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# CHEMISTRY

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**ONTENTS** 

Volume 25

May 2016

**Corporate Office:** 

Plot 99, Sector 44 Institutional area, Gurgaon -122 003 (HR).

Tel: 0124-6601200 e-mail: info@mtg.in website: www.mtg.in

No. 5

Read. Office:

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

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# **CHEMISTRY** MUSING

hemistry 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) / AIPMT / AIIMS / Other PMTs & PETs with additional study material.

In every issue of Chemistry Today, 10 challenging problems are proposed in various topics of JEE (Main and Advanced) / AIPMT. 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 34

Δ

#### **JEE MAIN/PMTs**

1. Identify the compound 'B' in the following reaction sequence.

$$CH_{2}(COOC_{2}H_{5})_{2} \xrightarrow{\text{NaOEt}} (A) \xrightarrow{CH_{3}CHBrCOOC_{2}H_{5}} (B)$$

$$H_{3}O^{+} \land A$$

$$CH_{3}-CH-COOH \leftarrow CH_{2}-COOH \leftarrow CH_{2}-COOH$$
(a) 
$$CH-CH(COOC_{2}H_{5})_{2}$$

$$COOH$$
(b) 
$$CH-CH_{2}-COOH \leftarrow CH_{3}$$
(c) 
$$CH-CH_{2}-COOH \leftarrow CH_{3}$$
(c) 
$$CH-CH_{2}-COOH \leftarrow CH_{3}$$
(c) 
$$COOH \leftarrow CH_{2}-COOH \leftarrow CH_{3}$$
(c) 
$$COOH \leftarrow CH_{3}$$
(c) 
$$CH - CH_{3}$$
(c) 
$$CH -$$

- 2. At 3 km altitude, water boils at 90°C and 300 seconds are taken to cook a '3 minute egg'. The temperature coefficient for the process of cooking is
  - (a) 2.66 (b) 1.66
  - (d) 0.6 (c) 3.66

3. The order of stability of the given compounds is



Identify the compound 'X' in the above reaction sequence.



- 5. Which one of the following statements does not govern the second law of thermodynamics?
  - (a) Total entropy of the universe is continuously increasing.
  - (b) Entropy of a perfectly crystalline solid at absolute zero is taken as zero.
  - (c) Without the help of an external agency, a spontaneous process cannot be reversed.
  - (d) All naturally occurring processes are irreversible.

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#### JEE ADVANCED

**6.** Which one of the following does not show optical activity?







#### COMPREHENSION

A powdered substance (A) on treatment with fusion mixture gives a green coloured compound (B). The compound (B) on acidification with dilute H<sub>2</sub>SO<sub>4</sub> gives a pink coloured compound (C). When (A) is treated with excess of NaOH and bromine water, (D) is obtained. Solution of (A) in dilute HCl on treatment with a solution of barium chloride gave a white precipitate of (E), which was insoluble in conc. HNO<sub>3</sub> and conc. HCl.

- 7. Green coloured compound (*B*) is
  - (a)  $Na_2MnO_4$  (b)  $MnO_2$
  - (c) BaCl<sub>2</sub> (d) NaMnO<sub>4</sub>
- 8. The compound (*D*) is

(a)  $MnSO_4$ (b)  $Na_2MnO_4$ (c)  $MnO_2$ (d)  $BaSO_4$ 

#### **INTEGER VALUE**

9. The total number of inner-orbital complexes among the following is

 $[Pt(NH_3)_6]^{4+}$ ,  $[Ni(H_2O)_6]^{2+}$ ,  $[Fe(CN)_6]^{4-}$ ,  $[Fe(H_2O)_6]^{3+}$ ,  $[Co(CN)_6]^{3-}$ ,  $[Ir(NH_3)_6]^{3+}$ ,  $[CoF_6]^{3-}$ 

**10.** 0.553 g of a boron-hydrogen compound  $(B_xH_y)$  created a pressure of 0.658 atm in a bulb of 407 mL at 100°C. Analysis showed the compound contains 85.7% boron. In the molecular formula  $B_xH_y$ , *y* is (Given : At. wt. of B = 10.8 u).

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#### PAPER-I

#### SECTION-1

- This section contains EIGHT questions
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive
- 1. A certain mass of a substance when dissolved in 100 g  $C_6H_6$  lowers the freezing point by 1.28 °C. The same mass of solute when dissolved in 100 g of water lowers the freezing point by 1.40 °C. If the substance has normal molecular mass in benzene and is completely dissociated in water, the number of ions formed when it dissociates in water is  $[K_f \text{ for } H_2O \text{ and } C_6H_6 \text{ are } 1.86 \text{ and } 5.12 \text{ K mol}^{-1} \text{ kg respectively}].$
- 2. A molecule of the type  $AX_5$  has square pyramidal geometry. Hence, number of lone pairs on *A* is
- 3. The percentage ionic character of the HBr molecule if the dipole moment is 0.63 D and HBr bond length 187.5 pm is
- 4. Ethylenediamine displaces  $H_2O$  in the complex  $[Fe(H_2O)_6]^{3+}$  in three steps.  $[Fe(H_2O)_6]^{3+} + 3en \longrightarrow [Fe(en)_3]^{3+} + 6H_2O$

 $[Fe(H_2O)_6] + 3en \longrightarrow [Fe(en)_3] + 6H_2V$ Stepwise formation constant are

log  $K_1$  = 4.34; log  $K_2$  = 3.31; log  $K_3$  = 2.05 Overall formation constant is  $A \times 10^B$  where the value of A is

- 5. In the Bohr's model of the hydrogen atom, the ratio of the kinetic energy to the total energy of the electron in a quantum state n is -x, where x is
- 6. The value of  $K_c$  for the following reaction at 25 °C is  $2.63 \times 10^x$ .

 $Cu^{2+}_{(aq)} + Sn^{2+}_{(aq)} \longrightarrow Sn^{4+}_{(aq)} + Cu_{(s)}$   $E^{\circ}_{Cu^{2+}/Cu} = 0.34 \text{ volt}, E^{\circ}_{Sn^{4+}/Sn^{2+}} = 0.15 \text{ volt}$ The value of x is

- The number of optical isomers for the compound [CH(OH)COOH]<sub>2</sub> is
- 8. Amongst the following, the total number of compounds soluble in aqueous NaOH is



#### SECTION-2

- This section contains TEN questions
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct
- **9.** The melting point of RbBr is 682°C while that of NaF is 988°C. The principal reason that the melting point of NaF is much higher than that of RbBr is that
  - (a) the two crystals are not isomorphous
  - (b) the molar mass of NaF is smaller than that of RbBr
  - (c) the bond in RbBr has more covalent character than the bond in NaF
  - (d) the internuclear distance  $(r_c + r_a)$  is greater for RbBr than for NaF.
- 10. Which is/are not the true statement(s) about KMnO<sub>4</sub>?

- (a) Its solution is unstable in acidic medium.
- (b) It gets reduced to  $MnO_2$  in neutral medium.
- (c)  $MnO_4^-$  changes to  $Mn^{2+}$  in basic solution.
- (d) It is self-indicator in  $Fe^{2+}$  or  $C_2O_4^{2-}$  titration.
- 11. Which of the following easily undergo(es) nucleophilic substitution by S<sub>N</sub>1 mechanism in butanol?
  - (a)  $C_6H_5CH_2Br$  (b)  $BrCH_2CH=CH_2$
  - (c)  $(CH_3)_3CBr$  (d)  $(CH_3)_3CCH_2Br$
- **12.** Extraction of metal from the ore cassiterite involves
  - (a) carbon reduction of an oxide ore
  - (b) self-reduction of a sulphide ore
  - (c) removal of copper impurity
  - (d) removal of iron impurity.
- **13.** Which of the following



 $V(m^3)$  -

→

- (c) w = 314 J
- (d) w = 31.4 J
- **14.** Which of the following statements is/are correct about HCOOH?
  - (a) It is a stronger acid than CH<sub>3</sub>COOH.
  - (b) It forms formyl chloride with PCl<sub>5</sub>.
  - (c) It gives CO and  $H_2O$  on heating with conc.  $H_2SO_4$ .
  - (d) It reduces Tollens' reagent.
- 15. End product(s) of the following reaction is/are



**16.** Which of the following monosaccharides yield(s) an optically active alditol on NaBH<sub>4</sub> reduction?



17. To an acidic solution of an anion, a few drops of KMnO<sub>4</sub> solution are added. Which of the following, if present, will not decolourise the KMnO<sub>4</sub> solution?

(a)	$CO_{3}^{2-}$	(b) $NO_2$
	-2-	(1)

- (c)  $S^{2-}$  (d)  $Cl^{-}$
- Pure ammonia is placed in a vessel at a temperature when its dissociation constant (α) is appreciable. At equilibrium,
  - (a)  $K_p$  does not change significantly with pressure
  - (b)  $\alpha$  does not change with pressure
  - (c) concentration of NH<sub>3</sub> does not change with pressure
  - (d) concentration of  $H_2$  is less than that of  $N_2$ .

#### **SECTION-3**

- This section contains TWO questions
- Each question contains two columns, Column I and Column II
- Column I has four entries (A), (B), (C) and (D).
- Column II has four entries (P), (Q), (R) and (S).
- Match the entries in Column I with the entries in Column II
- One or more entries in Column I may match with one or more entries in Column II
- **19.** Match the entries listed in Column I with appropriate entries listed in Column II.

	Column I		Column II
(A)	Poling	(P)	Titanium
(B)	Cupellation	(Q)	Copper
(C)	Electrorefining	(R)	Silver
(D)	van Arkel method	(S)	Tin



20. Match the entries listed in Column I with appropriate entries listed in Column II. Column I Column II

(A) 
$$\xrightarrow{\text{NaCN} + \text{H}_2\text{SO}_4} (X) \xrightarrow{\text{LiAlH}_4} (Y) \xrightarrow{\text{HNO}_2} (Z)$$

(B) 
$$\xrightarrow{\text{NH}_2\text{OH}} (X) \xrightarrow{\text{H}^+} (Y) \xrightarrow{\text{LiAlH}_4} (Z)$$

(C) 
$$CH_3 - C - CH_2 - CH_2 - CH_2 - CH_2 - C - H \xrightarrow{OH^-}{\Delta} Product$$
  
(D)  $H \xrightarrow{Ph}_{OH} + H^+_{A} \rightarrow Product$ 

- (P) Formation of six membered ring takes place
- (Q) Final product is a ketone
- (R) Final product formed will give positive Tollens' test
- (S) Final product will react with 2, 4-DNP
- (T) Final product have 5 membered ring

#### PAPER-II

#### **SECTION-1**

- This section contains EIGHT questions
- The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive
- 1. The first and second dissociation constant of  $H_2S$  are  $1 \times 10^{-7}$  and  $1.3 \times 10^{-14}$  respectively. Then the approximate pH of a 0.1 M  $H_2S_{(aq)}$  solution is
- 2. The number of possible isomers of the complex, Pt(NH<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub> are
- A 1.1 g sample of copper ore is dissolved and Cu<sup>2+</sup><sub>(aq)</sub> is titrated with excess KI. The liberated I<sub>2</sub> requires 12.12 mL of 0.1 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution for its titration. The percentage of copper by mass in the ore is
- 4.  $MCl_4 \xrightarrow{(i) Zn} (B)$  purple colour compound (A)

```
Colourless
liquid at room
temperature,
transition metal
Moist air
White fumes
```

The number of unpaired electrons in the compound (*B*) is

 Amongst the following, total number of compounds soluble in sodium bicarbonate is
 4, 6-trinitrophenol, benzoic acid, salicylic acid, trifluoroethanol, acetamide, benzenesulphonic acid

- 6. In a sample of pitchblende the ratio of  ${}^{206}\text{Pb}$ :  ${}^{238}\text{U} = 0.2$ : 1 by weight. If the disintegration constant of  ${}^{238}\text{U}$  is  $1.54 \times 10^{-10}$  per year and all Pb is supposed to be originated from uranium then, the age of the mineral is  $1.35 \times 10^{x}$  years. The value of x is
- 7. Oxidation number of Cr in the following complex is

$$(H_2O)_6Cr \swarrow O_2 O_0 Cr(H_2O)_6$$

- In the given list the number of compounds which cannot show tautomerism is acetophenone, acetaldehyde, cyclohexanone, acetylacetone, benzoquinone, acetone, benzaldehyde, butanone, ethyl acetoacetate
  - SECTION-2
- This section contains EIGHT questions
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct
- **9.** The pressure in a bulb dropped from 2000 mm to 1500 mm of Hg in 47 minutes when the contained oxygen leaked through a small hole. The bulb was then completely evacuated. A mixture of oxygen and another gas of molecular weight 79 in the molar ratio 1 : 1 at a total pressure of 4000 mm of Hg was introduced. The molar ratio of the two gases remaining in the bulb after a period of 74 minutes is
  - (a) 0.8089:1 (b) 1:0.8089 (c) 1:0.1499 (d) 0.1499:1

CHEMISTRY TODAY | MAY '16

B

**10.** What are *P*, *Q* and *R* in the following reactions?



- 11. A colourless mixture of two compounds 'A' and ('B' in excess) is soluble in H<sub>2</sub>O. 'A' turns blue litmus red and 'B' turns red litmus blue. 'A' gives white precipitate with 'B' which dissolves in excess of 'B' forming 'C'. 'A' when placed in atmosphere gives fumes and can form dimer. 'A' gives white precipitate with NH<sub>4</sub>Cl and NH<sub>4</sub>OH soluble in 'B'. 'A', 'B' and 'C' are respectively
  - (a) AgCl, KOH and KCl
  - (b) AlCl<sub>3</sub>, NaOH and NaAlO<sub>2</sub>
  - (c) PbCl<sub>2</sub>, KOH and Al(OH)<sub>3</sub>
  - (d) MgCl<sub>2</sub>, NaH, and NaAlO<sub>2</sub>
- 12. Which of the following statements is/are correct about the electrophilic substitution reactions in given compounds A and B?



- (a) Compound A is more reactive than compound B.
- (b) In A, ring Y will take part in electrophilic substitution reaction.

- (c) In B, ring Q will take part in electrophilic substitution reaction.
- (d) Compound *B* is more reactive than compound *A*.
- 13. In the reaction :  $2X + B_2H_6 \longrightarrow [BH_2(X)_2]^+[BH_4]^-$ , the amine(s) X is(are)
  - (a) NH<sub>3</sub> (b)  $CH_3NH_2$ (d) (CH<sub>3</sub>)<sub>3</sub>N (c)  $(CH_3)_2NH$
- **14.** The compound

$$R_1 > N - R_3$$

forms nitroso amines when the substituents are

- (a)  $R_1 = CH_3, R_2 = R_3 = H$
- (b)  $R_1 = R_2 = H, R_3 = C_2 H_5$
- (c)  $R_1 = H, R_2 = R_3 = CH_3$
- (d)  $R_1 = CH_3, R_2 = C_2H_5, R_3 = CH_3$
- 15. Which of the following statement(s) is/are not correct?
  - (a) All C–O bonds in  $CO_3^{2-}$  are equal but not in  $H_2CO_3$ .
  - (b) All C–O bonds in  $HCO_2^-$  are equal but not in HCO<sub>2</sub>H.
  - (c) C–O bond length in  $HCO_2^-$  is longer than C—O bond length in  $CO_3^{2-}$ .
  - (d) C–O bond length in  $HCO_2^-$  and C–O bond length in  $CO_3^{2-}$  are equal.
- **16.** A gas obeys P(V b) = RT. Which of the following statement(s) is/are correct about this gas?
  - (a) Isochoric curves have slope =  $\frac{R}{V-h}$ .
  - (b) Isobaric curves have slope =  $\frac{R}{p}$  and intercept = b.
  - (c) For the gas, compressibility factor =  $1 + \frac{Pb}{RT}$ .
  - (d) The attractive forces are overcome by repulsive forces.

#### **SECTION-3**

- This section contains TWO paragraphs
- Based on each paragraph, there will be TWO questions
- Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct

#### **PARAGRAPH 1**

Concrete is produced from a mixture of cement, water and small stones. Small amount of gypsum, CaSO<sub>4</sub>·2H<sub>2</sub>O is added in cement production to improve the subsequent hardening of concrete. The elevated temperature during the production of cement



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Available at all leading book shops throughout the country. To buy online visit www.mtg.in. For more information or for help in placing your order, call 0124-6601200 or email:*info@mtg.in*  may lead to the formation of unwanted hemihydrate  $CaSO_4 \cdot \frac{1}{2}H_2O$  according to reaction :  $CaSO_4 \cdot 2H_2O_{(s)} \longrightarrow CaSO_4 \cdot \frac{1}{2}H_2O_{(s)} + \frac{3}{2}H_2O_{(g)}$ The  $\Delta_f H^\circ$  of CaSO<sub>4</sub>·2H<sub>2</sub>O<sub>(s)</sub>, CaSO<sub>4</sub>· $\frac{1}{2}$ H<sub>2</sub>O<sub>(s)</sub>, H<sub>2</sub>O<sub>(g)</sub> are -2021.0 kJ mol<sup>-1</sup>, -1575.0 kJ mol<sup>-1</sup>, and -241.8 kJ mol<sup>-1</sup> respectively. The respective values of their standard entropies are 194.0, 130.0 and 188.0 J K<sup>-1</sup> mol<sup>-1</sup>. The values of R = 8.314 J K<sup>-1</sup> mol<sup>-1</sup> = 0.0831 L bar mol<sup>-1</sup> K<sup>-1</sup>. 17. Heat change occurring during conversion of 1 kg

of  $CaSO_4 \cdot 2H_2O_{(s)}$  (molar mass 172 g mol<sup>-1</sup>) to

CaSO<sub>4</sub> 
$$\cdot \frac{1}{2}$$
 H<sub>2</sub>O<sub>(s)</sub> is  
(a) 484 kJ (b) 400 kJ  
(c) -484.0 kJ (d) -1000 kJ

**18.** The formation of CaSO<sub>4</sub>  $\cdot \frac{1}{2}$ H<sub>2</sub>O at 298 K is

- (a) spontaneous
- (b) endothermic and non-spontaneous
- (c) endothermic and spontaneous
- (d) exothermic and non-spontaneous.

#### **PARAGRAPH 2**

S<sub>N</sub>2 reaction is bimolecular reaction which takes place by the formation of transition state. Velocity of the reaction depends on the concentration of the substrate as well as the nucleophile. The reaction is favoured by strong nucleophile and in the presence of polar aprotic solvent, optically active halides undergo Walden inversion by S<sub>N</sub>2 mechanism. The presence of hetero group (atom) at

 $\beta$  C-atom, unsaturation at  $\beta$  C-atom and  $\lfloor$ at  $\alpha$  C-atom favour S<sub>N</sub>2 mechanism.

Allyl halides and benzyl halides give S<sub>N</sub>1 and S<sub>N</sub>2 reactions. Allyl halides also give S<sub>N</sub>2 mechanism. Electron donating group at ortho- and para-positions in benzyl halides favours S<sub>N</sub>1 mechanism, whereas electron withdrawing group favours S<sub>N</sub>2 mechanism.

**19.** Which of the following will give  $S_N 2$  reaction

(a) 
$$C_2H_5Br$$
 (b)  $CH_3Br$   
O  
(c)  $Ph-C$  (d)  $Me_3C-CH_2Br$ 

20. In the reaction 
$$\begin{array}{c} Br \\ Me \end{array} \xrightarrow{O} \\ O^{-} \\ \hline AgNO_{3} \\ O^{-} \\ \hline AgNO_{3} \\ \hline X], [X] is$$
  
(a)  $C_{2}H_{5}Br \\ OH \\ (c) Me \\ O^{-} \\ O^{-} \\ O^{-} \\ O^{+} \\ (d) CH_{2} = CH_{2} \\ \hline SOLUTIONS \\ \hline COOAg \\ COOAg \\ CH_{2} = CH_{2} \\ \hline COOAg \\ CH_{3} = CH_{3} \\ \hline COOAg \\ CH_{3} \\ CH$ 

**PAPER-I** 

1. (3): 
$$\Delta T_f = \frac{1000 \times K_f \times w_2}{M_2 \times w_{1(\text{in g})}}$$

For the solution in benzene,

$$1.28 = \frac{1000 \times 5.12 \times w_2}{M_{\text{normal}} \times 100} \qquad \dots (i)$$

For the solution in water in which solute dissociates,

$$1.40 = \frac{1000 \times 1.86 \times w_2}{M_{\text{experimental}} \times 100} \qquad \dots (\text{ii})$$

Dividing eq. (ii) by (i),

•.•

4.

$$i = \frac{M_{\text{normal}}}{M_{\text{experimental}}} = \frac{1.40}{1.28} \times \frac{5.12}{1.86} = 3.01 \approx 3.0$$

Now, suppose that formula of the solute is  $A_x B_y$ . N ... A + ..

$$A_{x}B_{y} = xA + yB$$

$$1 \qquad 0 \qquad 0$$

$$(1-\alpha) \qquad x\alpha \qquad y\alpha$$

$$\therefore \quad i = 1 - \alpha + x\alpha + y\alpha$$

$$\therefore \quad i = 3 \text{ and } \alpha = 1$$
(Given that  $\alpha = 1$ )

$$\therefore$$
 No. of ions formed  $(x + y) = 3$ 

 $sp^3d^2$ (1): Square pyramidal geometry -2. hybridisation of central atom with 5 bond pairs and 1 lone pair.

3. (7): Calculated value of 
$$\mu = e \times l$$
  

$$= 4.8 \times 10^{-10} \text{ esu} \times 187.5 \times 10^{-10} \text{ cm}$$

$$= 9 \times 10^{-18} \text{ esu cm}$$

$$= 9 \text{ Debye} (1 \times 10^{-18} \text{ esu cm} = 1 \text{ Debye})$$
Observed value of  $\mu = 0.63$  Debye

% ionic character =  $\frac{\text{observed value} \times 100}{\text{calculated value}}$ 

$$= \frac{0.63}{9} \times 100 = 7\%$$
(5):  $[Fe(H_2O)_6]^{3+} + 3en \longrightarrow [Fe(en)_3]^{3+} + 6H_2O$   
 $\beta_3 = \frac{[Fe(en)_3]^{3+}}{[Fe(H_2O)_6]^{3+}[en]^3} = K_1 \times K_2 \times K_3$ 

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- $\Rightarrow \log \beta_3 = \log K_1 + \log K_2 + \log K_3$
- As  $\log K_1 = 4.34$ ,  $\log K_2 = 3.31$ ,  $\log K_3 = 2.05$  $\therefore \log \beta_3 = 4.34 + 3.31 + 2.05 = 9.7$
- $\beta_3 = 5 \times 10^9$  hence, A is 5.

5. (1): *K.E.* of an electron in an orbit = 
$$+\frac{1}{2}\frac{e^2}{r_n}$$

Total energy of an electron in an orbit =  $\frac{K.E.}{T F} = -1$  thus, x = 1

6. (6): The cell may be represented as  ${\rm Sn}^{2+} | {\rm Sn}^{4+} | | {\rm Cu}^{2+} | {\rm Cu}$ 

To calculate  $K_c$ , the cell reaction should be at equilibrium, *i.e.*,  $E_{cell} = 0$ 

$$E_{\text{cell}} = E_{\text{Cu}^{2+}/\text{Cu}} - E_{\text{Sn}^{4+}/\text{Sn}^{2+}} = 0$$
  
or  $\left\{ E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} + \frac{0.0591}{2} \log[\text{Cu}^{2+}] \right\} - \left\{ E_{\text{Sn}^{4+}/\text{Sn}^{2+}}^{\circ} + \frac{0.0591}{2} \log[\frac{(\text{Sn}^{4+})}{(\text{Sn}^{2+})} \right\} = 0$ 

or 
$$\left\{E_{Cu^{2+}/Cu}^{-} - E_{Sn^{4+}/Sn^{2+}}^{-}\right\} + \frac{0.0591}{2}\log\frac{[Cu^{2+}][Sn^{2+}]}{[Sn^{4+}]} = 0$$
  
or  $(+0.34 - 0.15) - \frac{0.0591}{2}\log\frac{[Sn^{4+}]}{[Sn^{4+}]} = 0$ 

or 
$$(+0.34 - 0.15) - \frac{0.0391}{2} \log \frac{[311]}{[Cu^{2+}][Sn^{2+}]} =$$

or 
$$0.19 - \frac{0.0391}{2} \log K_c = 0$$

- or  $\log K_c = 6.42$
- or  $K_c = 2.69 \times 10^6$
- 7. (3): The structure of the compound can also be written as

 $\therefore$  No. of asymmetric C atoms (C<sup>\*</sup>) = 2 but the two ends are similar or the molecule is divisible into equal halves.

Hence, No. of *d*- and *l*-forms,

$$a = 2^{n-1} = 2^{2-1} = 2$$

No. of *meso*-forms,

$$m = 2^{\frac{n}{2}-1} = 2^{\frac{2}{2}-1} = 2^{0} = 1$$

No. of optical isomers = a + m = 2 + 1 = 3

8. (4): Out of the given compounds, those soluble in aq. NaOH are :



9. (d): The melting point of a crystal is directly proportional to its lattice energy. The lattice energy in case of ionic crystals is itself dependent on the charge of the particles and the distance between them *i.e.*, the bond length.

Lattice energy 
$$\propto \frac{1}{r_c + r_a}$$

The charge in case of NaF as well as RbBr is the same but the bond length in case of RbBr is much more than NaF. Hence, the melting point of NaF is much higher than RbBr.

- 10. (c):  $MnO_4^-$  changes to  $MnO_4^{2-}$  or  $MnO_2$  in basic medium.
- 11. (a, b, c, d) : All form stable carbocations therefore, all options are correct.

(a)  $C_6H_5CH_2$  is stabilised by resonance over the phenyl ring.

(b)  $CH_2 = CH \stackrel{+}{\longrightarrow} \stackrel{+}{C}H_2 \longleftrightarrow \stackrel{+}{C}H_2 - CH = CH_2$  is also stabilised by resonance.

(c) 
$$CH_3 \rightarrow \overset{+}{C} \leftarrow CH_3$$
  
 $\downarrow \\ CH_3$ 

is stabilised by +I-effect of  $-CH_3$  groups.

(d) 
$$CH_3 - C - CH_2 - Br \xrightarrow{Ionisation}_{-Br}$$
  
(d)  $CH_3 - C - CH_2 - Br \xrightarrow{Ionisation}_{-Br}$   
Neopentyl bromide  
 $CH_3$   
 $CH_3 - C - CH_2 \xrightarrow{Rearranges} CH_3 - CH_3 - CH_2 - CH_3$   
 $CH_3 - C - CH_2 \xrightarrow{Ionisation}_{-Br}$   
 $CH_3 - CH_3 - CH_$ 

12. (a, c, d) : Tin is extracted from cassiterite ore. It is reduced by carbon.

 $SnO_2 + 2C \longrightarrow Sn + 2CO$ Crude metal contains impurities Fe, W and Cu.



**13.** (a, b, c) : For a cyclic process, dU = 0  $\therefore q = dU + (-w) \Rightarrow q = -w$ Also, w = Area covered by the curve

$$= \pi r^{2} = \pi \times \left[ \frac{(V_{2} - V_{1})}{2} \right]^{2}$$
$$= \frac{\pi \times (20)^{2}}{2^{2}}$$
$$= 100 \pi = 100 \times 3.14 = 314 \text{ J}$$

**14.** (**a**, **c**, **d**) : Formyl chloride being unstable decomposes to form CO + HCl



- 16. (a, b, d) : Only the alditol (monosaccharide having  $-CH_2OH$  at both ends) from structure (c) has a plane of symmetry hence, it will be optically inactive. The other three form optically active alditols.
- 17. (a): Oxidation state of C in  $CO_3^{2-}$  is +4, which is maximum. So, it will not be oxidised.
- **18.** (a):  $K_p$  is constant and does not change with pressure.
- 19.  $A \rightarrow Q$ , S;  $B \rightarrow R$ ;  $C \rightarrow Q$ , R, S;  $D \rightarrow P$

(A) **Poling :** Impure molten metal is stirred with green wooden poles, oxide impurities are removed, mainly used for Cu and Sn.

**(B)** Cupellation : It is used when impurities are of other metals, mainly used for silver.

**(C) Electrorefining :** Cu, Ag, Au, Al, Pb, Sn, etc., are mainly purified by removing insoluble impurities as anode mud.

**(D) van Arkel method (vapour phase refining):** Metals like titanium, zirconium and silicon are purified by this method.

20.  $A \rightarrow P, Q, S; B \rightarrow P, C \rightarrow P, Q, S; D \rightarrow P, Q, S$ HO CN HO  $CH_2 - NH_2$  (A) (V) (V)



#### PAPER-II

1. (4): Most of the H<sup>+</sup> ions result from primary dissociation, *i.e.*,

 $H_2S \rightleftharpoons H^+ + HS^-$ 

Let x be the concentration of  $[H^+]$  or  $[HS^-]$  at equilibrium.

$$\therefore \quad [H_2S] = 0.1 - x \approx 0.1 \qquad (\because x \text{ is very small.})$$
$$K_1 = \frac{[H^+][HS^-]}{[H_2S]}$$

or 
$$1 \times 10^{-7} = \frac{x \cdot x}{0.1} \implies x^2 = 1 \times 10^{-8}$$

or 
$$x = 1 \times 10^{-1}$$
  
or  $[H^+] = 1 \times 10^{-4}$ 

or 
$$[H^+] = 1 \times 10^{-1}$$

- :.  $pH = -log[H^+] = -log(10^{-4}) = 4$
- (6): [Pt(NH<sub>3</sub>)<sub>2</sub>(SCN)<sub>2</sub>]- *cis* and *trans*-isomers = 2 [Pt(NH<sub>3</sub>)<sub>2</sub>(NCS)(SCN)]- *cis* and *trans*-isomers = 2 [Pt(NH<sub>3</sub>)<sub>2</sub>(NCS)<sub>2</sub>] - *cis* and *trans*-isomers = 2 The complex is square planar; so it does not have a pair of enantiomers on account of the presence of plane of symmetry.

3. (7): 
$$2Cu^{2+} + 4I^{-} \longrightarrow Cu_{2}I_{2} + I_{2}$$
  
 $I_{2} + 2S_{2}O_{3}^{2-} \longrightarrow S_{4}O_{6}^{2-} + 2I^{-}$   
 $2S_{2}O_{3}^{2-} \equiv I_{2} \equiv 2Cu^{2+}$   
or  $S_{2}O_{3}^{2-} \equiv Cu^{2+}$ 

Equivalents of  $Na_2S_2O_3$  = Equivalents of  $I_2$ 

= Equivalents of Cu  

$$W_{(Pure Cu)} = \frac{0.1 \times 63.5 \times 12.12}{1000} = 0.077 \text{ g}$$
  
% of Cu =  $\frac{0.077}{1.1} \times 100 = 7\%$ 

4. (1): (*A*) is  $TiCl_4$  as it has no unpaired electron and is liquid at room temperature on account of covalent character because of high polarising power of



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Ti<sup>4+</sup>· TiCl<sub>4</sub> being covalent gets hydrolysed forming  $TiO_2 \cdot nH_2O$  and HCl(C) which fumes in air.

In [Ti(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> complex, Ti(III) has one unpaired electron  $(3d^1)$  which gives violet or purple colour due to d - d transition.

$$\begin{array}{c} \text{TiCl}_{4} \xrightarrow{Zn} \text{TiCl}_{3} \xrightarrow{\text{Hydrolysis}}_{\text{H}_{2}\text{O}} \Rightarrow [\text{Ti}(\text{H}_{2}\text{O})_{6}]\text{Cl}_{3} \\ \text{Purple or violet} \\ \text{Colourless} \\ & (B) \\ \hline \\ & & \text{Moist air} \\ & & \text{TiO}_{2} \cdot n\text{H}_{2}\text{O} + \text{HCl} \text{ (white fumes)} \\ & & (C) \end{array}$$

5. (4): Four compounds *i.e.*, 2, 4, 6-trinitrophenol, benzoic acid, salicylic acid and benzenesulphonic acid decompose NaHCO<sub>3</sub> and hence dissolve in it.

6. (9):  

$$2^{38}U \longrightarrow 2^{06}Pb$$
Initial moles :  

$$a 0$$
Moles after time t:  

$$(a-x) x$$

$$\frac{wt. of ^{206}Pb}{wt. of ^{238}U} = \frac{0.2}{1}$$

$$\therefore \frac{moles of Pb^{206}}{moles of U^{238}} = \frac{0.2/206}{1/238} = \frac{0.231}{1}$$
or  

$$\frac{x}{a-x} = 0.231$$
Add 1 to both sides,  

$$1 + \frac{x}{a-x} = 0.231 + 1 \Rightarrow \frac{a}{a-x} = 1.231$$
Now  $\lambda = \frac{2.303}{t} \log \frac{a}{a-x}$   
 $\Rightarrow 1.54 \times 10^{-10} = \frac{2.303}{t} \log 1.231$   
 $t = 1.35 \times 10^9$  years  
 $\therefore x = 9$ 

7. (3): 
$$\left[ (H_2O)_6Cr \underbrace{\bigcirc O_2}_{-1 & -1} Cr(H_2O)_6 \right]^{3+}$$

Thus, oxidation state of Cr = 2x - 1 + (-2) = +3x = +3

- 8. (2): Benzoquinone and benzaldehyde cannot show tautomerism.
- 9. (a): Suppose  $p_{O_2}$  and  $p_x$  be the pressure-drops per minute of  $O_2$  and the unknown gas *x* respectively.

$$\therefore \quad p_{O_2} = \frac{2000 - 1500}{47} = 10.64 \text{ mm/min}$$
$$\therefore \quad \frac{r_{O_2}}{r_x} = \frac{p_{O_2}}{p_x} = \sqrt{\frac{M_x}{M_{O_2}}}$$

$$\frac{10.64}{p_x} = \sqrt{\frac{79}{32}}; p_x = 6.77 \text{ mm/min.}$$

Since the bulb is now refilled with equal number of moles of  $O_2$  and x, the partial pressure of each gas will be 2000 mm as the total pressure is 4000 mm.  $\therefore$  pressure of O<sub>2</sub> after 74 min = partial pressure of  $O_2$  – pressure drop in 74 min  $= 2000 - (10.64 \times 74) = 1212.64$  mm of Hg

and pressure of *x* after 74 min

= partial pressure of x – pressure drop after 74 min  $= 2000 - (6.77 \times 74) = 1499.02 \text{ mm of Hg}$ Now,

Moles of 
$$x$$
 left after 74 min

$$= \frac{\text{Pressure of O}_2 \text{ after 74 min}}{\text{Pressure of } x \text{ after 74 min}}$$

$$=\frac{1212.64}{1499.02}-=0.8089$$

Hence, molar ratio of  $O_2$  and x after 74 minutes is 0.8089:1.

#### 10. (c)

**11.** (b): 'A' gives white ppt. with  $NH_4Cl$  and  $NH_4OH$  $\therefore$  'A' is Al<sup>3+</sup> and ppt. is of Al(OH)<sub>3</sub>.  $Al(OH)_3$  is soluble in 'B' therefore, 'B' is NaOH and 'C' is NaAlO<sub>2</sub> (sodium meta-aluminate). 'A' forms dimer indicating 'A' is electron-deficient that is the possible case of AlCl<sub>3</sub>. 'A' is thus AlCl<sub>3</sub> (acidic due to hydrolysis, turns blue litmus red). 'B' is NaOH (alkaline, turns red litmus blue).

$$\begin{array}{ccc} AlCl_{3} + 3NaOH \longrightarrow Al(OH)_{3} + 3NaCl \\ (A) & (B) & \text{white ppt.} \\ Al(OH)_{3} + NaOH \longrightarrow NaAlO_{2} + 2H_{2}O \\ (excess) & \text{soluble } (C) \\ AlCl_{3} + 3H_{2}O \longrightarrow Al(OH)_{3} + 3HCl \uparrow (fumes) \\ AlCl_{3} + 3NH_{4}OH \xrightarrow{NH_{4}Cl} Al(OH)_{3} \downarrow + 3NH_{4}Cl \\ 2AlCl_{3} \longrightarrow Al_{2}Cl_{6} \end{array}$$

12. (b, c, d) : In compound A, ring Y is both activated and deactivated while ring X is only deactivated, hence, Yis more electron rich than X and electrophilic substitution takes place on Y ring. In compound B, ring Q is both activated and deactivated while



ring *P* is only deactivated hence, *Q* will take part in electrophilic substitution reactions.

In *B*, ring *Q* is attached to N.

In *A*, ring *Y* is attached to O.

$$\stackrel{\text{N}}{\longrightarrow}$$
 group is a stronger +*R* group than  $-\stackrel{\text{O}}{\ominus}$ .

Hence, compound *B* is more reactive than compound *A*.

**13.** (a, b, c):  $B_2H_6$  reacts with NH<sub>3</sub>, 1° and 2° amines and form an ionic compound.

However, with 3° amine,  $B_2H_6$  forms an adduct.  $B_2H_6 + 2N(CH_3)_3 \longrightarrow 2(CH_3)_3N \rightarrow BH_3$ 

14. (c) :  $R_1 = H$  and  $R_2 = R_3 = CH_3$  $R_1 = H = H = H = H = H$  $R_2 = H = H = H = H = H$ 

Secondary amine reacts with nitrous acid to form nitroso amine (yellow liquid).

15. (c, d) : 
$$H - C \xrightarrow{O} H - C \xrightarrow{O} O^{-1}$$

B.O. = 
$$\frac{2+1}{2} = 1.5$$
  

$$\begin{bmatrix} 0 \\ || \\ 0 \\ 0 \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} 0 \\ || \\ 0 \\ 0 \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} 0 \\ || \\ 0 \\ 0 \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} 0 \\ 0 \\ 0 \end{bmatrix}^{2-} \longleftrightarrow \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \end{bmatrix}^{2-}$$

B.O.  $=\frac{2+1+1}{3}=\frac{4}{3}=1.33$ 

C-O bond length in HCOO<sup>-</sup> is less than C-O bond length in  $CO_3^{2-}$ .

**16.** (a, b, c, d): Isochoric curves, P(V - b) = RT

$$P = \frac{R}{(V-b)} \cdot T \quad \therefore \quad \text{slope} = \frac{R}{V-b}$$

Isobaric curves,

$$PV - Pb = RT$$

$$V = \frac{RT}{P} + b$$
 : slope =  $\frac{R}{P}$  and intercept = b

Compressibility factor,

$$\frac{PV}{RT} = 1 + \frac{Pb}{RT}; Z > 1$$

*i.e.*, repulsive forces predominate.

17. (a): 
$$\Delta_r H^\circ = \Sigma \Delta_f H^\circ_{\text{products}} - \Sigma \Delta_f H^\circ_{\text{reactants}}$$
  
=  $\left[ -1575.0 \text{ kJ mol}^{-1} - \frac{3}{2} \times 241.8 \text{ kJ mol}^{-1} \right]$   
-  $\left[ -2021.0 \text{ kJ mol}^{-1} \right]$ 

= +83.3 kJ mol<sup>-1</sup>  
For 1 kg of CaSO<sub>4</sub>·2H<sub>2</sub>O  
no. of moles = 
$$\frac{1000}{172}$$
 = 5.81  
∴ Heat change for 5.81 mol of CaSO<sub>4</sub>·2H<sub>2</sub>O  
= 5.81 mol × 83.3 kJ mol<sup>-1</sup>  
= 484 kJ

18. (b): 
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$
  
Now,  $\Delta S^\circ = \Sigma S^\circ_{\text{products}} - \Sigma S^\circ_{\text{reactants}}$   
⇒  $\Delta S^\circ = \left[ 130 + \left(\frac{3}{2} \times 188\right) \right] - 194$   
 $= 218 \text{ J K}^{-1} \text{ mol}^{-1} = 0.218 \text{ kJ K}^{-1} \text{ mol}^{-1}$   
∴  $\Delta G^\circ = 83.3 - (0.218 \times 298)$   
 $= 18.336 \text{ kJ mol}^{-1}$ 

 $\Delta H$  = +ve and  $\Delta G$  = +ve hence, reaction is endothermic and non-spontaneous.

- **19.** (a, b, c) : (a)  $1^{\circ}RX$ , (b)  $1^{\circ}RX$ ; (c)  $\begin{bmatrix} || \\ -C \end{bmatrix}$  group at  $\alpha$  C-atom favours  $S_N^2$  reaction. (d) Neopentyl halide does not undergo either  $S_N^1$  or  $S_N^2$ .
- **20.** (c) : Neighbouring group participation of COO<sup>-</sup> group, with retention of configuration takes place.



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NEWS



We are happy to inform our readers that most of the questions asked in JEE Main 2016 Exam are very similar to the problems given in **MTG JEE Main Chemistry.** 

1. At 300 K and 1 atm, 15 mL of a gaseous hydrocarbon requires 375 mL air containing 20%  $\mathrm{O}_2$  by volume for complete combustion. After combustion the gases occupy 330 mL. Assuming that the water formed is in liquid form and the volumes were measured at the same temperature and pressure, the formula of the hydrocarbon is

(a)  $C_3H_6$ (b)  $C_{3}H_{8}$ 

(c)  $C_4H_8$ (d)  $C_4H_{10}$ 

Two closed bulbs of equal volume (V) containing 2. an ideal gas initially at pressure  $p_i$  and temperature  $T_1$  are connected through a narrow tube of negligible volume as shown in the figure below. The temperature of one of the bulbs is then raised to  $T_2$ . The final pressure  $p_f$  is



3. A stream of electrons from a heated filament was passed between two charged plates kept at a potential difference V esu. If e and m are charge and mass of an electron respectively, then the value of  $h/\lambda$  (where  $\lambda$  is wavelength associated with electron wave) is given by

(a) 
$$meV$$
 (b)  $2meV$   
(c)  $\sqrt{meV}$  (d)  $\sqrt{2meV}$ 

4. The species in which the N atom is in a state of *sp* hybridisation is

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NEWS

(a) $NO_2^+$	(b) $NO_2^-$
(c) $NO_3^-$	(d) $NO_2$

The heats of combustion of carbon and carbon 5. monoxide are -393.5 and -283.5 kJ mol<sup>-1</sup> respectively. The heat of formation (in kJ) of carbon monoxide per mole is

- 6. 18 g glucose  $(C_6H_{12}O_6)$  is added to 178.2 g water. The vapour pressure of water (in torr) for this aqueous solution is
  - (b) 76.0 (a) 7.6
  - (c) 752.4 (d) 759.0

[From MTG JEE Main Chemistry, Page 327, Q-16]

- The equilibrium constant at 298 K for a reaction, 7.  $A + B \rightleftharpoons C + D$  is 100. If the initial concentration of all the four species were 1 M each, then equilibrium concentration of D (in mol  $L^{-1}$ ) will be
  - (a) 0.182 (b) 0.818
  - (c) 1.818 (d) 1.182

[From MTG JEE Main Chemistry, Similar Question, Page 206, Illustration-6]



- 8. Galvanization is applying a coating of
- (a) Pb (b) Cr (c) Cu (d) Zn [From MTG JEE Main Chemistry, Similar Question, Page 383, Q-17]
- 9. Decomposition of  $H_2O_2$  follows a first order reaction. In fifty minutes the concentration of  $H_2O_2$  decreases from 0.5 to 0.125 M in one such decomposition. When the concentration of  $H_2O_2$ reaches 0.05 M, the rate of formation of  $O_2$  will be
  - (a)  $6.93 \times 10^{-2} \text{ mol min}^{-1}$ (b)  $6.93 \times 10^{-4} \text{ mol L}^{-1} \text{ min}^{-1}$
  - (c)  $2.66 \text{ Lmin}^{-1}$  at STP
  - (d)  $1.34 \times 10^{-2}$  mol min<sup>-1</sup>

#### [From MTG JEE Main Chemistry, Similar Question, Page 416, Q-3]

- 10. For a linear plot of log (x/m) versus log p in a Freundlich adsorption isotherm, which of the following statements is correct? (k and n are constants)
  - (a) Both k and 1/n appear in the slope term.
  - (b) 1/n appears as the intercept.
  - (c) Only 1/n appears as the slope.
  - (d)  $\log(1/n)$  appears as the intercept.

#### [From MTG JEE Main Chemistry, Similar Question, Page 438, Q-23]

- **11.** Which of the following atoms has the highest first ionization energy?
  - (a) Rb (b) Na (c) K (d) Sc
- **12.** Which one of the following ores is best concentrated by froth floatation method?
  - (a) Magnetite (b) Siderite
  - (c) Galena (d) Malachite

[From MTG JEE Main Chemistry, Similar Question, Page 498, Q-11]

- **13.** Which one of the following statements about water is false ?
  - (a) Water is oxidized to oxygen during photosynthesis.
  - (b) Water can act both as an acid and as a base.
  - (c) There is extensive intramolecular hydrogen bonding in the condensed phase.
  - (d) Ice formed by heavy water sinks in normal water.
- **14.** The main oxides formed on combustion of Li, Na and K in excess of air are, respectively
  - (a)  $Li_2O$ ,  $Na_2O$  and  $KO_2$
  - (b)  $LiO_2$ ,  $Na_2O_2$  and  $K_2O$
  - (c)  $Li_2O_2$ ,  $Na_2O_2$  and  $KO_2$
  - (d) Li<sub>2</sub>O, Na<sub>2</sub>O<sub>2</sub> and KO<sub>2</sub>

**15.** The reaction of zinc with dilute and concentrated nitric acid, respectively produces

- (a)  $N_2O$  and  $NO_2$  (b)  $NO_2$  and NO
- (c) NO and  $N_2O$  (d)  $NO_2$  and  $N_2O$
- **16.** The pair in which phosphorus atoms have a formal oxidation state of + 3 is
  - (a) orthophosphorous and pyrophosphorous acids
  - (b) pyrophosphorous and hypophosphoric acids
  - (c) orthophosphorous and hypophosphoric acids
  - (d) pyrophosphorous and pyrophosphoric acids.
- **17.** Which of the following compounds is metallic and ferromagnetic?
  - (a)  $TiO_2$  (b)  $CrO_2$ (c)  $VO_2$  (d)  $MnO_2$
- **18.** The pair having the same magnetic moment is [At. No.: Cr = 24, Mn = 25, Fe = 26, Co = 27]
  - (a)  $[Cr(H_2O)_6]^{2+}$  and  $[CoCl_4]^{2-}$
  - (b)  $[Cr(H_2O)_6]^{2+}$  and  $[Fe(H_2O)_6]^{2+}$
  - (c)  $[Mn(H_2O)_6]^{2+}$  and  $[Cr(H_2O)_6]^{2+}$
  - (d)  $[CoCl_4]^{2-}$  and  $[Fe(H_2O)_6]^{2+}$
- **19.** Which one of the following complexes shows optical isomerism?
  - (a)  $[Co(NH_3)_3Cl_3]$
  - (b)  $cis[Co(en)_2Cl_2]Cl$
  - (c)  $trans[Co(en)_2Cl_2]Cl$
  - (d)  $[Co(NH_3)_4Cl_2]Cl (en = ethylenediamine)$
- **20.** The concentration of fluoride, lead, nitrate and iron in a water sample from an underground lake was found to be 1000 ppb, 40 ppb, 100 ppm and 0.2 ppm, respectively. This water is unsuitable for drinking due to high concentration of
  - (a) fluoride (b) lead
  - (c) nitrate (d) iron.
    - [From MTG JEE Main Chemistry, Similar Question, Page 774, Q-20]
- **21.** The distillation technique most suited for separating glycerol from spent-lye in the soap industry is
  - (a) simple distillation
  - (b) fractional distillation
  - (c) steam distillation
  - (d) distillation under reduced pressure.
- 22. The product of the reaction given below is

$$\xrightarrow{1. \text{ NBS}/hv} X$$

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**24.** 2-Chloro-2-methylpentane on reaction with sodium methoxide in methanol yields

(I) 
$$C_2H_5CH_2C - OCH_3$$
  
(II)  $C_2H_5CH_2C = CH_2$   
(III)  $C_2H_5CH_2C = CH_2$   
(III)  $C_2H_5CH = C - CH_3$   
(III)  $C_2H_5CH = C - CH_3$   
(a) all of these (b) I and III

- (d) I and II (c) III only
- **25.** The reaction of propene with HOCl  $(Cl_2 + H_2O)$ proceeds through the intermediate :
  - (a)  $CH_3 CH^+ CH_2 OH$
  - (b)  $CH_3 CH^+ CH_2 Cl$
  - (c)  $CH_3 CH(OH) CH_2^+$
  - (d)  $CH_3 CHCl CH_2^+$
- 26. In the Hofmann bromamide degradation reaction, the number of moles of NaOH and  $\mathrm{Br}_2$  used per mole of amine produced are
  - (a) one mole of NaOH and one mole of Br<sub>2</sub>
  - (b) four moles of NaOH and two moles of Br<sub>2</sub>
  - (c) two moles of NaOH and two moles of Br<sub>2</sub>
  - (d) four moles of NaOH and one mole of  $Br_2$ .
- 27. Which of the following statements about low density polythene is false?
  - (a) Its synthesis requires high pressure.
  - (b) It is a poor conductor of electricity.

- (c) Its synthesis requires dioxygen or a peroxide initiator as a catalyst.
- (d) It is used in the manufacture of buckets, dust-bins etc.
- 28. Thiol group is present in
  - (a) cytosine (b) cystine
  - (d) methionine. (c) cysteine
- 29. Which of the following is an anionic detergent?
  - (a) Sodium stearate
  - (b) Sodium lauryl sulphate
  - (c) Cetyltrimethyl ammonium bromide
  - (d) Glyceryl oleate

#### [From MTG JEE Main Chemistry, Similar Question, Page 1237, Q-24]

30. The hottest region of Bunsen flame shown in the figure below is



1. (b): Chemical equation for the combustion of hydrocarbon is

$$C_x H_{y(g)} + \left(x + \frac{y}{4}\right) O_{2(g)} \longrightarrow x CO_{2(g)} + \frac{y}{2} H_2 O_{(l)}$$

0

Initial 15 mL  $15\left(x+\frac{y}{4}\right)$ mL Final 0 0

15x mL

Now, volume of O<sub>2</sub> in air 
$$=\frac{20}{100} \times 375 = 75$$
 mL

$$\therefore \quad 75 = 15\left(x + \frac{y}{4}\right) \implies x + \frac{y}{4} = 5$$

Out of given four options, C<sub>3</sub>H<sub>8</sub> will satisfy the above equation.

2. (c) : Initially, number of moles of gas in each bulb is  $n_1 = \frac{p_i V}{RT_1}$  and  $n_2 = \frac{p_i V}{RT_1}$ 

After the temperature of second bulb is raised to  $T_2$ then the number of moles of gas in both the bulbs are



$$n'_{1} = \frac{p_{f}V}{RT_{1}}$$
 and  $n'_{2} = \frac{p_{f}V}{RT_{2}}$ 

Now, the total number of moles of gas in both the bulbs remains same in both the cases.

$$\begin{aligned} n_1 + n_2 &= n_1' + n_2' \\ \frac{2p_i V}{RT_1} &= \frac{p_f V}{RT_1} + \frac{p_f V}{RT_2} \\ \frac{2p_i V}{RT_1} &= \frac{p_f V}{R} \left(\frac{T_2 + T_1}{T_1 T_2}\right) \\ p_f &= \frac{2p_i T_2}{T_1 + T_2} \end{aligned}$$

3. (d): 
$$\lambda = \frac{h}{p} = \frac{h}{\sqrt{2mK.E.}} = \frac{h}{\sqrt{2meV}}$$
 (:: K.E. = eV]  
 $\frac{h}{\lambda} = \sqrt{2meV}$ 

4. (a):  $[O = N = O]^+$ *sp* hybridisation





5. (d): The required equation is

$$C_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}; \Delta H_f = ?$$

Given that,

$$C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H_1 = -393.5 \text{ kJ/mol}^{-1}$$
...(i)

$$CO_{(g)} + \frac{1}{2}O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H_2 = -283.5 \text{ kJ mol}^{-1}$$
...(ii)

Subtracting eqn (ii) from eqn (i) will give the required equation.

$$\Rightarrow \Delta H_f = \Delta H_1 - \Delta H_2 = -393.5 - (-283.5) \\= -110 \text{ kJ mol}^{-1}$$

6. (c) : Number of moles of glucose  $(n_{C_6H_{12}O_6})$ 

$$=\frac{18}{180}=0.1$$
 mol

Number of moles of water  $(n_{\text{H}_2\text{O}}) = \frac{178.2}{18} = 9.9 \text{ mol}$ 

Mole fraction of water in solution  $(x_{\rm H_2O})$ 

$$=\frac{n_{\rm H_2O}}{n_{\rm H_2O}+n_{\rm C_6H_{12}O_6}}=\frac{9.9}{10}=0.99$$

7.

Vapour pressure of water in aqueous solution,  $p_{\rm H_2O} = p_{\rm H_2O}^{\circ} x_{\rm H_2O} = 760 \text{ torr} \times 0.99 = 752.4 \text{ torr}$ 

$$\begin{array}{cccc}
(c): & A & + & B & \overleftarrow{\phantom{abc}} & C & + & D\\
\text{Initial conc.} & 1 & 1 & 1 & 1\\
\text{At equilibrium} & 1-x & 1-x & 1+x & 1+x\\
\text{Now,} & K_c = \frac{[C][D]}{[A][B]}\\
i.e., & 100 = \frac{(1+x)^2}{(1-x)^2} \implies 10 = \frac{1+x}{1-x}
\end{array}$$

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

8. (d): Galvanization is a method of rust prevention by applying zinc coating which acts as a sacrificial metal.

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9. (b): Decomposition of  $H_2O_2$  is represented as  $H_2O_2 \longrightarrow H_2O + \frac{1}{2}O_2$ 

Concentration of  $H_2O_2$  decreases from 0.5 M to

0.125 M in 50 minutes *i.e.*, reduced to  $\frac{1}{4}$  th . So, it can be represented as

$$0.5 \xrightarrow{t_{1/2}} 0.25 \xrightarrow{t_{1/2}} 0.125$$

$$50 \text{ min}$$

 $\Rightarrow 2t_{1/2} = 50 \text{ min} \Rightarrow t_{1/2} = 25 \text{ min}$ Now, for a first order reaction,

$$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{25} \operatorname{min}^{-1}$$

Rate of  $H_2O_2$  decomposition =  $k[H_2O_2]$ 

$$= \frac{0.693}{25} \times (0.05) = 1.386 \times 10^{-3} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$$
  
Rate of formation of  $\text{O}_2 = \frac{1}{2} \times \text{rate of } \text{H}_2\text{O}_2$ 

decomposition

$$=\frac{1}{2} \times 1.386 \times 10^{-3}$$

$$= 6.93 \times 10^{-4} \text{ mol } \text{L}^{-1} \text{ min}^{-1}$$

**10.** (c) : For the Freundlich adsorption isotherm, equation is

$$\log\left(\frac{x}{m}\right) = \log k + \frac{1}{n}\log p$$

Now, comparing this equation with y = mx + c, slope  $(m) = \frac{1}{n}$ ; intercept  $(c) = \log k$ 

- 11. (d): Rb, Na and K belong to group 1 which on losing one electron attain noble gas configuration and thus, have low value of ionisation energies. On the other hand, Sc with electronic configuration [Ar]  $3d^{1}4s^{2}$  loses its electron from 4*s*-orbital thus, it does not achieve that much stable configuration as in group 1 elements. Hence, it shows higher first ionisation energy.
- **12.** (c) : Froth floatation method is suitable for sulphide ores thus, PbS *i.e.*, galena is best concentrated by this method.
- **13.** (c): In the condensed phase, there is extensive intermolecular hydrogen bonding in water molecules but not intramolecular hydrogen bonding.

14. (d): Li + 
$$O_2 \longrightarrow Li_2O_{Normal oxide}$$
  
 $2Na + O_2 \longrightarrow Na_2O_2_{Peroxide}$   
 $K + O_2 \longrightarrow KO_2$   
 $Superoxide$   
15. (a):  $4Zn + 10HNO_{3(dil.)} \longrightarrow 4Zn(NO_3)_2$   
 $+ N_2O + 5H_2O$   
 $Zn + 4HNO_{3(conc.)} \longrightarrow Zn(NO_3)_2 + 2NO_2 + 2H_2O$   
16. (a): Name Formula Oxidation state  
Orthophosphorous acid  $H_3PO_3$  + 3  
Pyrophosphorous acid  $H_4P_2O_5$  + 3  
Hypophosphoric acid  $H_4P_2O_6$  + 4  
Pyrophosphoric acid  $H_4P_2O_7$  + 5  
17. (b):  $CrO_2$  is metallic and ferromagnetic.  
18. (b):  $[Cr(H_2O)_6]^{2+}$   
 $Cr^{2+} \rightarrow [Ar]3d^74s^0$   
 $\boxed{11111} \uparrow \uparrow \uparrow ]$   
 $3$  unpaired electrons  
 $[Fe(H_2O)_6]^{2+}$   
 $Fe^{2+} \rightarrow [Ar]3d^64s^0$ 

$$\frac{3d}{[1] \uparrow \uparrow \uparrow \uparrow} \qquad 4s$$

$$4 \text{ unpaired electrons} \qquad [Mn(H_2O)_6]^{2+}$$

$$Mn^{2+} \rightarrow [Ar]3d^54s^0$$

$$\begin{array}{c} 3d \\ \hline \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \uparrow \\ 5 \text{ unpaired electrons} \end{array}$$

Hence,  $[Cr(H_2O)_6]^{2+}$  and  $[Fe(H_2O)_6]^{2+}$  have same number of unpaired electrons *i.e.*, same magnetic moment.

**19.** (b): [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] has two geometrical isomers but both are optically inactive due to plane of symmetry.

 $cis[Co(en)_2Cl_2]Cl$  is optically active.





 $trans[Co(en)_2Cl_2]Cl$  is optically inactive due to plane of symmetry.

 $[Co(NH_3)_4Cl_2]Cl$  has two geometrical isomers but both are optically inactive due to plane of symmetry.

- **20.** (c) : Fluoride, lead and iron are present within their permissible limits but nitrate ion which has permissible value of 50 ppm, is present in much higher amount *i.e.*, 100 ppm which makes the water unfit for drinking.
- **21.** (d): Glycerol is separated from spent-lye by distillation under reduced pressure because under normal distillation glycerol having boiling point of 290°C may decompose.



23. (b):



24. (a) : The reaction can follow  $S_N 1$  or  $E_2$  mechanism thus, all the given three products are possible.



$$CH_{3}-CH \stackrel{!}{=} CH_{2} \stackrel{CI^{+}}{\longrightarrow} CH_{3}- \stackrel{+}{CH} - CH_{2}-CI$$

$$\xrightarrow{OH^{-}} CH_{3}-CH - CH_{2}-CI$$

$$\stackrel{I}{\longrightarrow} CH_{3}-CH - CH_{2}-CI$$

$$RNH_2 + 2NaBr + Na_2CO_3 + 2H_2O_3$$

27. (d): High density polythene is used to manufacture buckets, dust-bins, etc. while low density polythene is used for manufacturing flexible pipes, insulation of electrical wires etc. due to its poor conductivity and slight flexibility.

28. (c) : Cysteine : 
$$(HS) - CH_2 - CH_2$$
  
 $V$ 
Thiol group

- **29.** (b): Sodium lauryl sulphate :  $CH_3(CH_2)_{11}OSO_3^- Na^+$
- **30.** (b): Region-2 is the blue flame which is the hottest region of Bunsen flame.







Hello students!! Hope you all are doing fine. Chemistry is a subject of Concepts as you can see both of them starts with 'C' <sup>(()</sup>. This month, I am presenting Concepts of Acids and Bases and this is the first phase. You have seen that questions on Acids and Bases have always been an important topic in JEE. Hope you will like and appreciate my efforts as before.

\*Arunava Sarkar

### IMPACT OF ELECTRONIC EFFECTS ON ACIDITY AND BASICITY

#### **Acidity Corner**

○ Concept-1 : Electron withdrawing groups (EWGs) *i.e.*, -I and -R effect containing groups increase acidity whereas electron donating groups (EDGs) decrease acidity. EDGs are those groups which contain +I and +R effects.

Compound	pK <sub>a</sub>	
CH <sub>3</sub> COOH	4.8	
FCH <sub>2</sub> COOH	2.7	As per the power of $-I$
ClCH <sub>2</sub> COOH	2.8	$effect \Longrightarrow F > Cl > Br > I$
BrCH <sub>2</sub> COOH	2.9	
ICH <sub>2</sub> COOH	3.1	

So, according to the acidic strength the order is :  $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH > CH_3COOH$ 

• **Concept-2**: More will be the number of *-I* effect containing groups, more will be the acidity. For example,

Compound	pK <sub>a</sub>
CCl <sub>3</sub> COOH	0.64
ClCH <sub>2</sub> COOH	2.8
Cl <sub>2</sub> CHCOOH	1.3

So, as per the acidity the order is : CCl<sub>3</sub>COOH > Cl<sub>2</sub>CHCOOH > ClCH<sub>2</sub>COOH

• **Concept-3 :** Formic acid is stronger than benzoic acid.

Compound	р <i>К</i> а
НСООН	3.8
C <sub>6</sub> H <sub>5</sub> COOH	4.2

Both the compounds have stabilized corresponding carboxylates and therefore, they can release H<sup>+</sup>.



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This Ph-group has both -I and +R effects.

-I is electron withdrawing whereas +R is electron donating. Point to be noted is +R > -I. Hence, overall,

stability is lesser than that of HCO $\overline{O}$ . This is why as per acidity, HCOOH > PhCOOH.

• **Concept-4**:  $CF_3COOH$  is  $10^5$  times stronger than  $CH_3COOH$ .  $CF_3COOH$  is having a p $K_a$  value of 0.2 (in some books it is given as zero which is probably not correct). There are so many acids with the negative values of  $pK_a$  as shown below :

Compound	р <i>К<sub>а</sub></i>
HI	-10
HBr	-9
HCl	-7
$H_2SO_4$	-5
HNO <sub>3</sub>	-1.3
$\overset{o}{\overset{H}{\operatorname{CH}}}_{3}-\overset{H}{\overset{H}{\operatorname{CNH}}}_{2}$	0.0
$CH_3 - C \equiv NH$	-10.1
CH <sub>3</sub> - <sup>+</sup> <sub>5</sub> H <sub>2</sub>	-6.8
$CH_3CH_2 \overset{+}{O} -H$	-2.4
CH <sub>3</sub> SO <sub>3</sub> H	-1.2

Concept-5: Two chlorine atoms have more electron withdrawing power than that of single fluorine (-F) atom. *i.e.*, Cl<sub>2</sub>CHCOOH is more powerful acid than FCH<sub>2</sub>COOH.

Compound	F	oK <sub>a</sub>
Cl <sub>2</sub> CHCOOH	1.3	double
FCH <sub>2</sub> COOH	2.6	

• **Concept-6**: Among the weak inorganic acids (mostly those which is often used), the following acidity order is observed.

 $\mathrm{H_2CO_3} > \mathrm{H_2S} > \mathrm{HCN}$ 



Compound	pK <sub>a</sub>
H <sub>2</sub> CO <sub>3</sub>	6.4
H <sub>2</sub> S	7.0
HCN	9.1

• **Concept-7**: For alcohols, if *R* is bigger,  $pK_a$  will be more and more. So, as per acidity the following order between thiol, methanol, water and higher alcohol is observed.

Thiol (RSH) >  $CH_3OH$  >  $H_2O$  >  $CH_3CH_2OH$ 

	5 1
Compound	pK <sub>a</sub>
CH <sub>3</sub> CH <sub>2</sub> SH	10.5
CH <sub>3</sub> OH	15.5
H <sub>2</sub> O	15.7
CH <sub>3</sub> CH <sub>2</sub> OH	16.0
$\mathbf{v}$ Bigger alkyl(+ $R$ ) group	

 Concept-8 : Acidic character of the compounds (aliphatic or aromatic) containing carbonyl group (C=O) is given in the following table.

Compound	pK <sub>a</sub>
Organic acid (aliphatic) O $CH_3 - C - OH$	4.8
О СН <sub>3</sub> -С-Н	17
$CH_3 - C - CH_3$	20
$CH_3 - C - OEt$	24.5
$CH_3 - C - NH_2$	16
$CH_3 - C - O - O - H$	8.2
O C C C C C H <sub>3</sub>	16.0
О Н-С-ОН	3.8
$CH_{3} - C - CH_{2} - C - OEt$ ( $\beta$ -keto ester)	10.7

$\begin{array}{c} O & O \\ H_3 - C - C H_2 - C - C H_3 \end{array}$	8.9
НСНО	13.3
Organic acid (aromatic) C <sub>6</sub> H <sub>5</sub> COOH	4.2
C <sub>6</sub> H <sub>5</sub> CHO	14.9

The general acidity order of the compounds containing C=O group is :

Organic acid > peracid > aliphatic diketone >  $\beta$ -keto ester > HCHO > benzaldehyde (PhCHO) > acid amide > aliphatic aldehyde (other than HCHO) > aliphatic ketone > aromatic ketone > acid halide (-F > -Cl > -Br > -I) > acid anhydride > ester (In many occassions, exception to the above order is observed because for specific class or specific compound slight changes may appear).

• **Concept-9**: Acidity of hydrocarbons is always a great area of interest. Their acidity order is :

alkyne > alkene > alkane (decreasing order of acidity)

But when popular hydrocarbons intervene then the acidity can be written on the basis of  $pK_a$  values as given below :

Compound	pK <sub>a</sub>
$CH_4$	50
CH <sub>3</sub> —CH <sub>3</sub>	50
$CH_2 = CH_2$	44
СH <sub>2</sub> =СH-СH <sub>3</sub>	43
	43
<u>С</u> Н3	41
$\bigtriangledown$	46
$\begin{bmatrix} \mathrm{NH}_3 \\ \mathrm{CH}_3 \mathrm{NH}_2 \\ \mathrm{H}_2 \end{bmatrix}$	<ul> <li>36 This is just for comparative study with</li> <li>35 hydrocarbons</li> </ul>
HC≡CH	25

Hence, the acidity order is :

 $-C \equiv C \rightarrow H_2 > NH_3 > CH_3NH_2$  (other aliphatic amines) > toluene (for other alkyl substituted benzene it may differ) > benzene  $\approx CH_3CH = CH_2$  $sp^2$ 

> 
$$CH_2 = CH_2$$
 > alkanes  $(CH_4 \approx CH_3 - CH_3)$   
 $sp^2$   $sp^3$ 

- **Concept-10 :** In case of inorganic acids there are a few points which should be remembered.
  - (a) For oxy acids, with the increase in the oxidation number of the central element acidic nature increases. For example,  $u^{+7}_{+10} = u^{+6}_{+10} = u^{+4}_{+10} = u^{+2}_{+10}$

$$HClO_4 > H_2SO_4 > H_2SO_3 > HNO_2$$
  
The above rule is also valid for the same

- (b) The above rule is also valid for the same central element or key element. For example,  ${}^{+7}_{HClO_4} > {}^{+5}_{HClO_3} > {}^{+3}_{HClO_2} > {}^{+1}_{HOCl} ({}^{+1}_{HClO})$
- (c) For moving from left to right in the same period acidity increases.
   H<sub>2</sub>SiO<sub>4</sub> < H<sub>3</sub>PO<sub>4</sub> < H<sub>2</sub>SO<sub>4</sub> < HClO<sub>4</sub>
- (d) If electronegativity increases, acidic nature also increases. For example, HOCl > HOBr > HOI HClO<sub>4</sub> > HBrO<sub>4</sub> > HIO<sub>4</sub>
- (e) If you keep oxidation state same then bigger atom containing acid will be less acidic.
  HNO<sub>3</sub> > HPO<sub>3</sub> [as per size, N < P]</li>
  HClO<sub>4</sub> > HBrO<sub>4</sub>
  Point (e) can be correlated with point (d).

(f) If more electronegative atom is attached with H atom then this will create higher acidity in the compound. For example,

 $H-F > H-OH > H-NH_2 > H-CH_3$ 

(g) If the orbital overlapped with the 1s-orbital of H is bigger then the overlapping becomes weak and release of proton becomes easy. This is why, acidic order is HI > HBr > HCl > HF. or  $H_2Te > H_2Se > H_2S > H_2O$ 

The glimpse of acidic character of inorganic acids is represented in the following table.

Compound	pK <sub>a</sub>
HI	-10
HBr	-9
HCl	-7
H <sub>2</sub> SO <sub>4</sub>	-5
H <sub>3</sub> O <sup>+</sup>	-1.7
HNO <sub>3</sub>	-1.3
HF	3.2
HNO <sub>2</sub>	3.4

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H <sub>3</sub> PO <sub>4</sub>	2.1
$H_2CO_3$	6.4
H <sub>2</sub> S	7.0
HCN	9.2
H <sub>2</sub> O	15.7
Just for CH <sub>3</sub> OH	15.5
comparative $C_2H_5OH$	16.0
<sup>study</sup> PhOH	10.0
Just for $\begin{bmatrix} H_2 N - \dot{N} H_3 \\ N H_2 \end{bmatrix}$	8.1 36
study CH <sub>3</sub> NH <sub>2</sub>	40
H <sub>2</sub>	35
HCO <sub>3</sub>	10.2
$H_2PO_4^-$	7.2
$HSO_4^-$	2.0
$\begin{array}{c} \text{Just for}\\ \text{comparative}\\ \text{study} \end{array} \begin{array}{c} \text{CH}_{3}\text{COOH}\\ \text{NH}_{4}^{+} \end{array}$	4.75 or 4.8 9.2

Hence, the acidity order is :

$$\begin{split} &\text{HClO}_4 > \text{HI} > \text{HBr} > \text{HCl} > \text{H}_2\text{SO}_4 > \text{H}_3\text{O}^+ > \text{HNO}_3 \\ & > \text{HSO}_4^- > \text{H}_3\text{PO}_4 > \text{HF} > \text{CH}_3\text{COOH} > \text{H}_2\text{CO}_3 \\ & > \text{H}_2\text{S} > \text{H}_2\text{PO}_4^- > \text{H}_2\text{N} - \overset{+}{\text{NH}}_3 > \text{HCN} \approx \text{NH}_4^+ > \\ & \text{PhOH} > \text{CH}_3\text{OH} > \text{H}_2\text{O} > \text{C}_2\text{H}_5\text{OH} > \text{H}_2 > \text{NH}_3 > \\ & \text{CH}_3\text{NH}_2 > \text{CH}_4 \approx \text{CH}_3 - \text{CH}_3 \end{split}$$

Therefore, the basic strength of corresponding conjugate base will be

$$\begin{split} & \text{ClO}_{4}^{-} < \text{I}^{-} < \text{Br}^{-} < \text{Cl}^{-} < \text{HSO}_{4}^{-} < \text{H}_2\text{O} < \text{NO}_{3}^{-} < \\ & \text{SO}_{4}^{2^-} < \text{H}_2\text{PO}_{4}^{-} < \text{F}^{-} < \text{CH}_3\text{COO}^{-} < \text{HCO}_{3}^{-} < \text{HS}^{-} < \\ & \text{HPO}_{4}^{2^-} < \text{NH}_2 - \text{NH}_2 < \bar{\text{CN}} \approx \text{NH}_3 < \text{PhO}^{-} \\ & < \text{CH}_3\text{O}^{-} < \bar{\text{OH}} < \text{C}_2\text{H}_5\text{O}^{-} < \text{H}^{-} < \bar{\text{NH}}_2 < \text{CH}_3\bar{\text{NH}} \\ & < \bar{\text{CH}}_3 \approx \text{CH}_3 - \bar{\text{CH}}_2 \end{split}$$

O Concept-11 :

Compound	pK <sub>a</sub>
Benzene sulphonic acid	2.554
Benzoic acid	4.2

So, sulphonic acids are stronger than carboxylic acids.



Because sulphonate ion is very well resonance stabilized as dispersal of negative charge takes place over three oxygen atoms as shown below :



On the other hand,

$$\begin{array}{c} O \\ \parallel \\ Ph-C-O-H \xrightarrow{H_2O} & Ph-C-O^- + H_3O^+ \\ Benzoic acid & Benzoate ion \end{array}$$

The negative charge over oxygen atom can be dispersed in between two oxygen atoms as shown below :

$$Ph-C \xrightarrow{O} O^{-} \leftrightarrow Ph-C \xrightarrow{O} = \begin{bmatrix} O \\ I \\ Ph-C \xrightarrow{} O^{-} \leftrightarrow Ph-C \xrightarrow{} O = \begin{bmatrix} O \\ I \\ Ph-C \xrightarrow{} O \end{bmatrix}^{C}$$

So, due to more stability of the corresponding conjugate base, benzene sulphonic acid is stronger than benzoic acid. Moreover, due to presence of three highly electronegative oxygen atoms in benzene sulphonic acid, release of  $H^+$  gets facilitated.

• **Concept-12 :** Branching leads to lowering of acidity. Consider the following table.

Compound	pK <sub>a</sub>
CH <sub>3</sub> OH	15.5
CH <sub>3</sub> CH <sub>2</sub> OH	15.9 or 16.0
CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> OH	16.1
(CH <sub>3</sub> ) <sub>3</sub> COH	17

The reason behind this is that if conjugate base will be highly hindered then it cannot be well solvated so solvation energy will be less and it will lead to the destabilisation of the corresponding conjugate base and lowering of acidity of the corresponding acid.





- 1. Which of the following molecules will give maximum rate of reaction with  $S_N 2$  mechanism?
  - (a)  $CH_3 CH_2 Cl$  (b)  $CH_3 \overset{i}{C} CH_2 Cl_{i}$   $NO_2$ (c)  $CH_2 - CH_2 - Cl$  (d)  $CH_2 = CH - Cl$
- **2.** Which of the following compounds is maximum reactive towards nucleophile?



**3.** Which of the following is major product in given reaction?



**4.** Which of the following is major product in given reaction?

СН<sub>3</sub>

 $\xrightarrow{(i) \text{ KOH}} \text{Product } (P)$ 

CH<sub>3</sub>



5. Consider the following reaction, OH CH<sub>3</sub>-CH-CH<sub>3</sub>  $\xrightarrow{(i) CaOCl_2 + H_2O}$  A + B

If product A is  $CHCl_3$  then product B will be

(a) 
$$CH_3 = \overset{O}{\overset{}_{\text{C}}} = \overset{O}{\overset{}_{\text{O}}} H$$
 (b)  $CH_3 = \overset{O}{\overset{}_{\text{C}}} = CH_3$ 

(c) 
$$CH_3 - \ddot{C} - \ddot{C} - CH_3$$
  
O O  
 $\parallel$   $\parallel$ 

$$(d) CH_3 - C - O - C - CH_3$$

- **6.** *p*-type semiconductor is formed when
  - (i) As impurity is mixed in Si
  - (ii) Al impurity is mixed in Si
  - (iii) B impurity is mixed in Ge
  - (iv) P impurity is mixed in Ge
  - (a) (i) and (ii) (b) (i) and (iv)
  - (c) (ii) and (iii) (d) (ii) and (iv)
- 7. Plot of log x/m against log *P* is a straight line inclined at an angle of 45°. When the pressure is 0.5 atm and Freundlich parameter, *k* is 10, the amount of solute adsorbed per gram of adsorbent will be (log 5 = 0.6990)

8. Paramagnetic oxides are

(a) N<sub>2</sub>O<sub>4</sub>, NO<sub>2</sub>
(b) NO, ClO<sub>2</sub>
(c) P<sub>4</sub>O<sub>6</sub>, P<sub>4</sub>O<sub>10</sub>
(d) N<sub>2</sub>O<sub>5</sub>, O<sub>2</sub><sup>+</sup>

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9. The rate law for a reaction between the substances *A* and *B* is given by rate =  $k[A]^n[B]^m$ . On doubling the concentration of *A* and halving the concentration of *B*, the ratio of the new rate to the earlier rate of the reaction will be as

(a) $1/2^{m+n}$	(b) $(m + n)$
-----------------	---------------

(c) $(n - m)$	(d) $2^{(n-m)}$
---------------	-----------------

- **10.** Which of the following can exhibit geometrical isomerism?
  - (a)  $[MnBr_4]^{2-}$  (b)  $[Pt(NH_3)_3Cl]^+$

(c)  $[PtCl_2(PPh_3)_2]$  (d)  $[Fe(H_2O)_5NO]^{2+}$ 

- 11. Xenon oxytetrafluoride is
  - (a) square planar (b) square bipyramidal
  - (c) octahedral (d) square pyramidal.
- 12. Consider a binary mixture of volatile liquids. If at  $x_A = 0.4$  the vapour pressure of solution is 580 torr then the mixture could be
  - $(p_A^{\circ} = 300 \text{ torr}, p_B^{\circ} = 800 \text{ torr})$
  - (a) CHCl<sub>3</sub> CH<sub>3</sub>COCH<sub>3</sub> (b)  $C_6H_5Cl$   $C_6H_5Br$
  - (c)  $C_6H_6 C_6H_5CH_3$  (d)  $nC_6H_{14} nC_7H_{16}$
- 13. Solution having osmotic pressure nearer to that of an equimolar solution of  $K_4[Fe(CN)_6]$  is
  - (a)  $Na_2SO_4$  (b)  $BaCl_2$
  - (c)  $Al_2(SO_4)_3$  (d)  $C_{12}H_{22}O_{11}$
- **14.**  $4f^{14}$  configuration is observed in
  - (a) Dy and Pm (b) Lu and La
  - (c) Yb and Lu (d) Tm and Lu.
- **15.** Given that (at T = 298 K)

 $\begin{aligned} & \text{Cu}_{(s)} |\text{Cu}^{2+}(1.0 \text{ M})| |\text{Ag}^{+}(1.0 \text{ M})| \text{Ag}_{(s)}; \ E_{\text{cell}}^{\circ} = 0.46 \text{ V} \\ & \text{Zn}_{(s)} |\text{Zn}^{2+}(0.1 \text{ M})| |\text{Cu}^{2+}(1.0 \text{ M})| \text{Cu}_{(s)}; E_{\text{cell}}^{\circ} = 1.10 \text{ V} \\ & \text{Then } E_{\text{cell}} \text{ for} \\ & \text{Zn} |\text{Zn}^{2+}(0.1 \text{ M})| |\text{Ag}^{+}(1.0 \text{ M})| \text{Ag at } 298 \text{ K will be} \end{aligned}$ 

(a) 1.59 V (b) 1.53 V (c) 2.53 V

- (d) cannot be calculated due to insufficient data.
- **16.** Which of the following options show correct matches?

p.

Column I

**Column II**  $\Lambda_m^c$ 

 $\overline{\Lambda_m^{\circ}}$ 

(ii) Molar conductance,  $\Lambda_m$ 

Kohlrausch law

- (iii) Specific r.  $\Lambda_m^{\circ}$  of Ca<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> conductance ( $\kappa$ ) = 3( $\Lambda_m^{\circ}$ )<sub>Ca<sup>2+</sup></sub> + 2( $\Lambda_m^{\circ}$ )<sub>PO<sub>4</sub></sub><sup>3</sup>
- (iv) Degree of ionisation s.  $\frac{\kappa \times 1000}{M}$

- (a) (i) -r, (ii) -p, (iii) -q, (iv) -s(b) (i) -s, (ii) -p, (iii) -q, (iv) -s(c) (i) -r, (ii) -s, (iii) -q, (iv) -p(d) (i) -p, (ii) -s, (iii) -q, (iv) -r
- **17.** A fuel cell involves combustion of the butane at 1 atm and 298 Kelvin

$$C_4H_{10(g)} + \frac{13}{2}O_{2(g)} \longrightarrow 4CO_{2(g)} + 5H_2O_{(l)};$$
  
$$\Delta G^{\circ} = -2746 \text{ kJ/mole}$$

What is  $E^{\circ}$  of this cell?

(a) +4.74 V (b) +0.547 V

(c) +1.09 V (d) +4.37 V

- **18.** An element "A" has face centered cubic structure with edge length equal to 361 pm. The radius of atom "A" is
  - (a) 127.6 pm (b) 180.5 pm
  - (c) 160.5 pm (d) 64 pm
- **19.** LiF and CsI are less soluble in water. What factors are responsible for this?
  - (a) LiF : High ionic character CsI : High covalent character
  - (b) LiF: Strong reductant CsI : Strong reductant
  - (c) LiF : High Hydration CsI : Less Hydration
  - (d) LiF : High lattice energy CsI : Low hydration energy
- 20. In the disproportionation reaction :
  - $H_3PO_2 \rightarrow PH_3 + H_3PO_3$ ; if molecular weight of  $H_3PO_2$  is *m* then the equivalent mass of  $H_3PO_2$  will be

(a) 
$$\frac{3m}{4}$$
 (b)  $\frac{4}{3}m$ 

- (c)  $\frac{3m}{5}$  (d) none of these.
- **21.** Which of the following order is correct?
  - (a) Si Si > C C > Ge Ge (Bond energy)
  - (b) H H > F F > C C (Bond energy)

(c) Ge < Sn < Pb (Ability of  $ns^2e^-$  to participate in bonding)

- (d)  $SiH_4 > SnH_4 > PbH_4 > CH_4$  (ease of hydrolysis)
- **22.** Match the following :

Element			Property	
	(i)	С	p.	Used as semiconductor
	(ii)	Pb	q.	Forms most acidic oxide
	(iii)	Si	r.	Commonly found in +2 state
	(iv)	Ge	s.	Purified by zone refining



(i)

- (a) (i) s, (ii) r, (iii) q, (iv) p (b) (i) - p, (ii) - q, (iii) - r, (iv) - s (c) (i) - q, (ii) - s, (iii) - p, (iv) - r
- (d) (i) q, (ii) r, (iii) p, (iv) s
- **23.** The variation of extent of adsorption

with

pressure at a given constant temperature is given in following figure :



Which of the following relations between temperatures is correct?

- (a)  $T_1 = T_2 = T_3$ (b)  $T_1 < T_2 < T_3$
- (c)  $T_3 < T_2 < T_1$ (d) Cannot be predicted
- 24. Oxyacid with maximum P—H bonds is
  - (a) hypophosphorous acid
  - (b) cyclotrimetaphosphoric acid
  - (c) hypophosphoric acid
  - (d) orthophosphorous acid.
- **25.** 0.85% w/V solution of NaNO<sub>3</sub> is 90% dissociated at 27°C. Calculate its osmotic pressure (in atm).
  - (a) 4.67 atm (b) 5.74 atm
  - (c) 3.23 atm (d) 46.4 atm
- 26. Ozone can be quantitatively estimated by (a) KI, Na<sub>2</sub>SO<sub>4</sub> (b) PbS,  $Na_2SO_4$

(c) NO, 
$$I_2$$
 (d) KI, Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>

- 27. Which of the following orders is correct? (a) HF > HCl > HBr > HI (Melting point)
  - (b)  $F_2 > Cl_2 > Br_2 > I_2$  (Bond energy)
  - (c)  $HOCl > HClO_2 > HClO_3 > HClO_4$  (oxidising

nature)

- (d)  $F_2 > Br_2 > Cl_2 > I_2$  (oxidising nature)
- 28. Which of the following orders is correct?
  - (a) He > Ne > Ar > Kr (Adsorption tendency)
  - (b) He > Ne > Ar > Kr (Critical temperature)
  - (c) He > Ne > Ar > Kr (Boiling point)
  - (d) Xe > Kr > Ar > Ne (Polarisation)
- 29. 99% of a first order reaction was completed in 64 minutes, when will 99.9% of the reaction get completed?

(a)	50 min	(b)	48 min
( )	a.a	(1)	~ .

- (c) 32 min (d) 96 min
- **30.** For the reaction,

$$N_{2(g)} + 3H_{2(g)} \Longrightarrow 2NH_{3(g)}; K_p = 5 \times 10^{-5} \text{ at } 25^{\circ}C$$
  
 $\Delta G^{\circ}$  for the reaction will be ( $R = 8.31 \text{ J mol}^{-1} \text{ K}^{-1}$ )

(a) 24.5 kJ  
(b) 40.5 kJ  
(c) -7.3 kJ  
(d) -40.5 kJ  
31. 
$$CH_3 - C \equiv C - H \xrightarrow{2HCl} A \xrightarrow{Zn} B$$
; *B* is  
(a)  $CH_3 - C \equiv C - H$   
(b)  $CH_3 - C \equiv C - CH_3$   
(c)  $CH_3 - CH = CH_2$   
(d)  $CH_3 - C \equiv C - CH_3$   
 $CH_3 - C \equiv C - CH_3$   

- **32.** How many moles of  $Na^+$  ions are there in 20 mL of 0.4 M Na<sub>3</sub>PO<sub>4</sub>?
  - (a) 0.008 (b) 0.024 (c) 0.05 (d) 0.20

**33.** 
$$H_2NCOCH_2CH_2CONH_2 \xrightarrow{Br_2, OH}$$

- (a)  $H_2NCO(CH_2)_3NH_2$
- (b) BrNHCO(CH<sub>2</sub>)<sub>3</sub>CONH<sub>2</sub>
- (c) BrNHCO(CH<sub>2</sub>)<sub>3</sub>CONHBr
- (d)  $H_2N(CH_2)_2NH_2$

**34.** The IUPAC name of 
$$\checkmark \downarrow \downarrow \downarrow Cl O$$
 is

- (a) 3, 4-dimethylpentanoyl chloride
- (b) 1-chloro-1-oxo-2, 3-dimethylpentane
- (c) 2-ethyl-3-methylbutanoyl chloride
- (d) 2, 3-dimethylpentanoyl chloride.
- **35.** The products (*A*) and (*B*) of the following reaction,  $CH_3CH_2NH_2 + CH_3MgBr \rightarrow A + B$ are
  - (a) CH<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> and NH<sub>2</sub>MgBr
  - (b) CH<sub>3</sub>CH<sub>2</sub>NHCH<sub>3</sub> and MgBr<sub>2</sub>
  - (c) CH<sub>3</sub>CH<sub>2</sub>N(CH<sub>3</sub>)<sub>2</sub> and MgBr<sub>2</sub>
  - (d) CH<sub>3</sub>CH<sub>2</sub>NHMgBr and CH<sub>4</sub>
- 36. An example of Perkin's reaction is
  - (a)  $C_6H_5CHO + CH_3NO_2 \xrightarrow{KOH}$  $C_6H_5CH=CHNO_2$

(b) 
$$C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{Alc. NH_3} CH CH=CHCOOH$$

$$C_6 H_5 CH = CHCOOH$$

(c) 
$$C_6H_5CHO + CH_3CHO \xrightarrow{NaOH} C_6H_5CH=CHCHO$$

(d) 
$$C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa} C_6H_5CH=CHCOOH$$

- 37. Which of the following is known as oil of wintergreen?
  - (a) Phenyl benzoate (b) Phenyl salicylate
  - (c) Phenyl acetate (d) Methyl salicylate



38. Which of the following compounds has asymmetric centre?



39. Select the compound in which the lone pair of nitrogen is not delocalised over the benzene ring.



40. The final product(s) of this reaction is/are



**41.** What is *X* in the following reaction?



OH (b)  $H_3C - CH_2 - CH_2 - CH_2 - CH_2 - CHO$  $CH_3$ (c) CH<sub>3</sub>CH(CH<sub>3</sub>)CH<sub>2</sub>COCH<sub>3</sub> (d)  $H_3C - CH - CH - CH - CH_3$ Ĭ ÓН CH<sub>3</sub> 42. Rubber is a polymer of (b) ethylene (a) pyrene (c) isoprene (d) urea. ·H **43.**  $A \xrightarrow{\text{PCl}_5} B + H_2 -$ Pd-BaSO<sub>4</sub> A is NH<sub>2</sub> Η (b) (a)  $NH_2$ OH (c)

44. The correct order of ease of dehydration of the following compounds is



- 45. Which of the following statements is not correct? (a)  $K[PtCl_3(\pi-C_2H_4)]$  Zeise's salt has a planar anion.
  - (b)  $[Co(NH_3)_3Cl_3]$  will not have optical isomers.
  - (c) In optically active octahedral complex,  $[Fe(EDTA)]^{2-}$  coordination number of Fe is six.
  - (d) [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl and PtCl<sub>2</sub>.4NH<sub>3</sub> can be differentiated by AgNO3 solution qualitatively.

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





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SOLUTIONS 2. (b) 1. (c) Ph.  $C = O + CH_3CHO C = CH - CHO + H_2O$ (b): Aldol reaction 4. (b):  $CH_3 - CH - CH_3 \xrightarrow{CaOCl_2 + H_2O} (CH_3COO)_2Ca + CHCl_3 CH_3COCH_3 + CaCO_3 \xleftarrow{\Delta} (A)$ 6. (c) : Impurity of lower valency 7. (d):  $\log \frac{x}{m} = \log k + \frac{1}{n} \log P$ 8. (b) 9. (d) 10. (c) **11.** (d): XeOF<sub>4</sub> is square pyramidal. **12.** (a) :  $P_{\text{total}} = x_A p_A^{\circ} + x_B p_B^{\circ}$  $= 0.4 \times 300 + 0.6 \times 800 = 600$  torr  $P_{\text{observed}} < P_{\text{total}}$ ; thus, the deviation is negative. **13.** (c) : *i* = 5 **14.** (c) : Yb =  $4f^{14}5d^{0}6s^{2}$ ; Lu =  $4f^{14}5d^{1}6s^{2}$ 15. (a) : For cell,  $Cu_{(s)}|Cu^{2+}(1.0 \text{ M})||Ag^{+}(1.0 \text{ M})|Ag_{(s)}; E_{cell}^{\circ} = 0.46 \text{ V}$  $\Delta G^{\circ} = -2F \times 0.46 \qquad \dots (i)$ ...(i) For cell,  $Zn_{(s)}|Zn^{2+}(0.1 \text{ M})||Cu^{2+}(1.0 \text{ M})|Cu_{(s)}; E_{cell}^{\circ} = 1.10 \text{ V}$  $\Delta G^{\circ} = -2F \times 1.10$ Adding equations (i) and (ii), to get required equation,  $-2FE^{\circ}_{\text{cell}} = -2F \times 1.10 - 2F \times 0.46$  $-E_{\text{cell}}^{\circ} = -1.10 - 0.46$  $E_{\text{cell}}^{\circ} = 1.56 \text{ V}$  $E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Ag}^{+}]^{2}}$  $E_{\text{cell}} = 1.56 - \frac{0.059}{2} \log 0.1 = 1.56 + 0.03 = 1.59 \text{ V}$ 16. (c) **17.** (c) :  $\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$  $-2746 \times 10^{3} = -26 \times 96500 \times E_{cell}^{\circ}$  $E_{cell}^{o} = 1.09 \text{ V}$ **18. (a)**:  $r = \frac{a}{2\sqrt{2}} = \frac{361}{2\sqrt{2}}$  pm 19. (d) 20. (a)

**21.** (d): In option (c), inert pair effect; in option (d), octet expansion is maximum in Si.

22. (d) 23. (c)

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24. (a): H **25.** (a):  $i = 1 + \alpha = 1 + 0.9 = 1.9$ Osmotic pressure =  $i \times \frac{W_B}{M_B} \times \frac{RT}{V}$ Osmotic pressure =  $1.9 \times \frac{0.85}{85} \times \frac{0.082 \times 300}{100} \times 1000$ = 4.67 atm26. (d) 27. (c) 28. (d) **29.** (d):  $k = \frac{2.303}{64} \log \frac{100}{1}$ and  $k = \frac{2.303}{t} \log \frac{100}{0.1}$ ;  $t = 96 \min$ **30.** (a):  $\Delta G^{\circ} = -2.303 RT \log K_p$ 31. (d):  $CH_3 \xrightarrow[]{CH_3} CH_3 \xrightarrow[]{CH_3} CH_3$   $CH_3 \xrightarrow[]{CH_3} CH_3 \xrightarrow[]{CH_3} CH_3$   $CH_3 \xrightarrow[]{CH_3} CH_3 \xrightarrow[]{CH_3} CH_3$   $CH_3 CH_$  $+ ZnCl_{2}$ **32.** (b): No. of moles of Na<sub>3</sub>PO<sub>4</sub> =  $\frac{MV}{1000} = \frac{0.4 \times 20}{1000}$ No. of moles of Na<sup>+</sup> =  $3 \times \frac{0.4 \times 20}{1000} = 0.024$ 33. (d): Hofmann's bromamide reaction 34. (d) **35.** (d):  $CH_3CH_2 - NH - H + CH_3MgBr$ 37. (d) 36. (d) ×NH₂F ; no lone pair is present on 39. (c) nitrogen. 40. (b) 41. (a) COOH PCl COCl 43. (d): Rosenmund H<sub>2</sub>, (A)reduction Pd-BaSO<sub>4</sub> CHO

44. (b)

45. (d): [Pt(NH<sub>3</sub>)<sub>4</sub>]Cl<sub>2</sub> and [Co(NH<sub>3</sub>)<sub>5</sub>NO<sub>2</sub>]Cl both will give white ppt. with AgNO<sub>3</sub>.
[Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] will have geometrical isomers, *fac* and *mer*.



- 1. A  $S_N 2$  reaction at an asymmetric carbon of a compound always gives
  - (a) an enantiomer of the substrate
  - (b) a product with opposite rotation
  - (c) a mixture of diastereomers
  - (d) a single stereoisomer.
- 2. What volume of 2.5 M  $H_2SO_4$  is required to neutralize a solution containing 2.5 g NaOH?
  - (a) 10.2 mL (b) 18.4 mL
  - (c) 12.5 mL (d) 11.89 mL
- 3.  $0.1 \text{ M H}_2\text{SO}_4$  is diluted to  $0.01 \text{ M H}_2\text{SO}_4$ . Hence, its molar conductance will be
  - (b)  $\frac{1}{10}^{\text{th}}$  times (a) 10 times
  - (c) 100 times (d) 10000 times.
- 4. In the following sequence of reactions, *B* is
  - $CH_{3}CH_{2}COOH \xrightarrow{P/Br_{2}} A \xrightarrow{alc. KOH} B$ (a)  $CH_2 = CH - COOH$  (b)  $CH_2 - CH - COOH$ (c) CH<sub>3</sub>CH<sub>2</sub>COBr (d) CH<sub>3</sub>CH<sub>2</sub>OH
- 5. In  $NO_3^-$  ion, number of bond pairs and lone pairs of electrons on nitrogen atom are

(a)	2, 2	(b)	3, 1
(c)	1, 3	(d)	4,0

6. The chemical reaction,  $2O_3 \longrightarrow 3O_2$  proceeds as follows :

Step 1:  $O_3 \Longrightarrow O_2 + O$  ......(fast) Step 2 :  $O + O_3 \longrightarrow 2O_2$  ......(slow) The rate law expression should be (a)  $r = k' [O_3]^2$ (b)  $r = k' [O_3]^2 [O_2]^{-1}$ 

(c)  $r = k'[O_3][O_2]$ (d) unpredictable.

- 7. Which of the following phenols has lowest solubility in water?
  - (a) Phenol
- (b) o-Nitrophenol
- (d) *p*-Nitrophenol (c) *m*-Nitrophenol
- The complex  $[Fe(H_2O)_5NO]^{2+}$  is formed in the 8. brown ring test for nitrates when freshly prepared FeSO<sub>4</sub> solution is added to aqueous solution of NO<sub>3</sub><sup>-</sup> followed by addition of conc. H<sub>2</sub>SO<sub>4</sub>. Select the correct statement about this complex.
  - (a) Colour change is due to charge transfer.
  - (b) It has iron in +1 oxidation state and nitrosyl as NO<sup>+</sup>.
  - (c) It has magnetic moment of 3.87 BM confirming three unpaired electrons in Fe.
  - (d) All of these.
- 9. Amount of electricity that can deposit 108 g of silver from AgNO<sub>3</sub> solution is
  - (a) 1 ampere (b) 1 coulomb
  - (c) 1 faraday (d) none of these.
- **10.** The following sequence of reactions on *A* gives



11. Which of the following gases is evolved when ammonium dichromate (NH<sub>4</sub>)<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub>, is strongly heated?

(b) N<sub>2</sub>O (a)  $N_2$ (c) NO (d)  $NH_3$ 

- 12. Which of the following is a condensation polymer?
  - (b) Polythene (a) Polyisoprene
  - (c) Nylon (d) Polyacrylonitrile
- 13. The shape and hybridisation of some xenon oxyfluorides are given. Choose the wrong set.
  - (a) XeOF<sub>2</sub>-T-shape- $sp^3d$
  - (b) XeOF<sub>4</sub>-square pyramidal- $sp^3d^2$
  - (c)  $XeO_2F_2$ -distorted trigonal bipyramidal- $sp^3d$
  - (d)  $XeO_3F_2$ -octahedral- $sp^3d$ .
- 14. Benzene is first treated with conc. HNO<sub>3</sub> and conc. H<sub>2</sub>SO<sub>4</sub>. Then, the product formed is heated with chlorine and FeCl<sub>3</sub>. The final product is
  - (a) 2-chloronitrobenzene
  - (b) 4 -chloronitrobenzene
  - (c) 2,4,6-trichloronitrobenzene
  - (d) 3-chloronitrobenzene.
- **15.** For a reaction  $A \rightarrow B$ , the rate of reaction quadrupled when the concentration of A is doubled. The rate expression of the reaction is  $r = k(A)^n$ . The value of n is
  - (b) 0 (c) 3 (a) 1 (d) 2
- **16.** CH<sub>3</sub>OC<sub>2</sub>H<sub>5</sub> and (CH<sub>3</sub>)<sub>3</sub>C-OCH<sub>3</sub> are treated with hydroiodic acid. The fragments obtained after reactions are respectively
  - (a)  $CH_3I + HOC_2H_5$ ;  $(CH_3)_3C I + HOCH_3$
  - (b)  $CH_3OH + C_2H_5I$ ;  $(CH_3)_3CI + HOCH_3$
  - (c)  $CH_3OH + C_2H_5I$ ;  $(CH_3)_3C OH + CH_3I$
  - (d)  $CH_3I + HOC_2H_5$ ;  $CH_3I + (CH_3)_3C OH$
- 17. The vapour pressure of water at 20°C is 17.54 mm. When 20 g of a non-ionic substance is dissolved in 100 g of water, the vapour pressure is lowered by 0.30 mm. What is the molecular mass of the substance?
  - (a) 200.8 g (b) 206.88 g (d) 215.2 g
- (c) 210.5 g
- 18. Ferrimagnetism is in (a)  $\uparrow \uparrow \uparrow \uparrow \uparrow \uparrow$ (b)  $\uparrow \downarrow \uparrow \downarrow$

(c)  $\uparrow \uparrow \uparrow \downarrow \downarrow$ (d) none of these.

- 19. Methylamine is obtained when acetamide is treated with
  - (a)  $Br_2 + NH_4OH$ (b) NaOH +  $I_2$ (c)  $KOH + Br_2$ (d) none of these.
- 20. Helium atom is two times heavier than a hydrogen molecule at 298 K. The average kinetic energy of helium is
  - (a) 2 times of  $H_2$  molecule
  - (b) same as that of  $H_2$  molecule

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- (c) 4 times that of hydrogen molecule
- (d)  $\frac{1}{2}$  that of H<sub>2</sub> molecule.
- 21. Which of the following is not a characteristic of physical adsorption?
  - (a) Attraction due to weak van der Waals' forces
  - (b) Irreversible nature of adsorption
  - (c) Multimolecular adsorption layers
  - (d) Decrease in adsorption with increase in temperature.
- 22. Solubility of sulphates of group 2 elements decreases down the group due to
  - (a) decreasing hydration energy
  - (b) high ionisation energy
  - (c) increase in melting point
  - (d) all of these.

23. 
$$CH_3 \xrightarrow{CH_3COCl, Py} X \xrightarrow{KMnO_4} Y$$

The final product 'Y' is a medicine. Which of the following is incorrect regarding 'Y'?

- (a) It has analgesic as well as antipyretic properties.
- (b) It helps to prevent heart attack.
- (c) It has anti-blood clotting action.
- (d) It suppresses the gastric anomalies.
- 24. The number of alcohols that may have the molecular formula 'C<sub>4</sub>H<sub>10</sub>O' but do not have a chiral carbon is
  - (a) 1 (b) 2 (c) 3 (d) 4
- 25. Which of the following has the maximum electronegativity?
  - (a) C (b) F (c) N (d) O
- 26. When huge amount of sewage is dumped in a river, the BOD will
  - (a) increase (b) remain unchanged
  - (c) decrease (d) may increase or decrease.
- ·CH<sub>2</sub>CH=CH<sub>2</sub> on mercuration and demer-27.

curation produces

- CH<sub>2</sub>CHOHCH<sub>3</sub> (a)
- CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>OH (b) CH<sub>2</sub>CHOHCH<sub>2</sub>OH
- (c)
- (d) none of these.

28. The van der Waals' parameters for gases W, X, Y and Z are

Gas	$a (\operatorname{atm} \operatorname{L}^2 \operatorname{mol}^{-2})$	<i>b</i> (L mol <sup>-1</sup> )
W	4.0	0.027
X	8.0	0.030
Y	6.0	0.032
Z	12.0	0.027

Which one of these gases has the highest critical temperature?

(a)	W	(b) <i>X</i>
(c)	Y	(d) Z

**29.** Predict the product of reaction of  $I_2$  with  $H_2O_2$  in basic medium.

(a)	I-	(b)	$I_2O_3$
(c)	$IO_3^-$	(d)	$I_3^-$

- **30.** What is the free energy change when 1.0 mole of water at 100°C and 1 atm pressure is converted into steam at 100°C and 1 atm pressure?
  - (a) 540 cal (b) -9800 cal
  - (c) 9800 cal (d) 0 cal
- 31. The average osmotic pressure of human blood is 7.8 bar at 37°C. What is the concentration of an aqueous NaCl solution that could be used in the blood stream?
  - (a) 0.16 mol/L (b) 0.31 mol/L
  - (d) 0.45 mol/L (c) 0.60 mol/L
- 32. Which of the following compounds is thermally least stable?

(a)	Li <sub>2</sub> CO <sub>3</sub>	(b)	$MgCO_3$
(c)	BaCO <sub>3</sub>	(d)	BeCO <sub>2</sub>

33. Which of the following is most stable carbocation?



- **34.** The composition of carnallite is
  - (a) KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O (b) Na<sub>2</sub>Al<sub>2</sub>O<sub>3</sub>
  - (c)  $Fe_3O_4$ (d)  $Na_3AlF_6$
- 35. A tripeptide is written as Glycine-Alanine-Glycine. The correct structure of the tripeptide is





- **36.** Larger number of oxidation states are exhibited by the actinoids than those by the lanthanoids, the main reason being
  - (a) lesser energy difference between 5*f* and 6*d* than between 4f and 5d orbitals
  - (b) more energy difference between 5*f* and 6*d* than between 4f and 5d orbitals
  - (c) more reactive nature of the actinoids than the lanthanoids
  - (d) 4f orbitals are more diffused than the 5forbitals.
- 37. A compound on analysis was found to contain C = 18.5%, H = 1.55%, Cl = 55.04% and O = 24.81%. Its empirical formula is
  - (a)  $C_2H_2OCl$ (b) CH<sub>2</sub>ClO (c) CHClO (d) ClCH<sub>2</sub>O
- **38.**  $H_2S$  gas when passed through a solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because
  - (a) presence of HCl decreases the sulphide ion concentration
  - (b) sulphides of group IV cations are unstable in HCl
  - (c) solubility product of group II sulphides is more than that of group IV sulphides
  - (d) presence of HCl increases the sulphide ion concentration.
- **39.** The correct order of number of atoms in 1.6 g of  $CH_4$ , 1.7 g of  $NH_3$  and 1.8 g of  $H_2O$  is

(a)  $H_2O = NH_3 = CH_4$  (b)  $H_2O < NH_3 < CH_4$ (c)  $CH_4 < NH_3 < H_2O$  (d)  $CH_4 = NH_3 < H_2O$ 

- **40.** How many P=O bonds are present in  $(HPO_3)_3$ ?
  - (a) 0 (b) 3
  - (d) 9 (c) 6



#### **ASSERTION AND REASON**

**Directions :** In the following questions (41-60), a statement of assertion is followed by a statement of reason. Mark the correct choice as :

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.
- (b) If both assertion and reason are true but reason is not the correct explanation of assertion.
- (c) If assertion is true but reason is false.
- (d) If both assertion and reason are false.
- 41. Assertion : When a system in equilibrium is disturbed by changing the temperature, it will tend to adjust itself so as to overcome the effect of the change.

Reason : The endothermic reactions are favoured at lower temperature and exothermic reactions are favoured by high temperature.

42. Assertion : o-Nitrophenol is more volatile than *p*-nitrophenol.

Reason : Intramolecular hydrogen bonding is present in o-nitrophenol while intermolecular H-bonding is present in *p*-nitrophenol.

43. Assertion : Lyophilic colloids are called as reversible sols.

Reason : Lyophilic sols are liquid loving.

44. Assertion : Mixture of benzaldehyde and acetaldehyde in hot alkaline medium gives cinnamaldehyde.

Reason : Benzaldehyde is a strong electrophile than acetaldehyde.

45. Assertion : Anion vacancies in alkali halides are produced by heating the alkali halide crystals with alkali metal vapour.

Reason : Electrons trapped in anion vacancies are referred to as F-centres.

- **46.** Assertion : Hydrogen iodide cannot be prepared by the action of KI with conc.  $H_2SO_4$ . Reason: HI has poor thermal stability in comparison to other hydrogen halides.
- **47.** Assertion : Alkyl isocyanides in acidified water give alkyl formamides.

Reason : In isocyanides, carbon first acts as a nucleophile and then as an electrophile.

48. Assertion : van der Waals' equation is applicable only to non-ideal gases.

**Reason :** Ideal gases obey the equation PV = nRT.

49. Assertion : Diastereomers have different physical properties.

Reason : They are non-superimposable mirror images.

50. Assertion: Bond order can assume any value number including zero. Reason: Higher the bond order, shorter is bond length and greater is bond energy.

51. Assertion : Colloidal silver iodide is prepared by adding silver nitrate in slight excess to potassium iodide solution. When subjected to an electric field, the colloidal particles migrate to the anode.

Reason: Colloidal particles of a particular substance always carry the same charge irrespective of the method of preparation.

52. Assertion : Rate of reaction of alkyl halides in Williamson's synthesis reaction is  $1^{\circ}RX > 2^{\circ}RX > 3^{\circ}RX.$ 

Reason : It is a type of bimolecular substitution reaction ( $S_N$ 2).

53. Assertion : If 30 mL of H<sub>2</sub> and 20 mL of O<sub>2</sub> react to form water, 5 mL of H<sub>2</sub> is left at the end of the reaction.

**Reason :**  $O_2$  is the limiting reagent.

- 54. Assertion : The formal oxidation no. of sulphur in  $Na_2S_4O_6$  is 2.5. Reason : Two S-atoms are not directly linked with O-atoms.
- 55. Assertion : For a cell reaction  $\operatorname{Zn}_{(s)} + \operatorname{Cu}_{(aq)}^{2+} \rightarrow \operatorname{Zn}_{(aq)}^{2+} + \operatorname{Cu}_{(s)}$ ; at the equilibrium, voltmeter gives zero reading.

Reason : At the equilibrium, there is no change in the concentration of  $Cu^{2+}$  and  $Zn^{2+}$  ions.

56. Assertion : The position of an element in periodic table after emission of one  $\alpha$ - and two  $\beta$ - particles remains unchanged.

**Reason :** Emission of one  $\alpha$ - and two  $\beta$ -particles gives isotope of the element which acquires same position in periodic table.

57. Assertion : The boiling point of 0.1 M urea solution is less than that of 0.1 M KCl solution. Reason : Elevation of boiling point is directly proportional to the number of species present in the solution.





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58. Assertion : 
$$\left[ (en)_2 \text{Co} \underbrace{\text{OH}}_{\text{OH}}^{\text{NH}} \underbrace{\text{Co}(en)_2}_{\text{OH}} \right]^{3+}$$
 is named

as *tetrakis*(ethylenediamine)-µ-hydroxo-µ-imido dicobalt (III) ion.

**Reason :** In naming polynuclear complexes *i.e.*, containing two or more metal atoms joined by bridging ligands, the word  $\mu$  is added with hyphen before the name of such ligands.

**59.** Assertion : Ce<sup>4+</sup> is used as an oxidising agent in volumetric analysis.

**Reason :**  $Ce^{3+}$  has the tendency to change to  $Ce^{4+}$ .

**60.** Assertion :  $K_{sp}$  of  $AB_2$  salt for solubility 's' is  $4s^5$ . Reason :  $K_{sp}$  of a salt is its ionic product at any concentration.

### SOLUTIONS

1. (d): In  $S_N 2$  reactions, inversion of configuration occurs therefore, a single stereoisomer is produced. As this stereoisomer is not the enantiomer of the reactant therefore, a product with opposite sign of rotation is not necessarily produced.

2. (c) : 2.5 g NaOH = 
$$\frac{2.5}{40}$$
 equivalents of NaOH  
=  $\left(\frac{2.5}{40} \times 1000\right)$  = 62.5 milliequivalents of NaOH  
Now, meg of H<sub>2</sub>SO<sub>4</sub> = meg. of NaOH

Let the volume of  $H_2SO_4$  required is V mL. or  $2.5 \times 2 \times V = 62.5$  ( $\because$  *n*-factor for  $H_2SO_4 = 2$ )

$$V = \frac{62.5}{5} = 12.5 \,\mathrm{mL}$$

3. (c) : If dilution is made V-times molar conductance becomes V-times.
0.1 M H<sub>2</sub>SO<sub>4</sub> changes to 0.01 M H<sub>2</sub>SO<sub>4</sub> Thus, dilution is 100 times so, its molar conductance will be 100 times.

4. (a): 
$$CH_3CH_2COOH \xrightarrow{P/Br_2} CH_3CHCOOH$$
  
 $Br^{(A)}$   
 $alc. KOH$   
 $H^+$   
 $CH_2=CH-COOH + HBr^{(B)}$ 

 $P + Br_2$  is brominating agent that brominates the  $\alpha$ -position. The product then undergoes dehydrohalogenation in the presence of alcoholic potassium hydroxide.

5. (d): The structure of  $NO_3^-$  is represented as

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It has 4 bond pairs and no lone pair.

(b) : As the slowest step is the rate determining step, hence from eq. (2),
 r = k[O<sub>3</sub>][O]

From eq. (1), 
$$K_{eq} = \frac{[O_2][O]}{[O_3]}$$
 or  $[O] = \frac{K_{eq}[O_3]}{[O_2]}$   
Hence,  $r = k K_{eq} \frac{[O_3]^2}{[O_2]} = k'[O_3]^2[O_2]^{-1}$  [::  $k' = kK_{eq}$ ]

7. (b): *o*-Nitrophenol shows intramolecular hydrogen bonding and due to chelation, it has the lowest solubility.

8. (d): NO 
$$\longrightarrow$$
 NO<sup>+</sup> +  $e^-$   
Fe<sup>2+</sup> +  $e^- \longrightarrow$  Fe<sup>+</sup>  
Fe<sup>2+</sup> [Ar]  $3d^6$   $\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$   
Fe<sup>+</sup> [Ar]  $3d^7$   $\downarrow\uparrow\downarrow\downarrow\uparrow\uparrow\uparrow\uparrow\uparrow$   
Three unpaired electrons

$$\mu = \sqrt{n(n+2)} = \sqrt{3(3+2)} = 3.87$$
 B.M.

9. (c): 
$$Ag^+ + e^- \longrightarrow Ag; E_{Ag} = \frac{Atomic mass}{1} = 108$$

Number of faradays = 
$$\frac{W_{Ag}}{E_{Ag}} = \frac{108}{108} = 1$$

10. (c): 
$$(H_{2}COOCH_{3})$$

$$(H_{2}COOCH_{3})$$

$$(H_{2}CH_{2}CH_{2}CH_{3}CH$$

$$(H_{2}CH_{3}$$

- 11. (a):  $(NH_4)_2Cr_2O_7 \xrightarrow{\Delta} N_2 + Cr_2O_3 + 4H_2O_3$
- 12. (c) : Condensation polymerisation involves condensation reaction between two bifunctional monomers to produce dimer which in turn, produce, tetramer and so on with the loss of simple molecules like  $H_2O$ ,  $NH_3$ , HCl etc.
- **13.** (d): The structure of  $XeO_3F_2: O = Xe \bigcup_{F = O}^{F} O$

No. of lone pair of Xe = 0 and no. of bond pairs = 5 Hybridisation of Xe =  $sp^3d$ 

Hence, shape of  $XeO_3F_2$  should be trigonal bipyramidal and not octahedral.





3-chloronitrobenzene

- **15.** (d): Rate of reaction is quadrupled on doubling the concentration. Thus  $r \propto [A]^2$ .
- 16. (a): When mixed ethers are used, the alkyl iodide produced depends on the nature of alkyl groups. If one group is methyl and the other a primary or secondary alkyl group, then methyl iodide is produced. Here reaction occurs *via* S<sub>N</sub>2 mechanism and because of the steric effect of the larger group, I<sup>-</sup> attacks the smaller (Me) group.

$$CH_3OC_2H_5 + HI \longrightarrow CH_3I + C_2H_5OH$$

When the substrate is a methyl *t*-alkyl ether, the products are *t*-*R*I and MeOH. Here reaction occurs by  $S_N 1$  mechanism and formation of products is controlled by the stability of carbocation. Since carbocation stability order is  $3^\circ > 2^\circ > 1^\circ > CH_3$ , therefore alkyl halide is always derived from *tert*-alkyl group.

$$CH_{3} \xrightarrow[]{CH_{3}} CH_{3} - CH_{3} - CH_{3} + HI \xrightarrow[]{373 \text{ K}} S_{N^{1}} \xrightarrow[]{CH_{3}} CH_{3} \xrightarrow[]{CH_{3}} tert-Butyl iodide$$

17. (c) : Relative lowering in vapour pressure,  

$$\frac{p^{\circ} - p_{s}}{p^{\circ}} = \frac{w_{2}}{M_{2}} \times \frac{M_{1}}{w_{1}}$$

$$\frac{0.30 \text{ mm}}{17.54 \text{ mm}} = \frac{20}{M_{2}} \times \frac{18}{100}$$

$$\Rightarrow M_{2} = \frac{20 \times 18 \times 17.54}{0.30 \times 100} = 210.48 \approx 210.5 \text{ g}$$
18. (c)

**19.** (c) : The reaction involved is called as Hofmann's bromamide reaction.

 $RCONH_2 + Br_2 + 4KOH \longrightarrow RNH_2 + 2KBr + K_2CO_3$ Mechanism involved is :  $+ 2H_2O$ 

$$\begin{array}{c} O \\ R-C-NH_2 \xrightarrow{Br_2} R-C-NH-Br \xrightarrow{-OH} \\ \hline \\ -H_2OV \\ \hline \\ R-N=C=O \xleftarrow{R-C} N \xleftarrow{-Br^-} R-C-N \xrightarrow{-Br} Br \\ \hline \\ \hline \\ KOH \\ R-NH_2 + CO_2 \end{array}$$

- **20.** (b): Average kinetic energy  $=\frac{3}{2}kT$  where, *k* is Boltzmann constant. Average kinetic energy is the same for all gaseous molecules.
- 21. (b)
- **22.** (a): Heat of hydration is higher for small sized cations. Thus, solubility of sulphates of these metals decreases down the group.



- **25.** (b): Order of electronegativity is : F > O > N > C
- **26.** (a) : BOD is directly proportional to the amount of organic waste which is to be decomposed. Thus, the BOD will increase.
- 27. (a):



**28.** (d): For gas *Z*, critical temperature is highest.

$$T_c = \frac{8a}{27Rb}$$
$$\Rightarrow T_c = \frac{8 \times 12}{27 \times .0821 \times .027} = 1603.98 \text{ K}$$

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- **29.** (a) :  $I_{2(s)} + H_2O_{2(aq)} + 2OH_{(aq)} \longrightarrow 2I_{(aq)} + 2H_2O_{(l)} + O_{2(g)}$
- **30.** (d): It represents the condition of equilibrium hence,  $\Delta G = 0$ .

31. (b): 
$$\pi = CRT$$
  
 $C = \frac{\pi}{RT} = \frac{7.8}{0.082 \times 310} = 0.31 \text{ mol/L}$ 

32. (d)

- **33.** (c) : (1) (Tropylium) carbocation contains  $(4n + 2)\pi$  electrons hence, it is aromatic and most stable.
- **34.** (a): Carnallite is an ore of potassium and its formula is KCl·MgCl<sub>2</sub>·6H<sub>2</sub>O.



**36.** (a) : Energy difference between 5*f* and 6*d* orbitals is less so, actinoids have larger number of oxidation states.

37	(c)	۰ ۱
57.	$(\mathbf{r})$	•

Element	%	Atomic mass	Moles of atoms	Relative Simplest ratio of atoms
С	18.5	12	$\frac{18.5}{12} = 1.542$	1
Н	1.55	1	$\frac{1.55}{1} = 1.5$	1
Cl	55.04	35.5	$\frac{55.04}{35.5}$ = 1.55	1
О	24.81	16	$\frac{24.81}{16} = 1.55$	1

Therefore, empirical formula of the compound is CHClO.

38. (a)

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### **39.** (b):

Molecule	No. of moles	No. of molecules	No. of Atoms
$CH_4$	0.1	$0.1N_{0}$	$0.5N_{0}$
NH <sub>3</sub>	0.1	$0.1N_{0}$	$0.4N_{0}$
H <sub>2</sub> O	0.1	$0.1N_{0}$	$0.3N_{0}$



- **41.** (c) : An exothermic reaction is favoured by low temperature while an endothermic reaction is favoured by high temperature.
- **42.** (a): *p*-Nitrophenol has higher boiling point than *o*-nitrophenol, because of intermolecular hydrogen bonding present in *p*-nitrophenol. But intramolecular hydrogen bonding in *o*-nitrophenol makes it steam volatile.
- **43.** (b): If the dispersion medium is separated from the dispersed phase, the lyophilic sol can be reconstituted by simply remixing with the dispersion medium. That is why these sols are also called reversible sols.
- 44. (a): This is Claisen-Schmidt reaction.



**45.** (b): On heating the alkali halide crystals with alkali metal vapour the excess of alkali metal atoms deposit on the surface of the alkali halide crystal, halide ion then diffuse to the surface and combine with alkali metal atom which get ionised by losing electrons. After ionisation the alkali metal ion occupies cationic vacancy whereas electron occupies anionic vacancy.

46. (b): Hydrogen iodide cannot be prepared by the action of KI with conc. H<sub>2</sub>SO<sub>4</sub> because H<sub>2</sub>SO<sub>4</sub> oxidises HI to I<sub>2</sub>.

 $H_2SO_4 + 2HI \longrightarrow I_2 + SO_2 + 2H_2O$ 

47. (a): In an isocyanide, first an electrophile and then a nucleophile add at the carbon to form a species which usually undergoes further transformations.

$$R\overset{\mathsf{N}}{\mathsf{N}} \equiv C^{-} + E^{+} \longrightarrow R\overset{\mathsf{N}}{\mathsf{N}} \equiv CE \xrightarrow{\mathsf{N}}{\mathsf{N}} R \mathsf{N} \equiv C(\mathsf{N}\mathsf{u})E$$
$$R\overset{\mathsf{H}}{\mathsf{N}} \equiv C^{-} + H_{2}O \longrightarrow R \mathsf{N} \equiv \mathsf{CHOH} \xrightarrow{\mathsf{R}}{\mathsf{NHCHO}}_{Alkyl \text{ formamide}}$$

- 48. (b): In real gases, the intermolecular forces of attraction and the volume occupied by the gas molecules cannot be neglected.
- 49. (c): Stereoisomers which are not mirror images of each other are called diastereomers. They have similar chemical properties because they belong to the same family, but they do not have identical physical properties because of difference in their relative configurations.

**50.** (b): Bond order 
$$=\frac{1}{2}(N_b - N_a)$$
.  
Bond order zero indicates that the

e bond does not exist.

- 51. (d): As AgNO<sub>3</sub> is in excess, the AgI particles will adsorb Ag<sup>+</sup> ions and move towards cathode. Colloidal particles of AgI may be positively or negatively charged depending upon whether AgNO<sub>3</sub> is in excess or KI is in excess.
- 52. (a): Williamson's synthesis occurs by  $S_N 2$ mechanism and primary alkyl halides are most reactive in  $S_N 2$  reactions.

53. (d): 
$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$$
  
30 mL  $_{15 \text{ mL reacted}}$ 

Volume of  $O_2$  left = 20 – 15 = 5 mL Since H<sub>2</sub> is completely consumed, hence, it is the limiting reagent.

54. (a): 
$$\overset{+}{NaO} \overset{O}{=} \overset{O}{\underset{|}^{+50}} \overset{O}{=} \overset{O}{\underset{|}^{+50}} \overset{O}{=} \overset{O}{\underset{|}^{+5}} \overset{O}{=} \overset{O}{\underset{|}^{+5}} \overset{O}{=} \overset{O}{\underset{|}^{+5}} \overset{O}{=} \overset{O}{\underset{|}^{+5}} \overset{O}{=} \overset{O}{\underset{|}^{+5}} \overset{O}{=} \overset{O}{=}$$

Formal oxidation number of sulphur

$$=\frac{2\times5+2\times0}{4}=2.5$$

**55.** (a):  $Zn_{(s)} + Cu_{(aq)}^{2+} \rightarrow Zn_{(aq)}^{2+} + Cu_{(s)}$ 

As the time passes, the concentration of  $Zn^{2+}$  keeps on increasing while the concentration of Cu<sup>2+</sup> keeps on decreasing. At the same time voltage of the cell keeps on decreasing. When there is no change in concentration of Cu<sup>2+</sup> and Zn<sup>2+</sup> ions, voltmeter gives zero reading and this state is known as equilibrium.

- 56. (a): The loss of one  $\alpha$ -particle will reduce the mass number by four and atomic number by two. Subsequent two  $\beta$ -emissions will increase the atomic number by two without affecting the mass number. Hence, the new element will be only an isotope of the parent atom and hence its position in the periodic table remains unchanged.
- 57. (a)

58. (a): 
$$\left[ (en)_2 Co \right]^{3+}$$
 is named as

tetrakis(ethylenediamine)-µ-hydroxo-µ-imido dicobalt (III) ion. For more than one bridging group the word  $\mu$  is repeated before each bridging group.

- **59.** (c) :  $Ce^{4+}$  has the tendency to change to  $Ce^{3+}$  (as +3 oxidation state is more stable).
- **60.** (d):  $K_{sp}$  for  $AB_2 = 4s^3$  $K_{sp}$  equals ionic product in saturated solution.

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# **PRACTICE PAPER**

- 1. The chemical name of aspirin is
  - (a) methyl salicylate (b) acetylsalicylic acid
  - (c) sodium salicylate (d) salicylic acid.
- 2. The half life period of radon is 3.8 days. After how many days will only one-twentieth of radon sample be left over ?
  - (a) 8.54 days (b) 20 days
  - (c) 11.28 days (d) 16.46 days
- Which of the following acts as a sink for CO?
   (a) Plants
  - (b) Haemoglobin
  - (c) Microorganisms present in the soil
  - (d) Oceans
- 4. The plot of  $1/x_A$  versus  $1/y_A$  (where  $x_A$  and  $y_A$  are the mole fractions of A in liquid and vapour phases respectively) is linear whose slope and intercept respectively are given as

(a) 
$$\frac{p^{\circ}_{A}}{p^{\circ}_{B}}$$
,  $\frac{(p^{\circ}_{A} - p^{\circ}_{B})}{p^{\circ}_{B}}$  (b)  $\frac{p^{\circ}_{A}}{p^{\circ}_{B}}$ ,  $\frac{(p^{\circ}_{B} - p^{\circ}_{A})}{p^{\circ}_{B}}$   
(c)  $\frac{p^{\circ}_{B}}{p^{\circ}_{A}}$ ,  $\frac{(p^{\circ}_{A} - p^{\circ}_{B})}{p^{\circ}_{B}}$  (d)  $\frac{p^{\circ}_{B}}{p^{\circ}_{A}}$ ,  $\frac{(p^{\circ}_{B} - p^{\circ}_{A})}{p^{\circ}_{B}}$ 

- The standard reduction potentials of Pb and Zn electrodes are -0.126 and -0.763 volts respectively. The cell equation will be
  - (a)  $Pb^{2+} + Zn \rightarrow Pb + Zn^{2+}$
  - (b)  $Pb + 2Zn^{2+} \rightarrow Pb^{4+} + 2Zn$
  - (c)  $Zn^{2+} + Pb \rightarrow Zn + Pb^{2+}$
  - (d) none of the above.
- 6. Colourless solutions of the following four salts are placed separately in four different test tubes and a strip of copper is dipped in each one of these. Which solution will turn blue?
  - (a) KNO<sub>3</sub> (b) AgNO<sub>3</sub>
  - (c)  $Zn(NO_3)_2$  (d)  $ZnSO_4$

7. Amongst H<sub>2</sub>O, H<sub>2</sub>S, H<sub>2</sub>Se and H<sub>2</sub>Te, the one with the highest boiling point is

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- (a)  $H_2O$  because of hydrogen bonding
- (b)  $H_2$ Te because of higher molecular weight
- (c)  $H_2S$  because of hydrogen bonding
- (d)  $H_2$ Se because of lower molecular weight.
- 8. Of the following statements about enzymes which is/are true?
  - (i) Enzymes lack in nucleophilic groups.
  - (ii) Enzymes are highly specific both in binding chiral substrates and in catalysing their reactions.
  - (iii) Enzymes catalyse chemical reactions by lowering the energy of activation.
  - (iv) Pepsin is a proteolytic enzyme.
  - (a) (i) and (iv) (b) (i) and (iii)
  - (c) (ii), (iii) and (iv) (d) (i) only
- 9. Bakelite is made from phenol and formaldehyde. The initial reaction between them is the example of (a) electrophilic aromatic substitution
  - (b) nucleophilic aromatic substitution
  - (c) free radical reaction
  - (d) aldol reaction.
- **10.** Carbylamine test is performed in alcoholic KOH by heating a mixture of
  - (a) chloroform and silver powder
  - (b) trihalogenated methane and a primary amine
  - (c) an alkyl halide and a primary amine
  - (d) an alkyl cyanide and a primary amine.
- 11. When chlorine water is added to an aqueous solution of potassium halide in presence of chloroform, a violet colour is obtained. On adding more of chlorine water, the violet colour disappears, and a colourless solution is obtained. This test confirms the presence of \_\_\_\_\_ in aqueous solution.
  - (a) iodide (b) bromide
  - (c) chloride (d) iodide and bromide



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\_\_\_\_

- 12. Which of the following statements is incorrect?
  - (a) Brownian movement and Tyndall effect are shown by colloidal systems.
  - (b) Gold number is a measure of the protective power of a lyophillic colloid.
  - (c) The colloidal solution of a liquid in liquid is called gel.
  - (d) Hardy-Schulze rule is related with coagulation.
- 13. The reaction given below, involving the gases is observed to be first order with rate constant  $7.48 \times 10^{-3}$  sec<sup>-1</sup>. Calculate the time required for the total pressure (in a system containing A at an initial pressure of 0.1 atm) to rise to 0.145 atm and also, find the total pressure after 100 sec.

$$2A_{(g)} \rightarrow 4B_{(g)} + C_{(g)}$$

- (a) 46.5 sec, 0.12 atm (b) 47.7 sec, 0.18 atm
- (c) 50.2 sec, 0.16 atm (d) None of these
- 14. If a refrigerator's door is kept opened, then
  - (a) room gets cooled
  - (b) room gets heated
  - (c) more heat is passed out
  - (d) there is no effect.
- 15. The pH of pure water at 25°C and 35°C are 7 and 6 respectively. The heat of formation of water from H<sup>+</sup> and OH<sup>-</sup> is
  - (a) 64.55 kcal/mol (b) - 74.55 kcal/mol
  - (c) 84.55 kcal/mol (d) -54.55 kcal/mol
- **16.** The oxide which is used as white pigment is (d) CuO (a) ZnO (b) FeO (c) NiO
- 17. Stearic acid,  $C_{17}H_{35}COOH$  has a density of 0.85 g/cm<sup>3</sup>. The molecule occupies an area of 0.205 nm<sup>2</sup> in a closed packed surface film. Calculate the length of the molecule.
  - (a) 3.8073 nm (b) 8.3073 nm (c) 2.7073 nm (d) 1.8073 nm
- 18. An aqueous solution of 6.3 g oxalic acid dihydrate is made up to 250 mL. The volume of 0.1 N NaOH required to completely neutralize 10 mL of this solution is
  - (a) 40 mL (b) 20 mL (c) 10 mL (d) 4 mL
- 19. The pair of structures given below represent



- (a) enantiomers (b) diastereomers
- (c) structural isomers
- (d) two molecules of the same compound.
- 20. Which among the following statements are true for glycine?
  - (1) It exists in crystalline form.
  - (2) It is optically active.
  - (3) It is soluble in water.
  - (4) It can form zwitter ion.
  - (a) 1, 2 and 3 (b) 1, 2 and 4
  - (c) 1, 3 and 4 (d) 2, 3 and 4
- 21. Lemon juice normally has a pH of 2. If all the acid in the lemon juice is citric acid and there are no citrate salts present, then what will be the citric acid concentration (H.Cit) in the lemon juice? (Assume that only the first hydrogen of citric acid is important). (H.Cit  $\Longrightarrow$  H<sup>+</sup> + Cit<sup>-</sup>;  $K_a = 8.4 \times 10^{-4}$  mol lit<sup>-1</sup>) (a)  $8.4 \times 10^{-4}$  M (b)  $4.2 \times 10^{-4} \text{ M}$ 
  - (c)  $16.8 \times 10^{-4}$  M (d)  $12.0 \times 10^{-2}$  M
- **22.** The dissociation energy of  $H_2$  is 430.53 kJ mol<sup>-1</sup>. If hydrogen is dissociated by illumination with radiation of wavelength 253.7 nm, the fraction of the radiant energy which will be converted into kinetic energy is given by
  - (a) 100% (b) 8.78% (c) 2.22% (d) 1.22%
- **23.** For which of the following reactions  $\Delta H$  is less than  $\Delta E$ ?
  - (a)  $\text{HCl}_{(aq)} + \text{NaOH}_{(aq)} \longrightarrow \text{NaCl}_{(aq)} + \text{H}_2\text{O}_{(l)}$

(b) 
$$H_{2(x)} + I_{2(x)} \longrightarrow 2HI_{(x)}$$

(c) 
$$C_{(s)}^{2(g)} + O_{2(g)}^{2(g)} \longrightarrow CO_{2(g)}^{(g)}$$

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

24. Two students performed the same experiment separately and each one of them recorded two readings of mass which are given below. Correct reading of mass is 5.0 g. On the basis of given data, mark the correct option out of the following statements.

Students	Readings		
	(:)	(::)	

	(1)	(11)
Α	5.01	4.99

- В 5.05 4.95
- (a) Results of both the students are neither accurate nor precise.
- (b) Results of student A are both precise and accurate.
- (c) Results of student *B* are neither precise nor accurate.
- (d) Results of student B are both precise and accurate.



25. In the given reaction,

$$CH_3 - C - CH_3 \xrightarrow{SeO_2} X + Se + H_2O,$$

$$X \text{ is}$$

$$(a) CH_3 - C - C - H \qquad (b) CH_3 - C - OCH_3$$

$$O$$

$$(c) CH = C - CH OH \qquad (d) \text{ pape of these}$$

- (c)  $CH_3 C CH_2OH$  (d) none of these.
- **26.** In which isomer of  $C_7H_7NO_2$  there are two functional groups?
  - (a) Phenyl nitromethane (b) *m*-nitrotoluene
  - (d) Benzyl nitrite (c) Anthranilic acid
- 27. Which of the following is not correct representation of first law of thermodynamics?
  - (a) Isochoric process;  $\Delta E = q$
  - (b) Isothermal process; q = -w
  - (c) Adiabatic process; q = -w
  - (d) Cyclic process; q = -w
- 28. The incorrect statement among the following is
  - (a) the first ionization potential of Al is less than the first ionization potential of Mg
  - (b) the second ionization potential of Mg is greater than the second ionization potential of Na
  - (c) the first ionization potential of Na is less than the first ionization potential of Mg
  - (d) the third ionization potential of Mg is greater than the third ionization potential of Al.
- 29. In presence of peroxide, hydrogen chloride and hydrogen iodide do not give anti-Markownikoff's addition to alkenes because
  - (a) both are highly ionic
  - (b) one is oxidising and the other is reducing
  - (c) one of the step is endothermic in both the cases
  - (d) all the steps are exothermic in both the cases.
- 30. A mixture of benzaldehyde and formaldehyde on heating with aqueous NaOH solution gives
  - (a) benzyl alcohol and sodium formate
  - (b) sodium benzoate and methyl alcohol
  - (c) sodium benzoate and sodium formate
  - (d) benzyl alcohol and methyl alcohol.
- 31. The increase in the molar conductivity of HCl with dilution is due to
  - (a) increase in the self ionisation of water
  - (b) decrease in the self ionisation of water
  - (c) decrease in the interionic forces
  - (d) none of these.

32. Trimethylamine is a pyramidal molecule



- respectively.
- (b) *sp*<sup>3</sup>, *sp*<sup>2</sup>
  (d) *sp*<sup>2</sup>, *sp* (a)  $sp^2$ ,  $sp^2$
- (c)  $sp^3$ ,  $sp^3$
- 33. Which of the following processes will convert starch directly into glucose?
  - (a) Heating with dilute  $H_2SO_4$ .
  - (b) Fermentation by diastase.
  - (c) Fermentation by zymase.
  - (d) Heating with dilute NaOH.
- **34.**  $PbF_4$ ,  $PbCl_4$  exist but  $PbBr_4$  and  $PbI_4$  do not exist because of
  - (a) large size of Br<sup>-</sup> and I<sup>-</sup>
  - (b) strong oxidising character of Pb<sup>4+</sup>
  - (c) strong reducing character of  $Pb^{4+}$
  - (d) low electronegativity of Br<sup>-</sup> and I<sup>-</sup>.
- 35. Match list I with list II and select the correct answer using the codes given below :





- **36.** An alkyl halide with molecular formula,  $C_6H_{13}Br$ on treatment with alcoholic KOH gave two isomeric alkenes, A and B. Reductive ozonolysis of the mixture gave the following compounds : CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>CHO and (CH<sub>3</sub>)<sub>2</sub>CHCHO. The alkyl halide is
  - (a) 2-bromohexane
  - (b) 3-bromo-2-methylpentane
  - (c) 2,2-dimethyl-1-bromobutane
  - (d) 2-bromo-2, 3-dimethylbutane.
- **37.** Anhydride of nitric acid is (c)  $N_2O_5$  (d)  $N_2O_3$ (a)  $N_2O$ (b) NO<sub>2</sub>
- 38. How many grams of sucrose (mol. wt. = 342) should be dissolved in 100 g water in order to produce a solution with a 105.0°C difference between the freezing and the boiling temperatures?
  - $(K_f = 1.86^{\circ} \text{ C/m}, K_b = 0.51^{\circ} \text{ C/m})$ 72 g (c) 342 g (d) 460 g (a) 34.2 g (b) 72 g
- 39. The lower boiling point of helium is due to its (a) inertness (b) gaseous nature
  - (c) high polarisability
  - (d) weak van der Waals forces between atoms.
- 40. The correct order of basicity of the following compounds is\_

$$\begin{array}{c} \begin{array}{c} \begin{array}{c} & & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ & & \\ \end{array} \end{array} \xrightarrow[]{} \begin{array}{c} & & \\ & & \\ & & \\ \end{array} \\ \begin{array}{c} (H_3)_2 \\ (H_3)_2 \\ (H_3)_2 \\ (H_3)_2 \\ (H_3)_2 \\ (H_3)_2 \\ (H_3)_3 \\ (H_$$

#### SOLUTIONS

1. (b): Structural formula of aspirin is OCOCH<sub>3</sub>

COOH

IUPAC name : 2-Acetoxybenzoic acid Chemical name : Acetylsalicylic acid

(d): We know that,  $\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{3.8} = 0.182 \text{ day}^{-1}$ 2. Let the initial amount of radon be  $N_0$  and the

amount left after t days be N which is equal to  $\frac{N_0}{20}$ Applying the equation,

$$t = \frac{2.303}{\lambda} \log_{10} \frac{N_0}{N}$$
  
=  $\frac{2.303}{0.182} \log_{10} \frac{N_0}{N_0/20} = \frac{2.303}{0.182} \log_{10} 20$   
= 16.46 days

(c) : CO is converted into  $CO_2$  by microorganisms 3. present in soil.

(b): 
$$P_A = x_A p_A^{\circ}, P_B = x_B p_B^{\circ}$$
  
 $y_A = \frac{p_A}{p_A + p_B} = \frac{x_A p_A^{\circ}}{x_A p_A^{\circ} + x_B p_B^{\circ}}$   
 $= \frac{x_A p_A^{\circ}}{x_A p_A^{\circ} + (1 - x_A) p_B^{\circ}} = \frac{x_A p_A^{\circ}}{x_A (p_A^{\circ} - p_B^{\circ}) + p_B^{\circ}}$   
or,  $\frac{1}{y_A} = \frac{x_A (p_A^{\circ} - p_B^{\circ}) + p_B^{\circ}}{x_A p_A^{\circ}}$   
or,  $\frac{1}{y_A} = \frac{p_A^{\circ} - p_B^{\circ}}{p_A^{\circ}} + \frac{p_B^{\circ}}{p_A^{\circ}} \frac{1}{x_A}$   
or,  $\frac{1}{x_A} = \frac{p_A^{\circ}}{p_B^{\circ}} \frac{1}{y_A} + \frac{p_B^{\circ} - p_A^{\circ}}{p_B^{\circ}}$   
Hence, plot of  $\frac{1}{x_A} vs \frac{1}{y_A}$  will be linear with  
slope  $= \frac{p_A^{\circ}}{p_B^{\circ}}$  and intercept  $= \frac{(p_B^{\circ} - p_A^{\circ})}{p_B^{\circ}}$ .

- (a): The  $E^{\circ}_{red}$  of Zn is lower than that of Pb, hence Zn is a better reducing agent than Pb.
  - : The correct cell reaction will be  $Pb^{2+} + Zn \rightarrow Pb + Zn^{2+}$
  - (b): As Cu is more reactive than Ag.  $Cu + 2AgNO_3 \rightarrow Cu(NO_3)_2 + 2Ag$ Cu<sup>2+</sup> will give blue solution. Cu is below in electrochemical series than K and Zn hence, no reaction takes place with  $KNO_3$ ,  $Zn(NO_3)_2$  and ZnSO<sub>4</sub>.
- (a):  $H_2O$  has the highest boiling point due to 7. H-bonding.
- 8. (c)

6.

4.

9. (a): The reaction of phenol and formaldehyde is called Lederer Manasse reaction. It follows electrophilic addition and rearrangement mechanism.



**10.** (**b**): Trihalogenated methane (CH*X*<sub>3</sub>) and a primary amine, *i.e.*;

 $CHX_3 + RNH_2 + 3KOH \rightarrow RNC + 3KX + 3H_2O$ 

11. (a): 
$$2I^- + Cl_2 \longrightarrow I_2 + 2Cl^-$$
  
Violet  
 $5Cl_2 + I_2 + 6H_2O \longrightarrow 2HIO_3 + 10HCl$   
Excess  
Colourless

- **12.** (c) : Liquid-liquid system is known as emulsion.
- 13. (b):  $2A_{(g)} \rightarrow 4B_{(g)} + C_{(g)}$ Initial:  $P_0 = 0$  o 0 At time:  $t = P_0 - P' = 2P' = P'/2$   $P_{\text{total}} = P_0 - P' + 2P' + P'/2 = P_0 + \frac{3P'}{2}$   $P' = \frac{2}{3}(P_{\text{total}} - P_0)$   $P' = \frac{2}{3}(0.145 - 0.1) = 0.03 \text{ atm}$   $K = \frac{2.303}{t} \log \frac{P_0}{P_0 - P'}$   $t = \frac{2.303}{7.48 \times 10^{-3}} \log \frac{0.1}{0.07} = 47.7 \text{ sec}$ Also,  $k = \frac{2.303}{t} \log \frac{P_0}{P_0 - P'}$   $k = \frac{2.303}{100} \log \left(\frac{0.1}{0.1 - P'}\right)$   $\Rightarrow 0.1 - P' = 0.047 \text{ or } P' = 0.053$  $P_{\text{total}} = 0.1 + \frac{3}{2}(0.053) \approx 0.18 \text{ atm}$
- 14. (b): The room gets heated because to maintain the cooling inside the refrigerator its radiator radiates heat to the surroundings continuously.

15. (c) : At 25°C, [H<sup>+</sup>] = 10<sup>-7</sup>. 
$$\therefore K_{w_1} = 10^{-14}$$
  
At 35°C, [H<sup>+</sup>] = 10<sup>-6</sup>.  $\therefore K_{w_2} = 10^{-12}$   
Now using, 2.303 log  $\frac{K_{w_2}}{K_{w_1}} = \frac{\Delta H}{R} \left[ \frac{T_2 - T_1}{T_1 \times T_2} \right]$   
2.303 log  $\frac{10^{-12}}{10^{-14}} = \frac{\Delta H}{2} \left[ \frac{10}{298 \times 308} \right]$ 

 $\therefore \quad \Delta H = 84551.4 \text{ cal/mol} = 84.551 \text{ kcal/mol}$ Thus, H<sub>2</sub>O  $\rightleftharpoons$  H<sup>+</sup> + OH<sup>-</sup>;  $\Delta H = 84.551 \text{ kcal/mol}$  $\therefore \quad$  H<sup>+</sup> + OH<sup>-</sup>  $\rightleftharpoons$  H<sub>2</sub>O;  $\Delta H = -84.551 \text{ kcal/mol}$ 

- 16. (a): ZnO is used in white paints in place of white lead. It does not get blackened with hydrogen sulphide present in air as the white lead paint does. It is also known as Philosopher's wool.
- 17. (c) : Molar mass of stearic acid = 284 Mass of one molecule =  $\frac{284}{6.02 \times 10^{23}}$  g Volume of one molecule =  $\frac{284}{6.02 \times 10^{23} \times 0.85}$ = 55.5 × 10<sup>-23</sup> cm<sup>3</sup> Area occupied by the molecule = 0.205 nm<sup>2</sup> = 0.205 × 10<sup>-18</sup> m<sup>2</sup> = 0.205 × 10<sup>-14</sup> cm<sup>2</sup> Hence, length of the molecule =  $\frac{\text{volume}}{\text{area}}$ =  $\frac{55.5 \times 10^{-23}}{0.205 \times 10^{-14}}$  = 270.73 × 10<sup>-9</sup> cm = 2.7073 nm
- 18. (a): Normality of oxalic acid =  $\frac{6.3 \times 1000}{63 \times 250}$  = 0.4 N N<sub>1</sub>V<sub>1</sub> = N<sub>2</sub>V<sub>2</sub> or 0.1 × V<sub>1</sub> = 0.4 × 10 ∴ V<sub>1</sub> = 40 mL
- **19.** (c) : Convert these Newmann projections into open chain structures.

$$H \xrightarrow{CH_3} H \xrightarrow{CH_3} H \xrightarrow{H_3} H \xrightarrow{H_3}$$

Both structures have same molecular formula  $C_4H_9Cl$ , thus these are isomers. However, the two have different groups, *viz* CH<sub>3</sub> and CH<sub>2</sub>Cl, so these are neither enantiomers nor diastereomers. Hence, these are structural isomers.

21. (d): 
$$K_a = \frac{[H^+][cit^-]}{[H. cit]}$$
  
 $8.4 \times 10^{-4} = \frac{[10^{-2}][10^{-2}]}{[H. cit]}$   
 $8.4 \times 10^{-4} = \frac{10^{-4}}{[H. cit]}$   
 $[H. cit] = \frac{10^{-4}}{8.4 \times 10^{-4}} = 0.119$   
 $= 11.9 \times 10^{-2} M \approx 12 \times 10^{-2} M$ 



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22. (b): Energy of 1 mole of photons,

$$E = N_0 h \upsilon = \frac{N_0 \times h \times v}{\lambda}$$

Energy converted into K.E. = (472 - 430.53) kJ % of energy converted into K.E.

$$=\frac{(472-430.53)}{472}\times100=8.78\%$$

**23.** (d):  $\Delta n = 2 - 4 = -2$  $\therefore \quad \Delta H = \Delta E + (-2)RT \text{ or, } \Delta H = \Delta E - 2RT$ 

Hence,  $\Delta H < \Delta E$ 

- 24. (b): Results of student *B* is accurate but not precise.
- **25.** (a):  $SeO_2$  oxidises compounds containing active methylene group (*i.e.*  $CH_2$  next to the carbonyl group) to another CO group. *i.e.*,

$$CH_3 - CH_3 - CH_3 \xrightarrow{SeO_2} CH_3 - CH_3 - CHO + Se + H_2O$$

26. (c): 
$$COOH$$
  
NH<sub>2</sub> Anthranilic acid

- **27.** (c) : For adiabatic process, q = 0; so,  $\Delta E = w$
- **28.** (b):  $IE_2$  of Mg is lower than that of Na because in case of Mg<sup>+</sup>, one *s*-electron has to be removed where in case of Na<sup>+</sup>, an electron is to be removed from the stable inert gas configuration which is difficult.
- 29. (c): One of the steps, (*i.e.* the reaction of HCl with carbon radical in case of HCl and addition of iodine radical to double bond in case of HI) is endothermic in both the cases.
- **30.** (a): A mixture of benzaldehyde and formaldehyde undergoes cross Cannizzaro reaction.

$$C_6H_5CHO + HCHO \xrightarrow{NaOH} C_6H_5CH_2OH + HCOONa$$

- 31. (c) : Due to increase in volume of water, interionic forces of HCl will decrease. Hence, ionic mobility will increase and consequently, the molar conductivity will also increase.
- **32.** (b): In amine, the nitrogen is  $sp^3$  hybridised and in amide, the nitrogen is  $sp^2$  hybridised.
- 33. (a): Fermentation by diastase will convert starch into maltose but not into glucose. Zymase does not affect starch. Further, dilute NaOH will not hydrolyse starch because the various glucose units in it are linked to each other by glycosidic linkages which are resistant to hydrolysis by NaOH. Thus, only dilute H<sub>2</sub>SO<sub>4</sub> will hydrolyse starch into glucose.



34. (b):  $F_2$  and  $Cl_2$  are more oxidising in nature hence, they can form Pb in + 4 oxidation state but Br<sub>2</sub> and I<sub>2</sub> cannot. Secondly, Pb<sup>4+</sup> is strong oxidising agent and in its presence Br<sup>-</sup> and I<sup>-</sup> cannot exist.

**36.** (b): Out of CH<sub>3</sub>COCH<sub>3</sub>, CH<sub>3</sub>CHO, CH<sub>3</sub>CH<sub>2</sub>CHO and (CH<sub>3</sub>)<sub>2</sub>CHCHO, two pairs containing a total of six carbon atoms are :

(ii) CH<sub>3</sub>CHO + (CH<sub>3</sub>)<sub>2</sub>CHCHO

The alkenes which will give these pairs of compounds on ozonolysis are :

$$CH_3 \rightarrow C = CHCH_2CH_3$$
  
CH<sub>3</sub>  $2$ -Methyl-2-pentene

and 
$$CH_3 \rightarrow CH-CH=CHCH_3$$
  
4-Methyl-2-pentene

These two alkenes can be obtained as dehydrogenation products if the alkyl halide is Br CH->

$$CH_3$$
  $CH-CH-CH_2CH_3$   
3-Bromo-2-methylpentane

37. (c): 2HNO<sub>3</sub> 
$$\xrightarrow{P_2O_5}$$
 N<sub>2</sub>O<sub>5</sub> + H<sub>2</sub>O

**38.** (b): Boiling point  $(T_b) = 100 + \Delta T_b = 100 + K_b m$ Freezing point  $(T_f) = 0 - \Delta T_f = -K_f m$  $T_{l} - T_{f} = (100 + K_{l}m) - (-K_{f}m)$ 

$$105 = 100 + 0.51 m + 1.86 m$$

2.37 
$$m = 5$$
 or,  $m = \frac{5}{2.37} = 2.11$  m

- $\therefore$  Wt. of sucrose to be dissolved in 100 g water  $=\frac{2.11\times342}{1000}\times100=72 \text{ g}$
- 39. (d): Due to weak van der Waals forces, He has lowest boiling point.

40. (b): 
$$CH_3 - \overset{NH}{C} - \overset{NH_2}{H_2} + \overset{NH_2}{H^+} \longrightarrow CH_3 - \overset{H_2}{C} - \overset{NH_2}{H_2}$$
  
 $\overset{H_2}{\longleftrightarrow} CH_3 - \overset{NH_2}{C} - \overset{NH_2}{H_2} \xrightarrow{H_2}{H_2}$ 

The conjugate acid obtained by addition of a proton to I is stabilised by two equivalent resonance structures and hence, compound I is the most basic. Further 2° amines are more basic than 1° amines while amides are least basic due to delocalization of lone pair of electrons of N over the CO group. Thus the order is : I > III > II > IV



- Mass of one <sup>14</sup>/<sub>7</sub>N atom is

   (a) 14 amu
   (b) 7 amu
   (c) 14 g
   (d) 7 g
- 2. The incorrect IUPAC name is

(a) 
$$CH_3 - C - CH - CH_3$$
  
2-Methylbutan-3-one

(b) 
$$CH_3 - CH - CH - CH_3$$
  
 $| | | CH_3 - CH_2CH_3$   
2,3-Dimethylpentane

(c) 
$$CH_3 - C \equiv C - CH(CH_3)_2$$
  
4-Methylpent-2-yne

(d) 
$$CH_3 - CH - CH - CH_3$$
  
 $|$   $|$   $Cl$  Br  
2-Bromo-3-chlorobutane

- 3. Choose the correct statement.
  - (a) Saccharin is 650 times sweeter than sucrose.
  - (b) Aspartame is 550 times sweeter than sucrose.
  - (c) Sucralose is 160 times sweeter than sucrose.
  - (d) Alitame is 2000 times sweeter than sucrose.
- **4.** Which of the following represents the correct order of boiling points of the given substances?
  - (a) *n*-pentane > isopentane > neopentane
  - (b) isopentane > neopentane > *n*-pentane
  - (c) neopentane > *n*-pentane > isopentane
  - (d) *n*-pentane > neopentane > isopentane
- 5. For the non-stoichiometric reaction :
  - $2A + B \rightarrow C + D$ , the following kinetic data was obtained in three separate experiments, all at 298 K.

Initial concentration [A]	Initial concentration [ <i>B</i> ]	Initial rate of formation of C (mol L <sup>-1</sup> s <sup>-1</sup> )
0.1 M	0.1 M	$1.2 \times 10^{-3}$
0.1 M	0.2 M	$1.2 \times 10^{-3}$
0.2 M	0.1 M	$2.4  imes 10^{-3}$

The rate law for the formation of *C* is

(a) 
$$\frac{dC}{dt} = k[A]$$
 (b)  $\frac{dC}{dt} = k[A][B]$   
(c)  $\frac{dC}{dt} = k[A]^2[B]$  (d)  $\frac{dC}{dt} = k[A][B]^2$ 

(c) 
$$\frac{dC}{dt} = k[A]^2[B]$$
 (d)  $\frac{dC}{dt} = k[A][B]^2$ 

- 6. For the cell reaction,  $Cu_{(s)} + Cl_{2(g)} \longrightarrow Cu^{2+}_{(aq.)} + 2Cl^{-}_{(aq.)}$ Cell notation is
  - (a)  $Cu_{(s)}|Cu_{(aq.)}^{2+}||Cl_{(aq.)}^{-}|Cl_{2(g)}|C_{(s)}|$
  - (b)  $C_{(s)}|Cl_{(aq.)}|Cl_{2(g)}||Cu_{(aq.)}^{2+}|Cu_{(s)}|$
  - (c)  $\operatorname{Cu}_{(s)}|\operatorname{Cu}_{(aq.)}^{2+}||\operatorname{Cl}_{(aq.)}^{-}||\operatorname{Cl}_{2(g)}^{-}||$
  - (d)  $\operatorname{Cu}_{(s)}|\operatorname{Cu}_{(aq.)}^{2+}||\operatorname{Cl}_{2(g)}|\operatorname{Cl}_{(aq.)}^{-}|$
- 7. Aniline in a set of reactions yielded a product *D*. NH2

$$\bigcup_{\text{HCl}} \xrightarrow{\text{NaNO}_2} A \xrightarrow{\text{CuCN}} B \xrightarrow{\text{H}_2} C$$

$$\xrightarrow{\text{HNO}_2} D$$

The product *D* would be

- (a)  $C_6H_5CH_2NH_2$  (b)  $C_6H_5NHCH_2CH_3$ (c)  $C_6H_5NHOH$  (d)  $C_6H_5CH_2OH$
- 8. Which of the following has an ester linkage?
  (a) Nylon-6,6
  (b) Dacron
  (c) PVC
  (d) Bakelite
- 9. If  $K_1$  and  $K_2$  are respective equilibrium constants for the two reactions,

(i) 
$$\operatorname{XeF}_{6(g)} + \operatorname{H}_2O_{(g)} \Longrightarrow \operatorname{XeOF}_{4(g)} + 2\operatorname{HF}_{(g)}$$

(11) 
$$\operatorname{XeO}_{4(g)} + \operatorname{XeF}_{6(g)} \rightleftharpoons \operatorname{XeOF}_{4(g)} + \operatorname{XeO}_{3}F_{2(g)}$$
  
the equilibrium constant for the reaction,

$$XeO_{4(g)} + 2HF_{(g)} \Longrightarrow XeO_3F_{2(g)} + H_2O_{(g)}$$
  
will be

(a) 
$$\frac{K_1}{K_2^2}$$
 (b)  $K_1 \cdot K_2$ 

(c) 
$$\frac{K_1}{K_2}$$
 (d)  $\frac{K_2}{K_1}$ 

- **10.**  $XeF_6$  on complete hydrolysis gives
  - (a) XeO<sub>4</sub> (b) XeO<sub>3</sub>
  - (c) XeO<sub>2</sub> (d) Xe
- 11. Mark the correct order of decreasing acid strength of the following compounds.



- (a) V > IV > II > I > III(b) II > IV > I > III > V(c) IV > V > III > II > I(d) V > IV > III > II > I
- 12. Consider the following reaction :

$$O \xrightarrow{\text{COCl}} \xrightarrow{\text{H}_2/\text{Pd-BaSO}_4} A'$$

The product 'A' is

(a)	C <sub>6</sub> H <sub>5</sub> Cl	(b) C <sub>6</sub> H <sub>5</sub> CHO
(c)	C <sub>6</sub> H <sub>5</sub> OH	(d) $C_6H_5COCH_3$

- 13. Hinsberg's reagent is used to distinguish
  - (a) amines (b) alcohols
  - (d) amides. (c) acids
- 14. The vapour pressures of ethanol and methanol are 42.0 mm Hg and 88.5 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 46.0 g of ethanol with 16.0 g of methanol. What is the mole fraction of methanol vapour? (a) 0.467 (b) 0.502 (c) 0.513 (d) 0.556
- 15. Which of the following does not give a precipitate of AgCl with AgNO<sub>3</sub> solution?
  - (a)  $[Co(NH_3)_6]Cl_3$ (b)  $[Co(NH_3)_5Cl]Cl_2$
  - (c)  $[Co(NH_3)_4Cl_2]Cl$  (d)  $[Co(NH_3)_3Cl_3]$

**16.** 
$$\operatorname{Cr}_2\operatorname{O}_7^{2-} \xrightarrow{\mathrm{pH} = x} \operatorname{Cr}\operatorname{O}_4^{2-} \xrightarrow{\mathrm{pH} = y} \operatorname{Cr}_2\operatorname{O}_7^{2-}$$

pH values *x* and *y* can be

- (a) 4 and 5 (b) 4 and 8
- (c) 8 and 3 (d) 8 and 9

17. Among the following oxoacids, the correct decreasing order of acid strength is (a)  $HClO_2 > HClO_4 > HClO_3 > HOCl$ (b) HOCl >  $HClO_2 > HClO_3 > HClO_4$ 

- (c)  $HClO_4 > HOCl > HClO_2 > HClO_3$
- (d)  $HClO_4 > HClO_3 > HClO_2 > HOCl$
- 18. The increasing order of the rate of HCN addition to compounds I-IV is
  - I. HCHO II. CH<sub>3</sub>COCH<sub>3</sub>
  - III. PhCOCH<sub>3</sub> IV. PhCOPh
  - (a) I < II < III < IV(b) IV < II < III < I
  - (c) IV < III < II < I(d) III < IV < II < I
- 19. When first ionisation energy is plotted against the atomic number, the peaks in curve are occupied by (a) halogens (b) rare gases
  - (c) alkali metals (d) transition elements.
- 20. Which is not a correct representation of Boyle's law?



- 21. First ionisation enthalpy of Al is lower than that of Mg. This is because
  - (a) the size of Al is bigger than Mg
  - (b) ionisation enthalpy decreases in a period from left to right
  - (c) it is easier to remove electron from unpaired  $3p^1$  than from paired  $3s^2$
  - (d) aluminium is a passive metal while magnesium is active.
- **22.** The value of '*n*' in the reaction,  $\operatorname{Cr}_2\operatorname{O}_7^{2-}+14\operatorname{H}^+ + n\operatorname{Fe}^{2+} \longrightarrow 2\operatorname{Cr}^{3+} + n\operatorname{Fe}^{3+} + 7\operatorname{H}_2\operatorname{O}$ will be
  - (a) 2 (d) 7 (b) 3 (c) 6
- 23. In Hell-Volhard-Zelinsky reaction, the carboxylic acids are halogenated at A position by using B and C. Identify, A, B and C.
  - B С A (a) α NaOH Iodine (b) α Phosphorus Halogen (c) β Phosphorus H<sub>2</sub>O
  - (d) β NaOH  $PCl_5$

- **24.** What will be the emf of the given cell?  $Pt|H_2(P_1) | H^+_{(aq)} | H_2(P_2) | Pt$ 
  - (a)  $\frac{RT}{F} \ln \frac{P_2}{P_1}$  (b)  $\frac{RT}{2F} \ln \frac{P_1}{P_2}$ (c)  $\frac{RT}{2F} \ln \frac{P_2}{P_1}$  (d) None of these
- **25.** The number of atoms in 100 g of a *fcc* crystal with density, d = 10 g/cm<sup>3</sup> and cell edge equal to 100 pm, is equal to

(a)	$2 \times 10^{25}$	(b)	$1 \times 10$	) <sup>25</sup>
(c)	$4 \times 10^{25}$	(d)	$3 \times 10^{\circ}$	) <sup>25</sup>

**26.** At a given temperature, total vapour pressure (in torr) of a mixture of volatile components *A* and *B* is given by  $P_{\text{total}} = 120 - 75x_B$ .

The vapour pressures of pure *A* and *B* respectively (in torr) are

- (a) 120, 75 (b) 120, 195
- (c) 120, 45 (d) 75, 45
- **27.** The major product formed when 2-bromobutane is treated with alcoholic KOH is
  - (a) 2-butanol (b) 1-butene
  - (c) 1-butanol (d) *trans*-2-butene.
- 28. For a first order reaction, the graph log [A] vs t is given as follows :

x is equal to (a)  $\frac{0.693}{k}$  (b)  $\frac{k}{2.303}$  (c)  $-\frac{k}{2.303}$  (d)  $\log [A]_0$  (d)  $\log [A]_0$ 

29. The correct formula of plaster of Paris is

(a) 
$$CaSO_4 \cdot 2H_2O$$
 (b)  $CaSO_4 \cdot H_2O$ 

(c) 
$$CaSiO_4 \cdot 2H_2O$$
 (d)  $CaSO_4 \cdot \frac{1}{2}H_2O$ 

**30.**  $\Delta H_f^{o}$  of water is – 285.8 kJ mol<sup>-1</sup>. If enthalpy of neutralisation of monoacidic strong base is –57.3 kJ mol<sup>-1</sup>,  $\Delta H_f^{o}$  of OH<sup>-</sup> ion will be

(a) 
$$-114.25$$
 kJ mol<sup>-1</sup> (b)  $114.25$  kJ mol<sup>-1</sup>  
(c)  $228.5$  kJ mol<sup>-1</sup> (d)  $-228.5$  kJ mol<sup>-1</sup>

- **31.** A 4 : 1 mixture of helium and methane is contained in a vessel at 10 bar pressure. Due to a hole in the vessel, the gas mixture leaks out. The composition of the mixture effusing out initially is
  - (a) 8:1 (b) 8:3
  - (c) 4:1 (d) 1:1

- **32.** Four metals and their methods of refinement are given :
  - (i) Ni, Cu, Zr, Ga
  - (ii) Electrolysis, van-Arkel process, zone refining, Mond's process

Choose the right method for each.

- (a) Ni : Electrolysis, Cu : van-Arkel process, Zr : Zone refining, Ga : Mond's process
- (b) Ni : Mond's process, Cu : Electrolysis, Zr : van-Arkel process, Ga : Zone refining
- (c) Ni : Mond's process, Cu : van-Arkel process, Zr : Zone refining, Ga : Electrolysis
- (d) Ni : Electrolysis, Cu : Zone refining, Zr : van-Arkel process, Ga : Mond's process
- 33. Haemoglobin contains 0.334% of iron by weight. The molecular weight of haemoglobin is approximately 67200 u. The number of iron atoms (Atomic weight of Fe is 56 u) present in one molecule of haemoglobin is

- 34. Element A forms an oxide A<sub>2</sub>O<sub>3</sub>. What would be the formulae of its carbonate and phosphate?
  (a) A<sub>2</sub>(CO<sub>3</sub>), A(PO<sub>4</sub>) (b) A(CO<sub>3</sub>), A<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>
  (c) A<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, A(PO<sub>4</sub>) (d) A<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub>, A<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub>
- **35.** The two functional groups present in a typical carbohydrate are
  - (a) -OH and -COOH
  - (b) -CHO and -COOH
  - (c)  $\geq C \equiv O$  and -OH

- **36.** The total number of possible isomers of the complex compound [Cu<sup>II</sup>(NH<sub>3</sub>)<sub>4</sub>][Pt<sup>II</sup>Cl<sub>4</sub>] is
  - (a) 3 (b) 6 (c) 5 (d) 4
- 37. 2-Phenylethanol may be prepared by the reaction of phenyl magnesium bromide with(a) HCHO(b) CH<sub>2</sub>CHO

(c) 
$$CH_3COCH_3$$
 (d)  $\angle$ 

- **38.** C<sub>8</sub>H<sub>10</sub>(*A*) by oxidative cleavage forms C<sub>3</sub>H<sub>5</sub>COOH(*B*). Thus, *A* and *B* respectively are
  - (a)  $CH_2 = CHCH_2C \equiv CCH_2CH = CH_2$ ,  $CH_2 = CHCH_2COOH$

- (c) both (a) and (b) are correct
- (d) none of the above is correct.

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39. In which of the following orbital diagrams are both Pauli's exclusion principle and Hund's rule violated?



40. Which one of the following acts as an oxidising agent?

(a)	Tb⁴⁺	(b)	Sm <sup>2</sup>
	2		. 2.

- (c)  $Eu^{2+}$ (d)  $Yb^{2+}$
- 41. Nitrogen in an organic compound can be estimated by
  - (a) Kjeldahl's method
  - (b) Carius method
  - (c) Victor Meyer's method
  - (d) Lassaigne's method.
- 42. The maximum kinetic energy of the photoelectrons is found to be  $6.63 \times 10^{-19}$  J. When the metal is irradiated with a radiation of frequency  $2 \times 10^{15}$  Hz, the threshold frequency of the metal is about
  - (a)  $2 \times 10^{15} \, \mathrm{s}^{-1}$ (b)  $1 \times 10^{15} \text{ s}^{-1}$
  - (c)  $2.5 \times 10^{15} \, \mathrm{s}^{-1}$ (d)  $4 \times 10^{15} \text{ s}^{-1}$
- 43. Which of the following represents physical adsorption?



44. The number of possible resonance structures for  $CO_3^{2-}$  is

(a) 2	(b) 3
(c) 6	(d) 9

- 45. Amount of oxalic acid present in a solution can be determined by its titration with KMnO<sub>4</sub> solution in the presence of H<sub>2</sub>SO<sub>4</sub>. The titration gives unsatisfactory result when carried out in the presence of HCl, because HCl
  - (a) oxidises oxalic acid to carbon dioxide and water
  - (b) gets oxidised by oxalic acid to chlorine
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- (c) furnishes H<sup>+</sup> ions in addition to those from oxalic acid
- (d) reduces permanganate to  $Mn^{2+}$ .
- **46.** Which of the following is incorrect with respect to Frenkel defect?
  - (a) One or more ions (generally cations) shift from lattice points to interstitial sites.
  - (b) It appears in ionic compounds having high coordination number.
  - (c)  $r^+/r^-$  ratio should be low.
  - (d) All of the above.
- **47.**  $H_2O_2$  is manufactured these days by
  - (a) electrolysis of 50%  $H_2SO_4$
  - (b) the action of  $H_2SO_4$  on  $Na_2O_2$
  - (c) the action of  $H_2O_2$  on  $BaO_2$
  - (d) burning hydrogen in excess of oxygen.
- 48. 17.675 is rounded off to four significant figures as
  - (a) 17.68 (b) 17.67
  - (d) 17.7 (c) 17.6750
- 49. Ge(II) compounds are powerful reducing agents whereas Pb(IV) compounds are strong oxidants. This can be due to
  - (a) Pb is more electropositive than Ge
  - (b) ionization potential of Pb is less than that of Ge
  - (c) ionic radii of  $Pb^{2+}$  and  $Pb^{4+}$  are larger than those of Ge<sup>2+</sup> and Ge<sup>4+</sup>
  - (d) more pronounced inert pair effect in Pb than in Ge.
- 50. Rutherford's experiment which established the nuclear model of the atom used a beam of
  - (a)  $\beta$ -particles which impinged on a metal foil and got absorbed
  - (b) y-rays which impinged on a metal foil and ejected electrons
  - (c) helium atoms, which impinged on a metal foil and got scattered
  - (d) helium nuclei, which impinged on a metal foil and got scattered.
- **51.**  $E_1$ ,  $E_2$  and  $E_3$  are the emf values of the three given Galvanic cells respectively.

(i)  $Zn|Zn^{2+}(1 M)||Cu^{2+}(0.1 M)|Cu$ 

(ii)  $Zn|Zn^{2+}(1 M)||Cu^{2+}(1 M)|Cu$ (iii)  $Zn|Zn^{2+}(0.1 M)||Cu^{2+}(1 M)|Cu$ 

- Which one of the following is true?
- (a)  $E_2 > E_3 > E_1$ (b)  $E_3 > E_2 > E_1$
- (a)  $E_2 > E_3 > E_1$  (b)  $E_3 > E_2 > E_1$ (c)  $E_1 > E_2 > E_3$  (d)  $E_1 > E_3 > E_2$

- **52.** To prepare an ether by Williamson's synthesis, the reactants needed are
  - (a) ethyl alcohol and *tert*-butyl alcohol
  - (b) sodium ethoxide and tert-butyl bromide
  - (c) sodium *tert*-butoxide and ethyl bromide
  - (d) sodium ethoxide and sodium *tert*-butoxide
- **53.** The correct order of acidic nature of oxides is in the order
  - (a)  $NO < N_2O < N_2O_3 < NO_2 < N_2O_5$
  - (b)  $N_2O < NO < N_2O_3 < NO_2 < N_2O_5$
  - (c)  $N_2O_5 < NO_2 < N_2O_3 < NO < N_2O_3$
  - (d)  $N_2O_5 < N_2O_3 < NO_2 < NO < N_2O_3$
- **54.** Compound *X* is highly volatile and insoluble in water. Bonding in *X* is
  - (a) ionic (b) covalent
  - (c) polar covalent (d) coordinate.
- **55.** At a particular temperature under high pressure  $K_w(H_2O) = 1 \times 10^{-10}$ .

A solution of pH 5.4 under these conditions is said to be

- (a) acidic (b) basic
- (c) neutral (d) amphoteric.
- 56. In coagulating the colloidal solution of As<sub>2</sub>S<sub>3</sub> which of the following has the minimum coagulating value?
  (a) NaCl
  (b) KCl

(a)	NaCI	(D)	KCI
(c)	BaCl <sub>2</sub>	(d)	AlCl <sub>3</sub>

- **57.** In an irreversible process taking place at constant T and P and in which only pressure-volume work is being done, the change in Gibbs' free energy (*dG*) and change in entropy (*dS*) satisfy the criteria
  - (a)  $(dS)_{V,E} < 0, (dG)_{TP} < 0$
  - (b)  $(dS) > 0, (dG)_{TP} < 0$
  - (c)  $(dS) = 0, (dG)_{TP} = 0$
  - (d)  $(dS) = 0, (dG)_{TP} > 0$
- **58.** Which of the following statements about photochemical smog is incorrect?
  - (a) It is also called as Los Angeles smog.
  - (b) It has low concentration of oxidising agents.
  - (c) It can be controlled by controlling the release of NO<sub>2</sub>, hydrocarbons, etc.
  - (d) Plantation of some plants like pinus helps in controlling photochemical smog.
- **59.** Major product of the following  $S_N$ 1 reaction is

$$\begin{array}{c} \operatorname{CH}_{3}\operatorname{CHCHCH}_{3} + \overline{\operatorname{OC}}_{2}\operatorname{H}_{5} \longrightarrow \\ | & | \\ \operatorname{Br} & \operatorname{CH}_{3} \end{array}$$

(a) 
$$CH_3$$
  
 $OC_2H_5$   
(b)  $CH_3CHCH_2CH_2OC_2H_5$   
 $CH_3$   
(c)  $CH_3CH_2CCH_3$  (d) none is correct.  
 $OC_2H_5$ 

**60.** Aniline on treatment with HCl and NaNO<sub>2</sub> at low temperature gives

SOLUTIONS

- (a) aminophenol (b) chloroaniline
- (c) diazonium salt (d) nitroaniline.

C 
$$CH_3$$
  
1 2 || 3 4  
2. (a):  $CH_3 - C - CH - CH_3$   
3-Methylbutan-2-one

- 3. (d): Saccharin is 550 times sweeter than sucrose, aspartame is 100 times sweeter than sucrose. Sucralose is 600 times sweeter than sucrose.
- **4.** (a): Branching decreases the boiling point.
- 5. (a): For the reaction,  $2A + B \rightarrow C + D$ Rate of reaction

$$= -\frac{1}{2} \frac{d[A]}{dt} = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = \frac{d[D]}{dt}$$
Now, rate of reaction,  $\frac{d[C]}{dt} = k[A]^{x}[B]^{y}$ 
From table,  
 $1.2 \times 10^{-3} = k(0.1)^{x} (0.1)^{y}$  ...(i)  
 $1.2 \times 10^{-3} = k(0.1)^{x} (0.2)^{y}$  ...(ii)  
 $2.4 \times 10^{-3} = k(0.2)^{x} (0.1)^{y}$  ...(iii)  
On dividing equation (i) by (ii), we get  
 $\frac{1.2 \times 10^{-3}}{1.2 \times 10^{-3}} = \frac{k(0.1)^{x} (0.1)^{y}}{k(0.1)^{x} (0.2)^{y}}$   
 $1 = \left(\frac{1}{2}\right)^{y} \implies y = 0$ 

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

$$\frac{1.2 \times 10^{-3}}{2.4 \times 10^{-3}} = \frac{k(0.1)^x (0.1)^y}{k(0.2)^x (0.1)^y}$$
$$\left(\frac{1}{2}\right)^1 = \left(\frac{1}{2}\right)^x \implies x = 1$$
Hence,  $\frac{d[C]}{dt} = k[A]^1[B]^0 = k[A]$ 





8. (b): When a diacid is condensed with dialcohol, the polymer obtained contains ester linkage.



- 9. (d): Reaction (ii) and reverse of reaction (i) gives the desired reaction hence,  $K = K_2 \times \frac{1}{K_1} = \frac{K_2}{K_1}$ .
- 10. (b):  $XeF_6$  on complete hydrolysis yields xenon trioxide,  $XeO_3$ .  $XeF_6 + 3H_2O \rightarrow XeO_3 + 6HF$
- 11. (b): Phenols are acidic in nature due to resonance stabilisation of phenoxide ion. Presence of electron withdrawing groups (such as -NO<sub>2</sub>, -X, -NR<sup>+</sup><sub>3</sub>, -CHO, -COX, -COOR, -CN) in the ring stabilises phenoxide ion and increases the acidic nature of phenols. On the other hand, presence of electron releasing groups (such as -CH<sub>3</sub>, -OR) in the ring destabilises the phenoxide ion and decreases the acidic nature of phenols.

Furthermore, *meta*-isomer of nitrophenol is less acidic than *p*-and *o*-isomers because it is stabilised by inductive effect only. Similarly, *meta*-isomer of methoxyphenol is destabilised to lesser extent than the *para*-isomer.

Thus, correct order of acidic strength is II > IV > I > III > V.

12. (b): 
$$O = C - Cl_{H_2/Pd-BaSO_4/S} O = C - H$$

It is Rosenmund reduction.

- **13.** (a): Hinsberg's reagent  $(C_6H_5SO_2Cl)$  is used to distinguish amines.
- 14. (c):  $CH_{3}OH(A)$  $C_2H_5OH(B)$ Vapour pressure 88.5 mm Hg 42.0 mm Hg Mass 16.0 g 46.0 g No. of moles 0.5 1 :. Total moles = 1 + 0.5 = 1.5 $P_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B = \frac{88.5 \times 0.5}{1.5} + \frac{42 \times 1}{1.5}$  $P_{\text{total}} = 29.5 + 28 = 57.5 \text{ mm Hg}$ Mole fraction of methanol in vapour phase is  $y_A$ .  $p_A = y_A \times \text{Total pressure}$  $y_A = \frac{29.5}{57.5} = 0.513$ :.
- 15. (d): [Co(NH<sub>3</sub>)<sub>3</sub>Cl<sub>3</sub>] does not ionise to furnish Cl<sup>-</sup> ion as no chlorine atom is present outside the coordination sphere. Evidently, it would not give white precipitate with AgNO<sub>3</sub>.
- **16.** (c) :  $\operatorname{Cr}_2 \operatorname{O}_7^{2-} + 2\operatorname{OH}^- \longrightarrow 2\operatorname{Cr}\operatorname{O}_4^{2-} + \operatorname{H}_2\operatorname{O};$   $pH > 7 \ (x > 7)$  $2\operatorname{Cr}\operatorname{O}_4^{2-} + 2\operatorname{H}^+ \longrightarrow \operatorname{Cr}_2\operatorname{O}_7^{2-} + \operatorname{H}_2\operatorname{O};$   $pH < 7 \ (y < 7)$
- **17.** (d): No. of O-atoms (*i.e.* oxidation state)  $\propto$

Acidic strength

Hence, the decreasing order of acidic strength will be HClO<sub>4</sub> > HClO<sub>3</sub> > HClO<sub>2</sub> > HOCl

 (c) : Addition of HCN is a nucleophilic addition reaction. Greater the electron deficiency of carbonyl group, higher is the rate of reaction. Hence,

$$\begin{array}{cccc}
O & O & O \\
\parallel & \parallel & \parallel \\
Ph-C-Ph < Ph-C-CH_3 < CH_3-C-CH_3 \\
(IV) & (III) & (II) & O \\
< H-C-H \\
(I) \\
\end{array}$$

**19.** (b): Generally, the first ionization energy increases as we go across a period. Hence, the maximum peaks in curve are occupied by rare gases.

20. (c)

- **21.** (c) : Electronic configuration of Al  $1s^22s^22p^63s^23p^1$ Electronic configuration of Mg -  $1s^22s^22p^63s^2$ It is difficult to remove electron from paired  $3s^2$ -orbital than the unpaired  $3p^1$ . Hence, *I.E.*<sub>1</sub> of Al is lower than Mg.
- **22.** (c) :  $Cr_2O_7^{2+} + 14H^+ + nFe^{2+} \longrightarrow 2Cr^{3+} + nFe^{3+} + 7H_2O$  $Cr_2O_7^{2+} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$  (reduction) ...(i)

$$Fe^{2+} \longrightarrow Fe^{3+} + e^{-}$$
 (oxidation) ...(ii)

Eq. (ii) is multiplied by 6,  $6Fe^{2+} \longrightarrow 6Fe^{3+} + 6e^{-}$ Thus, balanced equation is  $Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$ Hence, the value of *n* is 6.

23. (b): 
$$RCH_2COOH \xrightarrow{(i) X_2/P} R-CH-COOH \downarrow_X (X=Cl, Br) \alpha-Halocarboxylic acid$$

- 24. (b): Anode :  $H_2(P_1) \longrightarrow 2H^+ + 2e^-$ Cathode :  $2H^+ + 2e^- \longrightarrow H_2(P_2)$   $H_2(P_1) \longrightarrow H_2(P_2)$  $E_{cell} = E_{cell}^\circ - \frac{RT}{nF} \ln \frac{P_2}{P_1} = \frac{RT}{2F} \ln \frac{P_1}{P_2}$
- **25.** (c) : Mass (m) = 100 g; Density (d) = 10 g/cm<sup>3</sup> and length (l) = 100 pm  $= 100 \times 10^{-12}$  m  $= 100 \times 10^{-10}$  cm We know that volume of the unit cell

$$= (a)^{3} = (100 \times 10^{-10} \text{ cm})^{3} = 10^{-24} \text{ cm}^{3}$$
  
volume of 100 g of element

and volume of 100 g of element

$$=\frac{\text{Mass}}{\text{Density}}=\frac{100}{10}=10 \text{ cm}^3$$

Therefore, number of unit cells =  $\frac{10}{10^{-24}} = 10^{25}$ 

Since each *fcc* cube contains 4 atoms, therefore total number of atoms in 100 g =  $4 \times 10^{25}$ .

26. (c) : 
$$P_{\text{total}} = p_A^\circ x_A + p_B^\circ x_B$$
  
  $= p_A^\circ (1 - x_B) + p_B^\circ x_B = p_A^\circ - (p_A^\circ - p_B^\circ) x_B$   
  $= 120 - 75 x_B \text{ (given)}$   
Thus,  $p_A^\circ = 120 \text{ torr}$   
  $p_A^\circ - p_B^\circ = 75 \text{ torr}$ ,  $\therefore p_B^\circ = 45 \text{ torr}$ 

27. (d) : 
$$CH_3 - CH - CH_2 - CH_3 \xrightarrow{\text{alc. KOH}}_{H_3C} H_3C \xrightarrow{H_{H_3C}}_{C=C} H_{H_3C}$$

28. (c): For first order reaction,



- **29.** (d): Plaster of Paris is calcium sulphate hemihydrate, CaSO<sub>4</sub>  $\cdot \frac{1}{2}$ H<sub>2</sub>O.
- **30.** (d):  $H_{2(g)} + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}; \Delta H_f^\circ = -285.8 \text{ kJ mol}^{-1}$ ...(i)

$$H^{+}_{(aq)} + OH^{-}_{(aq)} \longrightarrow H_2O_{(l)}; \Delta H^{\circ}_{neut} = -57.3 \text{ kJ mol}^{-1}$$
...(ii)
$$\frac{1}{2} H_{2(g)} \longrightarrow H^{+}_{(aq)} + e^{-}; \Delta H^{\circ}_f = 0 \text{ (by convention)}$$
...(iii)
(i) - (ii) - (iii) gives,

$$\frac{1}{2} H_{2(g)} + \frac{1}{2} O_{2(g)} + e^{-} \longrightarrow OH_{(aq)}^{-}$$
  

$$\Delta H_{f}^{\circ} \text{ of } OH^{-} = -285.8 + 57.3 = -228.5 \text{ kJ mol}^{-1}$$

**31.** (a) : Pressure of helium = 8 bar,  $CH_4 = 2$  bar According to Graham's law,

$$\frac{r_1}{r_2} = \frac{P_1}{P_2} \sqrt{\frac{M_2}{M_1}}$$
$$\frac{r_{\text{He}}}{r_{\text{CH}_4}} = \frac{P_{\text{He}}}{P_{\text{CH}_4}} \sqrt{\frac{M_{\text{CH}_4}}{M_{\text{He}}}} = \frac{8}{2} \sqrt{\frac{16}{4}} = \frac{8}{1} = 8:1$$

 32. (b): Ni — Mond's process; Cu — Electrolysis ; Zr — van-Arkel process; Ga — Zone refining

33. (c) : ∵ 100 g of haemoglobin contains = 0.334 g Fe
∴ 67200 g of haemoglobin contains

$$=\frac{0.334\times67200}{100}=224.45 \text{ g Fe}$$

Now,

 $\therefore$  56 g iron = 1 mole of Fe atoms

$$\therefore 224.45 \text{ g iron} = \frac{1 \times 224.45}{56}$$
$$= 4 \text{ moles of Fe atoms}$$
$$\therefore 1 \text{ molecule of haemoglobin} = 4 \text{ Fe atoms}$$

**34.** (c) :  $A_2O_3 \Rightarrow$  Valency of A is 3.

So, the formulae of carbonate  $(CO_3^{2-})$  will be  $A_2(CO_3)_3$  and that of phosphate  $(PO_4^{3-})$  will be  $A(PO_4)$ .

- **35.** (c) : Carbohydrates are essentially polyhydroxy aldehydes and polyhydroxy ketones. Thus, the two functional groups present are >C=O (aldehyde or ketone) and -OH.
- **36.** (d): For  $[Cu^{II}(NH_3)_4][Pt^{II}Cl_4]$ , four isomers are possible which are  $[Cu(NH_3)_4][PtCl_4]$ ,  $[CuCl_4][Pt(NH_3)_4]$ ,  $[PtCl_3(NH_3)][Cu(NH_3)_3Cl]$ and  $[Pt(NH_3)_3Cl]$   $[Cu(NH_3)Cl_3]$ .



Formation of *B* indicates that *A* is symmetrical.

- **39.** (d): Two electrons with parallel spins in the same orbital are violating Pauli's exclusion principle whereas pairing without single occupancy of all orbitals is violating Hund's rule.
- **40.** (a) : All those inner-transition elements having +2 oxidation state, change to +3, and act as reducing agents. While those having +4 oxidation state tend to change to +3 oxidation state and act as oxidising agents. Therefore, Tb<sup>4+</sup> acts as an oxidising agent.
- **41.** (a): Nitrogen can be estimated by Kjeldahl's method. This method cannot be used for organic compounds (i) containing nitrogen in the ring. *e.g.*, pyridine, quinoline etc. (ii) containing nitro and diazo groups. However, Lassaigne's test is used to detect nitrogen.

42. (b): Kinetic energy = 
$$h(v - v_0)$$
  
 $KE = hv - hv_0$   
 $v_0 = v - \frac{KE}{h} = 2 \times 10^{15} - \frac{6.63 \times 10^{-19}}{6.63 \times 10^{-34}}$   
 $= 1 \times 10^{15} \text{ s}^{-1}$ 

**43.** (a) : The amount of adsorption decreases with rise in temperature in case of physical adsorption.

**44.** (b): 
$$:\overset{.\dot{O}}{\underset{.\dot{O}}{:}} C - :\overset{.\ddot{O}}{\underset{.\dot{O}}{:}} \longleftrightarrow \overset{.\ddot{O}}{\underset{.\dot{O}}{:}} C = :\overset{.\ddot{O}}{\underset{.\dot{O}}{:}} C - :\overset{.\ddot{O}}{\underset{.\dot{O}}{:}} C - :\overset{.\ddot{O}}{\underset{.\dot{O}}{:}} C - :\overset{.\ddot{O}}{\underset{.\dot{O}}{:}} C - :\overset{.\dot{O}}{\underset{.\dot{O}}{:}} C - :\overset{.\dot{O}}{:} C - :\overset{.\dot{O}}{:} C - :\overset{.\dot{O}}{\underset{.\dot{O}}{:}} C - :\overset{.\dot{O}}{:} C - :; C - :$$

**45.** (d): Oxalic acid present in a solution can be determined by its titration with  $KMnO_4$  solution in the presence of  $H_2SO_4$ .

 $2KMnO_4 + 3H_2SO_4 + 5 \qquad \begin{array}{c} COOH \\ I \\ COOH \\ K_2SO_4 + 2MnSO_4 + 10CO_2 + 8H_2O \end{array}$ 

Titration cannot be done in the presence of HCl because KMnO<sub>4</sub> being a strong oxidising agent oxidises HCl to  $Cl_2$  and itself gets reduced to  $Mn^{2+}$ . So, actual amount of oxalic acid in solution cannot be determined.

- **46.** (b): Frenkel defect appears in ionic crystals having low coordination number, *i.e.*, low  $r^+/r^-$  ratio. The void can accommodate small cation easily.
- **47.** (a):  $H_2O_2$  is manufactured by electrolysis of 50% sulphuric acid.
- 48. (a)
- **49.** (d): Ge<sup>4+</sup> is more stable than Ge<sup>2+</sup> as a result of which Ge<sup>2+</sup> has a tendency to be oxidised to Ge<sup>4+</sup> so, Ge<sup>2+</sup> compounds act as powerful reducing agents. But Pb<sup>2+</sup> is more stable than Pb<sup>4+</sup> because of pronounced inert pair effect as a result of which Pb<sup>4+</sup> has a tendency to get reduced to Pb<sup>2+</sup> so, Pb<sup>4+</sup> compounds act as strong oxidising agents (*i.e.*, oxidants).
- **50.** (d): Rutherford used doubly charged helium particles ( $\alpha$ -particles).

51. (b): 
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{n} \log_{10} \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$
  
Higher the  $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$  ratio lower is the emf of cell  
(i)  $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 10$ ; (ii)  $\frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 1$ 

(iii) 
$$\frac{[Zn^{2+}]}{[Cu^{2+}]} = 0.1$$

So, order is  $E_3 > E_2 > E_1$ .

**52.** (c) : 1° alkyl halides on treatment with an alkoxide ion tend to undergo substitution to form ethers. So, sodium *tert*-butoxide and ethyl bromide reagent is used.

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53. (b): The acidic character of oxides increases with increase in oxidation number of element. However,

$$\begin{array}{c} \stackrel{+1}{\underset{N_2O,NO}{\underset{Neutral}{\overset{+2}{\underset{N_2O_3}{\underset{N_2O_3}{\underset{NO_2}{\underset{N_2O_5}{N_2O_5}{\underset{N_2O_5}{\underset{N_2O_5}{N_2O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{\underset{N}1O_5}{$$

54. (b): Compounds which are insoluble in water have covalent bonds. Due to their low boiling points, they are highly volatile.

55. (b): 
$$K_w = 1 \times 10^{-10}$$
  
∴ [H<sup>+</sup>] = [OH]<sup>-</sup> = 10<sup>-5</sup> M  
Thus, pH = 5 for neutral solution.  
pH < 5 acidic, pH > 5 basic

- **56.** (d):  $As_2S_3$  is a negative sol. For coagulating negative sol, Al<sup>3+</sup> is most effective. Higher the magnitude of the charge, lower is the coagulating value.
- 57. (b): An irreversible process is spontaneous hence, entropy increases and free energy decreases.
- 58. (b): Photochemical smog has high concentration of oxidising agents and it can be controlled by controlling the release of NO<sub>2</sub>, hydrocarbons, etc. Plantation of some plants like pinus helps in controlling photochemical smog.



Benzene diazonium chloride

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MATHEMATICS

 $2H_2O + NaCl$ 

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### SAWHORSE AND NEWMAN PROJECTIONS

Sawhorse projection is used to show relative spatial arrangement (arrangement in space) of atoms or groups attached to two adjacent carbons (not necessarily chiral). The backbone carbons are represented by a diagonal line and the terminal carbons are shown in groups. The top carbon of Fischer projection becomes the back carbon group of Sawhorse projection.



Note that in Sawhorse projection-1, while the Z and K groups are facing downward, L and Y are on the right and X and M are on the left as were in the Fischer projection. Whereas in Sawhorse projection-2, Z is facing upward (while K remains as it was), X is on the right and Y is on the left. This format is always true and can be used as a tip to convert Fischer to Sawhorse.

Free clockwise or anticlockwise rotation of one carbon keeping the other fixed is permissible in a Sawhorse projection, also called as 'Perspective Formula'.

The steric interaction between atoms or groups in three-dimensional space is nicely visualized by Newman projection formula. The central dot represents the first carbon and the 'circle' stands for the back carbon. Lines

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projected from the dot and the perimeter of the circle carry the atoms or groups attached to the respective carbons.

Newman projection formula in which the atoms or groups attached to two carbons, one shown by dot and the other by a circle, lie in a straight line is called the 'eclipsed form'. Atoms or groups attached to front carbon obscure or hide those attached to the rear (or back) carbon, hence the title. The other form of Newman projection though is generally called as 'staggered' but sometimes called as 'gauche' or 'skew' depending upon the nature and position of the substituents.



While converting a Sawhorse projection formula to a Newman form, simply the front and the rear carbons are copied along with their substituents.



Note that unlike Fisher projection formula, the carbons demonstrated in Sawhorse or Newman projection formulae are not necessarily chiral carbons.



**Problem-1:** Write Fischer projection formulae for the following compounds.



### **RELATIVE AND ABSOLUTE NAMING**

Naming the stereoisomers using prefixes *cis*, *trans*, *syn*, *anti*, *D* (not to be confused with *d* used for dextrorotatory substance) and *L* (not to be confused with *l* used for laevorotatory substance) is an attempt to show the relative configuration. For example, in *cis*-but-2-ene,  $-CH_3$  attached to one carbon is *cis* or on the same side as the  $-CH_3$  attached to the other carbon of the double bond. This is what is known as 'relative configuration'.



Without taking the spatial arrangement of groups around both the carbons simultaneously a stereoisomer cannot be called as *cis* or *trans*. Similar is the way for assigning D and L configuration for sugar molecules. The compound relative to which the configurations of sugars are described is the glyceraldehyde. It is taken as an arbitrarily standard. Glyceraldehyde molecule with -H on the left is given as 'D'. Any other aldose sugar molecules having -H on the left at the chiral carbon farthest from the -CHO functional group is termed as 'D'.





The idea though can be extended to other chiral centers but has a number of limitations. To overpower these difficulties, absolute system of naming stereocentres have been developed. In this method, one stereocentre can be directly named without comparing it with another stereocentre. The method is known as 'absolute configuration'.

#### THE SEQUENCE RULE

Consider the following rules without naming them as rule-1, 2 ... etc.

- The higher the atomic number of the immediate substituent atom, the higher is the priority.
   For example, -H < -C < -N < -O < -Cl.</li>
- For different isotopes, the heavier isotope takes precedence.
  - For example, -D > -H
- If the immediate substituent atoms are same, move to the next set of three atoms. The set with at least one atom having higher atomic number takes precedence.



Since (H, H, Cl = 1, 1, 17) takes superiority over (H, N, O = 1, 7, 8),  $-CH_2Cl$  gets the higher priority as compared to  $-CH(OH)NH_2$ .

• If a double or triple bond is attached to the substituent atom under consideration, the set of three atoms is picked as shown below.



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A doubly bonded atom attached to substituent is considered twice and a triply bonded atom is considered thrice to get the set of three atoms and then the previous priority rule is then applied to decide the precedence. The set (C, C, C = 6, 6, 6) takes preference over the set (H, C, C = 1, 6, 6). Thus,  $-C \equiv CH$  takes priority over  $-CH = CH_2$ . Consider another example,



The set (O, O, O = 8, 8, 8) takes priority over the set (O, O, H = 8, 8, 1). As a result, -COOH gets higher priority as compared to -CHO.

### *R/S* SYSTEM OF NOMENCLATURE (CAHN-INGOLD-PRELOG OR CIP SYSTEM)



CIP system is used to describe the configuration of the stereocentre directly without comparing it with any other stereocentre whose configuration is arbitrarily assigned (like glyceraldehyde). Follow the simple steps.

• Following the sequence rules, allot priority order to the substituents attached to the stereocentre.



• Hold the model in such a way so that the atom having lowest priority (H here) remains at farthest distance from your eyes.



• Draw an arrow mark in a circular way starting from atom of highest priority (iodine) to the third most priority (chlorine) *via* the second most (bromine) means,



• If the arrow mark moves in a clockwise manner, the configuration assigned is '*R*' and if in the anticlockwise manner, the configuration assigned is '*S*'. The alphabet '*R*' stands for 'rectus' or right and '*S*' stands for 'sinister' means left.



The method is most widely used on Fischer projections. So, here are the rules to assign the configurations of stereocentres in Fischer projection formulae.

• Assign priorities to the substituents attached to the stereocentre and then check whether the substituent with lowest priority is on the vertical line or not. If yes, draw the arrow mark starting from the top most priority to the third most *via* the second most



• If the atom with lowest priority is on the horizontal line, rotate the Fischer projection in such a way so that the atom or group with lowest priority is brought to the vertical line. While rotating the Fischer projection formula on the plane of the paper, the restrictions must be kept in mind.



Consider some more examples where more than one chiral carbon centers are there. In such cases, each individual center has to be checked separately.



In case the chiral center is a part of ring system, it can be proceeded as follows :



The configuration of chiral center is 'S' here. -OH group takes the highest priority. In order to decide the next, we move along the ring both in upward and in downward directions. In the first point, we come

across  $-CH_2$ - units in both the ways. Then comes the real difference, one -CO- group and another  $-CH_2$ - unit. -H gets the lowest priority. Priority order of the substituents then has been shown in circles as 1, 2, 3 and 4 (*A*) and the ring dropped for the sake of simplicity, then rotated the structure like a steering wheel towards right (*B*) and then have converted it into the proper Fischer projection formula (*C*).



The following steps are as usual to bring the lowest substituent to the vertical line and then to check the configuration.



### TIPS TO HANDLE R/S SYSTEM OF NOMENCLATURE

The following tips can help only in the final step; though small but it is extremely handy. When the substituent with the lowest priority remains in the horizontal line, normally rotate the Fischer projection in such a way so as to bring it to the vertical line. Then assign 'R' or 'S' to the chiral center. To recall it take another example.



Instead of bringing the fourth priority to the vertical line, if the configuration is assigned directly, the result will be wrong, wrong but exactly opposite of the correct answer.



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Without bringing the group with lowest priority to the vertical line, it can be done directly. The tips are:

- When the group with lowest priority is on the vertical line, check the direction of arrow mark from 1 to 2 to 3 and assign the configuration.
- When the group with lowest priority is on the horizontal line, check the direction of arrow mark from 1 to 2 to 3 and find out the configuration. If it is '*R*', then correct answer is '*S*' and vice-versa.

**Problem-2:** Assign '*R*' and '*S*' notation to the chiral centers in the following compounds.



**Problem-3:** Assign '*R*' and '*S*' notation to the chiral centers in the following compounds.



**Problem-4:** Assign '*R*' and '*S*' notation to the chiral centers of the following ring compounds.





**Problem-5:** Assign '*R*' and '*S*' notation to the chiral centers of the following spiro compounds.



### SOLUTIONS

Problem-1: CH3 (b) Br H↓\_\_он H-<u>—</u> — Н (a) H<sub>2</sub>N-ĊH<sub>3</sub> Ċ<sub>2</sub>H<sub>5</sub> CHO (d) Br—H Cl—H —Н (c) HO-—ОН H-ĊH3 CH<sub>3</sub>  $C_2H_5$ —ОН (e) H-HO-ĊH3

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### **Problem-3:**

The detail solutions for two bits are as follows :



Others are as follows :



After priority assignment and ignoring the ring, the molecule will look like



After assigning priority and ignoring the rings, it would look like





Since 4th priority is on the horizontal line, it is S



# CHEMISTRY MUSING

**SOLUTION SET 33** 

1. (a): In octahedral complexes,  $t_{2g}$  $e_g$  $d^8$ 11 11 11 1  $CFSE_{Octahedral} = -0.4n_x + 0.6n_y$  $(n_x = \text{no. of electrons in } t_{2g} \text{ and } n_y = \text{no. of electrons}$ in  $e_g$ )  $CFSE_{octahedral} = -0.4(6) + 0.6(2) = -1.2 \Delta_o$ In tetrahedral complexes, eg  $t_{2g}$  $d^8$ 11 1 11 11  $CFSE_{tetrahedral} = -0.6n_x + 0.4n_y$ 

$$= -0.6(4) + 0.4(4) = -0.8 \Delta_t$$
  
Now,  $\Delta_t = \frac{4}{9} \Delta_o$ 

$$\therefore \quad \text{CFSE}_{\text{tetrahedral}} = -0.8 \left(\frac{4}{9} \Delta_o\right) = -0.36 \Delta_o$$

2. (c) : In  $S_N 1$  reactions, formation of carbocation is the rate determining step. Hence, the alkyl halide which forms most stable carbocation intermediate will show highest reactivity.

In option (c), the benzylic carbocation formed is most stable due to resonance thus, it is most reactive.

$$\begin{array}{c} O & O \\ \parallel \\ \textbf{3. (a)}: R - C - Cl + R'NH_2 \longrightarrow R - C - NHR' + HCl \end{array}$$

HCl formed in this reaction protonates unreacted amine and since protonated amines are not nucleophiles, the further reaction with acyl chloride stops.

$$R'NH_2 + HCl \longrightarrow RNH_3 + Cl^-$$
No nucleophilic site
$$O$$

$$R - C - Cl + RNH_3 \longrightarrow no reaction$$

Hence, reaction must be carried out with twice as much amine as the acyl chloride.

$$\begin{array}{c} O \\ || \\ R-C-Cl + R'-OH \xrightarrow{\text{Pyridine}} R-C-OR' + HCl \\ \text{Acyl chloride} \end{array}$$

Reaction with acid chloride is carried out in presence of pyridine (base) to neutralise HCl formed during the reaction. It shifts the equilibrium towards right hand side.

4. (c): Let  $r_1$ ,  $r_2$ ,  $-r_3$  be the rotation per mole of sucrose, glucose and fructose respectively.

Sucrose 
$$\longrightarrow$$
 Glucose + Fructose  
at  $t = 0$   $a$   $0$   $0$   
at time  $t$   $a - x$   $x$   $x$   
 $ar_1 = 32.4 \implies a = \frac{32.4}{85} = 0.38$   
 $(a - x)r_1 + xr_2 - xr_3 = 28.8$   
 $x(r_2 - r_3 - r_1) = 28.8 - 32.4 = -3.6$   
 $x(74 - 86.04 - 85) = -3.6 \implies x = 0.037$   
For a first order reaction,

$$k = \frac{2.303}{t} \log\left(\frac{a}{a-x}\right)$$
$$k = \frac{2.303}{10} \log\left(\frac{0.38}{0.38 - 0.037}\right)$$
$$k = 9.21 \times 10^{-3} \text{ min}^{-1}$$
$$t_{1/2} = \frac{0.693}{k} = 75.2 \text{ min}$$

*.*..

5. (c) : Energy of scattered electron = Energy lost by photon Thus, difference of initial and final energies of

photon is the energy of scattered electron. he hc

$$\Rightarrow E_{\text{electron}} = \frac{nc}{\lambda_{\text{initial}}} - \frac{nc}{\lambda_{\text{final}}}$$
$$= hc \left(\frac{1}{\lambda_{\text{initial}}} - \frac{1}{\lambda_{\text{final}}}\right)$$
$$= 6.63 \times 10^{-34} \times 3 \times 10^8 \left(\frac{1}{1.4 \times 10^{-10}} - \frac{1}{2.8 \times 10^{-10}}\right)$$
$$= 7.10 \times 10^{-16} \text{ J}$$

### **EXAM DATES 2016**

AIPMT	:	1 <sup>st</sup> May
Karnataka CET	:	4 <sup>th</sup> & 5 <sup>th</sup> May
MHT-CET	:	5 <sup>th</sup> May
COMED K	:	8 <sup>th</sup> May
J & K CET	:	14 <sup>th</sup> & 15 <sup>th</sup> May
BITSAT	:	14 <sup>th</sup> to 28 <sup>th</sup> May
WB JEE	:	17 <sup>th</sup> May
JEE Advanced	:	22 <sup>nd</sup> May
AIIMS	:	29 <sup>th</sup> May
AMU (Med.)	:	1 <sup>st</sup> June
JIPMER	:	5 <sup>th</sup> June

6. (d): For case I, heat produced can be exchanged with surroundings due to slow process and hence, the change is isothermal *i.e.*;  $\Delta T = 0$ .

For case II, the change is adiabatic.

Thus, 
$$T_1 V_1^{\gamma - 1} = T_2 V_2^{\gamma - 1}$$
  
 $300 \times V^{(1.4 - 1)} = T_2 \times \left(\frac{V}{2}\right)^{(1.4 - 1)}$   
 $300 \times (2)^{(0.4)} = T_2$   
 $\log 300 + 0.4 \log 2 = \log T_2$ 

 $2.477 + 0.120 = \log T_2$  $2.597 = \log T_2$  $T_2 = \text{Antilog} (2.597) = 395.36 \text{ K}$ Change in temperature  $(\Delta T) = T_2 - T_1$ = 95.36 K

7. (a): Number of oxygen atoms in a unit cell arranged in *hcp* arrangement is 12. Contribution of oxygen atoms per unit cell

 $=12\times\frac{1}{2}=6$  atoms

Number of tetrahedral voids =  $2 \times no.$  of oxygen atoms per unit cell

$$= 2 \times 6 = 12$$

Number of metal (*M*) atoms =  $12 \times \frac{2}{3} = 8$  atoms

Thus, in a unit cell, there are 8 M atoms and 6 oxygen atoms.

Simple ratio of no. of *M* and O atoms = 8:6

= 4:3Hence, formula of the compound is  $M_4O_3$ .

8. (a): 
$$r_{\text{atom}} = \frac{\sqrt{3}}{4}a$$
; Also, closest approach in *bcc*  
lattice is  $\frac{1}{2}$  of body diagonal, *i.e.*,  $\frac{\sqrt{3}}{2}a = 1.73$  Å  
or  $a = \frac{1.73 \times 2}{\sqrt{3}} = 1.997$  Å = 199.7 pm  $\approx$  200 pm  
9. (3):

These three carbocations will give three different substituted alcohols.

10. (8): Percentage ionic character

$$= \frac{\text{Experimental value of dipole moment}}{\text{Theoretical value of dipole moment}} \times 100$$
$$= \frac{1.03}{6.12} \times 100 = 16.8 \approx 17\%$$
Thus,  $x + y = 1 + 7 = 8$ 

<br/>

### No weightage to Board examinations' marks in Entrance Exam

Class 12 board examination marks will not be taken into account for calculating ranks in the JEE Main, which is the gateway for admission into National Institutes of Technology (NITs) from the 2016-17 academic year, HRD ministry said on 7<sup>th</sup> April, 2016.

The JEE is a national common entrance examination conducted to provide admissions to several engineering courses, including the prestigious Indian Institutes of Engineering (IITs) and NITs.

According to the existing policy, 40% weightage is given to board exam marks in determining the ranks for JEE-Main score.

However, for the candidates to qualify in the JEE examination, they need to secure at least 75% marks or be in the top 20% percentile in the class 12 examination conducted by respective boards, a senior HRD official said.

For SC/ST students, this has been relaxed to 65% marks.

.....

The weightage system was introduced in 2012 by then HRD minister Kapil Sibal in the belief that students would pay more attention to board exams instead of concentrating on the curriculum of coaching institutes. Following the delay in publishing of ranking lists, the Smriti Irani-led HRD ministry formed a panel to study the weightage system and submit its recommendations.

This is the second UPA introduced decision related to examination reforms scrapped by the NDA government. Earlier, the controversial percentile system that governed students' eligibility for admissions into the IITs was changed in September last year.

The system required successful candidates to be among the top-20 percentile scorers in the Class 12 exams of their respective boards.





# Chemical Bonding and Molecular Structure, *d* - and *f* - Block Elements

### CHEMICAL BONDING AND MOLECULAR STRUCTURE

### **Chemical Bonding**

- The process of combination of atoms, called chemical bonding involves the union of two or more atoms through redistribution of electrons to acquire minimum energy.
- Kossel and Lewis proposed the electronic theory of chemical bonding according to which atoms achieve stable octet when they are linked by chemical bonds.
- □ Atoms combine together either by transferring or by sharing of valence electrons.
- The attainment of noble gas configuration *ns*<sup>2</sup> *np*<sup>6</sup>, in the valence shell is the driving force behind the formation of chemical bonds.
- There are mainly three types of bonds :
   (i) Ionic bond, (ii) Covalent bond
  - (iii) Coordinate bond

### Ionic Bond

□ The bonds formed between atoms by transferring of valence electrons from one atom to another is said to be electrovalent or ionic bond, and the compound so formed is an ionic compound.

# Conditions for the formation of electrovalent bond :

- *Number of valence electrons :* The atom which changes to a cation must contain 1, 2 or 3 electrons and the one changing to anion must contain 5, 6 or 7 valence electrons.
- *Electronegativity difference* : Higher the electronegativity difference between the atoms, more ionic will be the bond formed.
- *Low ionisation energy* : Ionisation energy of the element forming the cation *i.e.*, metal, should be low.
- *High electron affinity* : Electron affinity of the element forming anion *i.e.*, non-metal, should be high.

• *High lattice energy*: Higher the lattice energy, greater is the ease of formation of ionic compound.

### **Covalent Bond**

Bond formed by sharing of electrons between the combining atoms is called covalent bond and the compound so formed is a covalent compound.

### **Coordinate Bond**

A covalent bond in which both electrons of the shared pair are contributed by one of the atoms only, is called a coordinate bond or dative bond and the compound is called a coordinate compound.

### Polarisation

□ **Fajan's rule :** In ionic bond, some covalent character is introduced because of the tendency of the cation to polarise the anion. In fact, cation attracts the electron cloud of the anion and pulls electron density between two nuclei.



### According to Fajan's rule :

- Smaller the size of cation, larger is its polarising power.
- Larger the size of anion, more will be its polarisability.
- More the charge on cation and anion, more is the covalent character.
- Cations having 18 electrons in outermost shell bring greater polarisation than the other which have 8 electrons in outermost shell.

### **Bond Parameters**

- **Bond length :** It is the distance between the nuclei of two bonded atoms in a molecule.
  - *Covalent radius :* It is the radius of the core of an atom in contact with the core of an adjacent atom in a bonded situation.

- *van der Waals radius :* It is half the distance between two similar adjacent atoms belonging to two nearest neighbouring molecules of the same substance in solid state.
- **Bond angle :** It is the angle between the orbitals containing bonding electron pairs around the central atom in a molecule/complex ion.
- **Bond enthalpy :** It is the amount of energy required to break one mole of bonds of a particular type between the two atoms in the gaseous state.
- **Bond order :** It is the number of bonds between the two atoms in a molecule.

#### **Hydrogen Bonding**

- □ It is the force of attraction that exists between the hydrogen atom covalently bonded to highly electronegative atom (N or F or O) in a molecule and the electronegative atom of the same or neighbouring molecule. The bond is represented by a dotted line as shown below :
  - --- H F --- H F --- H F ---
- The hydrogen bond is of two types, intermolecular (formed between H-atom of one molecule and electronegative atom of neighbouring molecule) and intramolecular hydrogen bond (formed between H-atom and electronegative atom of the same molecule).

## Valence Shell Electron Pair Repulsion Theory (VSEPR) □ Postulates of the theory are as follows :

- Shape of a molecule depends upon the number of valence shell electron pairs (bonded or non-bonded) around the central atom.
- Electron pairs in the valence shell repel one another and the order of repulsion is :
   *lp lp* > *lp bp* > *bp bp*
- Electron pairs tend to occupy such positions in space that minimises repulsion and maximises the distance between them.

### Hybridisation (Valence Bond Approach)

- □ The process of mixing of atomic orbitals of nearly same energy to produce a set of entirely new orbitals of equivalent energy and same shape is known as hybridisation.
- □ The features of hybridisation are as follows :
  - Number of hybrid orbitals = Number of atomic orbitals undergoing hybridisation.
  - Hybrid orbitals are always equivalent in energy and shape.
  - Hybrid orbitals are more effective in forming stable bonds.
  - Hybrid orbitals are directed in space in preferred direction to have minimum repulsions between electron pairs and thus, from a stable arrangement. Hence, the type of hybridisation indicates the geometry of the molecules.

Snapes of some simple molecules										
Type of molecule	No. of bond pairs	No. of lone pairs	Total no. of electron pairs	Type of hybridisation involved	Geometry of molecules	Examples				
$AB_2$	2	0	2	sp	Linear	$BeF_{2}$ , $[Ag(NH_{3})_{2}]^{+}$				
$AB_3$	3	0	3	sp <sup>2</sup>	Trigonal planar	BF <sub>3</sub> , BCl <sub>3</sub>				
$AB_2L$	2	1	3	sp <sup>2</sup>	Bent or V-shaped	SnCl <sub>2</sub> , PbCl <sub>2</sub>				
$AB_4$	4	0	4	sp <sup>3</sup>	Tetrahedral	CH <sub>4</sub> , SiF <sub>4</sub> , CCl <sub>4</sub>				
AB <sub>3</sub> L	3	1	4	sp <sup>3</sup>	Trigonal pyramidal	$NH_3$ , $PX_3$ (X = F, Cl, Br, I)				
$AB_2L_2$	2	2	4	sp <sup>3</sup>	Bent or V-shaped	H <sub>2</sub> O, OF <sub>2</sub> , SCl <sub>2</sub>				
AB <sub>5</sub>	5	0	5	sp <sup>3</sup> d	Trigonal bipyramidal	PF <sub>5</sub> , PCl <sub>5</sub> , SbCl <sub>5</sub>				
$AB_4L$	4	1	5	sp <sup>3</sup> d	See-saw	SF <sub>4</sub> , TeBr <sub>4</sub>				
$AB_3L_2$	3	2	5	sp <sup>3</sup> d	T-shaped	ClF <sub>3</sub> , XeOF <sub>2</sub>				
$AB_2L_3$	2	3	5	sp <sup>3</sup> d	Linear	$XeF_2$ , $ICl_2^-$ , $I_3^-$				
AB <sub>6</sub>	6	0	6	sp <sup>3</sup> d <sup>2</sup>	Octahedral	$SF_6$ , $[SbF_6]^-$				
$AB_5L$	5	1	6	sp <sup>3</sup> d <sup>2</sup>	Square pyramidal	IF <sub>5</sub> , ClF <sub>5</sub> , BrF <sub>5</sub>				
$AB_4L_2$	4	2	6	$sp^2d^3$	Square planar	$XeF_4$ , $ICl_4^-$				
$AB_7$	7	0	7	sp <sup>3</sup> d <sup>3</sup>	Pentagonal bipyramidal	IF <sub>7</sub> , XeF <sub>6</sub>				







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### **Molecular Orbital Theory**

- According to this theory, all the atomic orbitals of the atoms participating in molecule formation get disturbed when the concerned nuclei approach nearer. They all get mixed up to give rise to an equivalent number of new orbitals that belong to the molecule now. These are called molecular orbitals.
- □ When two atomic orbitals overlap they can be in phase (added) or out of phase (subtracted). If they overlap in phase, constructive interference occurs and probability of finding the electrons in the region between two nuclei increases and a bonding molecular orbital is produced.
- When two atomic orbitals overlap out of phase, destructive interference reduces the probability of finding an electron in the region between the nuclei and antibonding molecular orbital is formed.
- □ The order of energy is as follows :
  - Antibonding M.O. > A.O. combining > Bonding M.O.
  - For diatomic homonuclear molecules such as Li<sub>2</sub>, Be<sub>2</sub>, B<sub>2</sub>, C<sub>2</sub>, N<sub>2</sub>, order of energy of molecular orbitals is

$$\sigma ls, \sigma^* ls, \sigma 2s, \sigma^* 2s, \frac{\pi 2p_x}{\pi 2p_y}, \sigma 2p_z, \frac{\pi^* 2p_x}{\pi^* 2p_y}, \sigma^* 2p_z$$

Energy increases

$$\sigma_{1s}, \sigma^{*}_{1s}, \sigma_{2s}, \sigma^{*}_{2s}, \sigma_{2}p_{z}, \frac{\pi^{2}p_{x}}{\pi^{2}p_{y}}, \frac{\pi^{*}2p_{x}}{\pi^{*}2p_{y}}, \sigma^{*}_{2}2p_{z}$$

### Energy increases d- AND f- BLOCK ELEMENTS

#### d - Block Elements

■ The *d*-block elements are also called as transition elements because their properties lie in between those of *s*-block and *p*-block elements and represent a transition from them. These elements are called *d*-block elements since in them 3d, 4d, 5d and 6d subshells are incomplete and the last electron enters the (n-1)d orbitals, *i.e.*, penultimate shell. Their general electronic configuration is

$(n-1)d^{1-10} ns^{0-2}$ where n is the outermost	t shell	l.
---	---------	----

Series	Elements					
First transition series or 3 <i>d</i> series	Sc (At. no. 21) to Zn (At. no. 30)					
Second transition series or 4 <i>d</i> series	Y (At. no. 39) to Cd (At. no. 48)					
Third transition series or 5 <i>d</i> series	La (At. no. 57), Hf (At. no. 72) to Hg (At. no. 80)					
Fourth transition series or 6 <i>d</i> series	Ac (At. no. 89), Rf (At. no. 104) to Uub (At. no. 112)					

#### Some important compounds of *d*-block elements

Compounds	Preparation	Physical properties	Uses			
K <sub>2</sub> Cr <sub>2</sub> O <sub>7</sub>	From sodium dichromate (obtained from chromite ore) $Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$	Orange red, crystalline solid, oxidising agent, melting point = 669 K	In dyeing, photography, leather industry			
KMnO <sub>4</sub>	From potassium manganate $2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$	Dark violet, crystalline solid, oxidising agent, melting point = 513 K	As disinfectant, germicide, Baeyer's reagent (alkaline $KMnO_4$ )			
$\begin{array}{l} \text{CuSO}_4 \cdot 5\text{H}_2\text{O} \\ \text{(Blue vitriol)} \end{array}$	From cupric oxide $CuO + H_2SO_4 \longrightarrow CuSO_4 + H_2O$	Blue (hydrated salt), at 403 K becomes anhydrous, readily dissolves in water	As electrolyte, mordant, fungicide			
AgNO <sub>3</sub> (Lunar caustic)	From silver metal $3Ag + 4HNO_3 \longrightarrow 3AgNO_3$ $+ NO^{\uparrow} + 2H_2O$	White crystalline, decomposes to give silver at high temperature	For making inks, hair dyes, photography, silvering of glass			
HgI <sub>2</sub>	From mercuric chloride HgCl <sub>2</sub> + 2KI → HgI <sub>2</sub> + 2KCl	It exists in two forms, <i>i.e.</i> , red and yellow, dissolves in excess of KI to form a complex, called as Nessler's reagent	To prepare Nessler's reagent, for making ointments for treating skin infections			





### f- Block Elements

- The general electronic configuration of the *f*-block elements is  $(n-2)f^{1-14}(n-1)d^{0-1}ns^2$ .
- **\Box** For lanthanoids, *n* is 6 while its value is 7 for actinoid series.

Lanthanoids	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Но	Er	Tm	Yb	Lu
Actinoids	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No	Lr

- Elements with atomic number greater than 92 (atomic number of uranium) are called transuranium elements. All these elements are man-made.
- Lanthanoid contraction : In lanthanoids, there is progressive decrease in atomic and ionic radii with increase in atomic number from La to Lu. This regular decrease is known as lanthanoid contraction.
  - *Cause of lanthanoid contraction* : As we move along the lanthanoid series, the nuclear charge increases by one unit at each successive element and a new electron enters the 4*f*-subshell. Due to the peculiar shape of *f*-orbitals, there is imperfect shielding of 4*f*-electrons by other electrons in this subshell from the nuclear attraction. As a result of this, the size of lanthanoid atoms keep on decreasing from La to Lu.









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# **N**Y

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1. Consider a class room of dimensions  $5 \times 10 \times 3 \text{ m}^3$ at temperature 20°C and pressure 1 atm. There are 50 people in the room, each loosing energy at the average of 150 watt. Assuming that the walls, ceiling, floor and furniture are perfectly insulated and none of them is absorbing heat, how much time will be needed for raising the temperature of air in the room to body temperature, i.e., 37°C?

For air  $C_p = \frac{7}{2}R$ . (Loss of air to the outside as the

- temperature rises may be neglected.)
- (a) 411.3 seconds (b) 500 seconds
- (d) 400 seconds (c) 430 seconds
- 2. In the following halogen-substituted hydrocarbon, the hydrogen atom that can be eliminated most readily is  $H_d$

(a) 
$$H_a$$
  $H_b$ 

(b) 
$$H_b$$
 /  $CH_3$ 

(c) 
$$H_c$$

(d) 
$$H_d$$
  $P H_c$  Cl  $H_a$ 

3. The wave function of 2s electron is given by

$$\Psi_{2s} = \frac{1}{4\sqrt{2\pi}} \left(\frac{1}{a_0}\right)^{3/2} \left(2 - \frac{r}{a_0}\right) e^{-r/a_0}$$

It has a node  $r = r_0$ . Then

(a) 
$$r_0 = a_0$$
 (b)  $r_0 = 2a_0$   
(c)  $r_0 = a_0/2$  (d)  $r_0 = 3a_0$ 

4. A dilute solution of KCl was placed between two Pt electrodes 10.0 cm apart, across which a potential difference of 6.0 volt was applied. How far would K<sup>+</sup> ions move in 2 hours at 25°C?

(Given : ionic conductivity of  $K^{\!+}$  at infinite dilution is 73.52 S cm<sup>2</sup> eq<sup>-1</sup> at 25°C.)

- (a) 4.26 cm (b) 3.292 cm
- (c) 5.341 cm (d) 2.264 cm

The major product of the following reaction is 5.



The spin magnetic moment of electrons in an ion is 6. 4.84 B.M. Its total spin will be

(a) ±1 (b)  $\pm 2$ 

(c) 
$$\pm 1.5$$
 (d) none of these.

Ethanol undergoes decomposition to form two sets 7. of products :

$$C_{2}H_{5}OH_{(g)} \xrightarrow{1} C_{2}H_{4(g)} + H_{2}O_{(g)};$$

$$\Delta H^{\circ} = -45.54 \text{ kJ}$$

$$C_{2}H_{5}OH_{(g)} \xrightarrow{2} CH_{3}CHO_{(g)} + H_{2(g)};$$

$$\Delta H^{\circ} = -68.91 \text{ kJ}$$

If the molar ratio of C<sub>2</sub>H<sub>4</sub> to CH<sub>3</sub>CHO in the product is 8 : 1, determine energy involved in the decomposition of 1 mole of ethanol.

(a) 
$$+ 52.02 \text{ kJ}$$
 (b)  $+ 48.13 \text{ kJ}$   
(c)  $-48.13 \text{ kJ}$  (d)  $-52.02 \text{ kJ}$ 

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- 8. The trade name of trichloroethylene is
  - (a) freon (b) westron
  - (c) westrosol (d) DDT.
- **9.** Which systematic diagram is correct about ionisation energy of coin metals?



- 10. The  $K_a$  values for formic acid and acetic acid are  $2.1 \times 10^{-4}$  and  $1.1 \times 10^{-5}$  respectively. Calculate relative strength for formic acid to acetic acid. (a) 1:1 (b) 1:2(c) 4.36:1 (d) 1:4.36
- **11.** Pick up the correct statement regarding the following resonating structures of the anilinium ion :



- (a) II is not acceptable because carbonium ions are less stable than ammonium ions.
- (b) II is not acceptable because it is non-aromatic.
- (c) II is not acceptable because here nitrogen has 10 valence electrons.
- (d) II is an acceptable canonical structure.
- 12. Consider the reaction,  $(NH_4)_2HAsO_3 + CuSO_4 \longrightarrow$

$$_{2}$$
HAsO<sub>3</sub> + CuSO<sub>4</sub>  $\longrightarrow \underbrace{\text{CuHAsO}_{3}}_{\text{Green ppt.}}$  + (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>

The green precipitate is also known as

- (a) Paris green (b) Scheele's green
- (c) Verdigris' green (d) Rinmann's green.

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- 13. 1.00 g of  $Cr_2O_7^{2-}$  is oxidised in an acidic solution by an excess of SO<sub>2</sub> to form HSO<sub>4</sub><sup>-</sup> and Cr<sup>3+</sup> ions. What is the minimum number of moles of H<sup>+</sup> that must be produced for this reaction to occur  $(Cr_2O_7^{2-} = 216)$ ?
  - (a) 0.0231 (b) 0.0282 (c) 0.0322 (d) 0.0268
- **14.** Extraction of Ag from sulphide ore and removal of unreacted silver bromide from photographic plate involve complexes
  - (a)  $[Ag(S_2O_3)_2]^{3-}$  in both
  - (b)  $[Ag(CN)_2]^-$  in both
  - (c)  $[Ag(S_2O_3)_2]^{3-}$ ,  $[Ag(CN)_2]^-$  respectively
  - (d)  $[Ag(CN)_2]^-$ ,  $[Ag(S_2O_3)_2]^{3-}$  respectively.
- **15.** Which of the statements about the following structures is false?



- (a) I and either II or III are *trans* and *cis*-isomers.
- (b) I and II are enantiomers.
- (c) II and III are optical isomers.
- (d) I, II and III are isomers.

(c) [

16. The radius of a soap bubble is 5 cm. The surface tension of the soap film is  $3.5 \times 10^{-2}$  N m<sup>-1</sup>. What is the work done in blowing the bubble?

(a) 
$$4.4 \times 10^{-2}$$
 J (b)  $1.1 \times 10^{-2}$  J

(c) 
$$1.1 \times 10^{-3}$$
 J (d)  $2.2 \times 10^{-2}$  J

17. 
$$\Box^{CH_2-CH_2-OH} \xrightarrow{HBr} A$$
In this reaction A will be
(a) 
$$CH_3 \qquad (b) \qquad CH_2-Br$$

(d)



- 18. Which of the following is a correct statement?
  - (a) In less acidic solution,  $K_2Cr_2O_7$  and  $H_2O_2$  give violet coloured diamagnetic  $[CrO(O_2)(OH)]^-$  ion.
  - (b) In alkaline H<sub>2</sub>O<sub>2</sub>, K<sub>3</sub>CrO<sub>8</sub> (with tetraperoxo species)  $[Cr(O_2)_4]^{3-}$  is formed.
  - (c) In ammoniacal solution, K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> gives  $(NH_3)_3CrO_4$ .
  - (d) All of these

 $\cap$ 

19. The oxidation potentials of H-electrodes set up in buffer solution of a weak acid HX and its salt NaX in the mole ratios of x : y and y : x are  $E_1$  and  $E_2$  volts respectively at 25°C. The  $pK_a$  value of the acid at 25°C is

(a) 
$$\frac{E_1 + E_2}{0.059}$$
 (b)  $\frac{E_1 - E_2}{0.118}$   
(c)  $\frac{E_2 - E_1}{0.118}$  (d)  $\frac{E_1 + E_2}{0.118}$ 

- 20. Which of the following compounds is not coloured?
  - (a)  $Na_2[CuCl_4]$ (b)  $Na_2[CdCl_4]$ (d) None of these (c)  $Fe_4[Fe(CN)_6]_3$

Identify (*A*) in the above reaction.



22. For a consecutive reaction,  $k_1$ k R

$$R_1 \longrightarrow R_2 \longrightarrow R_3$$

if initial concentration of  $R_1$  is 100 M, and  $k_1: k_2 = 1.0: 0.15$ , the value of  $[t]_{\text{max}}$  is

[Given :  $k_1 = 4.0 \times 10^{-2} \text{ min}^{-1}$ ]

- (b) 55.80 min (a) 80.55 min
- (d) 85.0 min (c) 58.50 min
- 23. One of the hazards of nuclear explosion is the generation of <sup>90</sup>Sr and its subsequent incorporation in bones. This nucleide has a half life of 28.1 years. Suppose one microgram was absorbed

by a new-born child, how much <sup>90</sup>Sr will remain in his bones after 20 years?

- (a)  $6.1 \times 10^{-7}$  g (c)  $6.1 \times 10^{-8}$  g (b)  $5.2 \times 10^{-4}$  g (d)  $5.2 \times 10^{-5}$  g
- 24. The given compound has



- (a) plane of symmetry (b) axis of symmetry
- (c) centre of symmetry (d) no symmetry.
- 25. Two sets of adsorption isotherms I and II for N<sub>2</sub> and O<sub>2</sub> respectively are shown in the figure. If wood charcoal is the adsorbent, the correct order of temperatures will be



**26.** Identify '*A*' in the given reaction,



- 27.  $Cl_2$  gas is passed into aqueous solution of KBr and KI and CHCl<sub>3</sub> added. It is observed that there is
  - (a) violet colour in CHCl<sub>3</sub> layer
  - (b) yellow colour in CHCl<sub>3</sub> layer
  - (c) yellow colour in aqueous layer
  - (d) violet colour in KI layer.
- 28. When an electron in an excited atom falls from L to K shell, an X-ray is emitted. These X-rays are diffracted at an angle of 7.75° by plane with a separation of 2.64 Å. The difference in energy between K-shell and L-shell in the atom is given by [assuming a first order diffraction  $(\sin 7.75 = 0.1349)]$

(a) 
$$\frac{6.62 \times 10^{-34} \times 3 \times 10^{10}}{0.7123 \times 10^{-10}}$$
 (b)  $\frac{6.62 \times 3 \times 10^{-16}}{0.7123}$ 

- $0.7123 \times 10^{14}$ (c)  $\frac{0.7123}{6.62 \times 3} \times 10^{14}$ (d)
- **29.** A compound 'X' discharges bromine water in  $CCl_4$ . The compound does not give effervescence of  $CO_2$ with aq. NaHCO3 solution. However, its hydrolysate with conc. KOH followed by acidification gives another compound 'Y' which gives colour with FeCl<sub>3</sub> solution as well as effervescences of CO<sub>2</sub> with NaHCO<sub>3</sub> solution. Compounds X and Y respectively are



30. In the following reaction sequence,

$$Na_{2}B_{4}O_{7} \cdot 10H_{2}O \xrightarrow{\Delta} NaBO_{2} + (A) + H_{2}O$$
$$(A) + MnO \xrightarrow{\Delta} (B)$$

- (A) and (B) respectively are
- (a)  $Na_3BO_3$  and  $Mn_3(BO_3)_2$
- (b)  $Na_2(BO_2)_2$  and  $Mn(BO_2)_2$
- (c)  $B_2O_3$  and  $Mn(BO_2)_2$
- (d) none of these.

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

#### **SOLUTIONS OF APRIL 2016 CROSSWORD**

	_		_	_	_		_	_	_		_	_		_		_	_		_		_	_	_	
												<sup>1</sup> A	U	<sup>2</sup> R	U	Μ						ЗT		
														Е			<sup>4</sup> C		<sup>5</sup> G			R		
														Α			Н		Α			Ι		<sup>6</sup> A
							<sup>7</sup> C							L			L		Ν			Т		С
	<sup>8</sup> K	L	Y	S	Т	R	0	Ν						G		°R	0	Ν	G	Α	L	Ι	Т	Е
							Α					10 U		Α			R		U			U		Т
							L			<sup>11</sup> P	0	L	Α	R	Ι	М	Е	Т	Е	R		М		Y
$B^{12}$	Е	С	Q	U	E	R	Е	L				Т					Т							L
							s					R					0							Е
<sup>13</sup> F							С					<sup>14</sup> A	N	Т	Ι	K	Ν	0	С	К				Ν
Α		15 A	М	В	Ι	D	Е	Ν	Т			М					Е							Е
R		Q					Ν					Α												
<sup>16</sup> B	Ι	U	R	Е	Т		<sup>17</sup> C	L	0	s	Т	R	I	$^{18}$ D	Ι	U	М				<sup>19</sup> E			
Е		Α					Е					Ι		Ι							х			
		S								20 C		Ν		S					21 T		0		22 W	
		0		$^{23}C$			24 G	Е	R	Α	D	Е		s			<sup>25</sup> P		R		Е		0	
		L		Α						s				Y			А		Ι		R		0	
				R		<sup>26</sup> M	А	G	Ν	Е	s	Ι	U	М			R		С		G		D	
				I						Ι				27 M	Е	Т	А	L	L	0	Ι	D	s	
			28 T	U	N	G	s	Т	Е	Ν				Е			F		I		С		Р	
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						29 L	A	v	0	I	s	Ι	Е	R			I		Ι				R	
-			1.1		a second s																			
														Y			Ν		С				Ι	

#### Winners of April 2016 Crossword

- Devjit Acharjee (Kolkata) Winners of March 2016 Crossword
- Sakchhi Kumari (Jharkhand)

#### Solution Senders of Chemistry Musing

#### Set 33

- 1. Indranil Roy, West Bengal
- 2. Swastik Biswas, Kolkata
- 3. Preyasi Das, West Bengal
- Ramakant Dutta, West Bengal 4

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Q1. In diffusion, the molecules go from denser to rarer solution but in osmosis the flow of molecules follow just the opposite pathway. Why does it happen?

#### (Taniya Mondal, West Bengal)

**Ans.** Diffusion is the migration of matter down the concentration gradient *i.e.*, matter migrates from the region of its higher concentration to the region of its lower concentration.



Osmosis is however, defined as the flow of solvent molecules only, from less concentrated solution (high concentration of solvent molecules) to more concentrated solution (low concentration of solvent molecules).



In osmosis, semipermeable membrane does not allow the solute molecules to pass through it. Thus, osmosis is not the opposite of diffusion but it is just the special case of diffusion in which only solvent molecules migrate from higher density region to lower density region.

Q2. The *d-d* transition is absent in mercury compounds but still some mercury compounds like cinnabar and many other are coloured. Why?

#### (Pinaki Chattopadhyay)

Ans. Most of the times the reason behind the colour of compounds of transition elements is d-d transition but when it is not possible such as in case of mercury then the another main reason is charge transfer. Charge can be transferred either from ligand to metal or from metal to ligand. In case of cinnabar (HgS), the colour arises due to ligand to metal charge tansfer. This charge transfer occurs due to relatively high energy lone pairs that are available on ligand S and the mercury metal has low-lying empty orbital. In HgS, there exist Hg<sup>2+</sup> and S<sup>2-</sup> ions, thus the lone pair available as  $\pi$ -electrons on S<sup>2-</sup> gets transferred to the empty 6s-orbital of Hg<sup>2+</sup> ion [Hg<sup>2+</sup> (6s)  $\leftarrow$  S<sup>2-</sup> (3p)] which imparts red colour to cinnabar.

### Q3. Carbon generally has valency four but in carbon monoxide it is two. Why?

#### (Arman Ameen)

Ans. Valency of an element is the number of valence electrons involved in bonding with other elements. In case of compounds like  $CH_4$ ,  $CO_2$  etc., carbon forms four bonds by sharing its four electrons with other elements while in the case of CO, the bonding is explained as follows:

#### :C**≦**0:

Here, out of four valence electrons of carbon only two electrons are shared with oxygen to form double bond. Then to complete the octet, the lone pair on oxygen atom is donated to carbon to form a coordinate bond and the molecule becomes stable. Here, it is clearly visible that two valence electrons on carbon atom exist as lone pair and the remaining two electrons are involved in bonding. Thus, carbon shows valency of two in carbon monoxide.



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#### ACROSS

- A volatile oil and the main constituent of lemon-grass oil. (6)
- 6. A quantum of light energy. (6)
- 8. The amount of energy that is not available for work in a closed thermodynamic system. (7)
- **10.** Trivial name of  $CF_3SO_3H$  acid. (7)
- 12. An amino acid which is abbreviated as 'Ala'. (7)
- 13. Type of mixtures for which Raoult's law is applicable. (5)
- **14.** Carbohydrate stereoisomers which differ only in configuration at the hemiacetal carbon atom. (7)
- Defect in a crystal lattice in which smaller ion (usually cation) is dislocated from its normal site to an interstitial site. (7)
- **18.** Dense form of calcium carbonate often used for decorative purpose. (6)
- A compound formed by the addition polymerisation of two molecules of a monomer. (5)
- **21.** An isotherm that relates the chemical potential at an interface and the change in surface tension. (5)
- 23. Trivial name of but-2-en-l-yl group. (6)
- **25.** Scientist who explained that in forming the solution, the salt dissociates into charged particles. (6)
- **28.** An electrical cell that produces electricity directly by the electrochemical conversion of gaseous or liquid chemicals in the cell. (4)
- **29.** A group which consists of a methylene bridge attached to vinyl group. (5)

#### DOWN

- 1. A pentose sugar present in all plant and animal cells. (6)
- 2. A reactive species containing a formally divalent carbon atom. (7)
- 4. An organic chemist who won the Nobel prize for his work on retrosynthetic analysis. (5)
- 5. A very rare carbon mineral. (7)
- Compound formed when highly electropositive metals combine with the moderately electronegative elements or metalloids or even metallic main group elements. (5)
- 9. The reserve carbohydrate of the animal cells. (8)

11. The transition element involved in the Vaska's compound. (7)

MORD

- **15.** An equation that relates emf of a cell with the activities of the reactants and products of the cell reaction. (6)
- **16.** Type of hydrides formed when the alkali metals are heated in hydrogen. (6)
- **17.** Group of CFCs used extensively as solvents, refrigerants, blowing agents and inert dispersing agents in aerosols. (6)
- **20.** Substance used as a fuel and as a reducing agent in blast furnace. (4)
- **22.** Coherent elastic scattering of monochromatic neutrons by a set of crystal planes was explained by \_\_\_\_\_\_. (5)
- 24. A highly ionised gas. (6)
- 26. A blend of metals prepared by mixing the components. (5)
- **27.** A naturally occurring sodium carbonate formed by evaporation of soda lakes. (5)



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