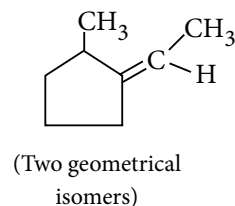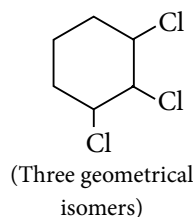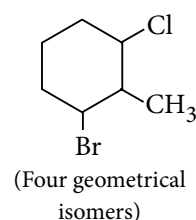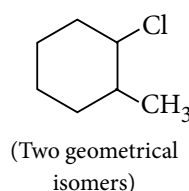
(Two geometrical isomers)

(Four geometrical isomers)

(Three geometrical isomers)

(Two geometrical isomers)

(No geometrical isomers)

(No geometrical isomers)

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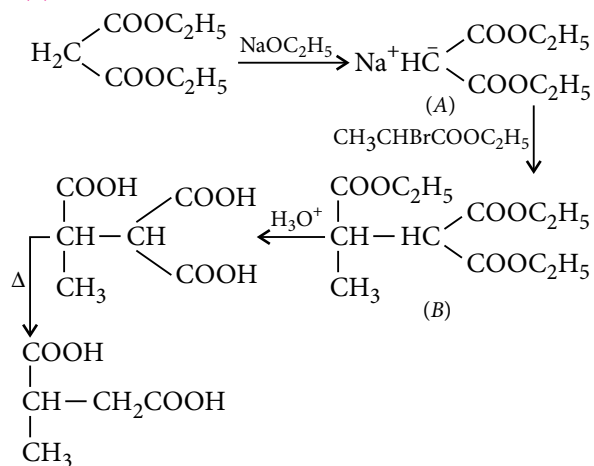
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Y?U ASK
WE ANSWER

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Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q 1. Why only promethium is radioactive in lanthanoids and not any other lanthanoid even it is in middle of the series?

(Pinaki Chattopadhyay)

Ans. Abundance of the elements and the number of naturally occurring isotopes vary regularly in lanthanides. Elements with even atomic number are more abundant than their neighbours with odd atomic numbers (Harkin's rule). Stability of a nucleus is related to both, the number of neutrons and the number of protons in the nucleus.

Element promethium ($Z = 61$) does not occur naturally. Its absence may be explained by Mattauch's rule which states that if two adjacent elements in the periodic table have isotopes of the same mass number, one of these isotopes must be radioactive. Two nuclides that have same mass number can both be stable only if their atomic number differ by more than one. Since elements 60 and 62 have seven isotopes each, there are not many stable mass numbers available for promethium.

According to Mattauch's rule, if promethium is to have a stable isotope, it must have a mass number outside the range of 142-150.

Q 2. Why chemotherapy for cancer treatments results in the side effects like loss of hair or anaemia?

(Bishal Modak, West Bengal)

Ans. Chemotherapy damages all rapidly dividing cells. Cancer cells divide much more often than most normal cells, so chemotherapy damages cancer cells and can destroy them.

But some types of normal cells also divide very often. This happens in tissues where there is need for a steady supply of new cells *e.g.*, skin, hair and nails. Chemotherapy can also damage those cells and this causes side effects. It may cause hair loss all over the body *e.g.*, eyelashes, eyebrows, etc. However, most of the times hair loss is temporary and lost hair regrow after sometime when the treatment ends.

Chemotherapy also affects the bone marrow which makes new blood cells. Hence, during chemotherapy the level of blood cells goes down.

Q 3. Photoelectric effect is quite common in metals. Can it occur in non-metals and other substances such as water?

(Sandhya Sharma, Mumbai)

Ans. Non-metals cannot exhibit photoelectric effect because only metals have extra electrons available in their outer shells that require lower ionisation energy. These extra electrons can be easily removed by a photon provided it has energy equal to the threshold energy *i.e.*, minimum energy required for the removal of an electron.

Some non-metals mostly in the metalloid group can exhibit weak photoelectric effect if the energy of the incoming photon is high enough like X-rays. Covalent compounds such as water are much less likely to show any photoelectric effect because all electrons are paired and are strongly held in shared electron shells.

Q 4. Can a crystalline substance change into amorphous on its own?

(Rohtash, U.P.)

Ans. The crystalline state is relatively more stable than the amorphous state. So the Gibbs' free energy ΔG, of a substance in the amorphous state is always higher than the Gibbs' free energy of same substance in its crystalline state. This accounts for the transformation of an amorphous solid into its crystalline state. The reverse transformation from the crystalline state to the amorphous state does not occur because it is energetically unfavourable. Transformation of amorphous substances into crystalline solids is rarely observed. This is attributed to the high viscosity of solids which allows change to occur but only very slowly. ◈◈
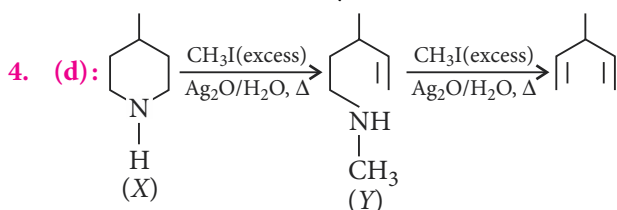
CHEMISTRY MUSING

SOLUTION SET 34

1. (a):

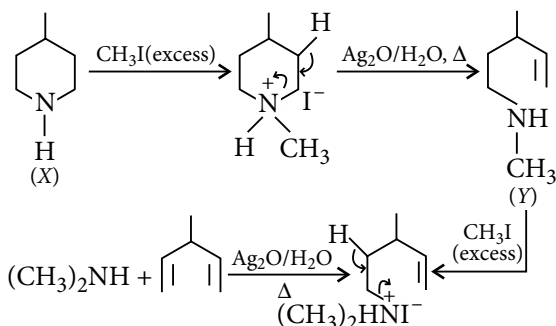**2. (b):** Temperature coefficient $= \dfrac{k_{373\ K}}{k_{363\ K}}$

$= \dfrac{(t)_{363\ K}}{(t)_{373\ K}} = \dfrac{300}{180} = 1.66 \qquad \left(k \propto \dfrac{1}{t}\right)$

3. (a): According to Baeyer's strain theory, stability decreases as the size of the ring decreases. Further, because of the presence of a double bond in a three-membered ring, cyclopropene (ii) is the least stable. Thus, the order of stability is (iv) > (iii) > (i) > (ii).
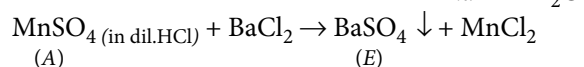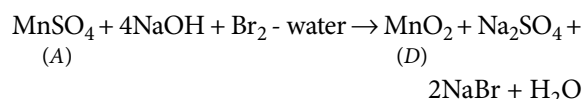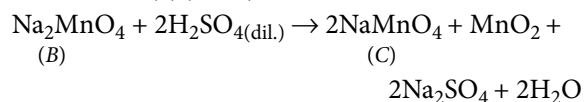
4. (d):

Mechanism :

5. (b): This statement governs the third law of thermodynamics.

6. (c): Compound (c) shows optical inactivity as there is no chiral C-atom and a plane of symmetry is present in the compound.

7. (a): $MnSO_4 + 2Na_2CO_3 + 2KNO_3 \xrightarrow{Fuse}$
   (A)

      $Na_2MnO_4 + 2KNO_2 + Na_2SO_4 + 2CO_2$
      (B) (Green)

$Na_2MnO_4 + 2H_2SO_{4(dil.)} \rightarrow 2NaMnO_4 + MnO_2 +$
 (B)   (C)

      $2Na_2SO_4 + 2H_2O$

$MnSO_4 + 4NaOH + Br_2 \text{-} water \rightarrow MnO_2 + Na_2SO_4 +$
 (A)   (D)

      $2NaBr + H_2O$

$MnSO_{4\ (in\ dil.HCl)} + BaCl_2 \rightarrow BaSO_4 \downarrow + MnCl_2$
 (A)   (E)
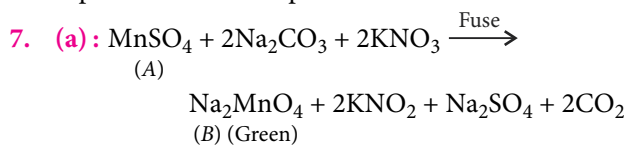
8. (c)

9. (4): $[Ni(H_2O)_6]^{2+}$, $[Fe(H_2O)_6]^{3+}$ and $[CoF_6]^{3-}$ are outer-orbital complexes having sp^3d^2 hybridisation. In these complexes, due to presence of weak field ligands *i.e.*, H_2O and F^-, pairing will not occur. Hence, shows sp^3d^2 hybridisation.
$[Pt(NH_3)_6]^{4+}$, $[Fe(CN)_6]^{4-}$, $[Co(CN)_6]^{3-}$ and $[Ir(NH_3)_6]^{3+}$ are inner-orbital complexes having d^2sp^3 hybridisation.
In these complexes, due to presence of strong field ligands *i.e.*, CN^- and NH_3, pairing will take place. Also Pt and Ir has high Δ_o value, therefore pairing will occur instead of filling electrons in other orbitals because of high energy requirement.

10. (9): For B-H compound,

$P = 0.658$ atm, $V = \dfrac{407}{1000}$ litre, $T = 373$ K, $w = 0.553$ g

$\therefore \quad PV = \dfrac{w}{M}RT;\ 0.658 \times \dfrac{407}{1000} = \dfrac{0.553}{M} \times 0.821 \times 373$

$M = 63.23$ g mol^{-1}

$\therefore$ 100 g of compound has 85.7 g of B

$\therefore$ 63.23 g of compound has $\dfrac{85.7 \times 63.23}{100}$

                        $= 54.19$ g of B

                        $= \dfrac{54.19}{10.8}$ g-atoms of B

$= 5$ g-atoms of B $[\because 10.8$ g $= 1$ g-atom of B]

$\therefore$ Formula becomes B_5H_y

$\therefore$ $5 \times 10.8 + y = 63.23$; $y = 9.23 \approx 9$

$\therefore$ Formula of compound is B_5H_9, hence y is 9.

                                    ◈◈

CROSSWORD

Readers can send their responses at editor@mtg.in or post us with complete address by 25th of every month to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.
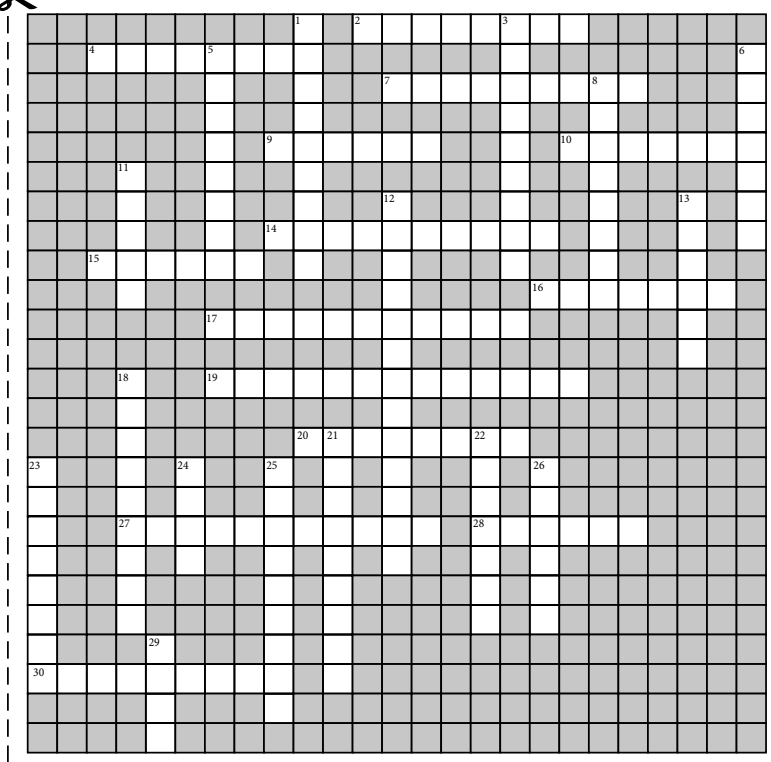
ACROSS

2. Ternary acids of hydrogen, oxygen and a non-metal. (8)

4. One of the polymorphs of zinc sulphide. (8)

7. Another name of sodium aluminosilicate. (9)

9. Colour imparted to glass when it is mixed with manganese dioxide. (6)

10. Electronegativity scale based upon bond energy data. (7)

14. Nature of reversible adiabatic processes. (10)

15. A crystalline halogen. (6)

16. Nickel based superalloys containing chromium and other additives like titanium and aluminium. (7)

17. An alcohol water mixture containing 57.1% of ethylalcohol by volume. (11)

19. The acidic hydride of nitrogen. (13)

20. The total life span of a radioactive element. (8)

27. Type of isomerism exhibited by urea. (11)

28. Geometry of $N(SiH_3)$. (6)

30. A reducing agent used in vat dyeing obtained from formaldehyde sodium bisulphite derivative. (9)

DOWN

1. Linear polymer of β-*D*-glucose is which C_1 of one glucose unit is connected to C_4 of the other through β-*D*-glucosidic linkage. (9)

3. Solutions of two electrolytes having same concentration of common ions. (9)

5. In *E-Z* notation for geometrical isomers, the word that signifies symbol *Z*. (8)

6. Synthesis of petrol by hydrogenation of coal was invented by _____. (7)

8. A highly toxic element of group 13. (8)

11. Drug used for treatment of cancer. (5)

12. Enzyme used to dissolve blood clots. (13)

13. Method of refining used when metal contains impurities of its own oxide. (6)

18. Another name of iron carbide. (9)

21. Complexes of NO with transition metal ions. (9)

22. Ground state of nitrenes. (7)

23. Non-protein component of enzyme. (8)

24. The difference between oxidation number of Mn in permanganate and Fe in haematite. (4)

25. Unsaturated hydrocarbons containing double bonds on adjacent or successive carbon atoms. (9)

26. A piezoelectric material. (6)

29. Can be used to put off metal fires. (4)

✂ *Cut Here*