2015 SOLVED PAPERS

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CHEMISTRY MONTHLY FOR
JEE (Main & Advanced) & PMTs

Chemistry Musing

Concept Map

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SERIES 2

Advanced Chemistry Bloc

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Contents

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Editor : Anil Ahlawat

editorial

Transferability of Skills in Totally Different Fields

A recent research in limited states has shown that former school athletes had always scored higher salaries in their job and were always taken in higher ranks. Our reason for this is simple. One who is very good in his field is bound to do well in any field, given the opportunity. We have seen that the toppers in I.A.S. or I.F.S. exams do very well in any field of administration or judiciary. Experience is good; but when the field is totally new such as atomic energy and nuclear studies, the top civil engineers or mechanical engineers show well in any field. There is no barrier between Chemistry and Physics. Both work hand in hand in the study of spectroscopy, crystallography or metallurgy and every field of atomic energy.

When starting some new research program, one has to grope one's own way.

It is surprising that among the top scientists of the world, many are great musicians, philosophers and Sanskrit scholars. The athletes and other successful persons have one thing in common. To excel in any field is their motivation. It may be related to their work or apparently unrelated. What is the common factor that can be observed in all the successful people? It is their will to excel in every field they touch.

Literature is so vast in every field of science and by going through them, one can find the problems faced by others. It is up to you to excel. The principle of success is "Milkha Theorem". Try to outdo your own success. Compete against yourself. This is the secret of success. Physicists, Chemists, Mathematicians are only labels. In research, there are no barriers.

Anil Ahlawat
Editor

CHEMISTRY MUSING

Chemistry Musing was started from August '13 issue of Chemistry Today with the suggestion of Shri Mahabir Singh. The aim of Chemistry Musing is to augment the chances of bright students preparing for JEE (Main and Advanced) / 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 24

JEE MAIN/PMTs

1. The physical properties of three substances *X*, *Y* and *Z* are shown below :

Substance	m.p. / °C	b.p. / °C	Electrical conductivity	
			in solid	in liquid
X	801	1413	poor	good
Y	2852	3600	poor	good
Z	3550	4827	good	not known

What could be the identities of *X*, *Y* and *Z*?

	X	*Y*	*Z*
(a)	NaF	KCl	Cu
(b)	NaBr	BaO	SiO_2
(c)	NaCl	MgO	$C_{(graphite)}$
(d)	NaBr	CaO	$C_{(diamond)}$

2. A transition metal '*A*' has spin only magnetic moment value of 1.8 B.M. When it is reacted with dilute H_2SO_4 in presence of air, its compound '*B*' is formed. '*B*' reacts with compound '*C*' to give compound '*D*' with liberation of iodine. Then, the metal *A*, compounds *B*, *C* and '*D*' are respectively

(a) Ti, $TiSO_4$, KI and TiI_2

(b) Zn, $ZnSO_4$, KI and ZnI_2

(c) Cu, $CuSO_4$, KI and Cu_2I_2

(d) Cu, $CuSO_4$, KI and CuI_2

3. The hydride ion (H^-) is stronger base than its hydroxide ion (OH^-). Which of the following reactions will occur, if sodium hydride (NaH) is dissolved in water?

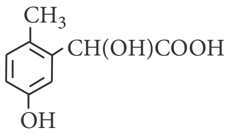
(a) $H^-_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$

(b) $H^-_{(aq)} + H_2O_{(l)} \rightarrow OH^-_{(aq)} + H_{2(g)}$

(c) $H^-_{(aq)} + H_2O_{(l)} \rightarrow$ No reaction

(d) None of the above.

4. *p*-Cresol reacts with chloroform in alkaline medium to give the compound '*X*' which adds hydrogen cyanide to form the compound '*Y*'. The latter on acidic hydrolysis gives chiral carboxylic acid. The structure of the carboxylic acid is

(a)


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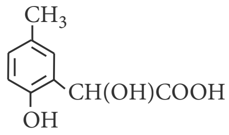

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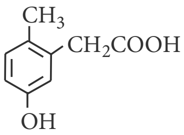

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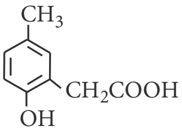
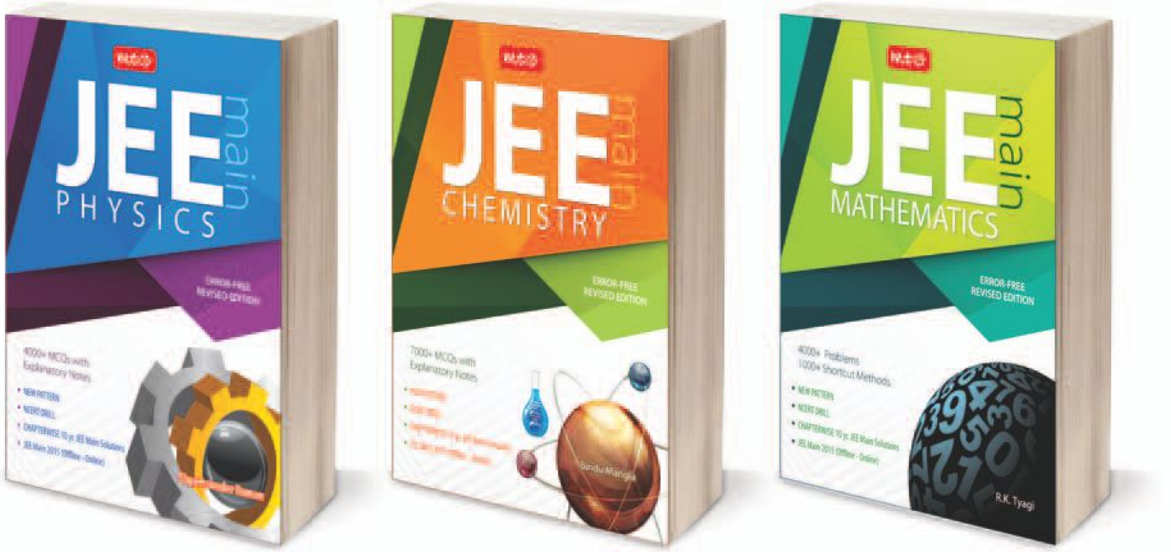


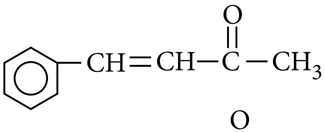
Solution Senders of Chemistry Musing

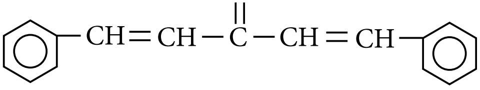
SET 23

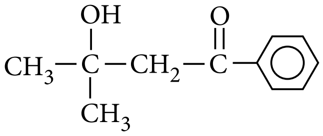
1. Swayangdipta Bera (WB)
2. Achala Pandita (J & K)
3. Ribhav Kapoor (Punjab)


JEE main PHYSICS
JEE main CHEMISTRY
JEE main MATHEMATICS
ERROR-FREE REVISED EDITION

5. A base-catalyzed reaction of 1 mole of acetone with 2 moles of benzaldehyde yields a yellow solid, $C_{17}H_{14}O$. What is the structure of the product?

(a) 

(b) 

(c) 

(d) None of the above

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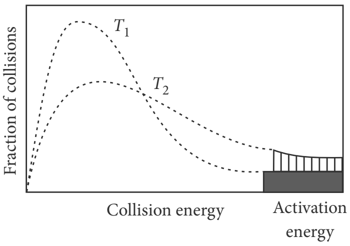
6. Which of the following order is not correct?
(a) $MeBr > Me_2CHBr > Me_3CBr > Et_3CBr(S_N2)$
(b) $Me_3CBr > Me_2CHBr > Me_2CHCH_2Br > MeCH_2CH_2CH_2Br(E2)$
(c) $PhCH_2Br > PhCHBrMe > PhCBrMe_2 > PhCBrMePh(S_N1)$
(d) $MeI > MeBr > MeCl > MeF\ (S_N2)$

COMPREHENSION

Very few collisions are productive because very few occur with a collision energy as large as the activation energy. The fraction of collisions with an energy equal to or greater than the activation energy E_a is represented as the given graph.



When E_a is large compared with RT, this fraction is approximated by the equation,

$$f = e^{-E_a/RT}$$

7. Which of the following statements is not correct?
(a) Total collision rate ∝ mean speed ∝ absolute temperature
(b) Total collision rate ∝ mean speed ∝ (absolute temperature)$^{1/2}$
(c) Activation energy is independent of temperature over wide range of the reaction.
(d) Activation energy of the reaction does not get lowered on adding a catalyst.

8. If activation energy for the reaction is 75 kJ/mol then the factor 'f' at 298 K, is
(a) 7.0×10^{-14}
(b) 3.5×10^{-14}
(c) 2.6×10^{-15}
(d) 1.4×10^{-13}

INTEGER VALUE

9. When the ion $Cr_2O_7^{2-}$ acts as an oxidant in acidic aqueous solution the ion Cr^{3+} is formed. The number of moles of Sn^{2+} which get oxidised to Sn^{4+} by one $Cr_2O_7^{2-}$ ion is

10. The vapour pressure of water at 20°C is 17.5 torr. The moles of water present in one litre of air at 20°C and 45% relative humidity is $x \times 10^{-4}$. The x is

◆

JEE Advanced

SOLVED PAPER 2015

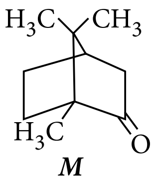
PAPER-1

SECTION 1 (Maximum Marks : 32)

- *This section contains EIGHT questions*
- *The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive*
- *For each question, darken the bubble corresponding to the correct integer in the ORS*
- *Marking scheme :*
  +4 If the bubble corresponding to the answer is darkened
  0 In all other cases

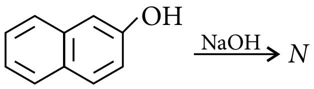
1. If the freezing point of a 0.01 molal aqueous solution of a cobalt(III) chloride-ammonia complex (which behaves as a strong electrolyte) is –0.0558°C, the number of chloride(s) in the coordination sphere of the complex is
[K_f of water = 1.86 K kg mol^{-1}]

2. The total number of stereoisomers that can exist for *M* is



M

3. The number of resonance structures of *N* is



4. The total number of lone pairs of electrons in N_2O_3 is

5. For the octahedral complexes of Fe^{3+} in SCN^- (thiocyanato-S) and in CN^- ligand environments, the difference between the spin-only magnetic moments in Bohr magnetons (when approximated to the nearest integer) is
[Atomic number of Fe = 26]

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

7. Not considering the electronic spin, the degeneracy of the second excited state (n = 3) of H atom is 9, while the degeneracy of the second excited state of H^- is

8. All the energy released from the reaction $X \longrightarrow Y$, $\Delta_r G° = -193$ kJ mol^{-1} is used for oxidizing M^+ as $M^+ \longrightarrow M^{3+} + 2e^-$, $E° = -0.25$ V.
Under standard conditions, the number of moles of M^+ oxidized when one mole of X is converted to Y is
[$F = 96500$ C mol^{-1}]

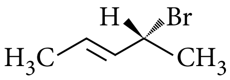
SECTION 2 (Maximum Marks : 40)

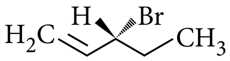
- *This section contains TEN questions*
- *Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct*
- *For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS*
- *Marking scheme :*
  +4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened
  0 If none of the bubbles is darkened
  –2 In all other cases

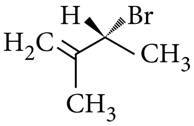
9. If the unit cell of a mineral has cubic close packed (*ccp*) array of oxygen atoms with *m* fraction of octahedral holes occupied by aluminium ions and *n* fraction of tetrahedral holes occupied by magnesium ions, *m* and *n*, respectively, are

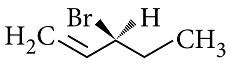
(a) $\frac{1}{2}, \frac{1}{8}$ (b) $1, \frac{1}{4}$ (c) $\frac{1}{2}, \frac{1}{2}$ (d) $\frac{1}{4}, \frac{1}{8}$

10. Compound(s) that on hydrogenation produce(s) optically inactive compound(s) is(are)

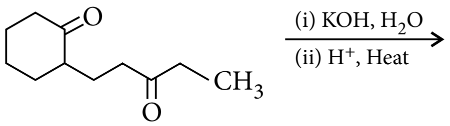
(a) 

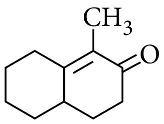
(b) 

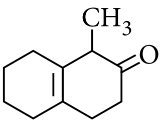
(c) 

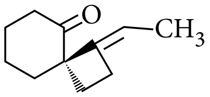
(d) 

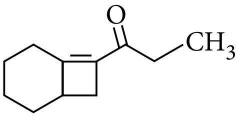
11. The major product of the following reaction is



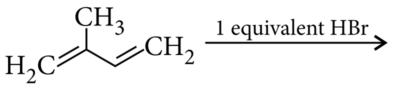
(a) 

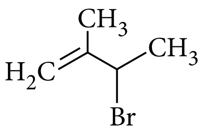
(b) 

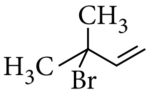
(c) 

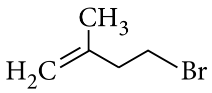
(d) 

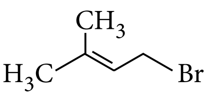
12. In the following reaction, the major product is



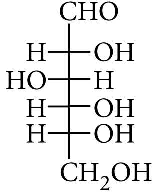
(a) 

(b) 

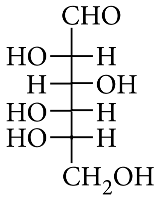
(c) 

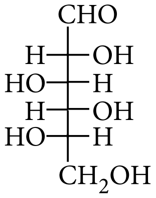
(d) 

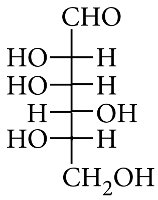
13. The structure of *D*-(+)-glucose is

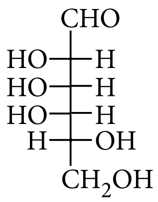


The structure of *L*-(–)-glucose is

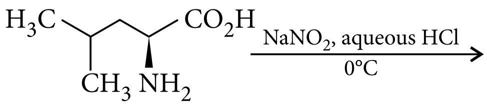
(a) 

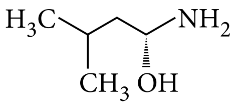
(b) 

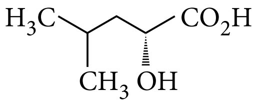
(c) 

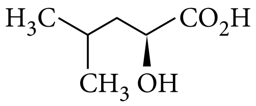
(d) 

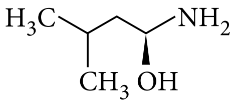
14. The major product of the reaction is



(a) 

(b) 

(c) 

(d) 

15. The correct statement(s) about Cr^{2+} and Mn^{3+} is(are)

[Atomic numbers of Cr = 24 and Mn = 25]

(a) Cr^{2+} is a reducing agent

(b) Mn^{3+} is an oxidizing agent

(c) both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration

(d) when Cr^{2+} is used as a reducing agent, the chromium ion attains d^5 electronic configuration.

16. Copper is purified by electrolytic refining of blister copper. The correct statement(s) about this process is(are)

(a) impure Cu strip is used as cathode

(b) acidified aqueous $CuSO_4$ is used as electrolyte

(c) pure Cu deposits at cathode

(d) impurities settle as anode-mud.

17. Fe^{3+} is reduced to Fe^{2+} by using

(a) H_2O_2 in presence of NaOH

(b) Na_2O_2 in water

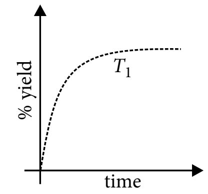
(c) H_2O_2 in presence of H_2SO_4

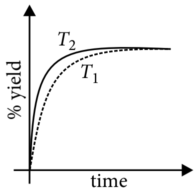
(d) Na_2O_2 in presence of H_2SO_4

18. The % yield of ammonia as a function of time in the reaction

$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, $\Delta H < 0$

at (P, T_1) is given below. If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by



(a)


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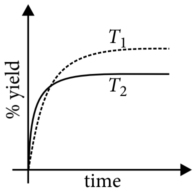

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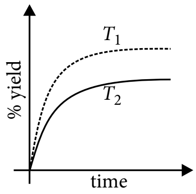

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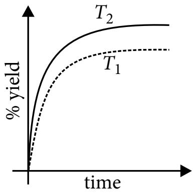


SECTION 3 (Maximum Marks : 16)

- *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 five entries (P), (Q), (R), (S) and (T).*
- *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*
- *The ORS contains a 4 × 5 matrix whose layout will be similar to the one shown below :*
- *For each entry in Column I, darken the bubbles of all the matching entries. For example, if entry (A) in Column I matches with entries (Q), (R) and (T), then darken these three bubbles in the ORS. Similarly, for entries (B), (C) and (D).*

(A)	(P)	(Q)	(R)	(S)	(T)
(B)	(P)	(Q)	(R)	(S)	(T)
(C)	(P)	(Q)	(R)	(S)	(T)
(D)	(P)	(Q)	(R)	(S)	(T)

- *Marking scheme :*
  For each entry in Column I
  +2 If only the bubble(s) corresponding to all the correct match(es) is(are) darkened
  0 If none of the bubbles is darkened
  −1 In all other cases

19. Match the anionic species given in Column I that are present in the ore(s) given in Column II.

Column I	Column II
(A) Carbonate	(P) Siderite
(B) Sulphide	(Q) Malachite
(C) Hydroxide	(R) Bauxite
(D) Oxide	(S) Calamine
	(T) Argentite

20. Match the thermodynamic processes given under Column I with the expressions given under Column II.

Column I	Column II
(A) Freezing of water at 273 K and 1 atm	(P) $q = 0$
(B) Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions	(Q) $w = 0$
(C) Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container	(R) $\Delta S_{sys} < 0$
(D) Reversible heating of $H_{2(g)}$ at 1 atm from 300 K to 600 K, followed by reversible cooling to 300 K at 1 atm	(S) $\Delta U = 0$
	(T) $\Delta G = 0$

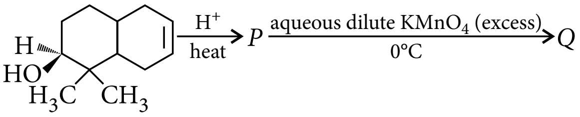
PAPER-2

SECTION 1 (Maximum Marks : 32)

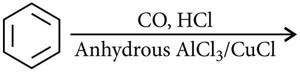
- *This section contains EIGHT questions*
- *The answer to each question is a SINGLE DIGIT INTEGER ranging from 0 to 9, both inclusive*
- *For each question, darken the bubble corresponding to the correct integer in the ORS*
- *Marking scheme :*
  +4 If the bubble corresponding to the answer is darkened
  0 In all other cases

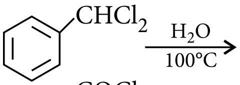
1. In dilute aqueous H_2SO_4, the complex diaquodioxalatoferrate (II) is oxidized by MnO_4^-. For this reaction, the ratio of the rate of change of $[H^+]$ to the rate of change of $[MnO_4^-]$ is

2. The number of hydroxyl group(s) in Q is

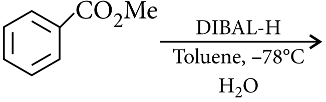


3. Among the following, the number of reaction(s) that produce(s) benzaldehyde is

I.


II.


III.


IV.


4. In the complex acetylbromidodicarbonylbis(triethyl phosphine)iron(II), the number of Fe — C bond(s) is

5. Among the complex ions,
$[Co(NH_2CH_2CH_2NH_2)_2Cl_2]^+$, $[CrCl_2(C_2O_4)_2]^{3-}$,
$[Fe(H_2O)_4(OH)_2]^+$, $[Fe(NH_3)_2(CN)_4]^-$,
$[Co(NH_2CH_2CH_2NH_2)_2(NH_3)Cl]^{2+}$ and
$[Co(NH_3)_4(H_2O)Cl]^{2+}$,
the number of complex ion(s) that show(s) *cis-trans* isomerism is

6. Three moles of B_2H_6 are completely reacted with methanol. The number of moles of boron containing product formed is

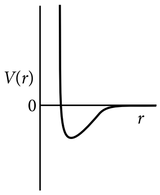
7. The molar conductivity of a solution of a weak acid H*X* (0.01 M) is 10 times smaller than the molar conductivity of a solution of a weak acid H*Y* (0.10 M). If $\lambda^{\circ}_{X^-} \approx \lambda^{\circ}_{Y^-}$, the difference in their pK_a values, $pK_a(HX) - pK_a(HY)$, is (consider degree of ionization of both acids to be << 1)

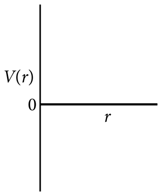
8. A closed vessel with rigid walls contains 1 mol of $^{238}_{92}U$ and 1 mol of air at 298 K. Considering complete decay of $^{238}_{92}U$ to $^{206}_{82}Pb$, the ratio of the final pressure to the initial pressure of the system at 298 K is

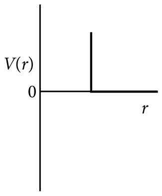
SECTION 2 (Maximum Marks : 32)

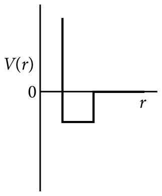
- *This section contains EIGHT questions*
- *Each question has FOUR options (a), (b), (c) and (d). ONE OR MORE THAN ONE of these four option(s) is(are) correct*
- *For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS.*
- *Marking scheme :*
  - *+4 If only the bubble(s) corresponding to all the correct option(s) is(are) darkened*
  - *0 If none of the bubbles is darkened*
  - *–2 In all other cases*

9. One mole of a monoatomic real gas satisfies the equation $p(V - b) = RT$ where b is a constant. The relationship of interatomic potential $V(r)$ and interatomic distance r for the gas is given by

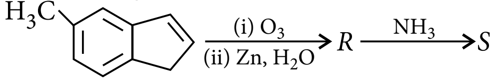
(a)


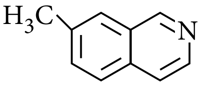
(b)


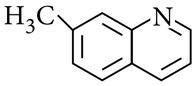
(c)


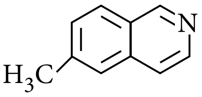
(d)


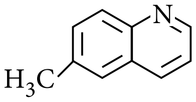
10. In the following reactions, the product *S* is



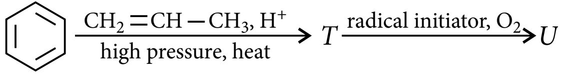
(a)


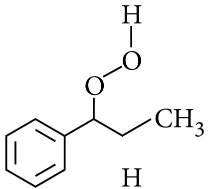
(b)


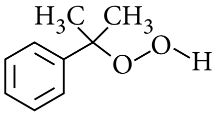
(c)


(d)


11. The major product *U* in the following reaction is



(a)


(b)


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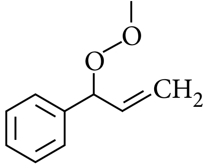
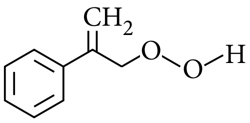
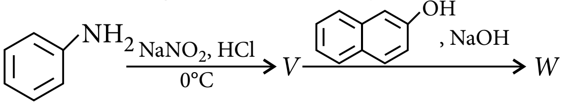
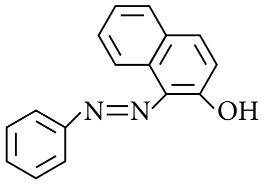
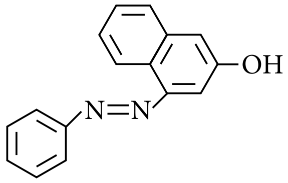


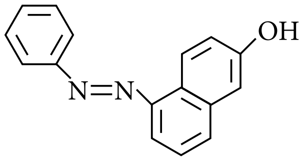
(d)


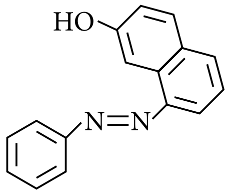
12. In the following reactions, the major product *W* is

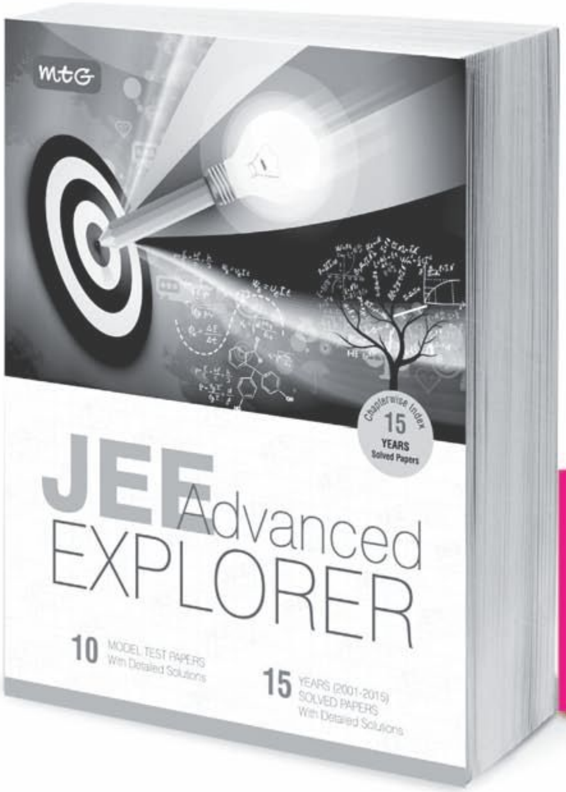


(a)


(b)


(c)


(d)



MTG
Chapterwise Index
15
YEARS
Solved Papers
JEE Advanced
EXPLORER
10 MODEL TEST PAPERS
With Detailed Solutions
15 YEARS (2001-2015)
SOLVED PAPERS
With Detailed Solutions

13. The correct statement(s) regarding, (i) HClO, (ii) $HClO_2$, (iii) $HClO_3$ and (iv) $HClO_4$, is(are)
(a) The number of $Cl{=}O$ bonds in (ii) and (iii) together is two
(b) The number of lone pairs of electrons on Cl in (ii) and (iii) together is three
(c) The hybridization of Cl in (iv) is sp^3
(d) Amongst (i) to (iv), the strongest acid is (i).

14. The pair(s) of ions where BOTH the ions are precipitated upon passing H_2S gas in presence of dilute HCl, is(are)
(a) Ba^{2+}, Zn^{2+} (b) Bi^{3+}, Fe^{3+}
(c) Cu^{2+}, Pb^{2+} (d) Hg^{2+}, Bi^{3+}

15. Under hydrolytic conditions, the compounds used for preparation of linear polymer and for chain termination, respectively, are
(a) CH_3SiCl_3 and $Si(CH_3)_4$
(b) $(CH_3)_2SiCl_2$ and $(CH_3)_3SiCl$
(c) $(CH_3)_2SiCl_2$ and CH_3SiCl_3
(d) $SiCl_4$ and $(CH_3)_3SiCl$

16. When O_2 is adsorbed on a metallic surface, electron transfer occurs from the metal to O_2. The TRUE statement(s) regarding this adsorption is(are)
(a) O_2 is physisorbed
(b) heat is released
(c) occupancy of π^*_{2p} of O_2 is increased
(d) bond length of O_2 is increased.

SECTION 3 (Maximum Marks : 16)

- *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*
- *For each question, darken the bubble(s) corresponding to all the correct option(s) in the ORS*
- *Marking scheme :*
  +4 If only bubble(s) corresponding to all the correct option(s) is(are) darkened
  0 If none of the bubbles is darkened
  –2 In all other cases

PARAGRAPH 1

When 100 mL of 1.0 M HCl was mixed with 100 mL of 1.0 M NaOH in an insulated beaker at constant pressure, a temperature increase of 5.7°C was measured for the beaker and its contents (Expt. 1). Because the enthalpy of neutralization of a strong acid with a strong base is a constant (-57.0 kJ mol^{-1}), this experiment could be used to measure the calorimeter constant.

In a second experiment (Expt. 2), 100 mL of 2.0 M acetic acid ($K_a = 2.0 \times 10^{-5}$) was mixed with 100 mL of 1.0 M NaOH (under identical conditions to Expt. 1) where a temperature rise of 5.6°C was measured.

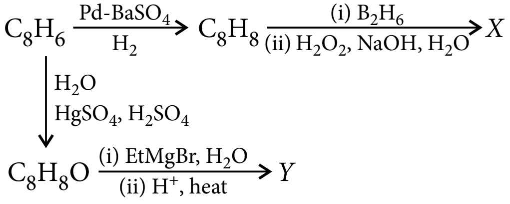
(Consider heat capacity of all solutions as 4.2 J g^{-1} K^{-1} and density of all solutions as 1.0 g mL^{-1})

17. Enthalpy of dissociation (in kJ mol^{-1}) of acetic acid obtained from the Expt. 2 is
(a) 1.0 (b) 10.0
(c) 24.5 (d) 51.4

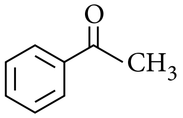
18. The pH of the solution after Expt. 2 is
(a) 2.8 (b) 4.7
(c) 5.0 (d) 7.0

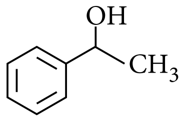
PARAGRAPH 2

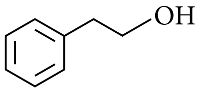
In the following reactions

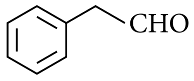


19. Compound *X* is

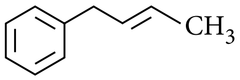
(a)


(b)


(c)


(d)


20. The major compound *Y* is

(a)


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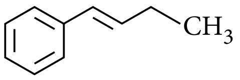
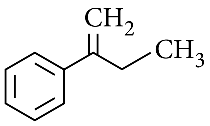
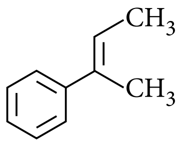


(c)


(d)


SOLUTIONS

Paper-1

1. **(1) :** $\Delta T_f = iK_f\, m$

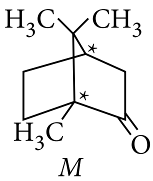
Given : $m = 0.01$ molal, $T_f = -0.0558°C$

$K_f = 1.86$ K kg mol^{-1}

$\Delta T_f = T_f^\circ - T_f = 0°C - (-0.0558°C) = 0.0558°C$

$$i = \frac{\Delta T_f}{K_f m} = \frac{0.0558}{1.86 \times 0.01} = 3$$

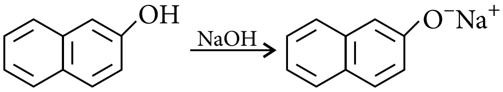
As, three ions are produced by the complex, the molecular formula of the complex is $[Co(NH_3)_5Cl]Cl_2$ Thus, only one Cl^- ion is in the coordination sphere.

2. **(2) :** 

M

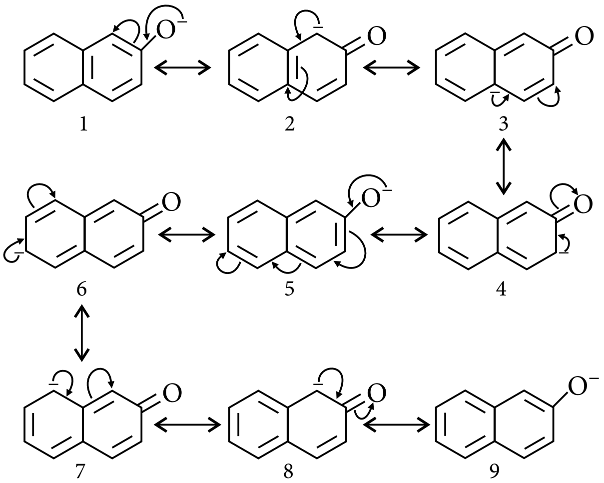
M has two chiral C–atoms thus, no. of stereoisomers $= 2^n = 2^2 = 4$.

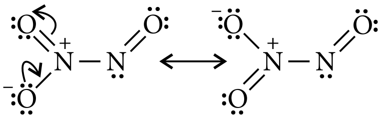
But due to bridging, rotation is not possible so, only two stereoisomers exist.

3. **(9) :** 

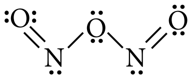
'*N*'

(It has 9 resonating structures)



4. **(8) :** 

Asymmetric form
(N_2O_3)

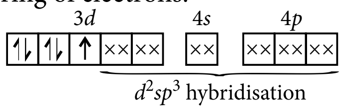


Symmetric form
(N_2O_3)

It has 8 lone pairs of electrons.

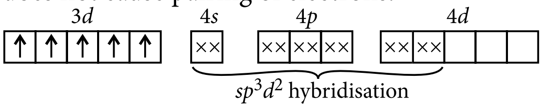
5. **(4) :** Fe (26) : $3d^6 4s^2$
Fe^{3+} : $3d^5$

In $[Fe(CN)_6]^{3-}$, CN^- is a strong field ligand which causes pairing of electrons.



$$\mu = \sqrt{n(n+2)} = \sqrt{1(1+2)} = \sqrt{3} = 1.732 \text{ BM}$$

In $[Fe(SCN)_6]^{3-}$, SCN^- being a weak field ligand does not cause pairing of electrons.



$$\mu = \sqrt{n(n+2)} = \sqrt{5(5+2)} = \sqrt{35} = 5.916 \text{ BM}$$

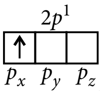
Difference = 5.916 – 1.732 = 4.184 ≈ 4 BM

6. **(4) :**

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

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

7. **(3) :** In case of H-atom, the energies of the orbitals are in the order :
$1s < 2s = 2p < 3s = 3p = 3d < 4s = 4p = 4d = 4f <$ ……
For multielectronic system, *i.e.*, H^- ion, the order is :
$1s < 2s < 2p$ …… [follow $(n + l)$ rule]
For H-atom, $Z = 1$, $1s^1$, the second excited state ($n = 3$) is : $3s = 3p = 3d$
Degenerate orbitals 1 3 5
∴ Degeneracy = 1 + 3 + 5 = 9
For H^- ion, $Z = 1$, $1s^2$, the first excited state would be $1s^1, 2s^1$.
And the second excited state would be $1s^1, 2s^0, 2p^1$



(3 degenerate orbitals)   ∴ degeneracy = 3

8. **(4) :** Given :
$X \longrightarrow Y;\ \Delta_r G° = -193 \text{ kJ mol}^{-1}$
$M^+ \longrightarrow M^{3+} + 2e^-;\ E° = -0.25$ V
$F = 96500 \text{ C mol}^{-1}$
Let 193 kJ is used for oxidising *x* moles of M^+.
For 1 mole of M^+,

$$\Delta G° = -nFE°$$
$$= -2 \times 96500 \times (-0.25)$$
$$= 48250 \text{ J mol}^{-1} = 48.25 \text{ kJ mol}^{-1}$$

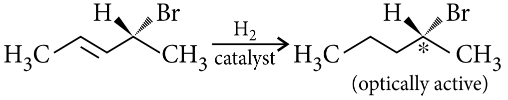
Thus, no. of moles of M^+ oxidized when one mole of *X* is converted to $Y = \dfrac{193}{48.25} = 4$.

9. **(a) :** For *ccp*, $Z = 4$ = no. of O-atoms
No. of octahedral voids = 4
No. of tetrahedral voids = $2 \times 4 = 8$
No. of Al^{3+} ions = $m \times 4$
No. of Mg^{2+} ions = $n \times 8$
Thus, the formula of the mineral is $Al_{4m}Mg_{8n}O_4$

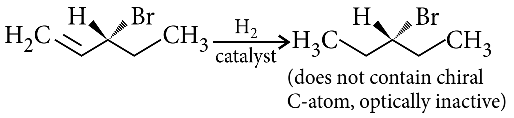
$$4m(+3) + 8n(+2) + 4(-2) = 0$$
$$12m + 16n - 8 = 0$$
$$4(3m + 4n - 2) = 0$$
$$3m + 4n = 2$$

Possible values of m and n are $\frac{1}{2}$ and $\frac{1}{8}$ respectively.

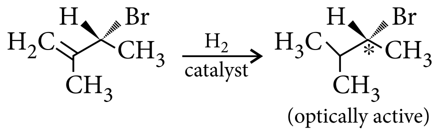
10. **(b, d) :**

(a)


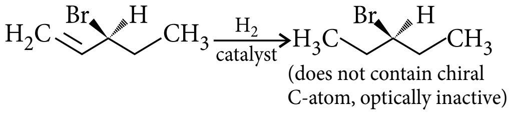
(optically active)

(b)


(does not contain chiral C-atom, optically inactive)

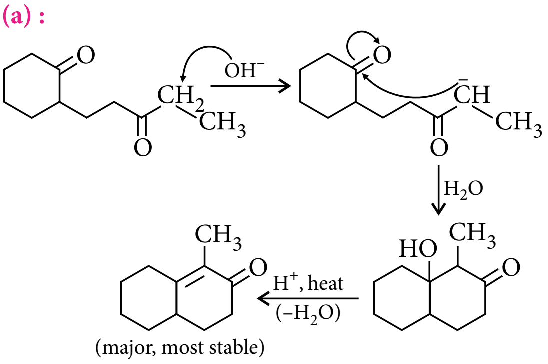
(c)


(optically active)

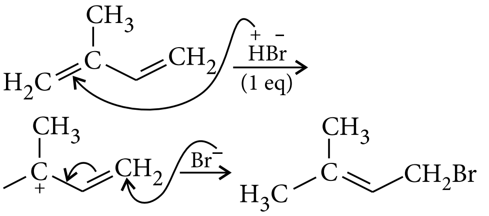
(d)


(does not contain chiral C-atom, optically inactive)

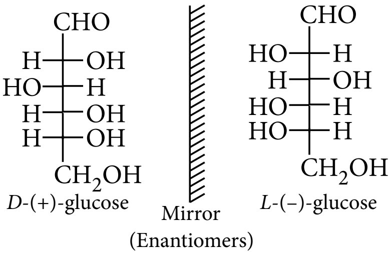
11. **(a) :**



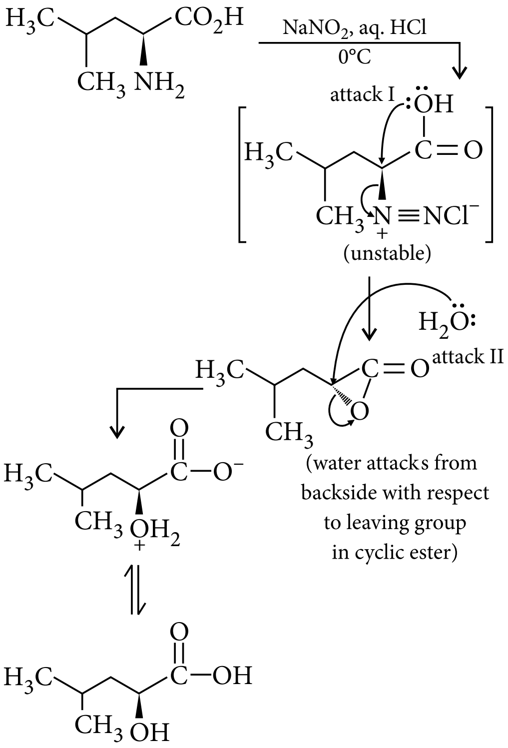
12. **(d) :**



13. **(a) :**



14. **(c) :**



In attack I, inversion of configuration takes place and in II^nd attack again inversion of configuration takes place which finally leads to retention of configuration.

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

(b) Mn^{3+} is an oxidizing agent, it gets reduced to Mn^{2+} ($3d^5$, most stable, half-filled configuration).

(c) Cr (24) : $3d^44s^2$ Mn (25) : $3d^54s^2$
Cr^{2+} : $3d^4$ Mn^{3+} : $3d^4$

Both Cr^{2+} and Mn^{3+} exhibit d^4 electronic configuration.

(d) When Cr^{2+} is used as a reducing agent, the chromium ion attains d^3 electronic configuration.

16. **(b, c, d) :** (a) Impure copper is made the anode and a thin sheet of pure copper is made the cathode, while copper sulphate solution acidified with sulphuric acid is taken as the electrolyte. Pure copper deposits at cathode and impurities settle as anode-mud.

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

17. **(a, b) :** (a) H_2O_2 in alkaline medium reduces Fe^{3+} to Fe^{2+},

$$2Fe^{3+}_{(aq.)} + H_2O_{2(aq.)} + 2\overset{-}{O}H_{(aq.)} \longrightarrow 2Fe^{2+}_{(aq.)} + O_{2(g)} + 2H_2O_{(l)}$$

(b) Na_2O_2 in water,

$$Na_2O_2 + 2H_2O \longrightarrow \underset{\substack{\text{(}H_2O_2\text{ in alkaline medium}\\ \text{reduces }Fe^{3+}\text{ to }Fe^{2+}\text{)}}}{2NaOH + H_2O_2}$$

(c) H_2O_2 in acidic medium oxidises Fe^{2+} to Fe^{3+}.

$$2Fe^{2+}_{(aq.)} + H_2O_{2(aq.)} + 2H^+_{(aq.)} \longrightarrow 2Fe^{3+}_{(aq.)} + 2H_2O_{(l)}$$

(d) Na_2O_2 in presence of H_2SO_4,

$$Na_2O_2 + H_2SO_4 \longrightarrow \underset{\text{(Neutral medium)}}{Na_2SO_4 + H_2O_2}$$

In alkaline medium, reducing action of H_2O_2 is more effective.

18. **(b) :** $N_{2(g)} + 3H_{2(g)} \underset{\text{endo}}{\overset{\text{exo}}{\rightleftharpoons}} 2NH_{3(g)}$; $\Delta H < 0$

Initially, with increase in temperature ($T_2 > T_1$) % yield increases.

Afterwards, equilibrium is reached and if the temperature is increased, *i.e.*, heat is supplied to the system, then according to Le Chatelier's principle, the equilibrium will shift in the backward direction, where the heat is absorbed. Hence, the % yield decreases.

19. **(A) → (P, Q and S)**

Carbonate ores are

(P) Siderite : $FeCO_3$
(Q) Malachite : $CuCO_3 \cdot Cu(OH)_2$
(S) Calamine : $ZnCO_3$

(B) → (T)

Sulphide ore is (T) Argentite : Ag_2S.

(C) → (Q and R)

Hydroxide ion is present in
(Q) Malachite : $CuCO_3 \cdot Cu(OH)_2$
(R) Bauxite : $Al_2O_3 \cdot 2H_2O$ or $AlO_x(OH)_{3-2x}$ where $0 < x < 1$

(D) → (R)

Oxide ore is bauxite (R) only.

20. **(A) → (R and T)**

Freezing of water,

$$H_2O_{(l)} \underset{273\text{ K}}{\overset{1\text{ atm}}{\rightleftharpoons}} H_2O_{(s)}$$

The system is cooled *i.e.*; heat is released during the process so, $q < 0$.

$$\underset{\text{(Less volume)}}{\text{Water}} \rightleftharpoons \underset{\text{(More volume)}}{\text{Ice}} + \text{heat}$$

Volume is increased *i.e.*; $\Delta V = +\text{ve}$.
$w = -P\Delta V = -\text{ve}$
i.e.; $w < 0$ (expansion)
Entropy of system is decreased, $\Delta S_{sys} < 0$.
$\Delta U = q + w$
As $q < 0$, $w < 0$ so, $\Delta U < 0$.
At equilibrium, $\Delta G = 0$.

(B) → (P, Q and S)

Expansion of 1 mol of an ideal gas into a vacuum under isolated conditions,

$w = 0$, $q = 0$ so, $\Delta U = 0$

For expansion, $\Delta S_{sys} > 0$ as entropy increases.

$$\Delta G = -nRT \ln \frac{V_2}{V_1}$$

For expansion, $V_2 > V_1$

$\Delta G = -\text{ve}$ *i.e.*; $\Delta G < 0$.

(C) → (P, Q and S)

Mixing of equal volumes of two ideal gases at constant temperature and pressure in an isolated container.

$q = 0$ (isolated)
$w = -P\Delta V$
$w = 0$ ($\because \Delta V = 0$)
$\Delta S_{sys} > 0$ (mixing of gases)
$\Delta U = q + w = 0$
$\Delta G = \Delta H - T\Delta S$
$\Delta G = q_p - T\Delta S$ (at constant P, T)
$\Delta G = 0 - T\Delta S = -T\Delta S$
$\Delta G < 0$ ($\because \Delta S_{sys} > 0$)

(D) → (P, Q, S and T)

$$\underset{(300\text{ K})}{H_{2(g)}} \underset{\text{cool}}{\overset{\text{heat, 1 atm}}{\rightleftharpoons}} \underset{(600\text{ K})}{H_{2(g)}}$$

Internal energy (U), entropy (S) and free energy (G) are state functions which depend only upon the state of the system and do not depend upon the path by which the state is attained.

Thus, $\Delta U = 0$, $\Delta S = 0$ and $\Delta G = 0$

Work and heat are path functions but the same path is retraced so, $q = 0$ and $w = 0$.

Paper-2

1. **(8) :** In complex, $\underset{\text{diaquodioxalatoferrate (II)}}{[Fe(C_2O_4)_2(H_2O)_2]^{2-}}$,

Fe is in +2 oxidation state.

In acidic medium, $KMnO_4$ oxidises Fe^{2+} to Fe^{3+},

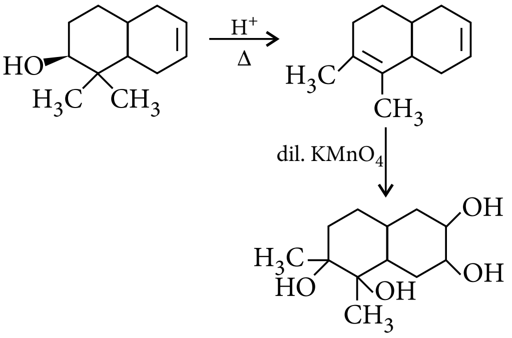
$$2MnO_4^- + 16H^+ + 10Fe^{2+} \longrightarrow 2Mn^{2+} + 8H_2O + 10Fe^{3+}$$

or

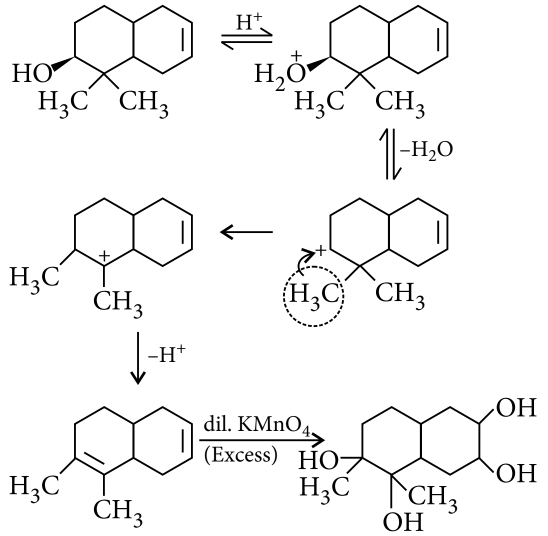
$$MnO_4^- + 8H^+ + 5Fe^{2+} \longrightarrow Mn^{2+} + 4H_2O + 5Fe^{3+}$$

$$\frac{\text{Rate of change of }[H^+]}{\text{Rate of change of }[MnO_4^-]} = \frac{8}{1} = 8$$

2. **(4) :**

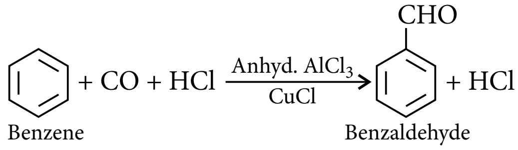


Mechanism :

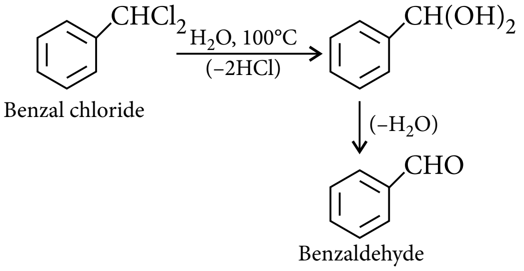


(Major product)

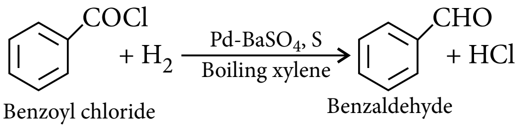
3. **(4) :** I. Gattermann-Koch aldehyde synthesis :



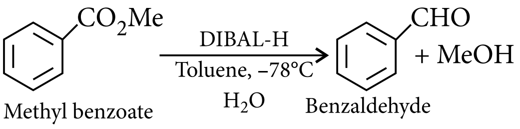
II. By hydrolysis of benzal chloride :



III. Rosenmund reduction :



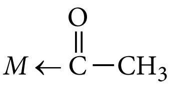
IV. Esters are reduced to aldehydes with DIBAL-H :



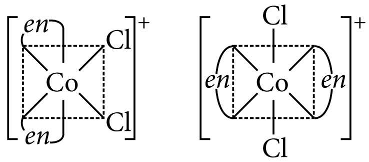
4. **(3) :** In the complex,

$[Fe(CH_3CO)(Br)(CO)_2(PEt_3)_2]$

acetylbromidodicarbonylbis(triethylphosphine)iron(II)

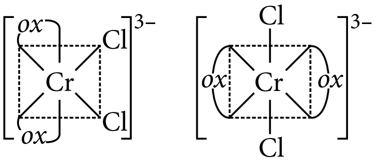
There are two $M \leftarrow CO$ bonds and one  $M \leftarrow \overset{\overset{O}{\|}}{C}-CH_3$ bond (where M = Fe).

5. **(6) :** $[Co(en)_2Cl_2]^+$ – $[M(AA)_2B_2]$ type complex, shows geometrical isomerism.



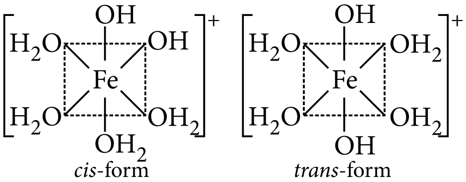
cis-form *trans*-form

$[CrCl_2(C_2O_4)_2]^{3-}$ – $[M(AA)_2B_2]$ type complex, shows geometrical isomerism.



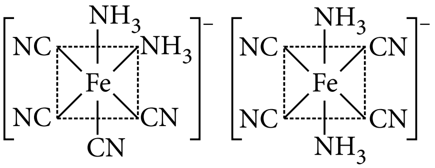
cis-form *trans*-form

$[Fe(H_2O)_4(OH)_2]^+$ – $[MA_4B_2]$ type complex, shows geometrical isomerism.



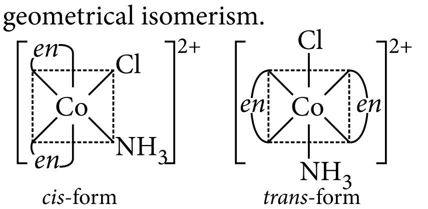
cis-form *trans*-form

$[Fe(NH_3)_2(CN)_4]^-$ – $[MA_4B_2]$ type complex, shows geometrical isomerism.



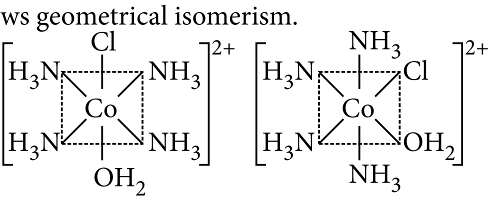
cis-form *trans*-form

$[Co(en)_2(NH_3)Cl]^{2+}$ – $[M(AA)_2BC]$ type complex, shows geometrical isomerism.



cis-form *trans*-form

$[Co(NH_3)_4(H_2O)Cl]^{2+}$ – $[MA_4BC]$ type complex, shows geometrical isomerism.



cis-form *trans*-form

6. (6) 7. (3) 8. (9) 9. (c) 10. (a)
11. (b) 12. (a) 13. (b, c) 14. (c, d) 15. (b)
16. (b,c,d) 17. (a) 18. (b) 19. (c) 20. (d)

For detail solutions refer :
MTG JEE Advanced Explorer, 38 years chapterwise solutions

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ADVANCED CHEMISTRY BLOC

(BAND THEORY)

Mukul C. Ray, Odisha

Emergence of Band – An application of MOT

Band theory is quite successful in explaining the electrical conductivity of metals and semiconductors. It is an extension of molecular orbital theory which is based on linear combination of atomic orbitals. If there are *N* atoms in a solid, each contributing one atomic orbital, *N* molecular orbitals will be formed, half at lower energies and half at higher energies.

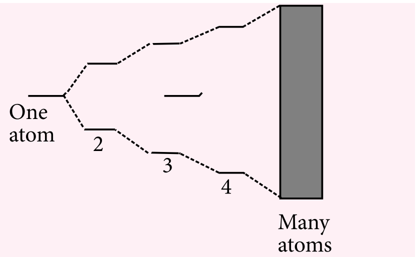


Figure showing development of bands. For three atoms there are non-bonding orbitals as well.

There is an important point that emerges from energy calculations. The separation between the highest energy and the lowest energy rapidly becomes constant as the number of atoms in the solid increases. However, as the number of energy levels that have to fit into this energy space is equal to the number of atoms in the solid, the energy levels get closer. When large numbers of atoms are included, the energy levels are so closely spaced that it is not too bad to take an approximation that a continuum of energies is found and this is called *band.*

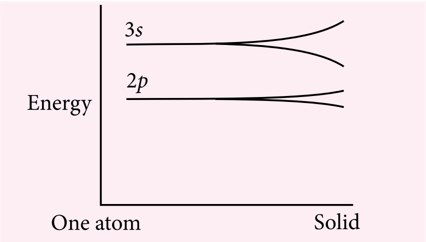


Figure showing broadening of energy levels in solids.

The gradual broadening of atomic orbitals into energy bands will happen to each of the atomic orbitals on each of the atoms in the crystal. The sharp energy level applicable to atom thus becomes translated into a set of bands. The energy spread in each band is related to the possibility of orbital overlap, which in turn depends on the extension of orbitals. The filled core orbitals are compact and are shielded from any interaction with orbitals on other atoms by the valence electron orbitals. No significant overlaps of these orbitals with orbitals on other atoms are possible. Thus core electron orbitals hardly broaden at all and form very narrow energy bands little different from those in a free atom. In contrast, the outer orbitals of adjacent atoms will interact strongly and the energy bands will be broad.

Bands are formed primarily by *s*-and *p*-orbitals. *d*-and *f*-orbitals are always shielded beneath outer *s*-and *p*-orbitals. They interact only weakly with orbitals on other atoms and form narrow *d*-or *f*-bands. These *d*- and *f*-orbitals however, play crucial role in explaining magnetic and optical properties of many solids.

Filling of Energy Levels in a Band

The electrons will feed into the energy levels in a band following Aufbau principle. For bonding to occur, an atomic orbital must contain a single unpaired electron. When all atoms have contributed one electron, the energy band will be half filled. The cohesive energy of a metal is due to this partial filling of the energy band.

The extent of filling of the highest occupied energy band determines the electrical properties of solids. If this band is incompletely filled, the electron may readily migrate through the crystal by gaining small increments of energy under the influence of an applied field. Such a solid is a *conductor*. If the band is completely filled at '0' K, the gap between this valence band and the conduction band is important. If this energy gap is large (several eV), electrons are not readily promoted to higher energy levels and the solid is an *insulator*. If the gap is small, at temperature above '0' K some electrons are thermally excited to the conduction band and the solid shows a low electrical conductivity, which increases with increase in temperature. This is an *intrinsic semiconductor.*

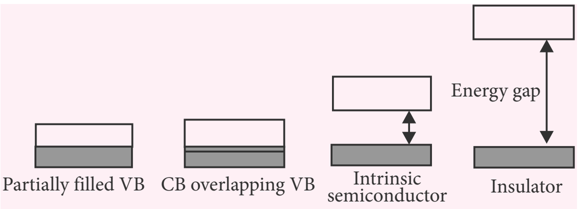


Figure showing the energy gaps in different materials. First two diagrams are for conductors. VB stands for Valence Band and CB for Conduction Band.

Intrinsic Semiconductor

Platform of semiconductor is good one to realize what is called band theory. Germanium and silicon are two important elementary semiconductors. Each atom in germanium crystal has four valence electrons. The inner ionic core of the atom has a positive charge of +4 units. The four valence electrons are held by covalent bonds with the valence electrons of four nearest neighbouring atoms. Since the valence electrons bind one atom to another, they are not available for electrical conduction in the absence of any thermal excitation. Hence at '0' K, a pure semiconductor behaves like an insulator. In the band picture the situation is described by saying that at '0' K the valence band is completely filled and the conduction band is empty.

At room temperature, some of the valence electrons have enough thermal energy to break their covalent bonds. These electrons are now free to move at random throughout the crystal. The energy required to break the covalent bond is the forbidden energy gap, which is 0.7 eV at room temperature. The vacancy caused by the bond cleavage is called as *hole*. In the band picture, the electrons are thermally excited from the valence band to conduction band where they become free. Holes left in the valence band contribute to conductivity in the following manner :

When an electron-hole pair is thermally generated, a valence electron in a neighbouring atom can have sufficient thermal energy to jump into the position of the hole and reconstruct a covalent bond. In doing so the electron leaves a hole in its initial position. Effectively the hole moves in an opposite direction to that of valence electrons. Thus hole behaves like a free positive charge equal in magnitude to the electronic charge.

In intrinsic semiconductors, the number of holes is equal to the number of free electrons. As new electron-hole pairs are generated by thermal agitation, some electron-hole pairs are lost due to recombination. At any temperature there is an equilibrium concentration of hole-electron pairs called *intrinsic carrier concentration*.

Drift of Electrons and Holes in External Applied Field

The electrons in the conduction band and the holes in the valence band move in a random fashion within the crystal due to their thermal energy. When an external voltage is applied to the semiconductor, a drift velocity is superimposed on the random thermal motion of the electrons and the holes. The drift of the electrons in the conduction band and that of the holes in the valence band produce electric current. Electrons move towards the positive electrode and holes towards the negative. Thus conventional current flows within the semiconductor from the positive electrode to the negative electrode.

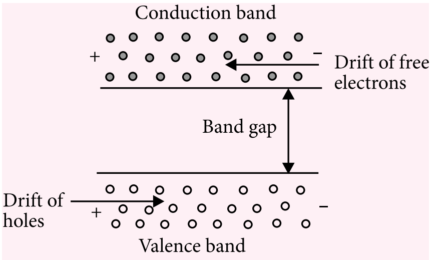
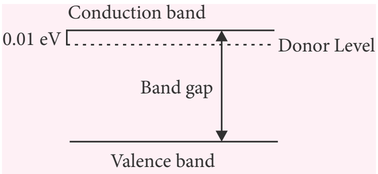


Figure showing drift of charge carriers in a biased semiconductor.

Extrinsic Semiconductor

When small amount of selected impurities are added to intrinsic semiconductors, their electrical properties change dramatically. A semiconductor having impurities is referred to as *doped*, *impure* or *extrinsic semiconductor*.



Donor level in the energy band diagram of *n*-type semiconductor.

Let a small amount of group-15 elements such as P, As or Sb be added to a Ge crystal. The impurity atom now displaces some of the host germanium atoms and fits into the crystal. Four of the five valence electrons of impurity atom form four covalent bonds with neighbouring host crystal atoms. The fifth electron is now loosely bound. This electron can be easily detached from the atom and set free. The energy necessary for this is about 0.01 eV. This energy required is much less than the band gap of intrinsic semiconductor, which is required to rupture a covalent bond. This small energy to release the fifth valence electron from the impurity is readily available from the thermal agitation of the crystal. As the electron is released from the impurity atom, the latter becomes an immobile positive ion. By default some electron-hole pairs exist in the semiconductor. The additional electrons coming from impurity are extra carriers. So, in *n*-type semiconductors, the charge carriers are predominantly electrons.

In the band picture when impurity atoms are added, an allowable energy level corresponding to the loosely bound valence electron is introduced in the forbidden gap just below the conduction band. Since the impurity atoms are located far apart in the crystal, their interaction is negligible. Therefore, the new energy level is discrete, called the *donor level*.

Similarly, in a *p*-type semiconductor, the impurities deliberately added are Al, B or In of Group-13 to Si or Ge. If a trivalent impurity atom replaces a host atom of Ge crystal, only three of the four covalent bonds can be filled. The trivalent impurity atom can accept one electron from a covalent bond of Ge crystal. The energy required for this purpose is only 0.01 eV. As an electron jumps to this hole, it breaks its original covalent bond and creates a new hole. These impurity atoms after accepting electron become immobile negative ions. In the band picture, as the electrons move into the acceptor level, holes are generated in the valence band. The number of these holes is greater than intrinsic carrier concentration and thus the semiconductor is called *p-type*.

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SOLUTIONS TO JUNE 2015 CROSSWORD

					C	A	R	B	A	M	I	D	E						N				C	
	N								M										I				U	
	O					S	U	S	P	E	N	S	O	I	D	S			T				P	
	R				C				H			C							R		R		R	
	B	E	R	N	O	U	L	L	I			I				P	Y	R	O	X	E	N	E	S
	I				L				P			N							S		G		N	
	D				L				R			T							Y		E		E	
	E			B	E	R	T	H	O	L	L	I	D	E					L		L			
		D			C				T			L							S		A			
		E			T		I		I			L									T		D	
		W			O		M		C			A		P	R	O	O	F	S	P	I	R	I	T
		P			R		I					T			O						O		O	
		O			S	O	D	I	U	M	S	I	L	I	C	A	T	E			N		X	
		I					O					O			H					G			O	
		N					G			K		N			E		T	H	I	O	K	O	L	
A	N	T	I	N	O	D	E			N					L		E			L			A	
L							N			O					L		C			D			N	
U							E			C	R	O	W	N	E	T	H	E	R	S			E	
N		M		A			S			K					S		N			C			S	
D		U		G						I		I			A		E			H				
U		F		E	M	U	L	S	I	N		N			L		T			M				
M		F		I						G		G			T		I			I				
		L	I	N	E	A	R					O					U			D				
		E		G					C	O	N	T	I	N	U	U	M			T				

Winners of June 2015 Crossword

- **Krishna Deori (Assam)**
- **Ramya Alva (Karnataka)**
- **Alok Bhushan (M.P.)**

EXAMINER'S MIND CLASS XI

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XI.
This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

SOME BASIC CONCEPTS OF CHEMISTRY | STRUCTURE OF ATOM

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. The total number of protons in 10 g of calcium carbonate is ($N_0 = 6.023 \times 10^{23}$)
(a) 1.5057×10^{24} (b) 2.0478×10^{24}
(c) 3.0115×10^{24} (d) 14.0956×10^{24}

2. The angular speed of the electron in n^{th} orbit of Bohr hydrogen atom is
(a) directly proportional to n
(b) inversely proportional to $\sqrt{n}$
(c) inversely proportional to n^2
(d) inversely proportional to n^3.

3. How many valence electrons are present in 0.53 g of Na_2CO_3?
(a) $40 \times 6.023 \times 10^{23}$ (b) $0.2 \times 6.023 \times 10^{23}$
(c) $0.4 \times 6.023 \times 10^{23}$ (d) $2 \times 6.023 \times 10^{23}$

4. The radii of maximum probability for 3s, 3p and 3d electrons are in the order
(a) $(r_{max})_{3d} > (r_{max})_{3p} > (r_{max})_{3s}$
(b) $(r_{max})_{3d} > (r_{max})_{3s} > (r_{max})_{3p}$
(c) $(r_{max})_{3s} > (r_{max})_{3p} > (r_{max})_{3d}$
(d) none of these.

5. When burnt in air, 14.0 g mixture of carbon and sulphur gives a mixture of CO_2 and SO_2 in the volume ratio of 2 : 1, volume being measured at the same conditions of temperature and pressure. Number of moles of carbon in the mixture is
(a) 0.75 (b) 0.5 (c) 0.40 (d) 0.25

6. Given below are the statements regarding d-orbitals.
I. Each orbital has 4 lobes and 2 angular nodes.
II. Each orbital has 4 lobes and 1 angular node.
III. The orbital angular momentum of electron in each orbital is $\sqrt{6}\dfrac{h}{2\pi}$.
IV. All are non-degenerate.
The correct statement(s) is/are
(a) only (I) (b) (I) and (III)
(c) (II) and (III) (d) (I) and (IV)

7. The vapour density of a mixture containing NO_2 and N_2O_4 is 27.6. Mole fraction of NO_2 in the mixture is
(a) 0.8 (b) 0.6 (c) 0.4 (d) 0.2

8. When light of frequency 3.2×10^{16} Hz is used to irradiate a metal surface, the maximum kinetic energy of the emitted photoelectron is $\frac{3}{4}$ of the energy of the irradiating photon. What is the threshold frequency of the metal?
(a) 2.4×10^{25} Hz (b) 2.4×10^{16} Hz
(c) 1.6×10^{15} Hz (d) 8×10^{15} Hz

9. The volume of water to be added to 100 cm^3 of 0.5 N H_2SO_4 to get decinormal concentration is
(a) 400 cm^3 (b) 450 cm^3
(c) 500 cm^3 (d) 100 cm^3

10. Correct set of four quantum numbers for valence (outermost) electron of rubidium (Z = 37) is
(a) 5, 0, 0, +1/2 (b) 5, 1, 0, +1/2
(c) 5, 1, 1, +1/2 (d) 6, 0, 0 +1/2

11. If 3.01×10^{20} molecules are removed from 98 mg of H_2SO_4, then the number of moles of H_2SO_4 left is
(a) 0.1×10^{-3} (b) 0.5×10^{-3}
(c) 1.66×10^{-3} (d) 9.95×10^{-2}

12. The frequency v of certain line of the Lyman series of the atomic spectrum of hydrogen satisfies the following conditions :
(i) It is the sum of frequencies of another Lyman line and a Balmer line.
(ii) It is the sum of the frequencies of a certain Lyman line, a Balmer line and a Paschen line.
(iii) It is the sum of the frequencies of a Lyman line, and a Paschen line but no Brackett line.
To what transition does v correspond?
(a) $n_2 = 3$ to $n_1 = 1$ (b) $n_2 = 3$ to $n_1 = 2$
(c) $n_2 = 2$ to $n_1 = 1$ (d) $n_2 = 4$ to $n_1 = 1$

13. 1 g alloy of Cu and Zn reacted with excess of dil. H_2SO_4 to give H_2 gas which occupies 60 mL at STP. The percentage of Zn in the alloy is
(a) 17% (b) 34% (c) 83% (d) 40%

14. When high speed electrons strike a target
(a) only heat is produced
(b) only continuous X-rays are emitted
(c) only continuous and characteristic X-rays are emitted
(d) heat is produced and simultaneously continuous and characteristic X-rays are emitted.

15. A 5 L vessel contains 2.8 g of N_2. When heated to 1800 K, 30% molecules are dissociated into atoms. Identify the correct statement.
(a) Total number of moles in the container will be 0.13.
(b) Total number of molecules in the container will be 0.78×10^{23}.
(c) Total number of atoms in the container will be 0.06.
(d) All of the above.

16. Which of the following pairs of nuclides are isodiaphers?
(a) $^{13}_{6}C$ and $^{16}_{8}O$ (b) $^{1}_{1}H$ and $^{2}_{1}H$
(c) $^{3}_{1}H$ and $^{4}_{2}He$ (d) $^{55}_{25}Mn$ and $^{65}_{30}Zn$

17. The density of 3 M sodium thiosulphate is 1.25 g mL^{-1}. Identify the correct statement(s) among the following.
(a) % by weight of sodium thiosulphate is 37.92.
(b) The mole fraction of sodium thiosulphate is 0.065.
(c) The molality of Na^+ is 7.74 and $S_2O_3^{2-}$ is 3.87.
(d) All of the above.

18. The de Broglie wavelength of electron in first Bohr orbit is exactly equal to
(a) half the circumference of the orbit
(b) equal to the circumference of the orbit
(c) twice the circumference of the orbit
(d) thrice the circumference of the orbit.

19. H_3BO_3 on heating decomposes in two ways :
I. $H_3BO_3 \longrightarrow HBO_2 + H_2O$
II. $H_3BO_3 \longrightarrow B_2O_3 + H_2O$
If 9 moles of H_3BO_3 are taken, some part decomposed like (I) and remaining like (II). If total 11 moles of water are formed, the moles of B_2O_3 formed is
(a) 6 (b) 5 (c) 3 (d) 2

20. The energy of the electron in Be^{3+} ion depends on
(a) the principal quantum number only
(b) the principal and azimuthal quantum numbers only
(c) the principal, azimuthal and magnetic quantum numbers only
(d) the principal, azimuthal, magnetic and spin quantum numbers.

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. SO_2 gas is slowly passed through an aqueous suspension containing 12 g $CaSO_3$ till the milkiness just disappears. What amount of SO_2 would be required?
(a) 12.8 g (b) 6.4 g
(c) 0.1 mole (d) 0.2 mole

22. For the radial probability distribution curves which of the following is/are correct?
(a) The number of maxima is $n - l$.
(b) The number of nodal points is $n - l - 1$.
(c) The radius of maximum charge density (r_{max}) increases in the order; $3s < 3p < 3d$.
(d) The number of angular nodes is l.

23. Which of the following statements is (are) true, if 1 mole of H_3PO_x is completely neutralized by 40 g of NaOH?
(a) $x = 2$ and acid is monobasic.
(b) $x = 3$ and acid is dibasic.
(c) $x = 4$ and acid is tribasic.
(d) $x = 2$ and acid does not form acidic salt.

24. Which of the following statements is/are correct?
(a) The mass of neutron is slightly greater than that of proton.
(b) e/m ratio of particle in anode rays depends upon the nature of the gas taken in the discharge tube.
(c) In H-atom, the electron revolves at a fixed distance of 0.53 Å.
(d) Angular momentum of all *s*-electrons is same.

25. Which of the following weighs equal to 32 g?
(a) 1 mole of sulphur atoms
(b) 1 mole of oxygen atoms
(c) 1 mole of carbon dioxide
(d) 22.4 L of oxygen molecule at S.T.P.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

When Schrödinger equation is solved for hydrogen atom, the solution gives the possible energy levels the electron can occupy and the corresponding wave function(s)

(ψ) of the electron associated with each energy level. These quantized energy states and corresponding wave functions which are characterized by a set of three quantum numbers (principal quantum number n, azimuthal quantum number l and magnetic quantum number m_l) arise as a natural consequence in the solution of the Schrödinger equation. When an electron is in any energy state, the wave function corresponding to that energy state contains all information about the electron.

26. Which quantum number determines orientation of the orbital?
(a) Principal (b) Azimuthal
(c) Magnetic (d) Spin

27. Radial nodes are maximum in
(a) $4s$ (b) $4p$ (c) $3d$ (d) $5f$

28. Consider following statements :
(i) Splitting of spectral line occurs when placed in a magnetic field or in an electric field.
(ii) In case of $1s$-orbital, the density of the charge cloud is the greatest at the nucleus and falls off with the distance. The density at a particular distance is uniform.
(iii) Electron-density is concentrated along a particular direction in case of $2p$-orbital.
(iv) A p-orbital can accommodate maximum of six electrons.

Select correct statements.
(a) (i), (ii), (iv) (b) (i), (ii), (iii)
(c) (ii), (iii), (iv) (d) (i), (iii), (iv)

Paragraph for Questions 29 to 31

There are different methods for calculation of molecular weight viz. osmotic pressure, lowering of vapour pressure, elevation in boiling point and depression in freezing point. The molecular weight of a volatile substance can be calculated from vapour density.

Molecular weight = Vapour density × 2

Vapour density

$$= \frac{1}{2} \times \frac{\text{Weight of volatile substance}}{\text{Volume at NTP}} \times 22400$$

29. The vapour density of a metal sulphate is 90 and its oxide contains 60 per cent metal. The atomic weight of metal is
(a) 12 (b) 24 (c) 36 (d) 40

30. The gram equivalent volume of oxygen at STP is
(a) 22.4 L (b) 20 L (c) 11.2 L (d) 5.6 L

31. The volume occupied by one mole of water vapours at STP is
(a) = 22.4 L (b) > 22.4 L
(c) < 22.4 L (d) 10 L

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the List I showing products of reactions to the List II showing amount of the product formed and select the correct answer using the code given below the lists :

	List I		List II
P.	$\underset{1\,g}{2H_2} + \underset{1\,g}{O_2} \longrightarrow 2H_2O$	1.	0.56 g
Q.	$\underset{1\,g}{N_2} + \underset{1\,g}{3H_2} \longrightarrow 2NH_3$	2.	1.333 g
R.	$\underset{1\,g}{CaCO_3} \xrightarrow{\Delta} CaO$	3.	1.125 g
S.	$\underset{1\,g}{2H_2} + \underset{1\,g}{C} \longrightarrow CH_4$	4.	1.214 g

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

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

	List I		List II
P.	Exclusion principle	1.	Intensity of electron wave
Q.	Zeeman effect	2.	Transition from higher shell to K shell
R.	Lyman series	3.	Effect of magnetic field on atomic spectra
S.	Schrödinger equation	4.	No two electrons in an atom can have all the four quantum numbers same.

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

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

	List I		List II
P.	4.5 m solution of $CaCO_3$ (density 1.45 g/mL)	1.	Mole fraction of solute = 0.2
Q.	100 mL of 3 M H_2SO_4 mixed with 300 mL of 1 M H_2SO_4 solution	2.	Mass of the solute is 360 g
R.	14.5 m solution of Ca	3.	Molarity = 4.5 M
S.	40 g of NaOH is added to 2 L of 4 M NaOH solution	4.	Molarity 1.5 M

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

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.

(b) If both assertion and reason are true but reason is not the correct explanation of assertion.

(c) If assertion is true but reason is false.

(d) If both assertion and reason are false.

35. **Assertion :** The kinetic energy of photoelectron ejected increases with the frequency of incident light.
Reason : Increase in intensity of incident light increases the photoelectric current.

36. **Assertion :** An electron can never be found in the nucleus.
Reason : Uncertainty of position of electron-wave is greater than 10^{-15} m.

37. **Assertion :** The molality of a solution does not change with change in temperature.
Reason : The molality is expressed in units of moles per 1000 g of solvent.

38. **Assertion :** The normality of 0.3 M aqueous solution of H_3PO_3 is equal to 0.6 N.
Reason : Equivalent weight of H_3PO_3

$$= \frac{\text{Molecular weight of } H_3PO_3}{3}$$

39. **Assertion :** Mass numbers of most of the elements are fractional.
Reason : Mass numbers are obtained by comparing with mass number of carbon taken as 12.

40. **Assertion :** The transition of electrons $n_3 \rightarrow n_2$ in H-atom will emit radiation of higher frequency than $n_4 \rightarrow n_3$.
Reason : Principal shells n_2 and n_3 have lower energy than n_4.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. The equivalent weight of an element is 4. Its chloride has a vapour density 59.25. Then the valency of the element is

42. The maximum number of electrons that can have principal quantum number, $n = 3$, and spin quantum number, $m_s = -1/2$ is

43. FeS on oxidation gives Fe_2O_3 and SO_2. The n-factor of FeS in the reaction is

44. Electron falls from 7th energy level and lower energy levels to produce bands in the Paschen series. The total number of bands obtained will be

45. A metal M on oxidation gives metal oxide MO that contains 80% oxygen. The atomic weight of metal is

46. To stop the flow of photoelectrons produced by electromagnetic radiation incident on a certain metal, a negative potential of 300 V is required. If the photoelectric threshold of metal is 1500 Å, the frequency of the incident radiation is $x \times 10^{16}$ Hz. the value of x is

47. A student performs a titration with different burettes and find titre values of 25.2 mL, 25.25 mL, and 25.0 mL. The number of significant figures in the average titre value is

48. In the Bohr's model of the hydrogen atom, if the ratio of the kinetic energy to the total energy of the electron in a quantum state n is $-x$, then x is

49. The volume of 90% alcohol which by weight ($d = 0.8$ g mL^{-1}) of ethanol which must be used to prepare 40 mL of 10% alcohol by weight ($d = 0.9$ g mL^{-1}) is

50. The highest excited state, the unexcited hydrogen atom can reach when they are bombarded with 12.2 eV electron is

SOLUTIONS

1. **(c) :** 10 g of $CaCO_3$ is $\frac{10}{100} = 0.1$ mol

Number of protons in 1 molecule of $CaCO_3$ =
(At. no. of Ca + At. no. of C + 3 At. no. of O)
= 20 + 6 + 24 = 50.

Number of protons in 1 mole of $CaCO_3$ =
$50 \times 6.023 \times 10^{23}$

Number of protons in 0.1 mole of $CaCO_3$ =
$0.1 \times 50 \times 6.023 \times 10^{23} = 3.0115 \times 10^{24}$

2. **(d) :** Angular speed = $\frac{V}{r}$; $V_n \propto \frac{1}{n}$ and $r_n \propto n^2$.

$\therefore$ Angular speed $\propto \frac{1}{n^3}$

3. **(b) :** In Na_2CO_3, sodium exists as Na^+ and carbonate exists as CO_3^{2-}. In Na^+, number of valence electrons are 8. In CO_3^{2-}, number of valence electrons are 24.
Total number of valence electrons in Na_2CO_3 =
2(8) + 24 = 40
Hence, 106 g of Na_2CO_3 contains $40 \times 6.023 \times 10^{23}$ valence electrons.

$\Rightarrow$ 0.53 g of Na_2CO_3 contains

$$0.53\times\frac{40}{106}\times6.023\times10^{23} = 0.2 \times 6.023 \times 10^{23}$$ valence electrons.

4. **(c)**

5. **(b):** Let weight of C be x g, then weight of S will be $(14 - x)$ g in a mixture.

$$\frac{x/12}{(14-x)/32}=\frac{2}{1} \quad (\because\ V \propto n)$$

$$\Rightarrow\ x = 6 \text{ g; Moles of C} = \frac{6}{12} = 0.5$$

6. **(b):** Number of angular nodes in any orbital = $l = 2$ ($l = 2$ for d-orbital)

Orbital angular momentum

$$=\sqrt{l(l+1)}\frac{h}{2\pi}=\sqrt{2(2+1)}\frac{h}{2\pi}=\sqrt{6}\frac{h}{2\pi}$$

Each d-orbital has 4 lobes and all d-orbitals are degenerate.

7. **(a):** $V.D._{\cdot mix} = x_{NO_2}(V.D.)_{NO_2} + x_{N_2O_4}(V.D.)_{N_2O_4}$

$$27.6 = x \times 23 + (1 - x) \times 46 \quad \left[\because\ V.D.=\frac{M}{2}\right]$$

$\therefore\ x_{NO_2} = 0.8$

8. **(d):** $K.E. = h\nu - h\nu_0$

$$K.E.=\frac{3}{4}h\nu \text{ (given)} \Rightarrow \frac{3}{4}h\nu=h\nu-h\nu_0$$

$$\therefore\ \nu_0=\frac{1}{4}\times\nu=\frac{1}{4}\times3.2\times10^{16}=8\times10^{15}\text{ Hz}$$

9. **(a):** $N_1V_1 = N_2V_2$

$\therefore\ 0.5 \times 100 = 0.1 \times V_2$

$\therefore\ V_2 = 500 \text{ cm}^3$

Volume of water to be added = 500 – 100 = 400 cm^3.

10. **(a):** For Rubidium, $Z = 37$

Electronic configuration of Rb = [Kr] $5s^1$

The outermost electron is in 5s-orbital.

Thus, Principal quantum number, $n = 5$

For an s-orbital, azimuthal quantum number, $l = 0$

Magnetic quantum number, $m_l = -l$ to $+ l$

For $l = 0$, $m_l = 0$

Spin quantum number can be $+\frac{1}{2}$ or $-\frac{1}{2}$.

$\therefore$ Correct set of quantum numbers = 5, 0, 0, $+\frac{1}{2}$

11. **(b):** Moles of H_2SO_4 in 98 mg of H_2SO_4

$$=\frac{1}{98}\times0.098=0.001$$

Moles of H_2SO_4 removed

$$=\frac{3.01\times10^{20}}{6.023\times10^{23}}=0.5\times10^{-3}=0.0005$$

Moles of H_2SO_4 left = 0.001 – 0.0005 = 0.5×10^{-3}

12. **(d):** For $n_2 = 4$ to $n_1 = 1$ transition,

$\nu = \nu_{\text{Balmer }(4\to2)} + \nu_{\text{Lyman }(2\to1)}$

Also, $\nu = \nu_{\text{Paschen }(4\to3)} + \nu_{\text{Balmer }(3\to2)} + \nu_{\text{Lyman }(2\to1)}$

Also, $\nu = \nu_{\text{Paschen }(4\to3)} + \nu_{\text{Lyman }(3\to1)}$

13. **(a):** Only Zn reacts with dil. H_2SO_4 to give H_2 gas.

$$Zn + H_2SO_4 \longrightarrow ZnSO_4 + H_2$$

Let the weight of Zn in the alloy is x g.

Eq. of Zn = Eq. of H_2

$$\frac{2x}{65.3}=\frac{60}{11200} \quad \left[\text{Eq. wt. of Zn}=\frac{65.3}{2}\right]$$

$$x=\frac{60\times65.3}{11200\times2}=0.1749\text{ g}$$

$$\%\text{ of Zn}=\frac{0.1749\times100}{1}=17.49\%$$

14. **(d)**

15. **(a):** 30% molecules are dissociated as $N_2 \longrightarrow 2N$

$$\text{Amount of } N_2 \text{ left (in moles)} = \frac{2.8}{28}\times\frac{70}{100}$$

$= 0.1 \times 0.7 = 0.07$

$$\text{No. of moles of N atoms formed} = 2\times\frac{30}{100}\times\frac{2.8}{28}$$

$= 0.06$

No. of atoms in container = $0.06 \times 6.023 \times 10^{23}$

$= 0.36 \times 10^{23}$

Total no. of moles = 0.07 + 0.06 = 0.13

Total number of molecules = $0.07 \times 6.023 \times 10^{23}$

$= 0.421 \times 10^{23}$

[$\because$ Product contains atoms of nitrogen and not molecules].

16. **(d):** Isodiaphers have same difference of number of neutrons and protons or $(A - 2Z)$ must be same.

Nuclides	**Neutrons (*n*) (*A* – *Z*)**	**Protons (*p*) (*Z*)**	***n* – *p***
$^{13}_{6}C$	13 – 6 = 7	6	7 – 6 = 1
$^{16}_{8}O$	16 – 8 = 8	8	8 – 8 = 0
$^{1}_{1}H$	0	1	0 – 1 = –1
$^{2}_{1}H$	2 – 1 = 1	1	1 – 1 = 0
$^{3}_{1}H$	3 – 1 = 2	1	2 – 1 = 1
$^{4}_{2}He$	4 – 2 = 2	2	2 – 2 = 0
$^{55}_{25}Mn$	55 – 25 = 30	25	30 – 25 = 5
$^{65}_{30}Zn$	65 – 30 = 35	30	35 – 30 = 5

17. **(d):** $$M=\frac{\text{Mass}\,\%\times d\times10}{M_2}$$

$$3=\frac{\text{Mass}\,\%\times1.25\times10}{158} \quad [\because\ M_{Na_2S_2O_3}=158\text{ g mol}^{-1}]$$

$$\text{Mass \%} = \frac{3\times158}{1.25\times10} = 37.92$$

Also, $\frac{1}{m} = \frac{d}{M} - \frac{M_2}{1000}$; $\frac{1}{m} = \frac{1.25}{3} - \frac{158}{1000}$

$\Rightarrow \quad m = \frac{3000}{776} = 3.87$ m

Thus, molality of Na^+ ions = 2 × 3.87 = 7.74 m

and molality of $S_2O_3^{2-}$ ions = 3.87 m

$\therefore$ Moles of $Na_2S_2O_3$ in 1000 g of water = 3.87

Moles of solvent = $\frac{1000}{18}$ = 55.55

Mole fraction of $Na_2S_2O_3 = \frac{n_2}{n_1+n_2} = \frac{3.87}{3.87+55.55}$

$= \frac{3.87}{59.42} = 0.065$

18. **(b) :** Angular momentum, $mvr = n\frac{h}{2\pi} = \frac{h}{2\pi}$

or $\quad mv = \frac{h}{2\pi r}$ or $\frac{h}{mv} = 2\pi r$

$\Rightarrow \quad \lambda = 2\pi r$

Hence, λ = circumference

19. **(d) :** Let x moles of H_3BO_3 decomposed by I way and $(9 - x)$ moles decomposed by II way.

$$\underset{x}{H_3BO_3} \longrightarrow HBO_2 + \underset{x}{H_2O}$$

$$\underset{(9-x)}{2H_3BO_3} \longrightarrow B_2O_3 + \underset{\frac{3}{2}(9-x)}{3H_2O}$$

Total moles of water = $\frac{3}{2}(9-x)+x = 11$

$\Rightarrow \quad x = 5$

$\therefore$ Moles of H_3BO_3 decomposed in II reaction = 4

2 moles of $H_3BO_3 \equiv$ 1 mole of B_2O_3

4 moles of $H_3BO_3 \equiv$ 2 moles of B_2O_3

20. **(a) :** For hydrogen and hydrogen like species (one electron system) energy of the electron depends only on the principal quantum number.

21. **(b,c) :** $CaSO_{3(s)} + H_2O_{(l)} + SO_{2(g)} \rightarrow \underset{\text{Soluble}}{Ca(HSO_3)_2}$

moles of SO_2 required = moles of $CaSO_3 = \frac{12}{120} = 0.1$;

mass of SO_2 = 0.1 × 64 = 6.4 g

22. **(a,b,d)**

23. **(a,d) :** No. of gram equivalents of NaOH

$= \frac{40}{40} = 1$ g equivalent.

As only 1 g equivalent of NaOH is required for neutralization hence, the acid should be monobasic *i.e.*, H_3PO_2.

Also, monobasic acids do not form any acidic salt.

24. **(a,b,d) :** (a) Mass of proton = 1.00727663 u

Mass of neutron = 1.0086654 u

(b) e/m ratio depends upon the nature of the gas taken inside the discharge tube.

(c) The radii of stationary states of hydrogen atom are given by $r_n = a_0 n^2$

where, a_0 = 52.9 pm = 0.53 Å, it is the radius of the first stationary state and n = no. of orbit.

Thus, the electron in H-atom does not revolve at a fixed distance.

(d) Angular momentum is given as $\sqrt{l(l+1)}\frac{h}{2\pi}$

For all s-orbitals, $l = 0$

$\therefore$ Angular momentum of all s-electrons is same, *i.e.* zero.

25. **(a,d) :** 1 mole of S atoms ≡ Gram atomic mass of 'S' = 32 g

1 mole of O atoms ≡ Gram atomic mass of 'O' = 16 g

1 mole of CO_2 = Gram molecular mass of CO_2 = 44 g

22.4 L of O_2 molecule at S.T.P. ≡ 1 mole of O_2 = 32 g

26. **(c)**

27. **(a) :** Radial nodes = $n - l - 1$

28. **(b)**

29. **(c) :** Molecular weight of metal sulphate

= 90 × 2 = 180

Equivalent mass of metal $= \frac{\text{Mass of element}}{\text{Mass of oxygen}} \times 8$

$= \frac{60}{40} \times 8 = 12$

Equivalent mass of metal sulphate = 12 + 48 = 60

Valency = $\frac{180}{60} = 3 \Rightarrow$ At. wt. of metal = 12 × 3 = 36

30. **(d) :** Gram equivalent volume of oxygen is the volume occupied by 1 gram equivalent of oxygen *i.e.* 8 g of oxygen.

32 g of O_2 = 22.4 L at STP

8 g of O_2 = 5.6 L at STP

31. **(c) :** Due to dipole-dipole attraction forces the volume occupied by one mole of water vapours at STP is less than Gram molar volume 22.4 L.

32. **(a) :** **P → 3 :** Here, oxygen is the limiting reagent.

32 g of oxygen gives 36 g of H_2O

1 g of oxygen gives $\frac{36}{32}$ = 1.125 g

Q → 4 : Here, N_2 is the limiting reagent.

28 g of N_2 gives 34 g of NH_3.

1 g of N_2 gives $\frac{34}{28} = \frac{17}{14}$ = 1.214 g of NH_3

R → 1 : 100 g of $CaCO_3$ gives 56 g of CaO.

1 g of $CaCO_3$ gives $\frac{56}{100}$ = 0.56 g of CaO

S → 2 : Here, carbon is the limiting reagent.
12 g of C gives 16 g of methane.

1 g of C gives $\frac{16}{12} = 1.33$ g

33. (a)

34. (c) : Relation between molarity (M) and molality (m) : $\frac{1}{m} = \frac{d}{M} - \frac{M_2}{1000}$

P → 3 : Molar mass of $CaCO_3 = 40 + 12 + 3 \times 16$
$= 100$ g mol^{-1}

$$\frac{1}{4.5} = \frac{1.45}{M} - \frac{100}{1000}\ ;\ \frac{1.45}{M} = \frac{14.5}{45}$$

$$\Rightarrow\ M = 1.45 \times \frac{45}{14.5} = 4.5\text{ M}$$

$$\textbf{Q} \rightarrow \textbf{4}:\ M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2} = \frac{3\times100 + 1\times300}{100+300}$$
$$= \frac{600}{400} = 1.5\text{ M}$$

$$\textbf{R} \rightarrow \textbf{1}:\ \text{Molality} = \frac{\text{No. of moles of solute}}{\text{Mass of solvent (in kg)}}$$

$$14.5 = \frac{\text{No. of moles of solute}}{1\text{ kg}}$$

No. of moles of solute, $n_2 = 14.5$

No. of moles of water,

$$n_1 = \frac{1\text{ kg}}{\text{Mol. mass of }H_2O} = \frac{1000}{18} = 55.55$$

Mole faction of solute,

$$x_2 = \frac{n_2}{n_1 + n_2} = \frac{14.5}{55.55 + 14.5} = \frac{14.5}{70.05} = 0.206 \simeq 0.2$$

$$\textbf{S} \rightarrow \textbf{2}:\ \text{Molarity} = \frac{\text{No. of moles of solute}}{\text{Volume of solution (in L)}}$$
$$= \frac{\text{No. of moles of NaOH}}{2}$$

No. of moles of NaOH = 4 × 2 = 8
Mass of NaOH = No. of moles × Molar mass of NaOH
= 8 × 40 = 320 g
As 40 g of NaOH is added,
∴ Mass of solute = 320 + 40 = 360 g

35. (b): $K.E. = h(\nu - \nu_0)$; $K.E.$ increases linearly with ν, the frequency. The rate of emission of photoelectrons *i.e.*, the photoelectric current is proportional to the rate of impinging photons *i.e.*, the intensity of light.

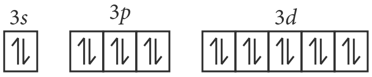
36. (a) **37. (a)** **38. (c)**

39. (d): Mass numbers are whole numbers, atomic masses are fractional. Atomic masses are obtained by comparing with mass of C-12 atom taken as 12.

40. (a) : $E_2 - E_1 > E_3 - E_2 > E_4 - E_3$ ...

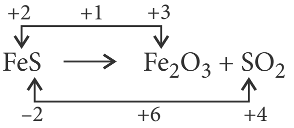
41. (3) : Valency of the element $= \frac{2 \times 59.25}{4 + 35.5} = 3$

42. (9) :



So, no. of electrons with spin quantum number $-\frac{1}{2}$ will be 1 + 3 + 5 = 9.

43. (7) : n-factor is the change in oxidation number per mole of FeS.



∴ $n = 6 + 1 = 7$

44. (4) : Paschen series is produced by jump to n = 3 energy level.
Starting from n = 7, the possible bands produced for transitions are :
7 → 3, 6 → 3, 5 → 3 and 4 → 3.

45. (4)

46. (7) : $K.E.$ of photoelectrons = e × stopping potential
$= 1.602 \times 10^{-19} \times 300 = 4.806 \times 10^{-17}$ J

$K.E.$ of photoelectrons $= h(\nu - \nu_0) = h\left(\nu - \frac{c}{\lambda_0}\right)$

(ν_0 = Threshold frequency)

$$4.806 \times 10^{-17} = 6.626 \times 10^{-34}\left(\nu - \frac{3\times10^8}{1500\times10^{-10}}\right)$$
$$= 6.626 \times 10^{-34}\ (\nu - 2 \times 10^{15})$$

$$\nu - 2 \times 10^{15} = \frac{4.806 \times 10^{-17}}{6.626 \times 10^{-34}} = 7.25 \times 10^{16}\text{ Hz}$$
$$\simeq 7 \times 10^{16}\text{ Hz}$$

47. (3) : Average titre value $= \frac{25.2 + 25.25 + 25.0}{3}$

$$= \frac{75.45}{3} = 25.15 = 25.2\text{ mL}$$

Number of significant figures will be 3.

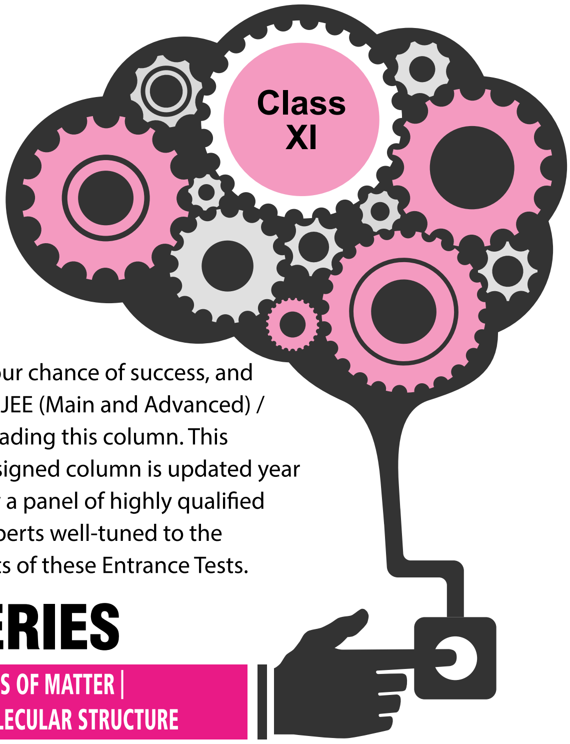
48. (1) **49. (5)**

50. (3) : $E_1 = -13.6$ eV
After absorption of 12.2 eV energy
$E_H = -13.6 + 12.2 = -1.4$ eV

Now, $E_n = \frac{E_1}{n^2}$ ∴ $n^2 = \frac{-13.6}{-1.4} = 9.71$

∴ $n = 3$

◆◆



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ACCELERATED LEARNING SERIES

Unit 1

SOME BASIC CONCEPTS IN CHEMISTRY | STATES OF MATTER | ATOMIC STRUCTURE | CHEMICAL BONDING AND MOLECULAR STRUCTURE

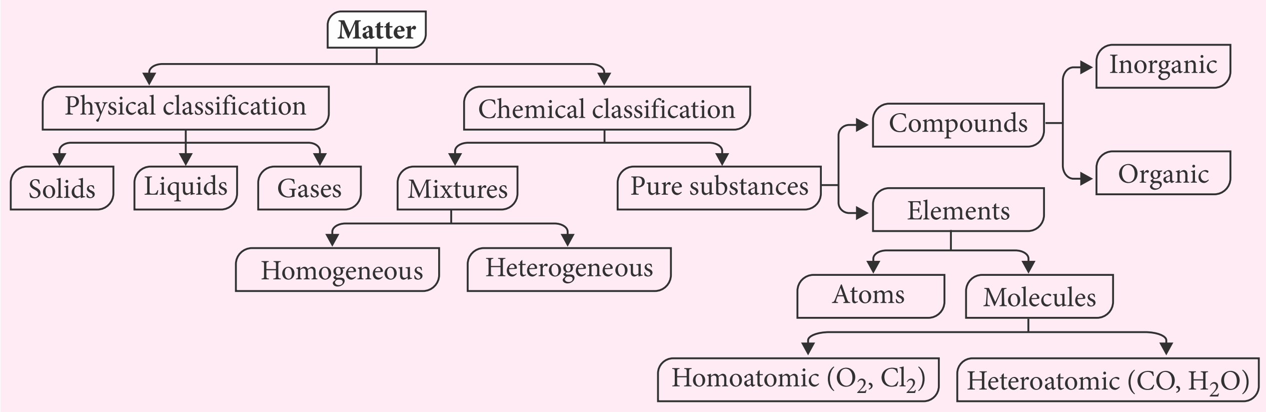
SOME BASIC CONCEPTS IN CHEMISTRY

- Introduction
- Classification of Matter
- Measurements in Chemistry
- Laws of Chemical Combinations and Dalton's Atomic Theory
- Atomic Mass, Molecular Mass and Equivalent Mass
- Mole Concept and Stoichiometry

TIPS TO REMEMBER

- ☐ Matter is the physical material of the universe and is anything that occupies *space* and has *mass*.
- ☐ Chemistry is the science that is primarily concerned with matter and the changes it undergoes. It is defined as the study of substances especially regarding their structures, properties, transformations and the energy changes accompanying these transformations.

Classification of Matter



Measurements in Chemistry

- ☐ The measurement is said to be *accurate* if the average value of different measurements is close to the actual value and the measurement is said to be *precise* if the values of different measurements are close to each other and hence close to their average value.
- ☐ The total number of digits in a number including the last digit whose value is uncertain is called the number of *significant figures.*
  Rules for determining the number of significant figures :
  - ○ All non-zero digits are significant.
  - ○ The zeros to the right of the decimal point are significant.

  - The zeros between two non-zero digits are significant.
  - Zeros to the left of the first non-zero digit are not significant.
- A *unit* is the standard of comparison for measurements.
  - According to SI system, there are *seven basic units* : length (m), mass (kg), time (s), electric current (A), temperature (K), amount of substance (mol), luminous intensity (cd) and *two supplementary units* : plane angle (rad), solid angle (Sr).
  - *Dimensional analysis* involves conversion of the given physical quantity from one unit to another using unit conversion factors. Some useful conversion factors are :

    Length – 1 Å = 10^{-8} cm = 10^{-10} m,
    1 nm = 10^{-9} m, 1 pm = 10^{-12} m
    Volume – 1 L = 1000 mL
    = 1000 cm^3 = 1 dm^3 = 10^{-3} m^3
    Pressure – 1 atm = 760 mm or torr
    = 101325 Pa or Nm^{-2}
    1 bar = 10^5 Nm^{-2} = 10^5 Pa
    Energy – 1 calorie = 4.184 J
    1 eV = 1.6022 × 10^{-19} J
    1 J = 10^7 ergs

Laws of Chemical Combinations

- **Law of Conservation of Mass (*Lavoisier*)**
  Matter can neither be created nor destroyed.
- **Law of Constant Composition or Definite Proportions (*Proust*)**
  A given compound always contains exactly the same proportion of elements by weight.
- **Law of Multiple Proportions (*Dalton*)**
  If two elements can combine to form more than one compound, the masses of one element that combine with a fixed mass of the other element, are in the ratio of small whole numbers.
- **Law of Reciprocal Proportions (*Richter*)**
  The ratio of the masses of two elements A and B which combine separately with a fixed mass of the third element C is either the same or some simple multiple of the ratio of the masses in which A and B combine directly with each other.
- **Gay Lussac's Law of Gaseous Volumes**
  When gases combine or are produced in a chemical reaction they do so in a simple ratio by volume provided all gases are at same temperature and pressure.
- **Avogadro's Law**
  Equal volumes of gases at the same temperature and pressure should contain equal number of molecules.

Dalton's Atomic Theory

- The main points of this theory are :
  - Matter consists of indivisible atoms.
  - All the atoms of a given element have identical properties including identical mass. Atoms of different elements differ in mass.
  - Compounds are formed when atoms of different elements combine in a fixed ratio.
  - Chemical reactions involve reorganisation of atoms. These are neither created nor destroyed in a chemical reaction.

Masses and their Methods of Determination

- **Atomic mass :** It is defined as the average relative mass of the atoms of the element as compared to the mass of C-12 isotope taken as 12 u.
- **Methods of Determining Atomic Mass**

Method	Formulae
Dulong and Petit's method	Approx. atomic mass = $\frac{6.4}{\text{Specific heat}}$
	Valency = $\frac{\text{Approx. atomic mass}}{\text{Equivalent mass}}$
	Exact atomic mass = Equivalent mass × Valency
Isomorphism method	Atomic mass = Equivalent mass × Valency
Specific heat/ Molar heat capacity method	Atomic mass of gaseous element = $\frac{\text{Molecular mass}}{\text{Atomicity}}$ (Mol. mass = 2 × Vapour density)
Volatile chloride method	Molecular mass of volatile chloride, MCl_x = Eq. mass of M × Valency of M + $35.5x$
	$x = \frac{2 \times \text{Vapour density}}{E + 35.5}$
	Atomic mass of M = Eq. mass of M × Valency of M

- **Molecular mass :** It is defined as the average relative mass of the molecules of a substance as compared to the mass of C-12 isotope taken as 12 u.

- **Methods of Determining Molecular Mass**

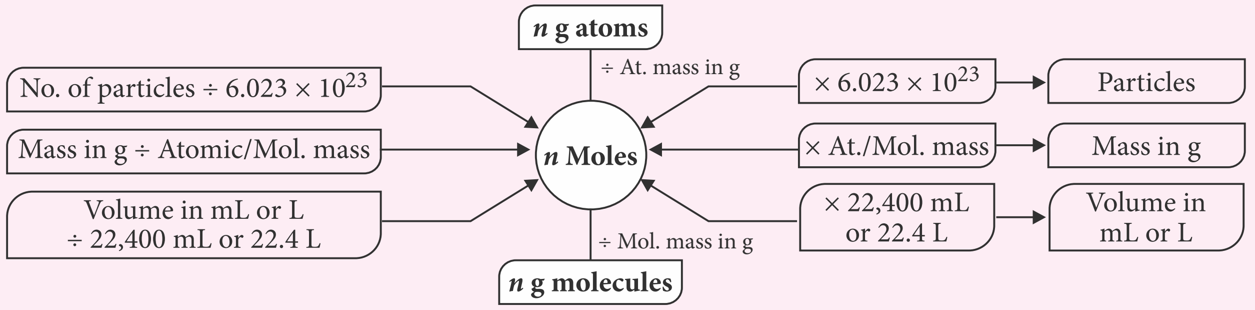
Method	Formulae
Vapour density method	Mol. mass = 2 × Vapour density
Diffusion method	$\frac{r_1}{r_2}=\sqrt{\frac{d_2}{d_1}}=\sqrt{\frac{2\times d_2}{2\times d_1}}=\sqrt{\frac{M_2}{M_1}}$
Colligative property method	$\Delta T_b = iK_b \times \frac{w_2\times 1000}{M_2\times w_1(\text{in g})}$ $\Delta T_f = iK_f \times \frac{w_2\times 1000}{M_2\times w_1(\text{in g})}$ $\pi = i\frac{w}{M}\frac{RT}{V}$ For dilute solutions (as $n_2 << n_1$), $\frac{p^\circ - p_s}{p^\circ} = i\frac{w_2/M_2}{w_1/M_1}$ For dilute as well as concentrated solutions, $\frac{p^\circ - p_s}{p_s} = \frac{w_2/M_2}{w_1/M_1}$

- **Equivalent mass :** It is defined as the number of parts by weight of the substance that combine with or displace directly or indirectly 1.008 parts by weight of hydrogen or 8 parts by weight of oxygen or 35.5 parts by weight of chlorine.

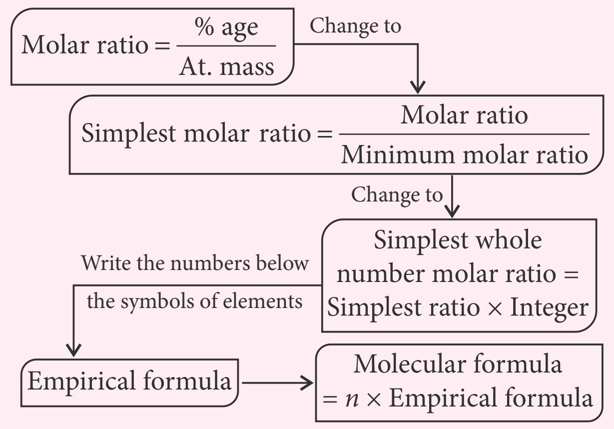
- **Methods of Determining Equivalent Mass**

Method	Formulae
Hydrogen displacement method	Eq.wt. of M = Mass of the metal which displaces 1.008 g or 11200 mL of H_2 at STP.
Oxide formation method	Eq.wt. of M = Mass of the metal which combines with or displaces 8 g or 5600 mL of O_2.
Chloride formation method	Eq.wt. of E = Mass of the element which combines with 35.5 g or 11200 mL of Cl_2.
Metal displacement method	$\frac{\text{Wt. of metal added}}{\text{Wt. of metal displaced}} = \frac{\text{Eq. mass of metal added}}{\text{Eq. mass of metal displaced}}$
Double decomposition method	$\frac{\text{Wt. of } AB \text{ taken}}{\text{Wt. of } AD \text{ formed}} = \frac{\text{Eq. mass of } A + \text{Eq. mass of } B}{\text{Eq. mass of } A + \text{Eq. mass of } D}$
Electrolytic method	$\frac{\text{Wt. of } X \text{ deposited}}{\text{Wt. of } Y \text{ deposited}} = \frac{\text{Eq. mass of } X}{\text{Eq. mass of } Y}$
Neutralization method	Eq. mass of an acid = Mass of acid neutralized by 1000 mL of 1 N base solution. Eq. mass of a base = Mass of base neutralized by 1000 mL of 1 N acid solution.
Silver salt method	$\frac{\text{Eq. mass of } RCOOAg}{\text{Eq. mass of Ag}} = \frac{\text{Wt. of silver salt}}{\text{Wt. of silver}}$
General methods	Eq. mass of an acid $= \frac{\text{Mol. mass of acid}}{\text{Basicity}}$ Eq. mass of a base $= \frac{\text{Mol. mass of base}}{\text{Acidity}}$ Eq. mass of a salt $= \frac{\text{Mol. mass of salt}}{\text{Total positive valency of metal atoms}}$

Mole Concept



Determination of Empirical and Molecular Formulae



Stoichiometry in Solutions

- ❑ Mass % of solute in solution $$= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 100$$
- ❑ Volume % of $A = \frac{V_A}{V_A + V_B} \times 100$
- ❑ Parts per million of $A = \frac{\text{Mass of } A}{\text{Mass of solution}} \times 10^6$
- ❑ Molarity $(M) = \frac{\text{Moles of solute}}{\text{Volume of solution (in mL)}} \times 1000$
- ❑ Molality $(m) = \frac{\text{Moles of solute}}{\text{Mass of solvent (in g)}} \times 1000$
- ❑ Normality $(N) = \frac{\text{No. of g eq. of solute}}{\text{Volume of solution (in mL)}} \times 1000$
- ❑ **Limiting reagent :** It is the reactant which is completely consumed during the reaction and hence limits the amount of product formed.
- ❑ **Relations between Different Concentration Units**

Concentration units	Relation
Molarity and Normality	$M \times$ Mol. mass of solute $= N \times$ Eq. mass of solute
Molarity and Mass percent	$M = \frac{\% \times d \times 10}{\text{Mol. mass}}$
Molarity and Molality	$m = \frac{100 \times M}{1000 \times d_{\text{soln}} - M \times GMM_{\text{solute}}}$
Molality and mole fraction of solute	$x_B = \frac{m \times GMM_{(\text{solvent})}}{1000 + m \times GMM_{(\text{solvent})}}$
Molarity and mole fraction of solute	$x_B = \frac{M \times GMM_{(\text{solvent})}}{M\left[GMM_{(\text{solvent})}\right] - GMM_{(\text{solute})} + 1000d}$

SELF CHECK

1. In the reaction,
$2Al_{(s)} + 6HCl_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 6Cl^{-}_{(aq)} + 3H_{2(g)}$
(a) 11.2 L $H_{2(g)}$ at STP is produced for every mole $HCl_{(aq)}$ consumed
(b) 6 L $HCl_{(aq)}$ is consumed for every 3 L $H_{2(g)}$ produced
(c) 33.6 L $H_{2(g)}$ is produced regardless of temperature and pressure for every mole Al that reacts
(d) 67.2 L $H_{2(g)}$ at STP is produced for every mole Al that reacts. (AIEEE 2007)

2. How many moles of magnesium phosphate, $Mg_3(PO_4)_2$ will contain 0.25 mole of oxygen atoms?
(a) 0.02 (b) 3.125×10^{-2}
(c) 1.25×10^{-2} (d) 2.5×10^{-2}
(AIEEE 2006)

KEY POINT

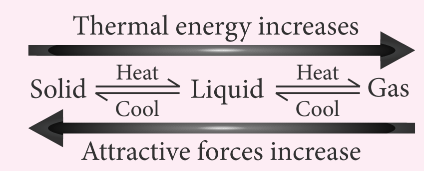
- During calculations involving more than one arithmetic operations, rounding off to the proper number of significant figures is done once at the end if all the operations are multiplications and/or divisions or if they are all additions and/or subtractions, but not if they are combinations of additions/subtractions with multiplications/divisions.
- If $w_{\text{solvent}} > 100$, then $M > m$
If $w_{\text{solvent}} < 100$, then $M < m$
If $w_{\text{solvent}} = 100$, then $M = m$

STATES OF MATTER

• Introduction	• Gaseous State
• Liquid State	• Solid State

TIPS TO REMEMBER

- ❑ Matter exists in three states – *solids*, *liquids* and *gases*.
- ❑ All the three states are associated with definite energy content and are interconvertible into each other.

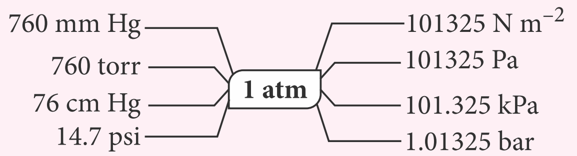


- The fourth state of matter known as *plasma* state is found at extremely high temperature in the interiors of sun and other stars or in the intense electrical fields as in discharge tubes and consists of gaseous mixtures of electrons and positively charged ions.
- Two other states, *fermionic condensate* and *Bose–Einstein's condensate* have also been observed during nuclear fusion reactions.

Gaseous State

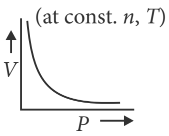
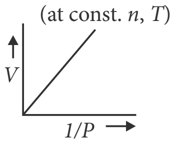
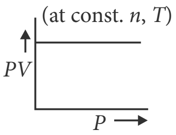
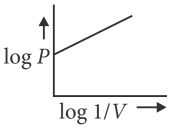
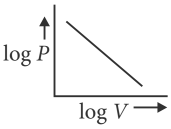
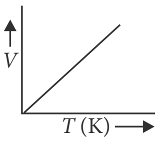
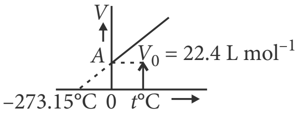
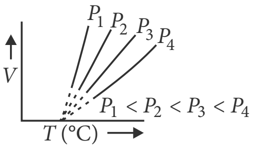
- Gaseous state exists in two different forms : vapour form (exists below critical temperature) and gas form (exists above critical temperature).
- **Measurable Properties of Gases**
  - Mass – generally expressed in grams (SI unit is kg)
  - Volume – generally expressed in units of L, m^3 or cm^3 or dm^3 (SI unit is m^3)
  - Temperature – generally expressed in °C or K.

    $T(K) = t°C + 273.15$
  - Pressure – generally expressed in the unit such as atm, mm, cm, torr, bar, etc. (SI units are Pa or kPa)



1 bar = 0.987 atm
1 bar = 10^2 kPa

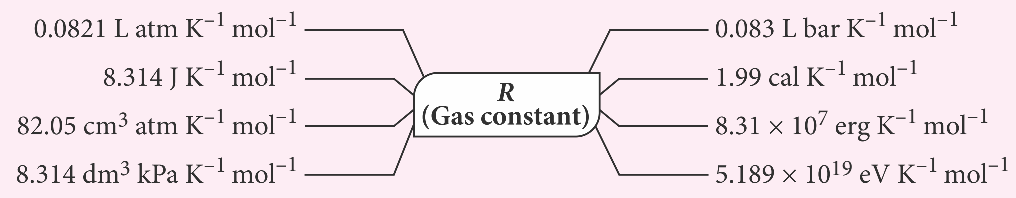
- **Standard States**
  - STP or NTP : P = 1 bar and T = 273.15 K
  - SATP : P = 1 bar (or 10^5 Pa) and T = 298.15 K
- **Gas Laws**

Laws	Mathematical expressions	Graphical representations
Boyle's law (*Robert Boyle*)	**At constant T** $V \propto \frac{1}{P}$ or PV = constant or $P_1V_1 = P_2V_2$	    
Charles' law (*Jacques Charles*)	**At constant P** $V_t = V_0 + \frac{t}{273.15}V_0$ or $V \propto T$ or $\frac{V_1}{T_1} = \frac{V_2}{T_2}$	  
Gay-Lussac's law/ Amonton's law	**At constant V** $P \propto T$ or $\frac{P_1}{T_1} = \frac{P_2}{T_2}$	
Avogadro's law	**At a given T and P** $V \propto n$	
Graham's law of diffusion	$\frac{r_1}{r_2} = \sqrt{\frac{d_2}{d_1}} = \sqrt{\frac{M_2}{M_1}}$	
Dalton's law of partial pressures	$P_{total} = p_1 + p_2 + p_3 + ... \; p_n$ $= (n_1 + n_2 + n_3 + ...)\frac{RT}{V}$	

KEY POINT

- Atmospheric pressure and density of air decrease with increase in altitude. At Mount Everest atmospheric pressure is reduced to 0.5 atm.
- Densities of gases are reported in g/L as they are quite low.
- Dalton's law is valid only for the mixtures of non-reacting gases.
- At SATP, the molar volume changes to 24.8 L.
- Nowadays the standard pressure is taken as 1 bar and the molar volume is 22.7 L and not 22.4 L.

- **Ideal gas equation :** $PV = nRT$
  - The constant R represents work done per degree per mole.



- **Kinetic Theory of Gases**
  - Kinetic theory of gases (presented by Bernoulli in 1738 and developed in 1860 by Clausius, Maxwell, Kroning and Boltzmann).
  - Various assumptions of the theory are :
    - All gases are made up of very large number of extremely small particles called *molecules*.
    - The molecules are separated from one another by large spaces so that the actual volume of the molecules is negligible as compared to the total volume of the gas.
    - The molecules are not at rest but possess rapid random motion. During their motion, they collide with one another and also against the walls of the container.
    - The pressure of the gas is due to bombardment of the gas molecules against the walls of the container.
    - The collisions of the molecules with each other and with the walls of the container are perfectly elastic, *i.e.*, there is no loss or gain of kinetic energy. However, there may be redistribution of energy during such collisions.
    - There are no attractive forces between the molecules of the gas. They are completely independent of each other.
    - At any instant, different molecules possess different velocities and hence, different energies. However, average kinetic energy of molecules is directly proportional to the absolute temperature.
  - *Kinetic gas equation :* $PV = \frac{1}{3} mNu^2$
  - *Relation between average kinetic energy and absolute temperature :* $K.E. = \frac{3}{2} PV = \frac{3}{2} RT$

- **Different Types of Molecular Speeds**
  - Most probable speed (u_{mp})

$$= \sqrt{\frac{2PV}{M}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2RT}{m \times N}}$$

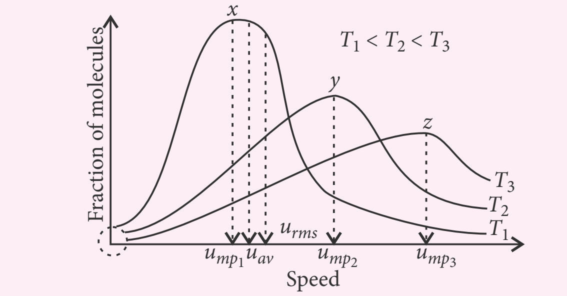
  - Average speed (u_{av})

$$= \frac{u_1 + u_2 + u_3 + ...u_n}{n} = \sqrt{\frac{8PV}{\pi M}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8kT}{\pi M}}$$

  - Root mean square speed (u_{rms})

$$= \sqrt{\frac{u_1^2 + u_2^2 + u_3^2 + ...u_n^2}{n}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3P}{d}}$$

- **Maxwell's Distribution of Speeds**

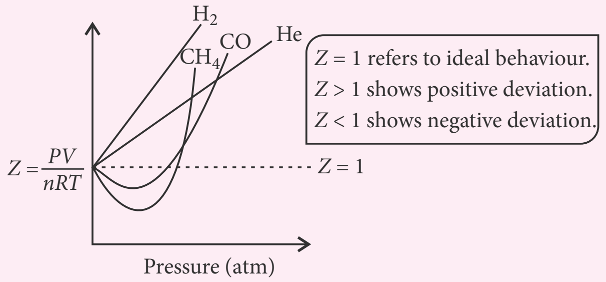


◌ Signifies that speed is never zero but it tends towards zero.

SELF CHECK

3. For gaseous state, if most probable speed is denoted by C^*, average speed by $\bar{C}$ and mean square speed by C, then for a large number of molecules the ratios of these speeds are
   (a) $C^* : \bar{C} : C = 1 : 1.225 : 1.128$
   (b) $C^* : \bar{C} : C = 1.225 : 1.128 : 1$
   (c) $C^* : \bar{C} : C = 1.128 : 1 : 1.225$
   (d) $C^* : \bar{C} : C = 1 : 1.128 : 1.225$ (JEE Main 2013)

- **Deviations from Ideal Behaviour and van der Waals Equation**
  - Gases which do not follow the ideal gas equation and other gas laws at all temperatures and pressures are called *real gases*.



where, Z is compressibility factor which measures the deviation from ideal behaviour.

- **van der Waals Equation of State for Real Gases**

$$\left(P + \frac{an^2}{V^2}\right)(V - nb) = nRT$$

where, a and b are van der Waals constants and their values depend on the nature of the gas.

van der Waals constant	Significance	Units
a	Measure of magnitude of attractive forces	atm L^2 mol^{-2} or bar dm^6 mol^{-2}
b	Measure of effective size of the gas molecules	L mol^{-1} or dm^3 mol^{-1}

SELF CHECK

4. If Z is a compressibility factor, van der Waals equation at low pressure can be written as

(a) $Z = 1 + \frac{Pb}{RT}$
(b) $Z = 1 + \frac{RT}{Pb}$
(c) $Z = 1 - \frac{a}{VRT}$
(d) $Z = 1 - \frac{Pb}{RT}$

(JEE Main 2014)

- **Boyle's temperature (or Boyle point):** It is the temperature at which a real gas obeys ideal gas law over an appreciable range of pressure.
- **Liquefaction of Gases and Critical Constants**
  - A gas can be liquefied by controlling two factors – lowering the temperature and increasing the pressure.
  - Gases like CO_2, NH_3 liquefy when temperature is lowered with increase in pressure and are called *temporary gases*.
  - Gases like H_2, N_2, O_2 etc. which are not liquefied under low temperature, high pressure conditions are called *permanent gases*.
  - The temperature above which a gas cannot be liquefied by application of pressure is called *critical temperature* (T_c).
  - The pressure required for liquefaction of a gas at its critical temperature is called *critical pressure* (P_c) and the volume occupied at critical temperature and pressure is called *critical volume* (V_c).
  - In terms of van der Waals constants,

$$V_c = 3b,\ P_c = \frac{a}{27b^2},\ T_c = \frac{8a}{27Rb} \text{ and } P_cV_c = \frac{3}{8}RT_c$$

Liquid State

- Liquid state is the intermediate state having some properties common with gases and some with solids.

- **Properties of Liquids and Effect of Temperature**

Property	Mathematical expression	Effect of temperature
Vapour pressure		
The pressure exerted by the vapours of the liquid in equilibrium with its surface at a particular temperature.	$\log\frac{P_2}{P_1} = \frac{\Delta H_{vap}}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$	Increases with increase in temperature due to decrease in the magnitude of interparticle forces.
Surface tension		
The force acting on the surface of liquid at right angle to any line of one centimetre length.	$\frac{\gamma_1}{\gamma_2} = \frac{n_1d_2}{n_2d_1}$ (γ_1 and d_1 are the surface tension and density of water and γ_2 and d_2 are the surface tension and density of liquid whose surface tension is to be determined.)	Decreases with increase in temperature.

Viscosity		
The internal resistance to flow in liquids which one layer offers to another layer trying to pass over it.	Force of friction between two adjacent layers of liquid having area A cm^2, separated by distance x and having a velocity difference of V cm s^{-1} is given as $f = \eta \frac{AV}{x}$ where η is coefficient of viscosity.	$\eta = Ae^{-E_a/RT}$, Decreases with increase in temperature (about 2% decrease per degree rise in temperature).

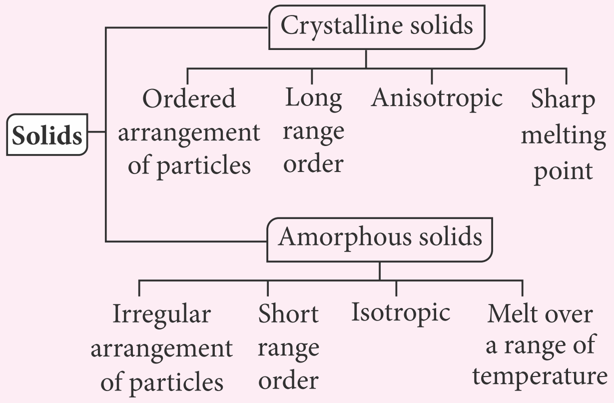
KEY POINT

- Normal boiling point of a liquid is approximately $\frac{2}{3}$ of its critical temperature.
- At critical state, the value of compressibility factor for 1 mole of gas is approximately constant.
  $Z = \frac{P_c V_c}{RT_c} = \frac{3}{8} = 0.375$
- Relation between u_{av}, u_{rms} and u_{mp}:
  $u_{mp} : u_{av} : u_{rms} = 1 : 1.128 : 1.224$
  $u_{av} = u_{rms} \times 0.9213;$
  $u_{rms} = u_{av} \times 1.085;$
  $u_{rms} = u_{mp} \times 1.244$

Solid State

❑ The solid state represents the physical state of matter in which constituents have no translatory motion although vibratory or rotational motions are possible about their position in solid lattice.

❑ On the basis of arrangement of constituent particles, solids are classified as :



❑ **Types of Crystalline Solids**

Solids	Constituent particles	Binding forces
Ionic solids	Ions of opposite charge	Electrostatic forces
Covalent solids	Atoms	Covalent bonds
Molecular solids	Molecules	van der Waals forces
Metallic solids	Kernels and electrons	Metallic bonds

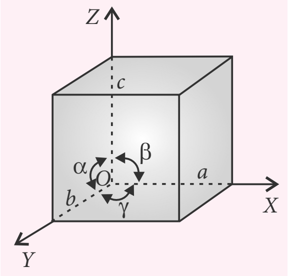
❑ **Bragg's law :** When a beam of X-rays of wavelength λ, strikes a crystal surface, the maximum intensity of reflected rays occur when

$$\sin\theta = \frac{n\lambda}{2d} \quad \text{or} \quad n\lambda = 2d\sin\theta \qquad (\textit{Bragg's equation})$$

- Bragg's law helps in the determination of crystal structure.

❑ **Space lattice :** Regular arrangement of constituent particles in three dimensional space.

❑ **Unit cell :** The smallest unit in space lattice which when repeated over and again in different directions produces the complete space lattice.



❑ Crystal system is a method to classify the substances on the basis of their unit cells.

❑ On the basis of primitives or axial distances and interfacial angles, there are seven crystal systems and fourteen Bravais lattices.

KEY POINT

- Out of the seven crystal systems, cubic is the most *symmetrical* while triclinic is the most *unsymmetrical.*

- **Unit cell constant (Z) for different types of unit cells :**

Type of unit cell	Simple cubic	*bcc*	*ccp*/*fcc*	*hcp*
No. of particles (Z)	$8\times\frac{1}{8}=1$	$8\times\frac{1}{8}+1=2$	$8\times\frac{1}{8}+6\times\frac{1}{2}=4$	$12\times\frac{1}{6}+2\times\frac{1}{2}+3=6$

- **Packing in Solids**

Simple cubic packing (*scp*)	Hexagonal close packing (*hcp*)	Cubic close packing (*ccp*)	Body centred cubic packing (*bcc*)
Arrangement			
Layers are packed over one another so that the sphere of second layer exactly lies over the sphere of first layer. *AAA* ... type of arrangement.	*ABABAB* ... type of packing arrangement is present.	*ABCABC*... type of packing arrangement is present.	The spheres in square close packing are slightly opened up, in second layer, the spheres are at the top of hollows and third layer is exactly over the first layer and so on.
Space occupied			
52.4%	74%	74%	68%
Coordination number			
6	12	12	8
It is least efficient so, rare in elements.	Efficient packing.	Efficient packing arrangement and is also referred as *fcc* arrangment.	Less efficient than *hcp* or *ccp* arrangement.
Examples			
Po	Mg, Zn, Mo, V, Cd	Cu, Ag, Au, Ni, Pt, etc.	Metals like Li, Na, K, Rb, Cs, Ba, Cd, Fe, Mn etc., crystallise in *bcc* arrangement.

Voids

- The empty space between atoms stacked together is known as *void*. These are of following types :
  - **Trigonal void :** This is the vacant space among three spheres (atoms/ions) touching each other in two dimensional space.
  - **Tetrahedral void :** When one sphere is placed over three other spheres touching each other, in three dimensional space, a tetrahedral void is produced.
  - **Octahedral void :** When three spheres are exactly placed over another three spheres, all touching each other, an octahedral void is created.
- If N is the number of close packed spheres, then
  - number of octahedral voids generated = N
  - number of tetrahedral voids generated = $2N$
- In *ccp* or *fcc*, total no. of voids per unit cell
  = 4 (octahedral) + 8 (tetrahedral) = 12
- In *hcp*, total no. of voids per unit cell
  = 6 (octahedral) + 12 (tetrahedral) = 18
- Regular tetrahedral voids and octahedral voids are found in *hcp* and *ccp*, whereas distorted tetrahedral voids and octahedral voids are found in *bcc* structures.
- Coordination number of an atom in tetrahedral void and octahedral void are respectively 4 and 6.
- **Calculations involving Unit Cell Parameters**

Density of unit cell (ρ) = $\dfrac{Z\times M}{N_0\times a^3}$

Unit cell type	Z	Radius of atom (r)	Packing fraction
Simple cubic	1	$\frac{a}{2}$	$\frac{\pi}{6}$
bcc	2	$\frac{\sqrt{3}}{4}a$	$\frac{\sqrt{3}}{8}\pi$

fcc	4	$\frac{a}{2\sqrt{2}}$	$\frac{\pi}{3\sqrt{2}}$
hcp	6	$\frac{a}{2}, \sqrt{\frac{3}{2}}\times\frac{h}{4}$	$\frac{\pi}{3\sqrt{2}}$

- **Limiting radius ratio:** It is the ratio of the radii of positive and negative ions in a crystal.

$$\text{Radius ratio} = \frac{\text{Radius of cation}}{\text{Radius of anion}} = \frac{r_+}{r_-}$$

- **Limiting radius ratio, coordination number and geometry**

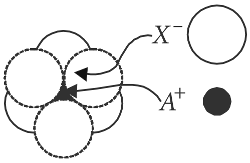
r_+/r_-	C. No.	Geometry
< 0.155	2	linear
0.155 - 0.225	3	plane triangular
0.225 - 0.414	4	tetrahedral
0.414 - 0.732	6	octahedral
0.732 - 1.000	8	cubic (body centred)

- For a tetrahedral void, $r = 0.225\ R$
  For an octahedral void, $r = 0.414\ R$
  where r is the radius of the void and R is the radius of the spheres in the close packed arrangement.

SELF CHECK

5. Sodium metal crystallizes in a body centred cubic lattice with a unit cell edge of 4.29 Å. The radius of sodium atom is approximately
(a) 5.72 Å (b) 0.93 Å
(c) 1.86 Å (d) 3.22 Å
(JEE Main 2015)

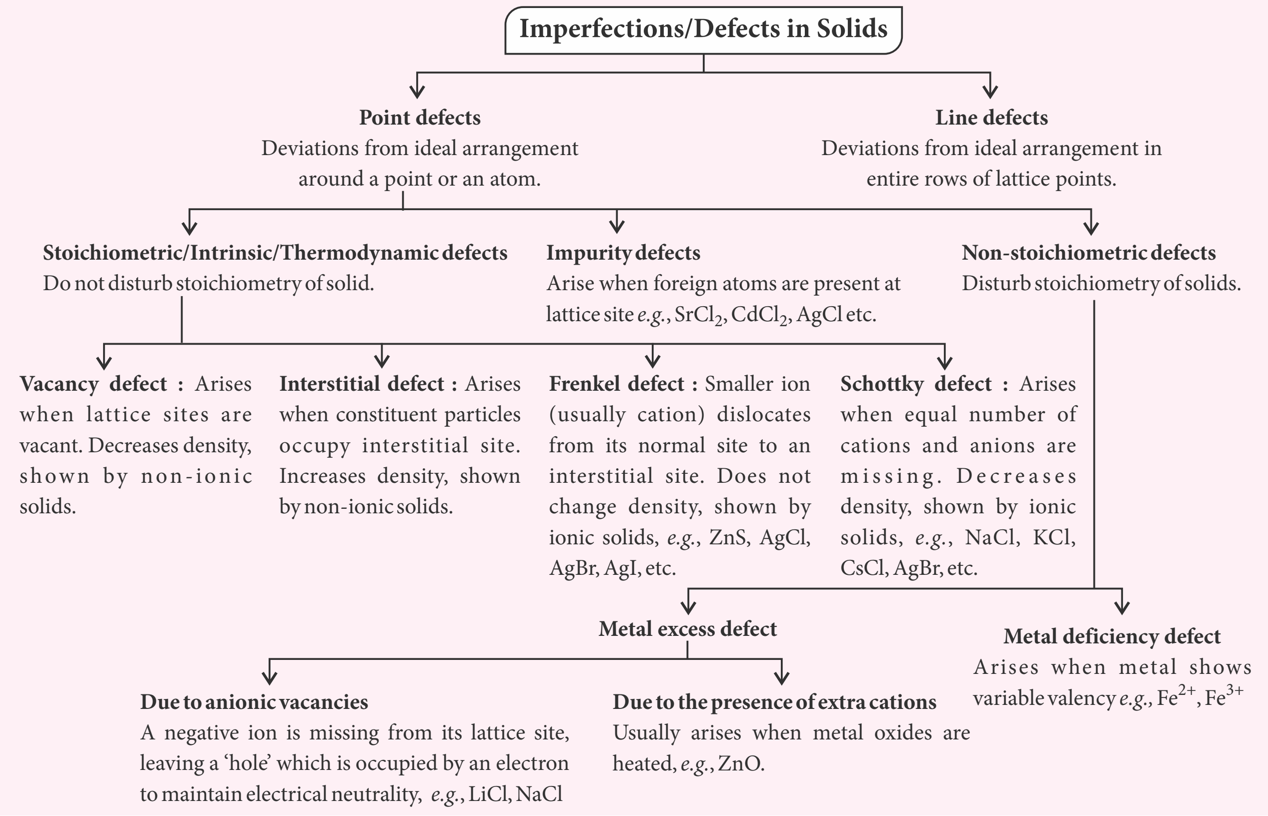
6. The arrangement of X^- ions around A^+ ion in solid AX is given in the figure (not drawn to scale). If the radius of X^- is 250 pm, the radius of A^+ is



(a) 104 pm (b) 125 pm
(c) 183 pm (d) 57 pm
(JEE Advanced 2013)

7. CsCl crystallises in body-centred cubic lattice. If 'a' is its edge length then which of the following expressions is correct?
(a) $r_{Cs^+} + r_{Cl^-} = \sqrt{3}a$ (b) $r_{Cs^+} + r_{Cl^-} = 3a$
(c) $r_{Cs^+} + r_{Cl^-} = \frac{3a}{2}$ (d) $r_{Cs^+} + r_{Cl^-} = \frac{\sqrt{3}}{2}a$
(JEE Main 2014)

- **Imperfections in solids :** Any deviation from the perfectly ordered arrangement of constituent particles in a crystal is called *imperfection* or *defect*.



Imperfections/Defects in Solids

Point defects
Deviations from ideal arrangement around a point or an atom.

Line defects
Deviations from ideal arrangement in entire rows of lattice points.

Stoichiometric/Intrinsic/Thermodynamic defects
Do not disturb stoichiometry of solid.

Impurity defects
Arise when foreign atoms are present at lattice site *e.g.*, $SrCl_2$, $CdCl_2$, AgCl etc.

Non-stoichiometric defects
Disturb stoichiometry of solids.

Vacancy defect : Arises when lattice sites are vacant. Decreases density, shown by non-ionic solids.

Interstitial defect : Arises when constituent particles occupy interstitial site. Increases density, shown by non-ionic solids.

Frenkel defect : Smaller ion (usually cation) dislocates from its normal site to an interstitial site. Does not change density, shown by ionic solids, *e.g.*, ZnS, AgCl, AgBr, AgI, etc.

Schottky defect : Arises when equal number of cations and anions are missing. Decreases density, shown by ionic solids, *e.g.*, NaCl, KCl, CsCl, AgBr, etc.

Metal excess defect

Metal deficiency defect
Arises when metal shows variable valency *e.g.*, Fe^{2+}, Fe^{3+}

Due to anionic vacancies
A negative ion is missing from its lattice site, leaving a 'hole' which is occupied by an electron to maintain electrical neutrality, *e.g.*, LiCl, NaCl

Due to the presence of extra cations
Usually arises when metal oxides are heated, *e.g.*, ZnO.

Electrical Properties

- **Piezoelectricity :** The electricity produced when mechanical stress is applied on polar crystals *e.g.*, $PbZrO_3$, $NH_4H_2PO_4$ and quartz.
- **Pyroelectricity :** The electricity produced when some polar crystals are heated.
- **Ferroelectricity :** In some piezoelectric crystals, the dipoles are permanently polarized even in the absence of electric field. However, on applying electric field, the direction of polarization changes. This phenomenon is called *ferroelectricity* due to analogy with *ferromagnetism e.g.*, $BaTiO_3$, Rochelle salt and KH_2PO_4.
- **Anti-ferroelectricity :** In some crystals, the dipoles in alternate polyhedra point up and down so that the crystal does not possess any net dipole moment. Such crystals are said to be *anti-ferroelectric e.g.*, $PbZrO_3$.
  - **Conductors :** Electrical conductivity, 10^4 to 10^7 ohm^{-1} m^{-1}.
  - **Insulators :** Electrical conductivity, 10^{-20} to 10^{-10} ohm^{-1} m^{-1}.
  - **Semiconductors :** Electrical conductivity, 10^{-6} to 10^4 ohm^{-1} m^{-1}.
    - ***n*-type semiconductors :** Group 14 elements doped with group 15 elements, free electrons increase conductivity.
    - ***p*-type semiconductors :** Group 14 elements doped with group 13 elements, holes increase conductivity.

Magnetic Properties

- **Paramagnetic substances :** They are weakly attracted by a magnetic field. They have one or more unpaired electrons and lose their magnetism in the absence of magnetic field, *e.g.*, O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}.
- **Diamagnetic substances :** They are weakly repelled by a magnetic field. They have no unpaired electrons and hence have zero magnetic moment, *e.g.*, H_2O, NaCl and C_6H_6.
- **Ferromagnetic substances :** They show permanent magnetism even in the absence of magnetic field as when placed in magnetic field, their unpaired electrons (or magnetic domains) get permanently oriented in one direction, *e.g.*, Fe, Ni, Co, Gd, CrO_2 etc.
- **Anti-ferromagnetic substances :** They are expected to possess paramagnetism or ferromagnetism but actually have zero net magnetic moment due to equal number of domains in opposite direction, *e.g.*, MnO.
- **Ferrimagnetic substances :** They are expected to have large magnetism but actually have small net magnetic moment due to unequal number of domains in opposite direction, *e.g.*, magnetite (Fe_3O_4), ferrites like $MgFe_2O_4$ and $ZnFe_2O_4$. These substances lose ferrimagnetism on heating and become paramagnetic.

KEY POINT

- Polonium is the only metal that crystallizes in simple cubic lattice.
- On pressurising a crystal its coordination number increases while on heating coordination number decreases.
- AgBr shows both Schottky as well as Frenkel defect.

ATOMIC STRUCTURE

- Introduction
- Nature of Electromagnetic Radiations
- Atomic Spectra
- Bohr's Atomic Model
- Dual Nature of Matter and Quantum Mechanics
- Quantum Numbers

TIPS TO REMEMBER

- *Atom* is not the smallest indivisible particle but have a complex structure of its own.
- At present, about 35 different *subatomic particles* are known but electrons, protons and neutrons are called *fundamental particles*.

Quantity	Unit	Electron (*e*)	Proton (*p*)	Neutron (*n*)
Mass	**amu**	0.000549	1.00728	1.00867
	gram	9.108×10^{-28}	1.673×10^{-24}	1.675×10^{-24}
	Relative	1/1837	1	1

Charge	**coulomb**	-1.602×10^{-19}	$+1.602 \times 10^{-19}$	zero
	esu	-4.803×10^{-10}	$+4.803 \times 10^{-10}$	zero
	Relative	-1	$+1$	zero
Discovered by		J.J. Thomson	Goldstein	Chadwick

Atomic Models

- ❑ According to Thomson's plum pudding model of atom, positive charge is spread over a sphere of radius ≈ 10^{-8} cm and electrons are embedded in it.
  - ❍ Thomson's model could explain the electrical neutrality of atom but not the other observations like spectra and α-scattering experiment.
- ❑ Rutherford's model was based upon the results of scattering experiments.
  - ❍ According to Rutherford's model, the nucleus of atom is hard dense core and consists of protons while electrons revolve around the nucleus.
- ❑ **Some important terms :**

Term	Description	Examples
Isotopes	Different atoms of same element having same atomic number but different mass numbers.	$^{1}_{1}H$, $^{2}_{1}H$, $^{3}_{1}H$; $^{35}_{17}Cl$, $^{37}_{17}Cl$
Isobars	Atoms of different elements having same mass number but different atomic numbers.	$^{40}_{18}Ar$, $^{40}_{19}K$, $^{40}_{20}Ca$
Isotones	Atoms of different elements containing same number of neutrons.	$^{14}_{6}C$, $^{15}_{7}N$, $^{16}_{8}O$
Isodiaphers	Atoms having same isotopic number (*i.e.*, no. of neutrons – no. of protons = same)	$^{235}_{92}U$, $^{231}_{90}Th$
Isosters	Molecules having same number of atoms and electrons.	CO_2, N_2O

Nature of Electromagnetic Radiations

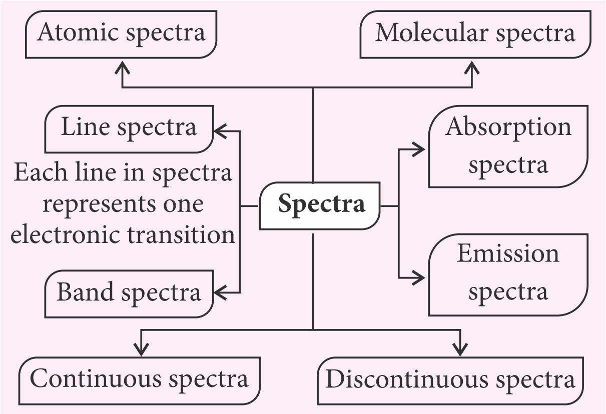
- ❑ **Electromagnetic wave theory :** Energy is emitted continuously from any source in the form of radiations travelling in the form of waves and associated with electric and magnetic fields, oscillating perpendicular to each other and to the direction of radiations.
- ❑ All electromagnetic radiations have wave characteristics and do not require any medium for their propagation.
- ❑ The arrangement of various radiations in the decreasing order of their frequencies or increasing order of their wavelengths is called *electromagnetic spectrum.*

Cosmic rays, γ-rays, X-rays, UV rays, visible, *IR*, microwaves, radiowaves

$\xrightarrow{\hspace{6em}}$

Decreasing frequency

- ❑ *Atomic spectra* represent the radiation or energy absorbed or emitted by an atom.
- ❑ Different types of spectra :



Atomic Spectra of Hydrogen

- ❑ Radiations emitted by hydrogen in discharge tube experiments when passed through prism gives five series of lines named after the researchers.

	Name of series	Wavelength	n_1	n_2	Region
1.	Lyman	$\frac{1}{\lambda} = R_H\left[\frac{1}{1^2} - \frac{1}{n^2}\right]$	1	$n > 1$	UV
2.	Balmer	$\frac{1}{\lambda} = R_H\left[\frac{1}{2^2} - \frac{1}{n^2}\right]$	2	$n > 2$	Visible
3.	Paschen	$\frac{1}{\lambda} = R_H\left[\frac{1}{3^2} - \frac{1}{n^2}\right]$	3	$n > 3$	IR
4.	Brackett	$\frac{1}{\lambda} = R_H\left[\frac{1}{4^2} - \frac{1}{n^2}\right]$	4	$n > 4$	IR
5.	Pfund	$\frac{1}{\lambda} = R_H\left[\frac{1}{5^2} - \frac{1}{n^2}\right]$	5	$n > 5$	far IR
6.	Humphrey	$\frac{1}{\lambda} = R_H\left[\frac{1}{6^2} - \frac{1}{n^2}\right]$	6	$n > 6$	far-far IR

- **Rydberg formula :** $\bar{\nu} = \frac{1}{\lambda} = R_H\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)Z^2$

  where, R_H is Rydberg constant and has a value equal to 109,677 cm^{-1}.

KEY POINT

- The number of spectral lines possible for hydrogen or hydrogen like species when the electrons from n^{th} energy level return to ground state in different atoms = $\frac{1}{2}n(n-1)$
- Absorption and emission spectra are complementary to each other. A line missing in absorption spectrum will appear in emission spectrum.

Bohr's Atomic Model

- The main postulates are :
  - Atom consists of a small, heavy and positively charged nucleus in centre, and electrons revolve around the nucleus in fixed paths called *orbits*.
  - Energy of an electron in the orbit does not change with time.
  - The electron can revolve only in those orbits whose angular momentum is an integral multiple of $h/2\pi$ *i.e.*,

    $$mvr = \frac{nh}{2\pi}, \quad n = 1, 2, 3, \ ....$$
  - When electron jumps from one level to another, energy is either emitted or absorbed.
    - The energy difference between two states is given by

      $$\Delta E = E_2 - E_1$$
    - As the distance of the orbits increases from the nucleus, the energy gap goes on decreasing, *i.e.*,

      $$E_2 - E_1 > E_3 - E_2 > E_4 - E_3 > ......$$
- **Derivations from Bohr's Theory (for n^{th} orbit)**

	For hydrogen	For H– like particles
Energy (E_n)	$\frac{-1312}{n^2}$ kJ/mol	$\frac{-1312\ Z^2}{n^2}$ kJ/mol
Radius (r_n)	$0.529 \times n^2$ Å	$\frac{0.529\ n^2}{Z}$ Å
Speed (v_n)	$\frac{2.18\times10^8}{n}$ cm sec^{-1}	$\frac{2.18\times10^8}{n}\times Z$ cm sec^{-1}

- **Limitations of Bohr's Model**
  - Mathematically, Bohr's model explains only monoelectronic atoms and fails to explain electronic repulsions in multielectronic atoms.
  - It does not explain the distribution of electrons in orbits.
  - It does not provide mathematical support to assumption, $mvr = \frac{nh}{2\pi}$.
  - It is against de-Broglie and Heisenberg's uncertainty principles.
  - It does not explain the splitting of spectral lines under the influence of electric field (*Stark effect*) and magnetic field (*Zeeman effect*).
- According to Planck's quantum theory, a body can emit or absorb energy not continuously but discontinuously in the form of small packets called *quanta* (called *photon* in case of light).

  Energy of photon, $E = h\nu = \frac{hc}{\lambda}$ (h is Planck's constant having value 6.62×10^{-34} J s)
- Ejection of electrons from the surface of a metal by irradiating it with light of suitable frequency is known as *photoelectric effect*.
  - The kinetic energy of emitted photoelectrons is mathematically given as

    $$K.E. = h\nu - h\nu_0 = h(\nu - \nu_0)$$

    $$K.E. = \frac{hc}{\lambda} - \frac{hc}{\lambda_0} = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda_0}\right)$$
  - Maximum kinetic energy of photoelectrons is directly proportional to frequency but is independent of intensity of the incident radiation.
  - Number of photoelectrons ejected per unit area per unit time is directly proportional to the intensity of the incident radiation.
  - Each photon can eject only one electron (provided frequency of the incident radiation is greater than the threshold frequency).
- The radiation emitted by a black body which is a perfect absorber and perfect radiator of energy is called *black body radiation*.
- Properties like diffraction, interference, refraction etc. explain the *wave like nature of radiations* while properties like photoelectric effect, black body radiation explain the *particle like properties*.

Dual Nature of Matter and de Broglie Relationship

- Every material particle in motion has dual nature *i.e.*, particle nature and wave nature and the relation between them is called *de Broglie relation.*
  - The wavelength of wave associated with such an object is given by
    $\lambda = \frac{h}{mv}$ (Significant only for microscopic particles)
- According to Heisenberg's uncertainty principle, it is impossible to measure simultaneously the position and momentum of a fast moving particle like electron with absolute accuracy. The product of uncertainty in the position (Δx) and uncertainty in the momentum (Δp) is always constant.

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

SELF CHECK

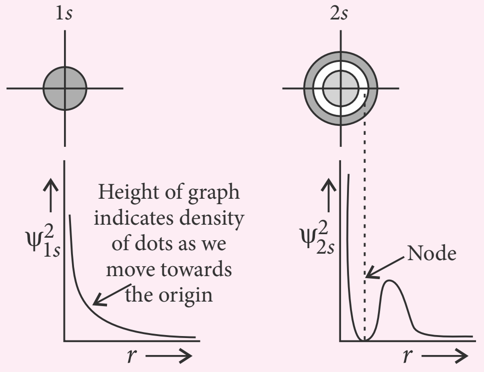
8. Which of the following is the energy of a possible excited state of hydrogen?
   (a) −3.4 eV (b) +6.8 eV
   (c) +13.6 eV (d) −6.8 eV
   (JEE Main 2015)

9. The kinetic energy of an electron in the second Bohr orbit of a hydrogen atom [a_0 is Bohr radius]
   (a) $\frac{h^2}{4\pi^2 m a_0^2}$ (b) $\frac{h^2}{16\pi^2 m a_0^2}$
   (c) $\frac{h^2}{32\pi^2 m a_0^2}$ (d) $\frac{h^2}{64\pi^2 m a_0^2}$
   (IIT-JEE 2012)

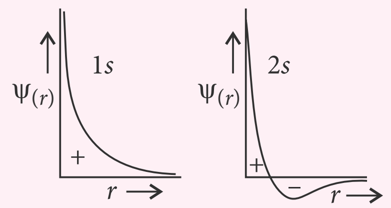
10. Energy of an electron is given by
    $$E = -2.178 \times 10^{-18}\ \text{J}\left(\frac{Z^2}{n^2}\right).$$
    Wavelength of light required to excite an electron in an hydrogen atom from level $n = 1$ to $n = 2$ will be ($h = 6.62 \times 10^{-34}$ J s and $c = 3.0 \times 10^8$ m s^{-1})
    (a) 8.500×10^{-7} m (b) 1.214×10^{-7} m
    (c) 2.816×10^{-7} m (d) 6.500×10^{-7} m
    (JEE Main 2013)

Quantum or Wave Mechanical Model of Atom

- Quantum mechanics developed by Erwin Schrodinger is based on the wave motion associated with the particles.
  Schrodinger wave equation :
  $$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$
- The wave function ψ for an electron in an atom has no physical significance as such but ψ^2 gives the intensity of electron wave at that point or the probability of finding the electron at that point.
- An atomic orbital may be defined as three dimensional space around the nucleus where the probability of finding an electron is maximum (upto 90-95%).
- Variation of ψ and ψ^2 with r :



Plots of ψ^2 *vs. r*



Plots of ψ *vs. r*

Quantum Numbers

- A set of four numbers which gives complete information about an electron in an atom.

Quantum number	Values	Information conveyed
Principal quantum number (n)	Any integer value *i.e.* 1, 2, 3, 4 etc.	– Main shell of the electron. – Approximate distance from the nucleus. – Energy of shell. – Maximum number of electrons present in the shell ($2n^2$). – Explains the main lines of spectrum.

Azimuthal quantum number (l)	For a particular value of n, $l = 0$ to $n - 1$ $l = 0$, s-subshell $l = 1$, p-subshell $l = 2$, d-subshell $l = 3$, f-subshell	– No. of subshells present in the main shell. – Relative energies of the subshells. – Shapes of orbitals. – Explains the fine structure of the line spectrum.
Magnetic quantum number (m_l)	For a particular value of l, $m = -l$ to $+l$ including zero.	– No. of orbitals present in any subshell. – Explains the splitting of lines in a magnetic field.
Spin quantum number (m_s)	$+\frac{1}{2}, -\frac{1}{2}$	– Direction of electron spin (clockwise or anticlockwise). – Explains the magnetic properties of substances.

- ☐ **Aufbau principle :** Orbitals are filled in the order of increasing energy. Lower the $(n + l)$ value, lower is the energy and if two orbitals have same $(n + l)$ value, orbital with lower value of n has lower energy.
- ☐ **Pauli's exclusion principle :** An orbital can accommodate maximum of two electrons and the electrons must have opposite spins.
- ☐ **Hund's rule of maximum multiplicity :** Pairing of electrons does not occur in orbitals of the same energy until each of them is singly filled.
- ☐ Exactly half-filled or completely filled electronic configurations are *extra stable* due to symmetrical distribution and greater exchange energy.

SELF CHECK

11. The electrons identified by quantum numbers n and l :
    (1) $n = 4, l = 1$ (2) $n = 4, l = 0$
    (3) $n = 3, l = 2$ (4) $n = 3, l = 1$
    can be placed in order of increasing energy as
    (a) (4) < (2) < (3) < (1) (b) (2) < (4) < (1) < (3)
    (c) (1) < (3) < (2) < (4) (d) (3) < (4) < (2) < (1)
    (AIEEE 2012)

KEY POINT

- Lowest limit of $\Delta p \cdot \Delta x$ *i.e.*, $h/4\pi$ is rarely attained and usually it is $h/2\pi$ or even h.
- Number of radial nodes increases with increasing value of principal quantum number (n).
- Radial nodes = $n - l - 1$
- Angular nodes = l
- Total nodes = $n - 1$
- For monoelectronic atoms, all the subshells and orbitals belonging to same shell, have same energy and depends on the value of n only.
- For multielectronic atoms, the energy depends on both n and l.

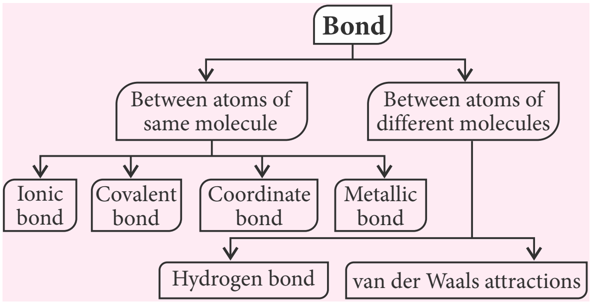
CHEMICAL BONDING AND MOLECULAR STRUCTURE

- Introduction
- VSEPR Theory
- Hybridisation
- Molecular Orbital Theory
- Types of Bonds
- Valence Bond Theory
- Resonance

TIPS TO REMEMBER

- ☐ The phenomenon of union of two or more atoms involving redistribution of electrons, so that each atom involved in bonding acquires stable configuration in order to gain stability is known as *chemical bonding*.
- ☐ The main reason for bonding between atoms is the tendency to acquire nearest noble gas configuration and the tendency to acquire minimum energy or maximum stability.
- ☐ Kossel and Lewis proposed that atoms combine so as to complete their octets or duplet.

Types of Bonds



- ☐ **Ionic or electrovalent bond :** It is the bond formed by transference of electrons from one atom to another so as to complete their octets or duplet.
  - ○ Factors affecting the formation of ionic bond :
    - – Low ionization enthalpy of metal.
    - – High electron gain enthalpy of non-metal.
    - – High lattice enthalpy of ionic compounds, for which charge on the ions should be high and size of ions should be small.

CONCEPT MAP

PHYSICAL CHEMISTRY (Part-I)

Solutions, Electrochemistry and Chemical Kinetics form the basis of physical chemistry and give an idea about the nature of solutions, relationship between chemical energy and electrical energy in redox reactions and also the rates of reactions.

SOLUTIONS

Expressing Concentration of Solutions

- **Mass percentage :** Grams of solute in 100 g of solution.
- **Strength :** Grams of solute in 1 L of solution.
- **Molarity :** Moles of solute in 1 L of solution.
- **Normality :** Gram equivalents of solute in 1 L of solution.
- **Molality :** Moles of solute in 1 kg of solvent.
- **Mole fraction :** Moles of the component/ total no. of moles of all components.
- **Parts per million :** Mass of solute in one million (10^6) parts by mass of solution.

Laws

- **Henry's law :** $m = K \cdot p$ or $p = K_H \cdot x$
  where K_H is Henry's constant having units of pressure.
- **Raoult's law :**
  For non-volatile solute : $\dfrac{p^\circ - p_s}{p^\circ} = \dfrac{n_2}{n_1 + n_2} = x_2$
  For volatile components :
  $p_A = x_A p_A^\circ$; $p_B = x_B p_B^\circ$ and $p_{\text{total}} = p_A + p_B$

Types of Solutions

- **Ideal solutions :** A–B interactions are of same magnitude as A–A and B–B interactions, $\Delta V_{\text{mix}} = 0$ and $\Delta H_{\text{mix}} = 0$.
- **Non-ideal solutions :** A–B interactions are of different magnitude than A–A and B–B interactions, $\Delta V_{\text{mix}} \neq 0$ and $\Delta H_{\text{mix}} \neq 0$.
  - **Non-ideal solutions showing +ve deviations :** A–B interactions are weaker than A–A and B–B interactions, ΔV_{mix} = +ve, ΔH_{mix} = +ve and resulting vapour pressure is higher than that expected.
  - **Non-ideal solutions showing –ve deviations :** A–B interactions are stronger than A–A and B–B interactions, ΔV_{mix} = –ve, ΔH_{mix} = –ve and resulting vapour pressure is lower than that expected.
- **Azeotropes:** Constant boiling mixtures.

Colligative Properties

- Colligative properties depend only on the number of particles of solute dissolved in a definite amount of solvent. These are :
  - **Elevation in boiling point :** Boiling point of solution is higher than that of pure solvent. $\Delta T_b = T_b - T_b^\circ = K_b m$
  - **Depression in freezing point :** Freezing point of solution is lower than that of pure solvent. $\Delta T_f = T_f^\circ - T_f = K_f m$
  - **Relative lowering of vapour pressure :**
    $\dfrac{p^\circ - p_s}{p^\circ} = x_2 = \dfrac{n_2}{n_1}$ (for dilute solutions, $n_2 <<< n_1$)
    $\dfrac{p^\circ - p_s}{p_s} = \dfrac{n_2}{n_1}$ (for dilute as well as concentrated solutions)
  - **Osmotic pressure :** $\pi = CRT$

van't Hoff Factor (i) and its Significance

$$i = \frac{\text{Observed value of colligative property}}{\text{Normal value of colligative property}}$$
$$= \frac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$$

- **For solute undergoing association :**
  $$\underset{\text{(Degree of association)}}{\alpha} = (1-i)\frac{n}{n-1};\ i<1$$
- **For solute undergoing dissociation :**
  $$\underset{\text{(Degree of dissociation)}}{\alpha} = \frac{i-1}{n-1};\ i>1$$
- **Modified colligative properties :**
  $\dfrac{p^\circ - p_s}{p^\circ} = ix_2$; $\Delta T_b = iK_b m$, $\Delta T_f = iK_f m$;
  $\pi = iCRT$

ELECTROCHEMISTRY

Basic Terms

- **Conductance :** Reciprocal of resistance.
  $C = \dfrac{1}{R}$; Unit : Ω^{-1} or S
- **Conductivity :** Conductance of 1 cm³ of the conductor.
  $\kappa = C \times \dfrac{l}{a}$; Unit : Ω^{-1} cm^{-1} or S cm^{-1}
- **Equivalent conductivity :** Conductance of a solution containing 1 g-equivalent of an electrolyte dissolved in V cm³ of the solution.
  $\Lambda_{eq} = \dfrac{\kappa \times 1000}{\text{Normality}}$; Unit : S cm^2 eq^{-1}
- **Molar conductivity :** Conductance of a solution containing 1 mole of an electrolyte dissolved in V cm³ of the solution.
  $\Lambda_m = \dfrac{\kappa \times 1000}{\text{Molarity}}$; Unit : S cm^2 mol^{-1}
- **Electrode potential :** Tendency of an electrode to lose or gain electrons when it is in contact with solution of its own ions.
- **Cell potential or EMF of the cell :** The difference between electrode potentials of two half-cells.

Types of Cells

- **Electrochemical cell :** Device used to convert chemical energy of a redox reaction into electrical energy.
- **Electrolytic cell :** Device which uses electricity to bring about a non-spontaneous redox reaction.

Laws

- **Faraday's first law :** $W = Zit$
- **Faraday's second law :** $\dfrac{W_1}{W_2} = \dfrac{E_1}{E_2}$
- **Kohlrausch's law :** For an electrolyte A_xB_y,
  $\Lambda^\circ_m = x\lambda^\circ_+ + y\lambda^\circ_-$ or $\Lambda^\circ_{eq} = \lambda^\circ_+ + \lambda^\circ_-$

Nernst Equation and Electrochemical Series

- **Nernst equation :** For the reaction :
  $M^{n+} + ne^- \longrightarrow M$,
  $$E = E^\circ - \frac{RT}{nF}\ln\frac{M}{[M^{n+}]} \text{ or}$$
  $$E = E^\circ - \frac{0.0591}{n}\log\frac{1}{[M^{n+}]} \text{ at 298 K}$$
- **For concentration cell :**
  $$E_{cell} = \frac{0.0591}{n}\log\frac{C_2}{C_1};\ E_{cell} = +\text{ve if } C_2 > C_1$$
- **For a reaction in equilibrium :**
  $$E^\circ_{cell} = \frac{0.0591}{n}\log K \text{ at 298 K}$$
- **Electrochemical series :** It is the arrangement of electrodes in order of increasing standard reduction potentials.
  - This series helps in comparing the relative oxidizing or reducing powers, relative activities of metals and to predict spontaneity of the redox reaction.

Commercial Cells/Batteries

- **Primary cells** cannot be recharged *e.g.*, dry cell, mercury cell.
- **Secondary cells** can be recharged *e.g.*, lead storage battery, Ni–Cd storage cell.
- **Fuel cells** convert the energy produced during combustion of fuels into electrical energy directly *e.g.*, H_2–O_2 fuel cell.

CHEMICAL KINETICS

Rate of Reaction

- For a reaction, $aA + bB \longrightarrow xX + yY$
  $$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = +\frac{1}{x}\frac{d[X]}{dt} = +\frac{1}{y}\frac{d[Y]}{dt}$$
- Greater the concentration of reactants, faster is the reaction.
- Rate becomes double for every 10° rise in temperature.
- Greater the surface area of reactants, faster is the reaction.

Order and Molecularity

- For a rate law equation, rate $= k[A]^a[B]^b$
  Order of reaction $= a + b$.
- **Molecularity** is the number of atoms, ions or molecules that must collide simultaneously with one another to result into a chemical reaction.

Integrated Rate Equation and Half-Life

Order	Integrated rate equation	Half-life $t_{1/2}$ =
0	$[A]_t = -kt + [A]_0$	$[A]_0/2k$
1	$\ln[A]_t = -kt + \ln[A]_0$	$0.693/k$
2	$1/[A]_t = kt + 1/[A]_0$	$1/k[A]_0$
2	$kt = \dfrac{1}{[A]_0 - [B]_0}\ln\dfrac{[B]_0[A]}{[A]_0[B]}$	–
n	$(n-1)kt = \dfrac{1}{[A]^{n-1}} - \dfrac{1}{[A_0]^{n-1}}$	$\dfrac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$

- Relationship between time for different fractions of a first order reaction to complete,
  $t_{3/4}$ or $t_{75\%} = 2t_{1/2}$
  $t_{87.5\%} = 3t_{1/2} = \dfrac{3}{2}t_{75\%}$
  $t_{93.75\%} = 4t_{1/2} = 2t_{75\%}$
  $t_{96.87\%} = 5t_{1/2}$
  $t_{99.9\%} = 10t_{1/2}$

Temperature Dependence of Rate of Reaction and Effect of Catalyst

- **Arrhenius equation :** $k = Ae^{-E_a/RT}$
  or $\log\dfrac{k_2}{k_1} = \dfrac{E_a}{2.303R}\left[\dfrac{T_2 - T_1}{T_1T_2}\right]$
- Activation energy
  = Threshold energy – Average kinetic energy of reactants
- **Collision theory :** $k = PZe^{-E_a/RT}$
  where P is steric factor and Z is collision frequency.
- *Catalyst* increases the rate of a reaction without itself undergoing any permanent chemical change.

HAVE A LOOK !

- ☞ Different solutions having same vapour pressure are called *isopiestic solutions*.
- ☞ *Deliquescent* substances absorb moisture because vapour pressure of their saturated solutions is less than that of water vapours in air at that temperature.
- ☞ *Efflorescent* substances lose their water of crystallisation because their hydrated crystals have vapour pressure larger than that of water vapours in air.
- ☞ Association generally occurs in non-aqueous solvents (non-polar) because high dielectric constant of water helps in the dissociation of the associated molecules.

- **Calculation of Lattice Enthalpy–Born Haber Cycle**
  - Born Haber cycle is based on Hess's law of constant heat summation and it correlates the energy changes taking place in various steps involved in the formation of ionic compounds.
  - The steps can be represented in the cycle as :

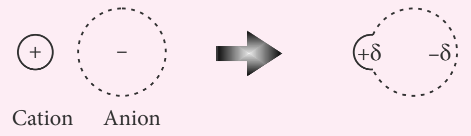
$$\begin{tikzcd}
M_{(g)} \arrow[rr, "IE"] & & M^+_{(g)} \\
& X_{(g)} \arrow[r, "\Delta H_{eg}"] & + \; X^-_{(g)} \arrow[d, "U"] \\
M_{(s)} \arrow[uu, "\Delta H_s"] & + \frac{1}{2} X_{2(g)} \arrow[u, "\frac{1}{2}\Delta H_d"'] \arrow[r, "\Delta H_f"] & MX_{(s)}
\end{tikzcd}$$

$$\Delta H_f = \Delta H_s + IE + \frac{1}{2}\Delta H_d + \Delta H_{eg} + U$$

where, ΔH_f = Enthalpy of formation,
ΔH_s = Enthalpy of sublimation,
IE = Ionisation energy,
ΔH_d = Enthalpy of dissociation,
ΔH_{eg} = Electron gain enthalpy
and U = Lattice energy.

- **Covalent bond :** It is formed by mutual sharing of one or more electron pairs between two atoms so that each atom involved in bonding attains nearest noble gas configuration in order to gain stability.
  - The sharing of one, two and three electron pairs between two atoms gives rise to the formation of single, double and triple bond respectively.
  - Covalent bond formed between two similar atoms is called *non-polar bond* because shared pair of electrons is attracted equally by two atoms.
  - Covalent bond formed between two dissimilar atoms is called *polar bond* because shared pair of electrons is more attracted towards more electronegative atom.
- **Coordinate bond :** It is a special type of covalent bond in which shared pair of electrons is donated by one atom called *donor atom* to the other atom called *acceptor*.
- **Percentage ionic character :**
  - *Pauling scale :*
    % ionic character = $18(\chi_A - \chi_B)^{1.4}$
  - *Hannay and Smith equation :*
    % ionic character = $16(\chi_A - \chi_B) + 3.5\,(\chi_A - \chi_B)^2$
  - Dipole moment (μ) = $q \times d$

- **Fajan's Rule :**



According to Fajan's Rules, the magnitude of covalent character in the ionic bond depends upon the extent of polarization caused by cation.
In general,

  - Smaller the size of cation, larger is its polarizing power.
  - Among two cations of similar size, the polarizing power of cation with noble gas configuration $ns^2np^6nd^{10}$ is larger than cation with noble gas configuration ns^2np^6.
    e.g., polarizing power of Ag^+ is more than K^+.
  - Larger the anion more will be its polarisibility.

Valence Shell Electron Pair Repulsion Theory (VSEPR)

- According to this theory the best arrangement of a given number of electron pairs is the one that minimizes the repulsion among them.
- Repulsive interactions between the pairs of electrons are in the order :
  lone pair–lone pair > lone pair–bond pair > bond pair–bond pair

Valence Bond Theory

- A bond is formed between two atoms when the new forces of attraction are greater than forces of repulsion.
- In terms of orbital overlap concept, the formation of a covalent bond between two atoms results by pairing of electrons present in the valence shell having opposite spins.
- A σ-bond is formed by head-on overlap of orbitals (stronger bond) while a π-bond is formed by sidewise overlap of orbitals (weaker bond).

Hybridisation

- It is the process of intermixing of orbitals with slightly different energies so as to redistribute their energies giving another set of orbitals (called *hybrid orbitals*) with same energy, size and shape.

- The structure of any molecule can be predicted on the basis of hybridisation by formula :
  No. of hybrid orbitals (H)

$$= \frac{1}{2}\left[\begin{pmatrix}\text{No. of valence}\\ \text{electrons of}\\ \text{central atom}\end{pmatrix} + \begin{pmatrix}\text{No. of}\\ \text{monovalent}\\ \text{atoms}\end{pmatrix} - \begin{pmatrix}\text{Charge}\\ \text{present}\\ \text{on the}\\ \text{cation}\end{pmatrix} + \begin{pmatrix}\text{Charge}\\ \text{present}\\ \text{on the}\\ \text{anion}\end{pmatrix}\right] \Rightarrow H = \frac{1}{2}[V + M - C + A]$$

Value of H (Hybrid orbitals)	2	3	4	5	6	7
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Shapes of Some Simple Molecules

Types of molecules	No. of electron pairs	No. of bond pairs	No. of lone pairs	Types of hybridisation involved	Geometry of molecule	Examples
AB_2	2	2	0	sp	Linear	BeF_2, $[Ag(NH_3)_2]^+$, $HgCl_2$
AB_3	3	3	0	sp^2	Trigonal planar	BF_3, $AlCl_3$, NO_3^-, CO_3^{2-}
AB_2L	3	2	1	sp^2	V-shaped or bent	$SnCl_2$, $PbCl_2$
AB_4	4	4	0	sp^3	Tetrahedral	CH_4, SiF_4, CCl_4, NH_4^+
AB_3L	4	3	1	sp^3	Trigonal pyramidal	NH_3, PX_3 (X = F, Cl, Br, I)
AB_2L_2	4	2	2	sp^3	V-shaped or bent	H_2O, OF_2, SCl_2
AB_5	5	5	0	sp^3d	Trigonal bipyramidal	PF_5, PCl_5, $SbCl_5$
AB_4L	5	4	1	sp^3d	See saw	SF_4, $TeBr_4$
AB_3L_2	5	3	2	sp^3d	T-shaped	ClF_3, $XeOF_2$
AB_2L_3	5	2	3	sp^3d	Linear	XeF_2, ICl_2^-, I_3^-
AB_6	6	6	0	sp^3d^2	Octahedral	SF_6, $[SbF_6]^-$
AB_5L	6	5	1	sp^3d^2	Square pyramidal	IF_5, ClF_5, BrF_5
AB_4L_2	6	4	2	sp^3d^2	Square planar	XeF_4, ICl_4^-
AB_7	7	7	0	sp^3d^3	Pentagonal bipyramidal	IF_7
AB_6L	7	6	1	sp^3d^3	Distorted octahedral	XeF_6

Resonance

- It is the phenomenon in which a molecule can be represented by more than one electronic arrangement none of which explains the known properties of the compound.
- The actual structure of the compound is intermediate of the various electronic arrangements and is called *resonance hybrid*.
- The difference between the energy of resonance hybrid and the most stable contributing structure is called *resonance energy*.

Molecular Orbital Theory

- The electrons in a molecule are present in the various molecular orbitals.
- The atomic orbitals of comparable energy and proper symmetry combine to form molecular orbitals.
- The electron in a molecular orbital is influenced by two or more nuclei depending upon the number of atoms in the molecule, thus a molecular orbital is *polycentric*.
- The number of molecular orbitals formed is equal to the number of combining atomic orbitals.

- The *bonding molecular orbital* has lower energy and greater stability than the corresponding *anti-bonding molecular orbital.*
- The molecular orbital gives electron probability distribution around a group of nuclei in a molecule.
- The molecular orbitals are filled in accordance with Aufbau principle obeying the Pauli's exclusion principle and the Hund's rule.
- The order of energies of molecular orbitals for simple homonuclear diatomic molecules like O_2, F_2 and Ne_2 is $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\sigma 2p_z$, $\pi 2p_x = \pi 2p_y$, $\pi^* 2p_x = \pi^* 2p_y$, $\sigma^* 2p_z$
- The order of energies of molecular orbitals for diatomic lighter elements like B_2, C_2 and N_2 is $\sigma 1s$, $\sigma^* 1s$, $\sigma 2s$, $\sigma^* 2s$, $\pi 2p_x = \pi 2p_y$, $\sigma 2p_z$, $\pi^* 2p_x = \pi^* 2p_y$, $\sigma^* 2p_z$
- The stability of molecules can be determined by *bond order*, higher the bond order higher is the stability. It can be calculated as :

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

  [N_b = No. of bonding electrons, N_a = No. of antibonding electrons]
- Higher the bond order, higher is the bond dissociation energy and smaller is the bond length.

Hydrogen Bonding

- The attractive force which binds hydrogen atom of one molecule with the electronegative atom (F, O or N) of another molecule is called *hydrogen bond.*
- **Intermolecular hydrogen bonding :** It is formed between the two different molecules of the same or different compounds *e.g.*, in case of HF, *R*OH or H_2O, etc.
- **Intramolecular hydrogen bonding :** The bond is formed between hydrogen atom and an electronegative atom (F, O or N) within the same molecule *e.g.*, in *o*-nitrophenol. An intramolecular hydrogen bond results in the cyclization of the molecules and prevents their association.
- **Applications of H-Bonding**
  - Intermolecular H-bonding increases the boiling point while intramolecular H-bonding decreases the boiling point.
  - Intermolecular H-bonding increases the solubility of covalent compounds in water while the intramolecular hydrogen bonding decreases the solubility.
  - Intermolecular H-bonding makes the compound more viscous and increases the surface tension.
  - Stability of proteins and nucleic acids is due to H-bonding.

Metallic Bonding

- Metallic bond is electrostatic force of attraction between positively charged kernels (nuclei with core electron) and mobile electrons which holds the metal atoms together.
- Strength of metallic bond increases with increase in the number of mobile electrons and increase in effective nuclear charge.

SELF CHECK

12. Assuming $2s$-$2p$ mixing is not operative, the paramagnetic species among the following is
    (a) Be_2 (b) B_2 (c) C_2 (d) N_2
    (JEE Advanced 2014)
13. Which one of the following properties is not shown by NO?
    (a) Its bond order is 2.5.
    (b) It is diamagnetic in gaseous state.
    (c) It is a neutral oxide.
    (d) It combines with oxygen to form nitrogen dioxide.
    (JEE Main 2014)
14. In which of the following pairs of molecules/ions, both the species are not likely to exist?
    (a) H_2^-, He_2^{2+} (b) H_2^+, He_2^{2-}
    (c) H_2^-, He_2^{2-} (d) H_2^{2+}, He_2
    (JEE Main 2013)

KEY POINT

- After the formation of coordinate bond, hybridisation of donor atom is not affected whereas that of acceptor gets changed.
- π-bonds are always formed in addition to σ-bonds.
- Shape of the molecule is decided by σ-bonds only.
- s-orbitals can form σ-bonds only.
- Strongest H-bond exists in KHF_2, $[F—H---F]^-$.

◆

ANSWER KEYS (SELF CHECK)

1. (a)	**2.** (b)	**3.** (d)	**4.** (c)	**5.** (c)
6. (a)	**7.** (d)	**8.** (a)	**9.** (c)	**10.** (b)
11. (a)	**12.** (c)	**13.** (b)	**14.** (d)	

Exam Café

QUESTIONS FOR PRACTICE

1. If each O-atom has two equivalents, volume of one equivalent of O_2 gas at STP is
   (a) 22.4 L
   (b) 11.2 L
   (c) 5.6 L
   (d) 44.8 L

2. Which of the following statements about gases is correct?
   (a) Kinetic energy is zero at 0°C.
   (b) *r.m.s.* velocity of O_2 at 27°C is 15.29 m s^{-1}.
   (c) Distribution of molecules is very small when $u \to 0$ or $u \to \infty$.
   (d) All of the above.

3. When the frequency of light incident on a metallic plate is doubled, the *K.E.* of the emitted photoelectrons will be
   (a) doubled
   (b) halved
   (c) increased but more than doubled of the previous *K.E.*
   (d) unchanged.

4. Number of bond pairs and lone pairs around the central atom in I_3^- ion, respectively are
   (a) 2, 2
   (b) 2, 3
   (c) 3, 2
   (d) 4, 3

5. Number of atoms in 20 g Ca is equal to number of atoms in
   (a) 20 g Mg
   (b) 1.6 g CH_4
   (c) 1.8 g H_2O
   (d) 1.7 g NH_3

6. Which gas has the highest partial pressure in atmosphere?
   (a) CO_2
   (b) H_2O
   (c) O_2
   (d) N_2

7. When an electron comes close to the nucleus, its
   (a) kinetic energy increases, potential energy and total energy decrease
   (b) kinetic energy and total energy increase, potential energy decreases
   (c) kinetic energy and total energy decrease, potential energy increases
   (d) kinetic energy, potential energy and total energy increase.

8. Identify the isostructural pairs.
   (a) [NF_3, NO_3^-] and [BF_3, H_3O^+]
   (b) [NF_3, HN_3] and [NO_3^-, BF_3]
   (c) [NF_3, H_3O^+] and [NO_3^-, BF_3]
   (d) [NF_3, H_3O^+] and [HN_3, BF_3]

9. For the formation of 5.00 moles of water, which reaction uses the most nitric acid?
   (a) $3Cu + 8HNO_3 \longrightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O$
   (b) $Al_2O_3 + 6HNO_3 \longrightarrow 2Al(NO_3)_3 + 3H_2O$
   (c) $4Zn + 10HNO_3 \longrightarrow 4Zn(NO_3)_2 + NH_4NO_3 + 3H_2O$
   (d) $Cu + 4HNO_3 \longrightarrow Cu(NO_3)_2 + 2NO_2 + 2H_2O$

10. For two gases, A and B with molecular masses M_A and M_B, it is observed that at a certain temperature T, the mean velocity of A is equal to the root mean square velocity of B. Thus, the mean velocity of A can be made equal to the mean velocity of B, if
    (a) A is at temperature T and B at T' where $T > T'$
    (b) A is lowered to a temperature $T_2 < T$ while B is at T
    (c) both A and B are raised to a higher temperature
    (d) both A and B are placed at lower temperature.

11. If each hydrogen atom is excited by giving 8.4 eV of energy, then the number of spectral lines emitted is equal to
    (a) none
    (b) two
    (c) three
    (d) four.

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

13. Mixture containing 1 mole each of $NaHCO_3$, Li_2CO_3 and Na_2CO_3 is heated strongly. CO_2 formed in this process will be
    (a) 3.0 mol
    (b) 2.5 mol
    (c) 1.0 mol
    (d) 1.5 mol

14. Element 'X' crystallizes in a 12 coordination *fcc* lattice. On applying high temperature, it changes to 8 coordination *bcc* lattice. Find the ratio of the density of the crystal lattice before and after applying high temperature.

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

(c) $\sqrt{2} : \sqrt{3}$ (d) $2(\sqrt{2})^3 : (\sqrt{3})^3$

15. The wavelength of a spectral line for an electronic transition is inversely related to

(a) the number of orbital undergoing the transition

(b) the nuclear charge of an atom

(c) the difference in energies of the levels involved in the transition

(d) the velocity of the electron undergoing the transition.

16. The correct order of the increasing ionic character is

(a) $BeCl_2 < BaCl_2 < MgCl_2 < CaCl_2$

(b) $BeCl_2 < MgCl_2 < BaCl_2 < CaCl_2$

(c) $BeCl_2 < MgCl_2 < CaCl_2 < BaCl_2$

(d) $BaCl_2 < CaCl_2 < MgCl_2 < BeCl_2$

17. If 10^{21} molecules are removed from 100 mg CO_2, then number of moles of CO_2 left are

(a) 6.10×10^{-4} (b) 2.8×10^{-3}

(c) 2.28×10^{-3} (d) 1.36×10^{-2}

18. How many unit cells are present in a cubic shaped ideal crystal of NaCl of mass 1.0 g?

(a) 1.28×10^{21} (b) 1.71×10^{21}

(c) 2.57×10^{21} (d) 5.14×10^{21}

19. In the given reaction,

$2H_2O_{2(l)} \longrightarrow 2H_2O_{(l)} + O_{2(g)}$

100 mL of 'X' molar H_2O_2 gives 3 L of $O_{2(g)}$ under the condition when 1 mole occupies 24 L. The value of 'X' is

(a) 2.5 (b) 1.0

(c) 0.5 (d) 0.25

20. Bond between A and B can be represented by

$A - B$	A^+B^-	A^-B^+
(I)	(II)	(III)

If A is more electronegative than B, then least contribution to the actual structure comes from

(a) I

(b) II

(c) III

(d) all the structures have equal contribution.

21. To what extent must a given solution containing 40 mg of $AgNO_3$ per mL be diluted to yield a solution containing 16 mg of $AgNO_3$ per mL?

(a) Each mL must be diluted to 2.5 mL.

(b) To each mL of solution, 2.5 mL of water should be added.

(c) To 1.5 mL of solution, 2 mL of water should be added.

(d) To 1.5 mL of solution, 1.5 mL of water should be added.

22. A liquid is in equilibrium with its vapours at its boiling point. On the average the molecules in the two phases have equal

(a) intermolecular forces

(b) potential energy

(c) total energy

(d) kinetic energy.

23. A 350 mL sample of ammonia at 1.00 bar and 27°C is absorbed by water to form 500 mL of solution at that temperature and pressure. Molar concentration of ammonia is

(a) 0.28 M (b) 0.02 M

(c) 2.8 M (d) 0.014 M

24. The AsF_3 molecule is trigonal pyramidal. The hybrid orbitals used by the As atoms for bonding are

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

(c) $s, p_x, p_y, p_z, d_{z^2}$ (d) $d_{x^2-y^2}, s, p_x, p_y, p_z$

25. If λ_0 and λ be the threshold wavelength and the wavelength of incident light, the velocity of photoelectrons ejected from the metal surface is

(a) $\sqrt{\frac{2h}{m}(\lambda_0 - \lambda)}$ (b) $\sqrt{\frac{2hc}{m}(\lambda_0 - \lambda)}$

(c) $\sqrt{\frac{2hc}{m}\left(\frac{\lambda_0 - \lambda}{\lambda\lambda_0}\right)}$ (d) $\sqrt{\frac{2h}{m}\left(\frac{1}{\lambda_0} - \frac{1}{\lambda}\right)}$

26. Percentages of free space in cubic close packed structure and in body-centred packed structure are respectively

(a) 48% and 26% (b) 30% and 26%

(c) 26% and 32% (d) 32% and 48%

27. Of these quantum state designations,

I. $n = 3, l = 2, m_l = -2$

II. $n = 3, l = 1, m_l = 0$

III. $n = 3, l = 0, m_l = -1$

IV. $n = 3, l = 2, m_l = 0$

V. $n = 3, l = 3, m_l = -2$

which does not describe an allowed state for an electron in an atom?

(a) I and IV (b) III and V
(c) II and V (d) IV and V

28. In which pair or pairs, the stronger bond is found in the first species?
I : O_2^{2-}, O_2; II : N_2, N_2^+; III : NO^+, NO^-
(a) Only I (b) Only II
(c) Only I and II (d) Only II and III

29. 0.24 g of a volatile gas, upon vaporisation, gives 45 mL vapours at STP. What will be the vapour density of the substance? (Density of H_2 = 0.089 g L^{-1})
(a) 95.39 (b) 59.93
(c) 39.95 (d) 95.73

30. The correct stability order of the following resonance structures is

$$H_2C{=}\overset{+}{N}{=}\overset{-}{N} \qquad H_2\overset{+}{C}{=}N{=}\overset{-}{N}$$

(I) (II)

$$H_2\overset{-}{C}{-}\overset{+}{N}{\equiv}N \qquad H_2\overset{-}{C}{-}N{=}\overset{+}{N}$$

(III) (IV)

(a) (I) > (II) > (IV) > (III)
(b) (I) > (III) > (II) > (IV)
(c) (II) > (I) > (III) > (IV)
(d) (III) > (I) > (IV) > (II)

SOLUTIONS

1. **(c) :** 1 O-atom ≡ 2 equivalents of oxygen (given)
2 O-atoms ≡ 4 equivalents of oxygen
1 mole of O_2 ≡ 22.4 L at STP

$$1 \text{ equivalent of } O_2 \equiv \frac{22.4}{4}\text{ L} = 5.6\text{ L}$$

2. **(c) :** (a) $K.E. = \frac{3}{2}nRT = \frac{3}{2}nR(0+273) = \frac{3}{2}nR\times 273$

Thus, (a) is incorrect.

(b) $u_{r.m.s.(O_2)} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3\times 8.314\times 300}{32\times 10^{-3}}}$
$= 483.56 \text{ m s}^{-1}$

(∵ Molar mass of O_2 in SI unit is 32×10^{-3} kg mol^{-1})

Thus, (b) is incorrect.

(c) The fraction of molecules with very low or very high speeds is very small.

Thus, (c) is correct.

3. **(c) :** The kinetic energy increases with increase in frequency.

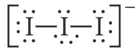
$(K.E.)_1 = h\nu - W$

If frequency is doubled, $(K.E.)_2 = 2h\nu - W$

$$\frac{(K.E.)_2}{(K.E.)_1} = \frac{2h\nu - W}{h\nu - W} = \frac{2h\nu - 2W + W}{h\nu - W} = 2 + \frac{W}{h\nu - W} > 2$$

i.e., kinetic energy will increase to slightly more than double value.

4. **(b) :** The structure of triiodide (I_3^-) ion is



Thus, number of bond pairs and lone pairs on the central atom respectively are 2 and 3.

5. **(b) :** $20 \text{ g Ca} = \frac{20}{40}\text{ mol} = 0.5 \text{ mol} = 0.5\, N_0 \text{ atoms}$

(a) $20 \text{ g Mg} = \frac{20}{24}\text{ mol} = 0.833 \text{ mol} = 0.833\, N_0 \text{ atoms}$

(b) $1.6 \text{ g } CH_4 = \frac{1.6}{16}\text{ mol} = 0.1 \text{ mol} = 0.1 \times 5\, N_0$
$= 0.5\, N_0 \text{ atoms}$

(c) $1.8 \text{ g } H_2O = \frac{1.8}{18}\text{ mol} = 0.1 \text{ mol} = 0.1 \times 3\, N_0$
$= 0.3\, N_0 \text{ atoms}$

(d) $1.7 \text{ g } NH_3 = \frac{1.7}{17}\text{ mol} = 0.1 \text{ mol} = 0.1 \times 4\, N_0$
$= 0.4\, N_0 \text{ atoms}$

6. **(d) :**

Gases in air	**% composition**	**% composition × atmospheric pressure**	**Partial pressure (mm Hg)**
Nitrogen (N_2)	79%	79% × 760 mm	600.40
Oxygen (O_2)	20.8%	20.8% × 760 mm	158.08
Carbon dioxide (CO_2)	0.03%	0.03% × 760 mm	0.30
Water (H_2O)	Trace	–	0.00

7. **(a) :** Let the total energy of the electron be E. It is the sum of kinetic energy and potential energy.

E = Kinetic energy + Potential energy

$$= \frac{1}{2}mv^2 - \frac{kZe^2}{r} \qquad \left[\because\ v^2 = \frac{kZe^2}{r\,m}\right]$$

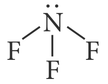
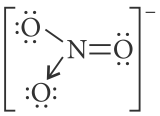
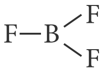
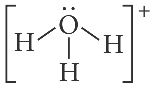
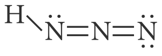
$$E = \frac{kZe^2}{2r} - \frac{kZe^2}{r} = -\frac{kZe^2}{2r}$$

$K.E. = \frac{1}{2}mv^2 = \frac{kZe^2}{2r}$, as an electron comes close to the nucleus, kinetic energy increases.

$P.E. = \frac{-kZe^2}{r}$, this indicates potential energy decreases as an electron comes close to the nucleus.

$E = \frac{-kZe^2}{2r}$, which also decreases as the radius of path of electron decreases.

8. (c) : Isostructural pairs have similar structures.

NF_3		Triangular pyramidal
NO_3^-		Triangular planar
BF_3		Triangular planar
H_3O^+		Triangular pyramidal
HN_3		Approx. linear

Thus, isostructural pairs are [NF_3, H_3O^+] and [NO_3^-, BF_3].

9. (c) : Ratio of HNO_3 per mole of H_2O for

(a) $\frac{8}{4} = 2$; (b) $\frac{6}{3} = 2$;

(c) $\frac{10}{3} = 3.33$; (d) $\frac{4}{2} = 2$

10. (b): $u_{av(A)} = \sqrt{\frac{8RT}{\pi M_A}}$; $u_{rms(B)} = \sqrt{\frac{3RT}{M_B}}$

At a certain temperature T,

$$u_{av(A)} = u_{rms(B)}$$

$$\sqrt{\frac{8RT}{\pi M_A}} = \sqrt{\frac{3RT}{M_B}} \quad \therefore \quad \frac{8}{3\pi} = \frac{M_A}{M_B}$$

For $u_{av(A)} = \sqrt{\frac{8RT_2}{\pi M_A}}$; $u_{av(B)} = \sqrt{\frac{8RT}{\pi M_B}}$

$$\frac{T_2}{T} = \frac{M_A}{M_B} = \frac{8}{3\pi}$$

$$T_2 = \frac{8}{3\pi}T \text{ or } T_2 < T$$

11. (a) : For excitation of electron from ground state, the minimum energy needed is $E_2 - E_1 = -3.4 - (-13.6) = 10.2$ eV. Hence, no excitation occurs.

12. (a)

13. (d): $$Li_2CO_3 \xrightarrow{\Delta} Li_2O + CO_2$$
$$\underset{1\text{ mol}}{Li_2CO_3} \qquad \underset{1\text{ mol}}{CO_2}$$

$$Na_2CO_3 \xrightarrow{\Delta} \text{No reaction}$$

$$\underset{\substack{2\text{ mol}\\1\text{ mol}}}{2NaHCO_3} \xrightarrow{\Delta} Na_2CO_3 + \underset{\substack{1\text{ mol}\\0.5\text{ mol}}}{CO_2} + H_2O$$

Total moles of CO_2 = 1 + 0.5 = 1.5 mol

14. (d): 12 coordination (*fcc*) : 8 coordination (*bcc*)

For *fcc* lattice, $a = \frac{4r}{\sqrt{2}}$

For *bcc* lattice, $a = \frac{4r}{\sqrt{3}}$

Ratio of densities is $\frac{4 \times M}{N_A \times a^3} : \frac{2 \times M}{N_A \times a^3}$

Ratio of densities is $\frac{4 \times M}{N_A \times \left(\frac{4r}{\sqrt{2}}\right)^3} : \frac{2 \times M}{N_A \times \left(\frac{4r}{\sqrt{3}}\right)^3}$

$$= 2(\sqrt{2})^3 : (\sqrt{3})^3$$

15. (c) : The difference in energies of the levels involved in the transition *i.e.*, $\Delta E = h\nu = \frac{hc}{\lambda}$.

16. (c) : $BeCl_2$ has covalent bond. Amongst Mg, Ca and Ba, the ionic character increases from top to bottom in the group due to increase in size and decrease in ionisation energy.

17. (a) : Number of molecules in 100 mg CO_2

$$= \frac{\text{Mass}}{\text{Molar mass}} \times 6.023 \times 10^{23} = \frac{0.1}{44} \times 6.023 \times 10^{23}$$
$$= 1.368 \times 10^{21}$$

Molecules remaining $= 1.368 \times 10^{21} - 10^{21}$
$= 0.368 \times 10^{21}$

No. of moles of CO_2 remaining $= \frac{0.368 \times 10^{21}}{6.023 \times 10^{23}}$
$= 6.1 \times 10^{-4}$

18. (c) : Gram formula mass of NaCl = 23 + 35.5 g = 58.5 g

No. of formula units of NaCl in 1.0 g of NaCl

$$= \frac{6.023 \times 10^{23}}{58.5} \times 1.0$$

There are four formula units per unit cell in NaCl.

$$\therefore \text{ No. of unit cells } = \frac{6.023 \times 10^{23} \times 1.0}{58.5 \times 4} = 2.57 \times 10^{21}$$

19. (a) : $\underset{\text{2 moles}}{2H_2O_{2(l)}} \longrightarrow 2H_2O_{(l)} + \underset{\text{24 L}}{O_{2(g)}}$

Under given conditions, 1 mole occupies 24 L of O_2

24 L of O_2 is formed from 2 moles of H_2O_2

$$3\text{ L of }O_2\text{ is formed from} = \frac{2\times3}{24} = 0.25\text{ mole of }H_2O_2$$

in 100 mL of solution

$$\text{Thus, molarity of }H_2O_2 = \frac{0.25\times1000}{100} = 2.5\text{ mol L}^{-1}$$

20. (b) : As *A* is more electronegative than *B*, it cannot carry positive charge.

21. (a) : Millimoles of conc. $AgNO_3$ = Millimoles of dil. $AgNO_3$

$$i.e., \frac{40\times10^{-3}}{170}\times1 = \frac{16\times10^{-3}}{170}\times V \Rightarrow V = 2.5\text{ mL}$$

22. (d) : At liquid $\rightleftharpoons$ vapour equilibrium, the *K.E.* of both the states is same *K.E.* = 3*RT*/2

23. (b) : $\text{Moles of ammonia} = \frac{PV}{RT} = \frac{1\times0.350}{0.083\times300}$

$= 0.01$ mol

$$\text{Molar concentration} = \frac{\text{Number of moles}}{\text{Volume (in L)}} = \frac{0.01}{0.500}$$

$= 0.02$ M

24. (c) : AsF_3 molecule has trigonal pyramidal shape *i.e.*, sp^3d hybridization. Hybrid orbitals involved in this hybridization is one *s*, three $p(p_x, p_y, p_z)$ and one $d(d_{z^2})$ orbitals.

25. (c) : From Einstein's equation of photoelectric effect,

$$h\nu = h\nu_0 + K.E. \qquad \left(\because K.E. = \frac{1}{2}mv^2\right)$$

$$\therefore \quad \frac{1}{2}mv^2 = h\nu - h\nu_0 = \frac{hc}{\lambda} - \frac{hc}{\lambda_0}$$

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

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

26. (c) : The packing efficiency in a *ccp* structure = 74%

∴ Percentage of free space = 100 – 74 = 26%

Packing efficiency in a body-centred structure = 68%

Percentage of free space = 100 – 68 = 32%

27. (b) : When *n* = 3, the possible values of *l* will be 0, 1, 2, not 3. Also, when *l* = 0, 'm_l' will also be equal to 0, not –1.

28. (d) :

	Species	Bond order	Bond strength
I.	O_2^{2-} O_2	1 2	 Stronger
II.	N_2 N_2^+	3 2.5	Stronger
III.	NO^+ NO^-	3 2	Stronger

Larger is the bond order, greater is the bond energy.

29. (b) : $$V.D. = \frac{\text{Wt. of 45 mL of vapours at STP}}{\text{Wt. of 45 mL of }H_2\text{ at STP}}$$

$$= \frac{0.24\text{ g}}{4.5\times0.000089} = 59.93$$

($\because$ density of H_2 = 0.089 g L^{-1} = 0.000089 g/mL)

30. (b) : (I) will be the most stable as it maintains conjugation.

(IV) will be the least stable as it loses conjugation and lesser electronegative carbon acquires negative charge.

(III) will be more stable than (II) as it maintains a triple bond between two nitrogens.

Hence, the correct order of stability is

I > III > II > IV

KCET

SOLVED PAPER 2015

1. 0.30 g of an organic compound containing C, H and O on combustion yields 0.44 g CO_2 and 0.18 g H_2O. If one mol of compound weighs 60, then molecular formula of the compound is
(a) C_3H_8O (b) $C_2H_4O_2$
(c) CH_2O (d) C_4H_6O

2. For one of the element various successive ionization enthalpies (in kJ mol^{-1}) are given below :

I.E.	1st	2nd	3rd	4th	5th
	577.5	1810	2750	11,580	14,820

The element is
(a) P (b) Mg
(c) Si (d) Al

3. The aqueous solution of following salt will have the lowest pH
(a) NaClO (b) $NaClO_4$
(c) $NaClO_3$ (d) $NaClO_2$

4. One of the following is an essential amino acid.
(a) Cysteine (b) Serine
(c) Tyrosine (d) Isoleucine

5. The formation of cyanohydrin from a ketone is an example of
(a) nucleophilic addition
(b) electrophilic substitution
(c) nucleophilic substitution
(d) electrophilic addition.

6. 100 cm^3 of 1 M CH_3COOH was mixed with 100 cm^3 of 2 M CH_3OH to form an ester. The change in the initial rate if each solution is diluted with equal volume of water would be
(a) 4 times (b) 0.25 times
(c) 2 times (d) 0.5 times.

7. How many coulombs of electricity are required for the oxidation of one mol of water to dioxygen?
(a) 1.93×10^4 C (b) 19.3×10^5 C
(c) 9.65×10^4 C (d) 1.93×10^5 C

8. Cheilosis and digestive disorders are due to the deficiency of
(a) ascorbic acid (b) pyridoxine
(c) thiamine (d) riboflavin.

9. One of the following amides will not undergo Hoffmann bromamide reaction :
(a) $CH_3CONHCH_3$ (b) $CH_3CH_2CONH_2$
(c) CH_3CONH_2 (d) $C_6H_5CONH_2$

10. Iodoform can be prepared from all, except
(a) butan-2-one (b) acetophenone
(c) propan-2-ol (d) propan-1-ol.

11. The arrangement of following compounds :
(i) bromomethane (ii) bromoform
(iii) chloromethane (iv) dibromomethane
In the increasing order of their boiling point is
(a) iv < iii < i < ii (b) i < ii < iii < iv
(c) iii < i < iv < ii (d) ii < iii < i < iv

12. The complex ion having minimum magnitude of Δ_o(CFSE) is
(a) $[Co(NH_3)_6]^{3+}$ (b) $[Cr(H_2O)_6]^{3+}$
(c) $[Cr(CN)_6]^{3-}$ (d) $[CoCl_6]^{3-}$

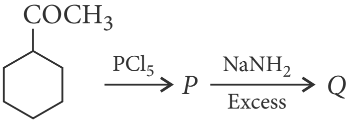
13. Which of the following colloids cannot be easily coagulated?
(a) Multimolecular colloids
(b) Irreversible colloids
(c) Lyophobic colloids
(d) Macromolecular colloids

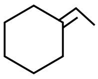
14. After adding non-volatile solute freezing point of water decreases to −0.186°C. Calculate ΔT_b if $K_f = 1.86$ K kg mol^{-1} and $K_b = 0.521$ K kg mol^{-1}
(a) 0.0521 K (b) 0.0186 K
(c) 0.521 K (d) 1.86 K

15. Which of the following compounds of xenon has pyramidal geometry?
(a) XeF_2 (b) XeF_4
(c) $XeOF_4$ (d) XeO_3

16. Cryolite is
(a) Na_3AlF_6 and is used in the electrolysis of alumina for lowering the melting point of alumina only
(b) Na_3AlF_6 and is used in the electrolytic refining of alumina
(c) Na_3AlF_6 and is used in the electrolysis of alumina for decreasing electrical conductivity
(d) Na_3AlF_6 and is used in the electrolysis of alumina for lowering the melting point and increasing the conductivity of alumina.

17. Identify '*Q*' in the following sequence of reactions :



(a)


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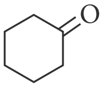
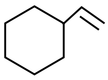
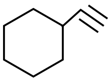


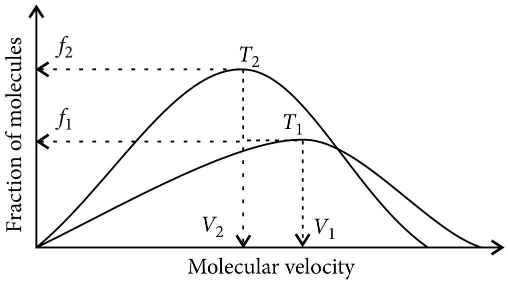
(c)


(d)


18. What amount of dioxygen (in gram) contains 1.8×10^{22} molecules?
(a) 0.960 (b) 96.0
(c) 0.0960 (d) 9.60

19. The pair of compound which cannot exist together in solution is
(a) $NaHCO_3$ and H_2O
(b) Na_2CO_3 and NaOH
(c) $NaHCO_3$ and NaOH
(d) $NaHCO_3$ and Na_2CO_3

20. Plot of Maxwell's distribution of velocities is given below :



Which of the following is correct about this plot?
(a) $f_1 > f_2$ (b) $V_1 < V_2$
(c) $T_1 < T_2$ (d) $T_1 > T_2$

21. Arrange the following compounds in the increasing order of their acidic strength :
(i) *m*-Nitrophenol (ii) *m*-Cresol
(iii) Phenol (iv) *m*-Chlorophenol
(a) ii < iv < iii < i (b) ii < iii < i < iv
(c) iii < ii < i < iv (d) ii < iii < iv < i

22. In the reaction :

$$S + \frac{3}{2}O_2 \longrightarrow SO_3 + 2x \text{ kJ and}$$

$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3 + y \text{ kJ}$$

heat of formation of SO_2 is
(a) $x - y$ (b) $2x + y$
(c) $x + y$ (d) $2x - y$

23. Which of the following is not true?
(a) Ampicillin is not a natural antibiotic.
(b) Vancomycin is a broad spectrum antibiotic.
(c) Erythromycin is a bacteriostatic antibiotic.
(d) Prontosil is not converted into sulphanilamide in the body.

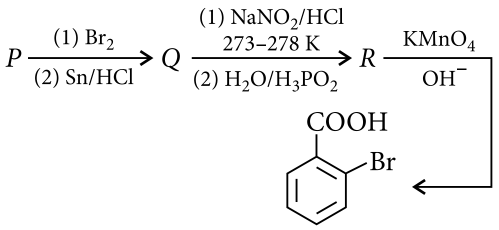
24. Using MOT, compare O_2^+ and O_2^- species and choose the incorrect option.
(a) O_2^- is less stable.
(b) Both O_2^+ and O_2^- are paramagnetic.
(c) O_2^+ have higher bond order than O_2^-.
(d) O_2^+ is diamagnetic while O_2^- is paramagnetic.

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

26. The correct statement is
(a) BI_3 is the weakest Lewis acid among the boron halides
(b) there is minimum $p\pi$-$p\pi$ back bonding in BF_3
(c) BF_3 is the strongest Lewis acid among the other boron halides
(d) there is maximum $p\pi$-$p\pi$ back bonding in BF_3.

27. Acetic acid is treated with $Ca(OH)_2$ and the product so obtained is subjected to dry distillation. The final product is
(a) propanal (b) ethanol
(c) ethanal (d) propanone.

28. In the sequence of following reactions :



The starting compound 'P' is
(a) m-nitrotoluene (b) p-nitrotoluene
(c) o-nitrotoluene (d) o-bromotoluene.

29. An alkali metal hydride (NaH) reacts with diborane in 'A' to give a tetrahedral compound 'B' which is extensively used as reducing agent in organic synthesis. The compound 'A' and 'B' respectively are
(a) CH_3COCH_3 and $B_3N_3H_6$
(b) $(C_2H_5)_2O$ and $NaBH_4$
(c) C_2H_6 and C_2H_5Na
(d) C_6H_6 and $NaBH_4$

30. Water softening by Clark's process uses
(a) $NaHCO_3$ (b) $Ca(OH)_2$
(c) $Ca(HCO_3)_2$ (d) Na_2CO_3

31. One of the following conversion results in the change of hybridization and geometry.
(a) NH_3 to NH_4^+ (b) H_2O to H_3O^+
(c) CH_4 to C_2H_6 (d) BF_3 to BF_4^-

32. In presence of HCl, H_2S results the precipitation of group-2 elements but not group-4 elements during qualitative analysis. It is due to
(a) higher concentration of H^+
(b) lower concentration of H^+
(c) higher concentration of S^{2-}
(d) lower concentration of S^{2-}.

33. The two electrons have the following sets of quantum numbers :

$$P = 3,\ 2, -2, +\frac{1}{2},\ Q = 3,\ 0,\ 0,\ +\frac{1}{2}$$

Which of the following statements is true?
(a) P has greater energy than Q.
(b) P and Q represent same electron.
(c) P and Q have same energy.
(d) P has lesser energy than Q.

34. Orlon has monomeric unit
(a) glycol (b) isoprene
(c) acrolein (d) vinyl cyanide.

35. Adenosine is an example of
(a) purine base (b) nucleoside
(c) nucleotide (d) pyrimidine base.

36. While charging the lead storage battery
(a) $PbSO_4$ on cathode is reduced to Pb
(b) $PbSO_4$ on anode is oxidized to PbO_2
(c) $PbSO_4$ on anode is reduced to Pb
(d) $PbSO_4$ on cathode is oxidized to Pb.

37. The unit cell with crystallographic dimensions, $a \neq b \neq c$, $\alpha = \gamma = 90°$ and $\beta \neq 90°$ is
(a) monoclinic (b) tetragonal
(c) triclinic (d) orthorhombic.

38. Sodium metal crystallizes in bcc lattice with edge length of 4.29 Å. The radius of sodium atom is
(a) 1.601 Å (b) 1.857 Å
(c) 2.857 Å (d) 2.145 Å

39. On heating with concentrated NaOH solution in an inert atmosphere of CO_2, white phosphorus gives a gas. Which of the following statements is incorrect about the gas?
(a) It is more basic than NH_3.
(b) Its solution in water decomposes in the presence of light.
(c) It is less basic than NH_3.
(d) It is highly poisonous and has smell like rotten fish.

40. In the given set of reactions :

$$\text{2-Bromopropane} \xrightarrow[\text{heat}]{\text{alc. AgCN}} X \xrightarrow{\text{LiAlH}_4} Y$$

The IUPAC name of product Y is
(a) N-isopropylmethanamine
(b) N-methylpropan-2-amine
(c) N-methylpropanamine
(d) butan-2-amine.

41. H_2O_2 cannot oxidise
(a) Na_2SO_3 (b) KI
(c) PbS (d) O_3

42. Which of the following will be able to show geometrical isomerism?
(a) MA_2B_2-Tetrahedral
(b) $MABCD$-Tetrahedral
(c) MA_3B-Square planar
(d) $MABCD$-Square planar

43. Copper is extracted from copper pyrites by heating in a Bessemer converter. The method is based on the principle that

(a) iron has less affinity for oxygen than sulphur at high temperature
(b) sulphur has less affinity for oxygen at high temperature
(c) copper has more affinity for oxygen than sulphur at high temperature
(d) copper has less affinity for oxygen than sulphur at high temperature.

44. The electrolyte having maximum flocculation value for AgI/Ag^+ sol is
(a) Na_2S (b) Na_3PO_4
(c) $NaCl$ (d) Na_2SO_4

45. In a first order reaction, the concentration of the reactant is reduced to 12.5% in one hour. When was it half completed?
(a) 20 min (b) 15 min
(c) 3 hr (d) 30 min

46. 0.06% (*w*/*v*) aqueous solution of urea is isotonic with
(a) 0.6% glucose solution
(b) 0.1 M glucose solution
(c) 0.06% glucose solution
(d) 0.01 M glucose solution.

47. In H_2—O_2 fuel cell the reaction occurring at cathode is
(a) $O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-_{(aq.)}$
(b) $H^+_{(aq.)} + OH^-_{(aq.)} \longrightarrow H_2O_{(l)}$
(c) $2H_{2(g)} + O_{2(g)} \longrightarrow 2H_2O_{(l)}$
(d) $H^+ + e^- \longrightarrow \frac{1}{2}H_2$

48. The distinguishing test between methanoic acid and ethanoic acid is
(a) Tollens' test
(b) sodium bicarbonate test
(c) litmus test
(d) esterification test.

49. The hydrolysis of optically active 2-bromobutane with aqueous NaOH results in the formation of
(a) (–)-butan-2-ol (b) (±)-butan-2-ol
(c) (+)-butan-2-ol (d) (±)-butan-1-ol.

50. $MSO_4 \xrightarrow{NH_4OH} \underset{\text{white}}{X\downarrow} \xrightarrow[\text{Excess}]{NH_4OH} Y \xrightarrow{H_2S} Z\downarrow$

Here *M* and *Z* are
(a) Zn, ZnS (b) Al, Al_2S_3
(c) Cu, ZnS (d) Fe, FeS

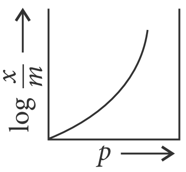
51. The electronic configuration of Gd^{2+} is
(at. no. of Gd is 64)
(a) $[Xe]4f^7$ (b) $[Xe]\ 4f^7\ 5d^1$
(c) $[Xe]\ 4f^8$ (d) $[Xe]\ 4f^7\ 5d^1\ 6s^2$

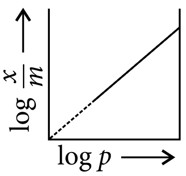
52. Number of possible alkynes with formula C_5H_8 is
(a) 3 (b) 5
(c) 2 (d) 4

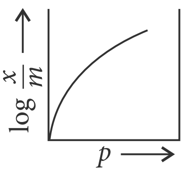
53. Glycogen is
(a) a structural polysaccharide
(b) structurally similar to amylopectin but extensively branched
(c) a polymer of β-*D*-glucose units
(d) structurally very much similar to amylopectin.

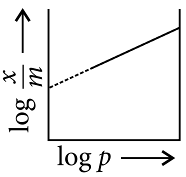
54. How many ions per molecule are produced in the solution when Mohr salt is dissolved in excess of water?
(a) 5 (b) 10
(c) 4 (d) 6

55. Which of the following curves is in accordance with Freundlich adsorption isotherm?

(a)


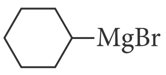
(b)


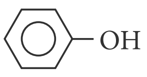
(c)


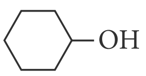
(d)


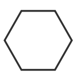
56.


The product '*B*' is

(a)


(b)


(c)


(d)


57. On heating potassium permanganate, one of the following compound is not obtained
(a) MnO (b) K_2MnO_4
(c) O_2 (d) MnO_2

58. The salt which responds to dilute and concentrated H_2SO_4 is
(a) $Ba(NO_3)_2$ (b) Na_3PO_4
(c) CaF_2 (d) Na_2SO_4

59. Half-life period of a first order reaction is 10 min. Starting with initial concentration 12 M, the rate after 20 min is
(a) 0.693×3 M min^{-1}
(b) 0.0693×4 M min^{-1}
(c) 0.0693 M min^{-1}
(d) 0.0693×3 M min^{-1}

60. Which of the following aqueous solutions has the highest freezing point?
(a) 0.01 M NaCl (b) 0.01 M Na_2SO_4
(c) 0.1 M Sucrose (d) 0.1 M NaCl

SOLUTIONS

1. **(b) :** $\text{Percentage of C} = \frac{12}{44} \times \frac{0.44}{0.30} \times 100 = 40\%$

$\text{Percentage of H} = \frac{2}{18} \times \frac{0.18}{0.30} \times 100 = 6.6\%$

Percentage of O = 100 – (40 + 6.6) = 53.4%

Element	%	Molar ratio	Simplest ratio
C	40	$\frac{40}{12} = 3.3$	$\frac{3.3}{3.3} = 1$
H	6.6	$\frac{6.6}{1} = 6.6$	$\frac{6.6}{3.3} = 2$
O	53.4	$\frac{53.4}{16} = 3.3$	$\frac{3.3}{3.3} = 1$

Hence, empirical formula = CH_2O

$$n = \frac{\text{Molecular mass}}{\text{Empirical formula mass}} = \frac{60}{30} = 2$$

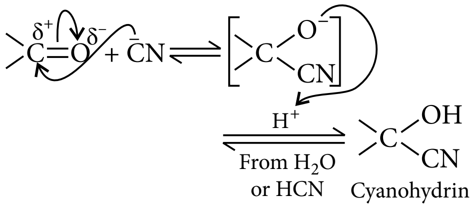
$\Rightarrow$ Molecular formula of the compound = $(CH_2O)_2$
$= C_2H_4O_2$

2. **(d) :** Large jump between IE_3 and IE_4 suggests that the element has three valence electrons.

3. **(b) :** $NaClO + H_2O \longrightarrow NaOH + HClO$
$NaClO_4 + H_2O \longrightarrow NaOH + HClO_4$
$NaClO_3 + H_2O \longrightarrow NaOH + HClO_3$
$NaClO_2 + H_2O \longrightarrow NaOH + HClO_2$
As $HClO_4$ is the strongest acid, its solution will have lowest pH.

4. **(d)**

5. **(a) :**



6. **(b) :** $\underset{1\,M}{CH_3COOH} + \underset{2\,M}{CH_3OH} \longrightarrow CH_3COOCH_3 + H_2O$

$r_1 = k[CH_3COOH][CH_3OH] = k(1)(2) = 2k$

When solution is diluted with equal volume of water, concentration is reduced to half.

$$\therefore \quad r_2 = k\left(\frac{1}{2}\right)\left(\frac{2}{2}\right) = \frac{k}{2}$$

$$\frac{r_1}{r_2} = \frac{2k}{k/2} = 4 \Rightarrow r_2 = \frac{r_1}{4} = 0.25\,r_1$$

7. **(d) :** $H_2O \longrightarrow 2H^+ + \frac{1}{2}O_2 + \underset{2F}{2e^-}$

Hence coulombs of electricity required for the oxidation of one mole of water to dioxygen
$= 2 \times 96500 = 193000\text{ C} = 1.93 \times 10^5\text{ C}$

8. **(d)**

9. **(a) :** Only primary amides undergo Hoffmann bromamide reaction.

10. **(d) :** Iodoform can be prepared from compounds containing $-CH_3CO$ group or $CH_3-\overset{|}{C}HOH$ group.
Propan-1-ol does not contain any such group.

11. **(c) :** The intermolecular forces of attraction become stronger with the increase in size of the molecules. Hence the order of boiling points will be :
$CH_3Cl < CH_3Br < CH_2Br_2 < CHBr_3$

12. **(d) :** The magnitude of Δ_o follows the order :
$Cl^- < H_2O < NH_3 < CN^-$

13. **(d) :** Macromolecular colloids are quite stable and resemble true solution in many respects.

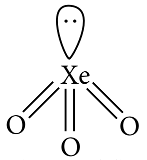
14. **(a) :** $\Delta T_f = T_f^\circ - T_f = 0 - (-0.186) = 0.186°C$

$\Delta T_f = K_f \times m$

$$\Rightarrow \quad m = \frac{\Delta T_f}{K_f} = \frac{0.186}{1.86} = 0.1\text{ m}$$

$\Delta T_b = K_b \times m = 0.521 \times 0.1 = 0.0521\text{ K}$

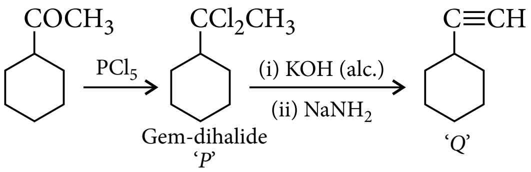
15. **(d) :**



(Pyramidal)

16. **(d)**

17. **(d) :**



18. **(a) :** 6.022×10^{23} molecules are present in 32 g of O_2

$\therefore$ 1.8×10^{22} molecules will be present in

$$\frac{32}{6.022 \times 10^{23}} \times 1.8 \times 10^{22}\,g$$

$$= 0.960 \text{ g of } O_2$$

19. **(c) :** $NaHCO_3$ being an acidic salt will react with NaOH.

$$NaHCO_3 + NaOH \longrightarrow Na_2CO_3 + H_2O$$

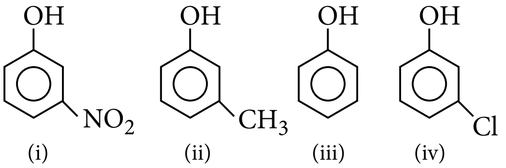
20. **(d) :** In Maxwell's distribution of velocities, the curve shifts forward and downward at higher temperature.

$T_1 > T_2$

$V_1 > V_2$

$f_2 > f_1$

21. **(d) :**



Nitro group has both $-R$ effect and $-I$ effect, but $-R$ effect predominates. Due to stronger electron withdrawing nature of $-NO_2$ group, phenoxide ion is stabilized more. Hence nitrophenol is more acidic than phenol.

Methyl group destabilizes the phenoxide ion by $+I$ effect and hyperconjugation. Hence *m*-cresol is weaker acid than phenol.

Chlorine have both $+R$ and $-I$ effect, but $-I$ effect predominates. Hence *m*-chlorophenol is more acidic than phenol.

$-R$ effect of nitro group is stronger than $-I$ effect of chlorine, hence *m*-nitrophenol is more acidic than *m*-chlorophenol.

Therefore the correct order of acidic strength is

m-nitrophenol > *m*-chlorophenol > phenol > *m*-cresol

22. **(None) :** $S + \frac{3}{2} O_2 \longrightarrow SO_3 + 2x \text{ kJ}$ ...(i)

$SO_2 + \frac{1}{2} O_2 \longrightarrow SO_3 + y \text{ kJ}$ ...(ii)

$S + O_2 \longrightarrow SO_2 + q \text{ kJ}$ ...(iii)

Equation (iii) can be obtained by subtracting equation (ii) from (i)

$\Rightarrow \quad q = 2x - y \text{ kJ}$

Enthalpy of formation $(\Delta H_f) = -q = -(2x - y)$

$= y - 2x$

23. **(d)**

24. **(d) :** Molecular orbital configuration of O_2^+ :

$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_z^2\, \pi 2p_x^2 = \pi 2p_y^2\, \pi^* 2p_x^1$

Bond order $= \frac{1}{2}(10 - 5) = 2.5$

Number of unpaired electrons = 1, hence paramagnetic.

Molecular orbital configuration of O_2^- :

$\sigma 1s^2\, \sigma^* 1s^2\, \sigma 2s^2\, \sigma^* 2s^2\, \sigma 2p_z^2\, \pi 2p_x^2 = \pi 2p_y^2$

$\pi^* 2p_x^2 = \pi^* 2p_y^1$

Bond order $= \frac{1}{2}(10 - 7) = 1.5$

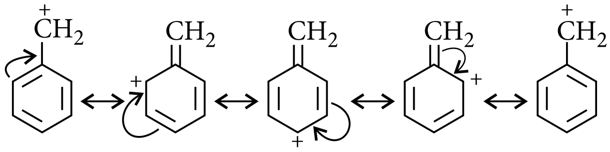
Number of unpaired electron = 1, hence paramagnetic.

Both O_2^+ and O_2^- are paramagnetic.

O_2^+ have higher bond order than O_2^-.

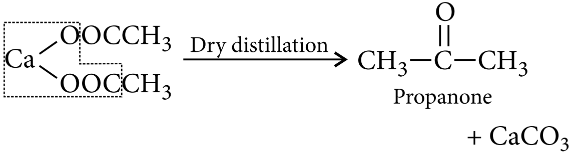
O_2^- is less stable.

25. **(c) :** Toluene will form the most stable carbocation hence, bond dissociation energy of "C—H" bond will be minimum in case of toluene.

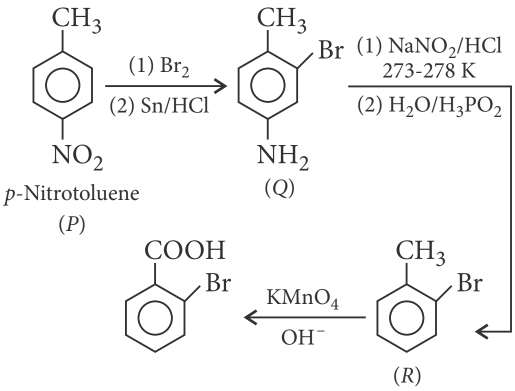


26. **(d) :** There is maximum $p\pi$–$p\pi$ back bonding in BF_3 due to identical size of $2p$ orbitals of B and F.

27. **(d) :** $2CH_3COOH + Ca(OH)_2 \longrightarrow \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca} + 2H_2O$



28. **(b) :**



29. **(b) :** $2NaH + B_2H_6 \xrightarrow[\text{'A'}]{(C_2H_5)_2O} \underset{\substack{\text{Sodium borohydride} \\ \text{'B'}}}{2NaBH_4}$

30. (b) : Clark's process is a commercial method of water softening.

A calculated amount of quick lime is added to hard water, bicarbonates are converted into insoluble calcium and magnesium carbonates which are filtered off.

$CaO + H_2O \longrightarrow Ca(OH)_2$

$Ca(HCO_3)_2 + Ca(OH)_2 \longrightarrow 2CaCO_3\downarrow + 2H_2O$

31. (d) :

NH_3 sp^3 hybridization Tetrahedral geometry	$\longrightarrow$	NH_4^+ sp^3 hybridization Tetrahedral geometry
CH_4 sp^3 hybridized C Tetrahedral geometry	$\longrightarrow$	C_2H_6 sp^3 hybridized C Tetrahedral geometry
H_2O sp^3 hybridization Tetrahedral geometry	$\longrightarrow$	H_3O^+ sp^3 hybridization Tetrahedral geometry
BF_3 sp^2 hybridization Trigonal planar geometry	$\longrightarrow$	BF_4^- sp^3 hybridization Tetrahedral geometry

32. (d) : Dissociation of H_2S is suppressed in presence of HCl due to common ion effect. This decreases the S^{2-} ion concentration and hence, only group II radicals having low solubility product are precipitated.

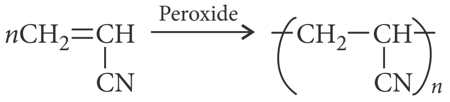
33. (a) : From the given quantum numbers, it can be inferred that :

P electron belongs to 3*d* orbital.

Q electron belongs to 3*s* orbital.

Hence, *P* has greater energy than *Q*.

34. (d) :



$$n\underset{\displaystyle CN}{CH_2{=}CH} \xrightarrow{\text{Peroxide}} \left(CH_2-\underset{\displaystyle CN}{CH}\right)_n$$

Vinyl cyanide or Acrylonitrile — Polyacrylonitrile or Orlon

35. (b) : A nucleoside contains only two components of nucleic acids – a pentose sugar and a nitrogenous base.

In adenosine, nitrogenous base is adenine.

36. (c) : Reactions occurring during charging are :

Anode: $PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO_{4(aq)}^{2-}$

Cathode: $PbSO_{4(s)} + 2H_2O \longrightarrow PbO_{2(s)} + SO_{4(aq)}^{2-} + 4H_{(aq)}^+ + 2e^-$

$2PbSO_{4(s)} + 2H_2O \longrightarrow Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)}$

37. (a)

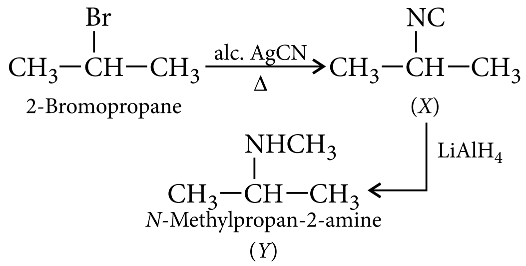
38. (b) : $a = 4.29$ Å

For *bcc*, $r = \frac{\sqrt{3}}{4}a = \frac{\sqrt{3}}{4} \times 4.29 = 1.857$ Å

39. (a) : $P_4 + 3NaOH + 3H_2O \xrightarrow[CO_2]{\Delta} 3NaH_2PO_2 + \underset{\text{Phosphine}}{PH_3\uparrow}$

PH_3 is less basic than NH_3 as the electron density is diffused over the larger phosphorus atom.

40. (b) :



$$CH_3-\overset{\displaystyle Br}{CH}-CH_3 \xrightarrow[\Delta]{\text{alc. AgCN}} CH_3-\overset{\displaystyle NC}{CH}-CH_3 \xrightarrow{LiAlH_4} CH_3-\overset{\displaystyle NHCH_3}{CH}-CH_3$$

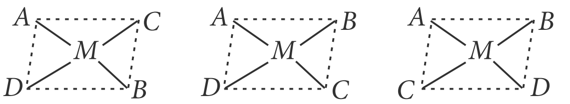
41. (d) : H_2O_2 oxidises Na_2SO_3 to Na_2SO_4, KI to I_2, PbS to $PbSO_4$ and reduces O_3 to O_2.

$H_2O_2 + O_3 \longrightarrow H_2O + 2O_2$

42. (d) : Tetrahedral complexes do not show geometrical isomerism because due to symmetrical structure, relative positions of the ligands is same with respect to each other.

Square planar complexes of the type MA_3B do not show geometrical isomerism because the possible spatial arrangements are equivalent.

MABCD type square planar complexes show three isomers which can be obtained by fixing the position of one ligand and placing any of the remaining three ligands at the *trans* position one by one.



trans *cis* *cis*

43. (d) : $2Cu_2S + 3O_2 \longrightarrow 2Cu_2O + 2SO_2$

$Cu_2S + 2Cu_2O \longrightarrow 6Cu + SO_2$

44. (c) : Flocculation value is inversely proportional to flocculation power.

For the flocculation of positively charged sol PO_4^{3-} ions have maximum flocculation power while Cl^- have minimum flocculation power. Hence, NaCl will have maximum flocculation value.

45. (a) : For a first order reaction :

$$k=\frac{2.303}{t}\log\frac{[A]_0}{[A]}=\frac{2.303}{60}\log\frac{100}{12.5}=0.0346\ \text{min}^{-1}$$

$$\text{Now } t_{1/2}=\frac{0.693}{k}=\frac{0.693}{0.0346}=20\ \text{min}$$

46. (d) : Molarity of 0.06% (w/v) aqueous solution of

$$\text{urea}=\frac{0.06\times1000}{60\times100}=0.01\ \text{M}$$

As osmotic pressure (π) = CRT

$\therefore$ 0.01 M solution of urea will be isotonic with 0.01 M glucose solution.

47. (a) : The reactions occurring in H_2–O_2 fuel cell are

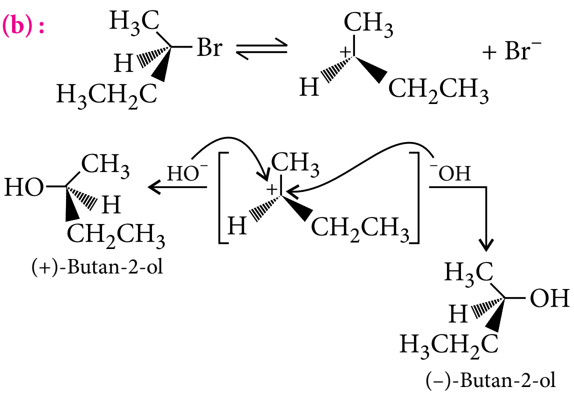
At anode : $2H_{2(g)}+4OH^-_{(aq)}\longrightarrow 4H_2O_{(l)}+4e^-$

At cathode : $O_{2(g)}+2H_2O_{(l)}+4e^-\longrightarrow 4OH^-_{(aq)}$

Overall reaction : $2H_{2(g)}+O_{2(g)}\longrightarrow 2H_2O_{(l)}$

48. (a) : Formic acid contains a hydrogen atom and behaves like an aldehyde as well as a carboxylic acid. Like aldehydes it reduces Tollens' reagent.

49. (b) :



50. (a) :

$$\begin{tikzcd}
ZnSO_4 \arrow[r, "NH_4OH"] & \underset{\text{(White)}}{\underset{(X)}{Zn(OH)_2\downarrow}} \arrow[d, "NH_4OH", "\text{Excess}"'] \\
 & \underset{(Z)}{ZnS\downarrow} \quad \underset{(Y)}{\text{Clear solution}} \arrow[l, "H_2S"']
\end{tikzcd}$$

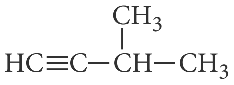
M is Zn.

51. (b)

52. (a) : Three possible structures are

(i) $HC\equiv C-CH_2-CH_2-CH_3$

(ii) $H_3C-C\equiv C-CH_2-CH_3$

(iii) 

$HC\equiv C-\underset{|}{\overset{CH_3}{CH}}-CH_3$

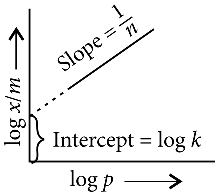
53. (b) : Glycogen is called animal starch because its structure is similar to that of amylopectin. The main difference between glycogen and amylopectin is that amylopectin chains consist of about 20-25 glucose units but glycogen chains are much shorter and consist of about 10-14 glucose units, *i.e.*, glycogen is highly branched.

54. (a) : $FeSO_4\cdot(NH_4)_2SO_4\cdot6H_2O \xrightarrow{\text{Excess } H_2O} Fe^{2+}+2NH_4^+ + 2SO_4^{2-}+6H_2O$

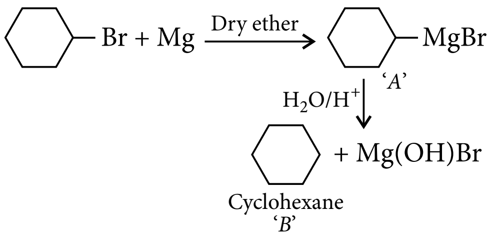
55. (d) : The relationship between the amount adsorbed (x/m) and the equilibrium pressure (p) is given as :

$$\log\frac{x}{m}=\log k+\frac{1}{n}\log p$$

Hence, the curve will be



56. (d) :



57. (a) : $2KMnO_4 \xrightarrow{\Delta} K_2MnO_4+MnO_2+O_2$

58. (a)

59. (d) : $\underset{\text{Initial conc.}}{12\ \text{M}} \xrightarrow{t_{1/2}} 6\ \text{M} \xrightarrow{t_{1/2}} 3\ \text{M}$

$t_{1/2}$ = 10 min

$$k=\frac{0.693}{10}=0.0693\ \text{min}^{-1}$$

As $t_{1/2}$ is 10 min, after 20 minutes the concentration will be 3 M.

Hence, Rate = 0.0693 × 3 M min^{-1}

60. (a) : Depression in freezing point, $\Delta T_f = iK_f m$

ΔT_f will follow the order :

$\underset{i=2}{0.1\ \text{M NaCl}} > \underset{i=1}{0.1\ \text{M Sucrose}} > \underset{i=3}{0.01\ \text{M } Na_2SO_4} > \underset{i=2}{0.01\ \text{M NaCl}}$

Depression in freezing point is minimum in case of 0.01 M NaCl solution hence, it will have maximum freezing point.

◆

ACE YOUR WAY CBSE XII

Series 2

CHAPTERWISE PRACTICE PAPER : ELECTROCHEMISTRY | CHEMICAL KINETICS

Time Allowed : 3 hours

Maximum Marks : 70

GENERAL INSTRUCTIONS

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

1. Write the name and polarity of the electrode where oxidation takes place in galvanic cell.

2. In which type of reactions, order and molecularity of the reaction are equal?

3. What is overpotential?

4. What is the effect of temperature on rate constant?

5. The cell potential of mercury cell remains constant during its life time. Why?

6. Estimate the minimum potential difference needed to reduce Al_2O_3. Free energy change for the decomposition reaction :

$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2$ is

$\Delta G = +960$ kJ ($F = 96500$ C mol^{-1})

7. **(i)** Draw a schematic graph showing how the rate of a first order reaction changes with change in concentration of the reactant.

(ii) Rate of a reaction is given by

Rate = $k[A]^2[B]$

What are the units for the rate and the rate constant for this reaction?

8. **(i)** Express the relation between the conductivity (κ) and the molar conductivity (Λ_m) of a solution.

(ii) Electrolytic conductivity of 0.30 M solution of KCl at 295 K is 3.72×10^{-2} S cm^{-1}. Calculate the molar conductivity.

9. **(i)** How much time is required for the completion of a zero order reaction?

(ii) How does the value of rate constant vary with reaction concentration?

10. Zinc rod is dipped in 0.1 M solution of $ZnSO_4$. The salt is 95% dissociated at this dilution at 298 K. Calculate the electrode potential.

[Given : $E°_{Zn^{2+}/Zn} = -0.76$ V]

OR

The $E°$ values corresponding to the following two reduction electrode processes are :

$Cu^+/Cu = +0.52$ V

$Cu^{2+}/Cu^+ = +0.16$ V

Formulate the galvanic cell for their combination. What will be the standard cell potential for it? Calculate $\Delta_r G°$ for the cell reaction.

[$F = 96500$ C mol^{-1}]

11. A certain reaction is 50% completed in 20 min at 300 K and the same reaction is again 50% completed in 5 min at 350 K. Calculate the activation energy if it is a first order reaction.

[$R = 8.314$ J K^{-1} mol^{-1}, log 4 = 0.602]

12. Write the overall reaction that occurs during the use of nickel-cadmium cell. Is it a primary or a secondary cell? Mention its one merit over the lead storage cell.

13. For the reaction :

$$2NO_{(g)} + Cl_{2(g)} \longrightarrow 2NOCl_{(g)}$$

the following data were collected. All the measurements were taken at 263 K.

Exp. No.	**Initial [NO]/(M)**	**Initial [Cl_2]/(M)**	**Initial rate of disapp. of Cl_2 / (M/min)**
1	0.15	0.15	0.60
2	0.15	0.30	1.20
3	0.30	0.15	2.40
4	0.25	0.25	?

(i) Write the expression for the rate law.

(ii) Calculate the value of rate constant and specify its units.

(iii) What is the initial rate of disappearance of Cl_2 in exp. 4?

14. (i) Solutions of two electrolytes '*A*' and '*B*' are diluted. It is found that Λ_m value of '*B*' increases 2 times while that of '*A*' increases 20 times. Which of the two is a strong electrolyte?

(ii) A galvanic cell has $E^\circ_{\text{cell}} = 1.1$ V. If an opposing potential of 1.1 V is applied to this cell, what will happen to the cell reaction and current flowing through the cell?

(iii) How will the pH of brine solution be affected on electrolysis?

15. (i) What aspect of the reaction is influenced by the presence of catalyst which increases the rate of the reaction?

(ii) In some cases it is found that a large number of colliding molecules have energy more than threshold energy, yet reaction is slow, why?

16. (i) How much charge is required for the reduction of 1 mol of MnO_4^- to Mn^{2+}?

(ii) A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5 amperes for 20 minutes. What mass of Ni is deposited at the cathode? [Given : Ni = 58.7]

17. (i) For the reaction at 500 K,

$$NO_{2(g)} + CO_{(g)} \longrightarrow CO_{2(g)} + NO_{(g)}$$

the proposed mechanism is as below :

$$NO_2 + NO_2 \longrightarrow NO + NO_3 \text{ (slow)}$$

$$NO_3 + CO \longrightarrow CO_2 + NO_2 \text{ (fast)}$$

What is the rate law for the reaction?

(ii) The decomposition of NH_3 on platinum surface is a zero order reaction. What are the rates of production of N_2 and H_2 if $k = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}?

(iii) A reaction is first order w.r.t. *A* and second order w.r.t. *B*. How is the rate affected when the concentrations of both *A* and *B* are doubled?

18. The rate constant for the decomposition of a certain reaction is described by the equation :

$$\log_{10} k(s^{-1}) = 14 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

(i) What is the pre-exponential factor?

(ii) What is the energy of activation (in cal)?

(iii) At what temperature, rate constant is equal to pre-exponential factor?

OR

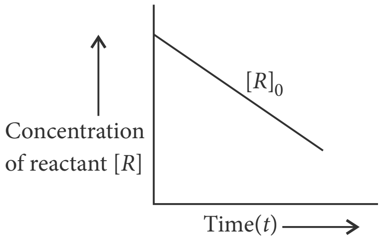
(i) A first order reaction is 15% completed in 20 minutes. How long will it take to complete 60%?

(ii) The activation energy of a reaction is 75.2 kJ mol^{-1} in the absence of a catalyst and 50.14 kJ mol^{-1} with a catalyst. How many times will the rate of reaction grow in the presence of the catalyst if the reaction proceeds at 25°C?

[R = 8.314 J K^{-1} mol^{-1}]

19. (i) The half life period for a first order reaction is 5×10^4 s. What percentage of the initial reactant will react in 2 hours?

(ii) A reaction, Reactant → Product is represented by



Predict

(a) The order of the reaction in this case.

(b) What does the slope of the graph represent?

20. (i) State Ksohlrausch's law for electrical conductance of an electrolyte at infinite dilution.

(ii) At 291 K, molar conductivities at infinite dilution of NH_4Cl, NaOH, NaCl are 129.8, 217.4, 108.9 ohm^{-1} cm^2 respectively. If molar conductivity of normal solution of NH_4OH is 9.33 ohm^{-1} cm^2 then what is the degree of dissociation of NH_4OH solution?

(iii) State reason for the following :
Rusting of iron is said to be an electrochemical phenomenon.

21. (i) From the rate expression of the given reaction,

$CH_3CHO_{(g)} \longrightarrow CH_{4(g)} + CO_{(g)}$

Rate = $k[CH_3CHO]^{3/2}$

determine the dimensions of rate constant.

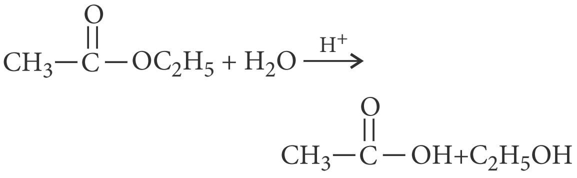
(ii) A reaction is 50% completed in 2 hours and 75% completed in 4 hours. What is the order of the reaction.

(iii) List two factors on which rate constant of a reaction depends.

22. (i) How do conductivity and molar conductivity vary with concentration?

(ii) How does molar conductivity vary with concentration for (a) weak electrolyte and (b) strong electrolyte? Give reasons for the variations.

23. Udit, a student of class XII was performing an experiment to study the kinetics of acid hydrolysis of ester by titration method using 0.1 N NaOH. He recorded his observations in the table given below as instructed by his teacher.



$$CH_3-\overset{\overset{\large O}{||}}{C}-OC_2H_5 + H_2O \xrightarrow{H^+} CH_3-\overset{\overset{\large O}{||}}{C}-OH + C_2H_5OH$$

Time (min)	Volume of 0.1 N NaOH (mL)
0.00	5
10.00	20
1.00 h (complete)	45

(i) Mention the values displayed by Udit.

(ii) What is the order of reaction?

(iii) Why did the volume of 0.1 N NaOH increase, as reaction proceeded?

(iv) What did the role of H^+ ion?

24. (i) Predict the products of electrolysis in each of the following :

(a) An aqueous solution of $AgNO_3$ with silver electrodes.

(b) An aqueous solution of $AgNO_3$ with platinum electrodes.

(ii) What type of a cell is the lead storage battery? Write the anode and the cathode reactions and the overall reaction occurring in a lead storage battery while operating.

OR

(i) Predict the products of electrolysis in each of the following :

(a) A dilute solution of H_2SO_4 with platinum electrodes.

(b) An aqueous solution of $CuCl_2$ with platinum electrodes.

(ii) A voltaic cell is setup at 25°C with the half cells, Al/Al^{3+} (0.001 M) and Ni/Ni^{2+} (0.50 M). Write the equation for the reaction that occurs when the cell generates an electric current and determine the cell potential.

[Given: $E°_{Ni^{2+}/Ni} = -0.25$ V, $E°_{Al^{3+}/Al} = -1.66$ V]

25. (i) Define activation energy. How is it affected by

(a) the use of catalyst and

(b) a rise in temperature?

(ii) The following data were obtained during the first order thermal decomposition of SO_2Cl_2 at a constant volume :

$SO_2Cl_{2(g)} \longrightarrow SO_{2(g)} + Cl_{2(g)}$

Experiment	Time/s	Total pressure/atm
1	0	0.4
2	100	0.7

Calculate the rate constant.

[Given : log 4 = 0.6021, log 2 = 0.3010]

OR

(i) For a first order reaction, show that time required for 99% completion is twice the time required for the completion of 90% of reaction.

(ii) Rate constant k of a reaction varies with temperature T according to the equation,

$$\log k = \log A - \frac{E_a}{2.303R}\left(\frac{1}{T}\right)$$

where E_a is the activation energy. When a graph is plotted for $\log k$ *vs.* $\frac{1}{T}$, a straight line with a slope of – 4250 K is obtained. Calculate E_a for the reaction. ($R = 8.314\ \text{J K}^{-1}\ \text{mol}^{-1}$)

26. (i) How many moles of mercury will be produced by electrolysing 1.0 M $Hg(NO_3)_2$ solution with a current of 2.00 A for 3 hours?

(ii) Calculate the cell emf at 25°C for the following cell : $Mg_{(s)} \mid Mg^{2+}\ (0.01\ M) \parallel Sn^{2+}\ (0.10\ M) \mid Sn_{(s)}$

[Given : $E^\circ_{(Mg^{2+}/Mg)} = -2.34$ V, $E^\circ_{(Sn^{2+}/Sn)} = -0.136$ V, 1 F = 96500 C mol^{-1}].

Calculate the maximum work that can be accomplished by the operation of this cell.

OR

(i) Explain why electrolysis of aqueous solution of NaCl gives H_2 at cathode and Cl_2 at anode. Write the overall reaction.

[Given : $E^\circ_{Na^+/Na} = -2.71$ V, $E^\circ_{H_2O/H_2} = -0.83$ V, $E^\circ_{Cl_2/Cl^-} = +1.36$ V, $E^\circ_{H^+/H_2/H_2O} = +1.23$ V]

(ii) The resistance of a conductivity cell containing 0.001 M KCl solution at 298 K is 1500 Ω. Calculate the cell constant if conductivity of 0.001 M KCl solution at 298 K is $0.146 \times 10^{-3}\ \text{S cm}^{-1}$.

SOLUTIONS

1. In galvanic cell, oxidation takes place at zinc electrode and it is the negative electrode (anode).

2. In elementary reactions (single step reactions), order and molecularity are same.

3. Extra potential required for the deposition of an ion at the electrode is called overpotential.

4. Rate constant is directly proportional to temperature *i.e.*, it increases with increase in temperature.

5. The cell potential of mercury cell remains constant during its life time because its cell reaction does not involve any ion whose concentration can change.

6.

$$Al_2O_3 \longrightarrow 2Al + \frac{3}{2}O_2$$

$$2Al^{3+} + 6e^- \longrightarrow 2Al,\quad n = 6$$

$$\frac{2}{3}Al_2O_3 \longrightarrow \frac{4}{3}Al + O_2,\quad n = \frac{6\times 2}{3} = 4$$

$$\Delta G = -nFE$$

[$\Delta G = 960 \times 10^3$ J, $n = 4$, $F = 96500$ C mol^{-1}]

$$\therefore\quad 960 \times 10^3 = -4 \times 96500 \times E$$

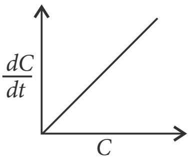
$$E = -\frac{960\times 10^3}{4\times 96500} = -2.487\ \text{V}$$

∴ Minimum potential difference needed to reduce $Al_2O_3 = -2.487$ V

7. (i) For a first order reaction, rate of reaction is directly proportional to the concentration of the reactant.

Rate = $k \cdot C$

Hence, graph between rate of reaction and change in concentration will be straight line passing through the origin.



(ii) Given : Rate = $k[A]^2[B]$

Unit of rate = $\text{mol L}^{-1}\ \text{s}^{-1}$

Unit of rate constant,

$$k = \frac{\text{Rate}}{[\text{Conc.}]^3}\quad \text{or,}\quad k = \frac{\text{mol L}^{-1}\ \text{s}^{-1}}{(\text{mol L}^{-1})^3} = \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}$$

8. (i)

$$\Lambda_m = \frac{\kappa \times 10^3}{M}$$

where M is the concentration of solution in molarity.

(ii) Electrolytic conductivity, $\kappa = 3.72 \times 10^{-2}\ \text{S cm}^{-1}$

Molar conductivity,

$$\Lambda_m = \frac{\kappa(\text{S cm}^{-1}) \times 1000(\text{cm}^3\ \text{L}^{-1})}{M(\text{mol L}^{-1})}$$

$$= \frac{3.72 \times 10^{-2} \times 1000}{0.30} = 124\ \text{S cm}^2\ \text{mol}^{-1}$$

9. (i) Time required for the completion of a zero order reaction is $\frac{[A]_0}{k}$ units of time.

(ii) Rate constant is independent of the concentration of the reactants.

10. $[Zn^{2+}_{(aq)}] = 0.1 \times \frac{95}{100} = 0.095$

$$Zn^{2+}_{(aq)} + 2e^- \longrightarrow Zn_{(s)}$$

According to the Nernst equation,

$$E = E^\circ - \frac{0.0591}{n}\log\frac{[Zn_{(s)}]}{[Zn^{2+}_{(aq)}]}$$

$$= -0.76 - \frac{0.0591}{2}\log\frac{1}{0.095}$$

$$= -0.76 - 0.02955 \times (1.0223) = -0.76 - 0.03021$$

$$= -0.79\ \text{V}$$

OR

At cathode : $Cu^+ + e^- \longrightarrow Cu \qquad E° = +0.52\ V$

At anode : $Cu^+ \longrightarrow Cu^{2+} + e^- \qquad E° = +0.16\ V$

Cell reaction : $2Cu^+ \longrightarrow Cu + Cu^{2+}$

Cell representation is

$Cu^+ \mid Cu^{2+} \parallel Cu^+ \mid Cu$

$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = 0.52 - 0.16 = 0.36\ V$

$\Delta_r G° = -nE°F = -1 \times 0.36 \times 96500$

$= -34740\ J\ mol^{-1}$

11. At 300 K, $t_{1/2} = 20$ min

At 350 K, $t_{1/2} = 5$ min

$$\text{At 300 K,}\ k_1 = \frac{0.693}{20}\ min^{-1}$$

$$\text{At 350 K,}\ k_2 = \frac{0.693}{5}\ min^{-1}$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\text{or,}\quad \log\frac{20}{5} = \frac{E_a}{2.303 \times 8.314}\left[\frac{350 - 300}{350 \times 300}\right]$$

$$\text{or,}\quad \log 4 = \frac{E_a}{2.303 \times 8.314} \times \frac{50}{350 \times 300}$$

$$\text{or,}\quad E_a = \frac{0.602 \times 2.303 \times 8.314 \times 300 \times 350}{50}$$

$= 24206\ J\ mol^{-1} = 24.2\ kJ\ mol^{-1}$

12. Nickel-cadmium batteries are rechargeable storage batteries. It has anode cadmium metal and cathode nickel (III) compound like NiO(OH) supported on nickel.

Reactions during discharging,

At anode : $Cd_{(s)} + 2OH^-_{(aq)} \rightarrow Cd(OH)_{2(s)} + 2e^-$

At cathode :

$NiO_{2(s)} + 2H_2O_{(l)} + 2e^- \rightarrow Ni(OH)_{2(s)} + 2OH^-_{(aq)}$

$$\overline{\underline{Cd_{(s)} + NiO_{2(s)} + 2H_2O_{(l)} \rightarrow Cd(OH)_{2(s)} + Ni(OH)_{2(s)}}}$$

When charging takes place, reactions are reversed. It is a secondary cell.

It has longer life than the lead storage cell but is more expensive to manufacture.

Since reactant and product are metals or solids, emf remains constant throughout in its operation.

13. (i) Let m be the order w.r.t. [NO] and n be the order w.r.t. $[Cl_2]$.

Rate, $r = k[NO]^m[Cl_2]^n$

$$\frac{r_1}{r_2} = \frac{0.60}{1.20} = \frac{k(0.15)^m(0.15)^n}{k(0.15)^m(0.30)^n}$$

$$\text{or}\quad \frac{1}{2} = \left(\frac{1}{2}\right)^n \Rightarrow n = 1$$

$$\frac{r_2}{r_3} = \frac{1.20}{2.40} = \frac{k(0.15)^m(0.30)^1}{k(0.30)^m(0.15)^1}$$

$$\text{or}\quad \frac{1}{2} = \left(\frac{1}{2}\right)^m \times \frac{2}{1}\ \text{ or }\ \frac{1}{4} = \left(\frac{1}{2}\right)^m \Rightarrow m = 2$$

Hence, expression for the rate law is

$r = k[NO]^2\,[Cl_2]^1$

(ii) Substituting the values in experiment 1

$0.60\ M\ min^{-1} = k(0.15\ M)^2(0.15\ M)^1$

$$\text{or}\quad k = \frac{0.60\ M\,min^{-1}}{0.0225 \times 0.15\ M^3} = 177.77\ M^{-2}\ min^{-1}$$

(iii) Substituting the values in experiment 4

$r = 177.7\ M^{-2}\ min^{-1} \times (0.25\ M)^2\ (0.25\ M)$

$= 2.77\ M\ min^{-1}$

14. (i) For strong electrolytes, Λ_m increases slowly with dilution. Since there is no wide effect on Λ_m value of electrolyte 'B' on dilution. On dilution, interionic attraction decreases. Thus, 'B' is a strong electrolyte.

(ii) If an external opposite potential is applied in the galvanic cell and increased slowly, reaction continues to take place till the opposing voltage reaches the value 1.1 V. After that reaction stops and no further chemical reaction takes place. Hence, no current flows through the cell.

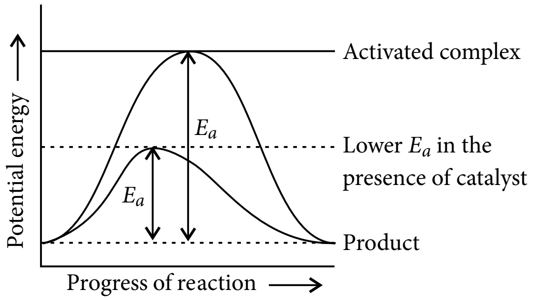
(iii) The overall reaction for electrolysis of brine solution can be written as

$$NaCl_{(aq)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + \frac{1}{2}H_{2(g)} + \frac{1}{2}Cl_{2(g)}$$

Hence, the pH of brine solution which is neutral will increase due to formation of NaOH.

15. (i) In the presence of catalyst, the rate of reaction increases because catalyst lowers down the activation energy and reaction becomes possible at lower temperature.

The graph first shows higher activation energy of reactants. When the catalyst is added to reactants a new path of lower activation energy is adopted. So, the reaction becomes possible at lower temperature.



(ii) The colliding molecules may not be in proper orientation at the time of collision.

16. (i) The given reaction is

$$\underset{1\text{ mole}}{MnO^-_{4(aq)}} + 8H^+_{(aq)} + \underset{5\text{ moles}}{5e^-} \longrightarrow Mn^{2+}_{(aq)} + 4H_2O_{(l)}$$

∴ 5 moles of electrons are needed for the reduction of 1 mole of MnO_4^- to Mn^{2+}.

5 moles of electrons = 5 Faraday

= 5 × 96500 coulombs = 4.825×10^5 coulombs

(ii) Given : $I = 5$ A; $t = 20 \times 60$ s, $w = ?$

$Q = I \times t = 5 \times 20 \times 60 = 6000$ C

Reaction for deposition of Ni,

$$Ni^{2+} + 2e^- \longrightarrow Ni$$

2 mol 1 mol

2 × 96500 C 58.7 g

Thus, 2 × 96500 C of electricity produces 58.7 g Ni

∴ 6000 C of electricity would produce

$$= \frac{58.7 \times 6000}{2 \times 96500} = 1.825\text{ g}$$

17. (i) The slow step of the reaction mechanism is

$NO_2 + NO_2 \rightarrow NO + NO_3$

Hence, rate of the reaction, $r = k[NO_2][NO_2]$

Rate = $k[NO_2]^2$

(ii) $$2NH_{3(g)} \xrightarrow{Pt} N_{2(g)} + 3H_{2(g)}$$

As Rate = $k[\text{Reactant}]^0$

Rate = $2.5 \times 10^{-4} \times 1 = 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

∴ Rate of formation of N_2

$$= \frac{d[N_2]}{dt} = 2.5 \times 10^{-4}\text{ mol L}^{-1}\text{ s}^{-1}$$

and, Rate of formation of $H_2 = \dfrac{d[H_2]}{dt}$

= 3 × Rate of reaction = $3 \times 2.5 \times 10^{-4}$ mol L^{-1} s^{-1}

= 7.5×10^{-4} mol L^{-1} s^{-1}

(iii) $r_1 = k[A]^1[B]^2$

∴ $r_2 = k[2A]^1[2B]^2$ or $r_2 = 8 \times r_1$

Hence, rate becomes 8 times the initial rate.

18. $$\log_{10} k = \log_{10} A - \frac{E_a}{2.303\ RT} \quad ...(1)$$

Given, $$\log_{10} k\,(s^{-1}) = 14 - \frac{1.25 \times 10^4\text{ K}}{T} \quad ...(2)$$

(i) From equations (1) and (2),

$\log_{10} A = 14$

∴ A(pre-exponential factor) = 10^{14} s^{-1}

(ii) $$\frac{E_a}{2.303\,R} = 1.25 \times 10^4$$

$E_a = 2.303R \times 1.25 \times 10^4$

$= 2.303 \times 2 \times 1.25 \times 10^4$ cal

$= 57575$ cal

(iii) $\log_{10} k = \log_{10} A$ if $T \rightarrow \infty$

or $k = A$ if $T \rightarrow \infty$.

OR

(i) $$t_{15\%} = \frac{2.303}{k} \log \frac{a}{a - x}$$

$$\text{or, } 20 = \frac{2.303}{k} \log \frac{100}{100 - 15}$$

$$\text{or, } k = \frac{2.303 \times 0.0706}{20}\text{ min}^{-1}$$

$$\text{Now, } t_{60\%} = \frac{2.303}{k} \log \frac{100}{40}$$

$$t_{60\%} = \frac{2.303 \times 20}{2.303 \times 0.0706} \log \frac{10}{4}$$

$$t_{60\%} = \frac{20 \times 0.3979}{0.0706} = 112.73\text{ min}$$

(ii) $k = Ae^{-E_a/RT}$

In the absence of catalyst, $k_1 = Ae^{-75.2/RT}$

In the presence of catalyst, $k_2 = Ae^{-50.14/RT}$

$$\therefore \frac{k_1}{k_2} = \frac{e^{-75.2/RT}}{e^{-50.14/RT}} = e^{-25.06/RT}$$

$$2.303 \log_{10} \frac{k_2}{k_1} = \frac{25.06}{RT}$$

$$\log_{10} \frac{k_2}{k_1} = \frac{25.06}{2.303 \times 8.314 \times 10^{-3} \times 298}$$

$$\log_{10} \frac{k_2}{k_1} = 4.3920 \Rightarrow \frac{k_2}{k_1} = 24660$$

Thus, rate of reaction increases by 24660 times.

19. (i) Given: $t_{1/2} = 5 \times 10^4$ s, $t = 2$ hrs $= 2 \times 60 \times 60$ s

$$\frac{[R]}{[R]_0} = ?$$

For a first order reaction, $k = \dfrac{2.303}{t} \log_{10} \dfrac{[R]_0}{[R]}$

$$k = \frac{0.693}{t_{1/2}}$$

or $\dfrac{0.693}{5\times10^4}=\dfrac{2.303}{2\times60\times60}\log_{10}\dfrac{[R]_0}{[R]}$

or $\log_{10}\dfrac{[R]_0}{[R]}=\dfrac{0.693\times2\times3600}{5\times10^4\times2.303}=0.0433$

or $\dfrac{[R]_0}{[R]}=\text{antilog}\ (0.0433)=1.105$

% of reactant reacted $=\dfrac{1}{1.105}\times100=90.49\ \%$

(ii) (a) The reaction is of zero order.

(b) Slope of the straight line graph gives

$$-k=\frac{d[R]}{dt}$$

20. (i) Kohlrausch's law states that at infinite dilution, when the dissociation of electrolyte is complete each ion makes a definite contribution towards the molar conductivity of electrolyte, irrespective of the nature of other ion with which it is associated.

$$\Lambda_m^\infty=\nu_+\lambda_+^\infty+\nu_-\lambda_-^\infty$$

(ii) According to Kohlrausch's law,

$$\Lambda^\infty_{NH_4OH}=\lambda^\infty_{NH_4^+}+\lambda^\infty_{OH^-}$$

$$\therefore\ \Lambda^\infty_{NH_4OH}=\Lambda^\infty_{NH_4Cl}+\Lambda^\infty_{NaOH}-\Lambda^\infty_{NaCl}$$

$$=129.8+217.4-108.9$$

$$=238.3\ \text{ohm}^{-1}\ \text{cm}^2$$

Given : $\Lambda^c=9.33\ \text{ohm}^{-1}\ \text{cm}^2$

Degree of dissociation,

$$\alpha=\frac{\Lambda^c}{\Lambda^\infty}=\frac{9.33}{238.3}=0.039$$

(iii) According to electrochemical theory, during the formation of rust the impure iron surface behaves like a small electrochemical cell. In such cells pure iron acts as anode and impure surface acts as cathode. Moisture containing dissolved oxygen or CO_2 is the electrolytic solution. Hence, rusting is an electrochemical phenomenon.

21. (i) Rate $=k[CH_3CHO]^{3/2}$

$$k=\frac{\text{Rate}}{[CH_3CHO]^{3/2}}=\frac{\text{mol L}^{-1}\text{s}^{-1}}{(\text{mol L}^{-1})^{3/2}}$$

$$=\text{L}^{1/2}\ \text{mol}^{-1/2}\ \text{s}^{-1}$$

(ii) $A\xrightarrow{2\,\text{hours}}\dfrac{A}{2}\xrightarrow{2\,\text{hours}}\dfrac{A}{4}$

The concentration is reduced to exactly half after every 2 hours, thus half life period is independent of inital concentration of the reactant. Thus, reaction is of first order.

(iii) Rate constant of a reaction depends upon :

(a) nature of reaction and

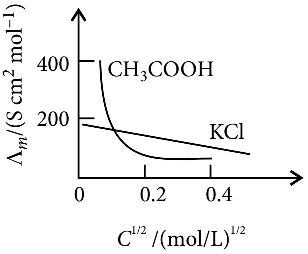
(b) the temperature of the reaction.

22. (i) **Variation of conductivity and molar conductivity with concentration :** Conductivity always decreases with decrease in concentration, for both weak and strong electrolytes. This is because the number of ions per unit volume that carry the current in a solution decreases on dilution.

Molar conductivity increases with decrease in concentration. This is because that total volume, V, of solution containing one mole of electrolyte also increases. It has been found that decrease in κ on dilution of a solution is more than compensated by increase in its volume.

(ii) (a) **Weak electrolyte :** When the concentration of weak electrolyte becomes very low, its degree of ionisation rises sharply. There is sharp increase in the number of ions in the solution. Hence, the molar conductivity of a weak electrolyte rises steeply at low concentration.

(b) **Strong electrolyte :** The molar conductivity of strong electrolyte decreases slightly with the increase in concentration. This increase is due to increase in attraction as a result of greater number of ions per unit volume. With dilution the ions are far apart, interionic attractions become weaker and conductance increases.



Molar conductivity *vs* $C^{1/2}$ for acetic acid (weak electrolyte) and potassium chloride (strong electrolyte) in aqueous solutions.

23. (i) The values displayed by Udit are :

(a) Keen observation

(b) Discipline and critical thinking.

(ii) It is a pseudo first order reaction. As water is present in large excess, its concentration will remain almost constant during the reaction. Therefore, the rate of reaction will depend only on the concentration of the reactant present in smaller amount *i.e.*, ester.

$$\text{Rate}=k[CH_3COOC_2H_5]$$

(iii) The volume of 0.1 N NaOH increased, as reaction proceeded due to the formation of CH_3COOH. Volume of NaOH consumed depends on both the acetic acid produced during the reaction and the acid present originally as catalyst as it is an acid-catalysed reaction. During the reaction, as the amount of acetic acid produced increased, the volume of NaOH used also increased.

(iv) H^+ ion acts as a catalyst acts as a reaction.

24. (i) (a) Electrolysis of aqueous solution of $AgNO_3$ with silver electrodes :

$AgNO_3 \rightleftharpoons Ag^+ + NO_3^-$

Cathode : Reduction of Ag^+ and H_2O is possible.

Since $E°_{cell}$(reduction potential of Ag^+) is greater than that of H_2O, Ag will be deposited at cathode.

$Ag^+ + e^- \longrightarrow Ag$

Anode : As silver anode is attacked by NO_3^- ions, it would be oxidised as :

$Ag \rightarrow Ag^+ + e^-$

Thus, Ag dissolves from anode,

(b) Electrolysis of aqueous solution of $AgNO_3$ with platinum electrodes :

Cathode : Ag will be deposited at cathode.

Anode : Platinum anode (inert) is not attacked by NO_3^- ions.

Out of OH^- and NO_3^- ions, the discharge potential of OH^- is lower and it would be discharged as :

$4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$

Thus, $O_{2(g)}$ is liberated at anode.

(ii) Lead storage battery is a secondary cell.

Cell reactions during operation are

At anode : $Pb_{(s)} + SO_4^{2-}{}_{(aq)} \rightarrow PbSO_{4(s)} + 2e^-$

At cathode : $PbO_{2(s)} + SO_4^{2-}{}_{(aq)} + 4H^+_{(aq)} + 2e^- \rightarrow PbSO_{4(s)} + 2H_2O_{(l)}$

$Pb_{(s)} + PbO_{2(s)} + 2H_2SO_{4(aq)} \rightarrow 2PbSO_{4(s)} + 2H_2O_{(l)}$

OR

(i) (a) Electrolysis of dilute solution of H_2SO_4 with platinum electrodes :

Cathode : Both water and H_2SO_4 furnish H^+ ions which are discharged at the cathode as

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

and $H_{2(g)}$ is liberated at cathode.

Anode : Water furnishes OH^- and H_2SO_4 furnishes SO_4^{2-} ions. Out of these the discharge potential of OH^- is lower and these are discharged as

$4OH^-_{(aq)} \rightarrow 2H_2O_{(l)} + O_{2(g)} + 4e^-$

Thus, $O_{2(g)}$ is liberated at anode.

(b) Electrolysis of an aqueous solution of $CuCl_2$ with platinum electrodes :

$CuCl_2 \rightarrow Cu^{2+} + 2Cl^-$

$H_2O \rightarrow H^+ + OH^-$

Cathode : $CuCl_2$ furnishes Cu^{2+} ions and H_2O furnishes H^+ ions. Out of these, discharge potential of Cu^{2+} ions is lower hence, they are discharged as

$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$

Hence, Cu is deposited at cathode.

Anode : $CuCl_2$ furnishes Cl^- ions and H_2O furnishes OH^- ions. Due to overvoltage Cl^- ions are discharged as :

$2Cl^-_{(aq)} \rightarrow Cl_{2(g)} + 2e^-$

Thus, $Cl_{2(g)}$ is liberated at anode.

(ii) From an electrochemical series, Al will act as anode and Ni as cathode.

The cell reactions are

At anode : $2Al_{(s)} \rightarrow 2Al^{3+}_{(aq)} + 6e^-$

At cathode : $3Ni^{2+}_{(aq)} + 6e^- \rightarrow 3Ni_{(s)}$

$2Al_{(s)} + 3Ni^{2+}_{(aq)} \rightarrow 2Al^{3+}_{(aq)} + 3Ni_{(s)}$

The cell may be represented as

$Al_{(s)} | Al^{3+}_{(aq)} || Ni^{2+}_{(aq)} | Ni_{(s)}$

$$E°_{cell} = E°_{cathode} - E°_{anode}$$
$$= -0.25\text{ V} - (-1.66\text{ V}) = 1.41\text{ V}$$

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{6}\log\frac{[Al^{3+}]^2}{[Ni^{2+}]^3}$$

$$= 1.41 - \frac{0.0591}{6}\log\frac{(10^{-3})^2}{(5\times10^{-1})^3}$$

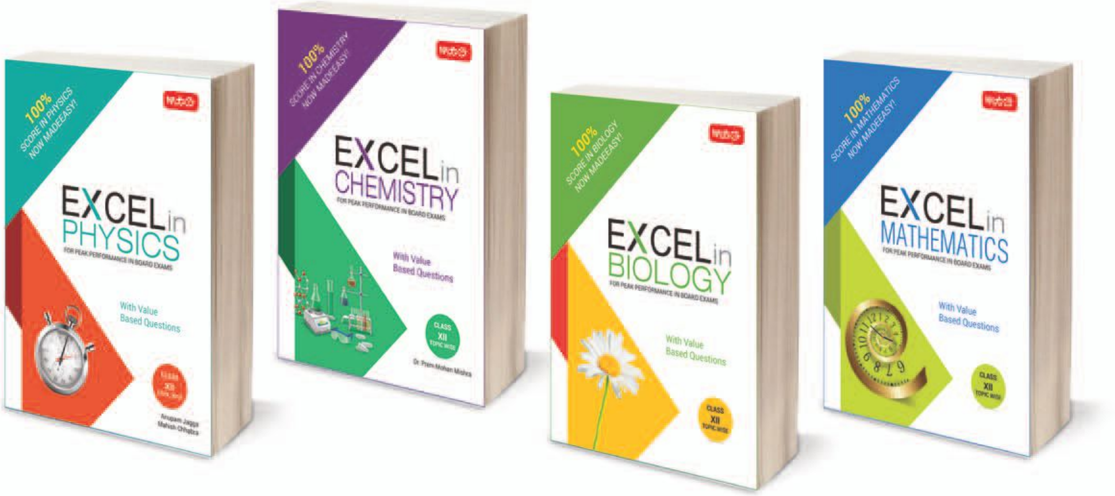
$$= 1.41 + 0.0502 = 1.46\text{ V}$$

25. (i) The minimum extra energy which must be supplied to the reactants to enable them to cross over the energy barrier between reactants and products is called activation energy.

Activation energy = Threshold energy–average energy of reactants

(a) Activation energy of the reactants decreases by the use of catalyst.

(b) Activation energy of the reactants decreases with rise in temperature.


EXCEL in PHYSICS
EXCEL in CHEMISTRY
EXCEL in BIOLOGY
EXCEL in MATHEMATICS
With Value Based Questions

(ii) The given reaction is

$$\begin{array}{llll} & SO_2Cl_{2(g)} & \longrightarrow SO_{2(g)} & + \ Cl_{2(g)} \\ \text{At } t = 0, & 0.4 \text{ atm} & 0 & 0 \\ \text{At time } t, & (0.4 - x) \text{ atm} & x \text{ atm} & x \text{ atm} \end{array}$$

Total pressure at time t will be

$P_{\text{Total}} = (0.4 - x) + x + x = 0.4 + x$

$x = (P_{\text{Total}} - 0.4)$

Pressure of SO_2Cl_2 at time t will be

$p_{SO_2Cl_2} = 0.4 - x = 0.4 - (P_{\text{Total}} - 0.4)$

$= 0.8 - P_{\text{Total}}$

At time ($t = 100$ s), $P_{\text{Total}} = 0.7$ atm

$\therefore \ p_{SO_2Cl_2} = 0.8 - 0.7 = 0.1$ atm

According to first order kinetic equation,

$$k = \frac{2.303}{t} \log \left(\frac{p_{SO_2Cl_2 (\text{initial})}}{p_{SO_2Cl_2 (\text{after reaction})}} \right)$$

$$= \frac{2.303}{100} \log \left(\frac{0.4}{0.1} \right) = 1.3 \times 10^{-2} \text{ s}^{-1}$$

OR

(i) For a first order reaction, $t = \dfrac{2.303}{k} \log \dfrac{[R]_0}{[R]_t}$

For 99% completion of reaction,

$t = t_{0.99}$, $[R]_0 = 1$, $[R]_t = (1 - 0.99) = 0.01 = 10^{-2}$

$$t_{0.99} = \frac{2.303}{k} \log \frac{1}{10^{-2}} = \frac{2.303}{k} \log 10^2$$

$$= \frac{2.303}{k} \times 2 \quad \text{...(1)}$$

For 90% completion of reaction,

$t = t_{0.90}$, $[R]_0 = 1$, $[R]_t = (1 - 0.90) = 0.1 = 10^{-1}$

$$t_{0.90} = \frac{2.303}{k} \log \frac{1}{10^{-1}} = \frac{2.303}{k} \log 10$$

$$= \frac{2.303}{k} \quad \text{...(2)}$$

Comparing equations (1) and (2),

$t_{0.99} = 2 \times t_{0.90}$

(ii) Given : Slope = – 4250 K, $R = 8.314$ J K^{-1} mol^{-1}

$E_a = ?$

$$\log k = \log A - \frac{E_a}{2.303\,R} \left(\frac{1}{T} \right)$$

Comparing with $y = mx + c$

$$\text{Slope} = -\frac{E_a}{2.303\,R} = -4250 \text{ K}$$

$E_a = 2.303 \times 8.314$ J K^{-1} mol^{-1} $\times$ 4250 K

$= 81{,}375.35$ J mol^{-1} = 81.37 kJ mol^{-1}

26. **(i)** Quantity of electricity passed,

$Q = I \times t = 2.0 \times 3 \times 60 \times 60 = 21600$ C

$$\underset{\text{2 moles}}{Hg^{2+} + 2e^-} \longrightarrow \underset{\text{1 mole}}{Hg}$$

2 × 96500 C electricity produces 1 mole of Hg

∴ 21600 C will produce

$$= \frac{21600}{2 \times 96500} = 0.112 \text{ mole of Hg}$$

(ii) $Mg_{(s)} \rightarrow Mg^{2+}_{(aq)} + 2e^-$ (Anodic half reaction)

$Sn^{2+}_{(aq)} + 2e^- \rightarrow Sn_{(s)}$ (Cathodic half reaction)

$Mg_{(s)} + Sn^{2+}_{(aq)} \rightarrow Mg^{2+}_{(aq)} + Sn_{(s)}$

$E^\circ_{\text{cell}} = E^\circ_{Sn^{2+}/Sn} - E^\circ_{Mg^{2+}/Mg}$

$= -0.136 + 2.34 = 2.20$ V

$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2} \log \frac{0.01 \text{ M}}{0.10 \text{ M}}$$

$= 2.20 - (0.0295 \times -1) = 2.2295$ V

$w_{\max} = -\Delta G^\circ = -(-nFE^\circ_{\text{cell}}) = nFE^\circ_{\text{cell}}$

$= 2 \times 96500 \times 2.20 = 424600$ J = 424.6 kJ

OR

(i) Aqueous NaCl solution ionises as

$NaCl \longrightarrow Na^+ + Cl^-$

Following reactions are possible at cathode,

$2Na^+_{(aq)} + 2e^- \longrightarrow 2Na_{(s)}$; $E^\circ = -2.71$ V

$2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$; $E^\circ = -0.83$ V

The reaction with higher E° value will take place, hence H_2 is produced at cathode.

Following reactions may take place at anode,

$2Cl^-_{(aq)} \longrightarrow Cl_{2(g)} + 2e^-$; $E^\circ = +1.36$ V

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+ + 2e^- ; E^\circ = +1.23 \text{ V}$$

Due to overvoltage, Cl_2 is liberated at anode.

Hence, the overall reaction is

$$2NaCl_{(aq)} + 2H_2O_{(l)} \longrightarrow 2Na^+_{(aq)} + 2OH^-_{(aq)} + H_{2(g)} + Cl_{2(g)}$$

(ii) Given, [KCl] = 0.001 M, $R = 1500\ \Omega$,

$\kappa = 0.146 \times 10^{-3}$ S cm^{-1}, $G^* = ?$

$$\text{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}} = \text{Conductivity} \times \text{Resistance}$$

$= (0.146 \times 10^{-3} \text{ S cm}^{-1}) \times (1500\ \Omega)$

$= 0.219$ cm^{-1}

◆◆

YOU ASK WE ANSWER

Do you have a question that you just can't get answered?

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q1. Why SO_2 is more powerful reducing agent in an alkaline solution than in acidic one?

Pankaj Mishra (Mughalsarai, U.P.)

Ans. The aqueous solution of SO_2 acts as a reducing agent as sulphurous acid changes into sulphuric acid and liberates nascent hydrogen in the presence of moisture. The reaction is as follows :

$$H_2O + SO_2 \longrightarrow \underset{\text{Sulphurous acid}}{H_2SO_3}$$

$$H_2SO_3 + H_2O \longrightarrow \underset{\substack{\text{Sulphuric}\\ \text{acid}}}{H_2SO_4} + \underset{\substack{\text{Nascent}\\ \text{hydrogen}}}{2[H]}$$

or

The reducing nature of SO_2 can be represented by the following equation :

$$SO_2 + 2OH^- \longrightarrow SO_4^{2-} + 2H^+ + 2e^-$$

Any increase in OH^- ion concentration (alkaline medium) will favour the forward reaction while increase in H^+ ion concentration (acidic medium) will favour the backward reaction.

Q2. Although inert gases are non-reactive, yet they are dangerous. Explain.

Jai Saini (Ambala, Haryana)

Ans. Most gases have some dangerous properties. They may be combustible, corrosive, toxic, asphyxiating or oxidising.

Inert gases or *neutral gases* are mainly nitrogen and rare gases like helium, neon, argon, krypton and xenon. They are not toxic, do not support breathing and react rarely with other substances. Being odourless, colourless and tasteless, they can be more dangerous than toxic gases such as chlorine, ammonia or hydrogen sulphide which can be detected by their odour at very low concentrations.

Inert gases can displace enough air to reduce oxygen levels (~21%). If oxygen levels are low or no oxygen present, inhalation of only 1-2 breaths of nitrogen or any other inert gas can cause sudden loss of consciousness or even death due to asphyxiation.

To avoid these effects, some precautions should be taken :

- Mark off the areas where there is a danger of asphyxiation.
- Never enter a suspicious area without first checking its oxygen concentration.
- If the concentration is less than 18%, use a breathing apparatus.
- Proper ventilation of dangerous areas.

Q3. Why is molality preferred over molarity in handling solutions?

Anita Mathur (Bhopal, M.P.)

Ans. Molarity is no. of moles of solute dissolved in 1L of solution.

$$M = \frac{\text{Moles of solute}}{\text{Volume of solution (in L)}}$$

whereas, molality is no. of moles of the solute per kg of the solvent.

$$m = \frac{\text{Moles of solute}}{\text{Mass of solvent (in kg)}}$$

Molality involves masses which do not change with temperature whereas, molarity involves volume which changes with temperature.

Q4. Ether, a non-polar solvent is essential for the preparation of Grignard reagent. Why?

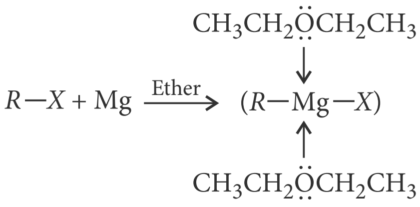
Chandana Das (W. Bengal)

Ans. For the preparation of Grignard reagent, the most critical aspect of the solvent is that it must be dry (< 0.02 wt% of H_2O) and free of O_2.

Diethyl ether is usually the preferred solvent because it can be readily obtained in anhydrous form, is less expensive and easy to remove after the reagent has been used owing to its low boiling point (36°C).

Magnesium is essentially divalent and electron deficient when it reacts with alkyl halide to form *RMgX*. A full octet around the metal atom requires two additional pairs of electrons.

These two pairs of electrons are obtained from the coordination of two molecules of the ether with Mg. This association increases the solubility and stability of the Grignard reagent in the non-polar ether solvent.



$$R{-}X + \text{Mg} \xrightarrow{\text{Ether}} \begin{array}{c} CH_3CH_2\ddot{O}CH_2CH_3 \\ \downarrow \\ (R{-}\text{Mg}{-}X) \\ \uparrow \\ CH_3CH_2\ddot{O}CH_2CH_3 \end{array}$$

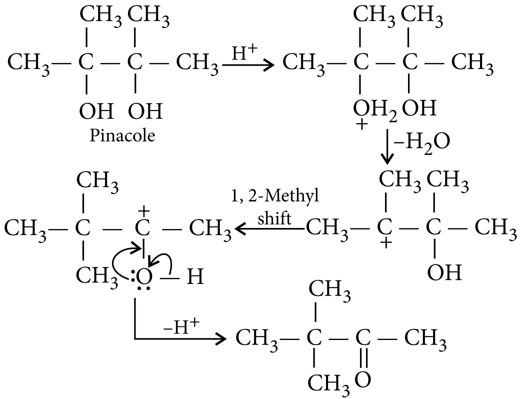
◆◆

CHEMISTRY MUSING

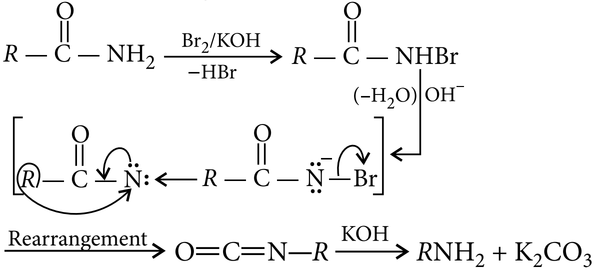
SOLUTION SET 23

1. **(c) :** In pinacol–pinacolone rearrangement, the group or atom migrates to electron deficient carbon, while in Hofmann rearrangement migration to electron deficient nitrogen takes place.

Pinacole–pinacolone rearrangement :

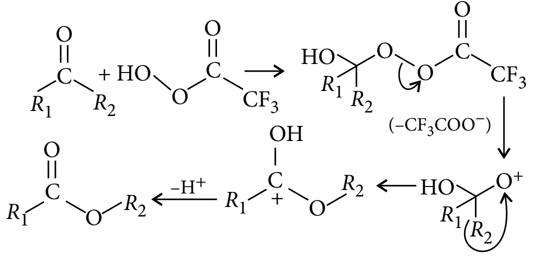


Hofmann rearrangement :



$$O{=}C{=}N{-}R \xrightarrow{KOH} RNH_2 + K_2CO_3$$

Baeyer–Villiger rearrangement :



2. **(b)**

3. **(d):** $P_{Total} = \frac{1}{2}(75 + 22) = 48\frac{1}{2} = 48.5$ torr

$$P_{Total} = \frac{1}{2}(75 + 10) = 42.5 \text{ torr}$$

$$P_{Total} = \frac{1}{2}(22 + 10) = 16 \text{ torr}$$

$$P_{Total} = \frac{1}{3}(75 + 22 + 10) = 35\frac{2}{3} = 35.66 \text{ torr}$$

4. **(b):** This is an example of Hofmann elimination which generally takes place by E2 mechanism and requires a strong base (OH^- is a strong base than I^-). The NH_2^-, being a strong base, cannot be eliminated easily.

5. **(b):** Large jump between IP_4 and IP_5 shows that there are four valence electrons.

6. **(a) :** SO_2 is oxidised by MnO_4^- in acidic medium,

$$5SO_2 + 2MnO_4^- \longrightarrow 2Mn^{2+} + 5SO_4^{2-}$$

$$2 \text{ moles of } MnO_4^- \equiv 5 \text{ moles of } SO_2$$

Hence, 0.4 moles of $MnO_4^- \equiv \frac{5}{2} \times 0.4 = 1$ mole of SO_2

	$2SO_2$	$+ O_2$	$\rightleftharpoons 2SO_3$
Initially :	2	1	0
At equil :	$(2 - 2x)$	$(1 - x)$	$2x$

$(2 - 2x) = 1$ mole of SO_2 (as determined by MnO_4^-)

$x = 0.5$ and $V = 1$ L

$$[SO_3] = \frac{2x}{V} = 1\text{M},\ [SO_2] = \frac{2 - 2x}{V} = 1\text{M and}$$

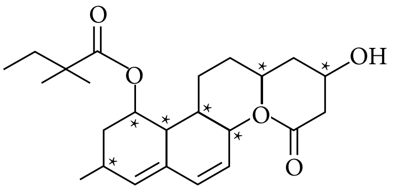
$$[O_2] = \frac{1 - x}{V} = 0.5\text{M} \quad \therefore \quad K_c = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} = 2$$

7. **(d):** Liquification of Xe is explained by London forces which arise as a result of momentary, imbalance in electronic distribution.

8. **(d):** AlF_3 has highest melting point because it is an ionic compound and others are covalent.

	PH_3	AsH_3	SbH_3
b.p. (°C) :	–87.5	–62.4	–18.4
	HBr	HCl	HF
b.p. (°C) :	–66.4	–84.8	19.7
	CH_3OCH_3	CH_3SCH_3	CH_3SeCH_3
b.p. (°C) :	24	37	54
	AlF_3	SiF_4	PF_5
m.p. (°C) :	1040	–90	–94

9. **(7):**



10. **(3):** According to Dalton's law,

$$P_{Total} = p_X + p_Y$$

$$1.5 = 1.0 + p_Y \text{ or } p_Y = 0.5 \text{ atm}$$

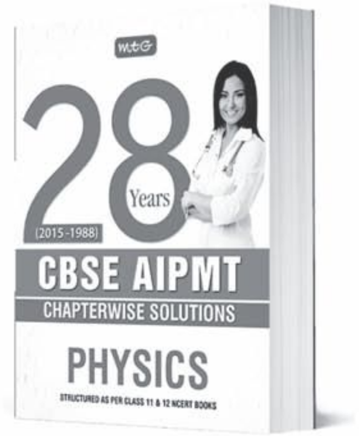
$$PV = nRT \Rightarrow P = \frac{w}{M}RT$$

For gas X, $p_X \times V = \frac{2}{M_X}RT$

For gas Y, $p_Y \times V = \frac{3}{M_Y}RT$

$$\frac{p_X}{p_Y} = \frac{2M_Y}{3M_X} \text{ or } \frac{M_Y}{M_X} = \frac{3}{2} \times \frac{p_X}{p_Y} = \frac{3 \times 1.0}{2 \times 0.5} = 3$$

◆ ◆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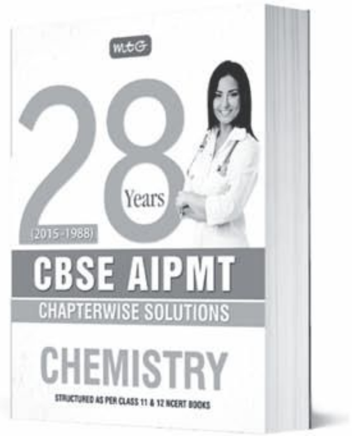
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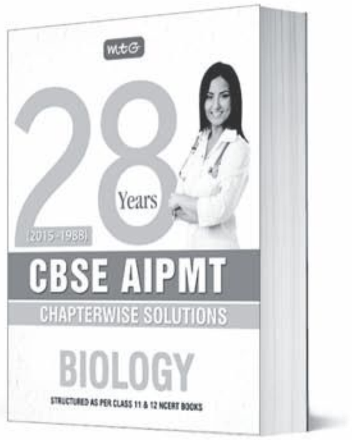
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EXAMINER'S MIND CLASS XII

The questions given in this column have been prepared strictly on the basis of NCERT Chemistry for Class XII.
This year JEE (Main & Advanced)/AIPMT/AIIMS/other PMTs have drawn their papers heavily from NCERT books.

THE SOLID STATE | SOLUTIONS

SECTION - I

Only One Option Correct Type

This section contains 20 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

1. TiO_2 is a well known example of
(a) triclinic system (b) tetragonal system
(c) monoclinic system (d) none of these.

2. Select the incorrect statement.
(a) Higher the value of K_H (Henry's law constant) at a given pressure, lower is the solubility of the gas in the liquid.
(b) Solubility of a gas in a liquid decreases with increase in temperature and pressure.
(c) To minimize the painful effects accompanying the decompression sickness in deep sea divers, O_2 diluted with less soluble He gas is used as breathing gas.
(d) The solubility of a gas in a liquid is governed by Henry's law.

3. Superconductors are derived from compounds of
(a) p-block elements (b) lanthanides
(c) actinides (d) transition elements.

4. During depression of freezing point in a solution the following are in equilibrium
(a) liquid solvent, solid solvent
(b) liquid solvent, solid solute
(c) liquid solute, solid solute
(d) liquid solute, solid solvent.

5. If the ratio of the coordination number of P to that of Q is $y : z$, then the formula of the solid is
(a) P_yQ_z (b) P_zQ_y
(c) $P_{2y}Q_z$ (d) none of these.

6. The values of observed and calculated molecular masses of calcium nitrate are 65.6 and 164 respectively. The degree of dissociation of calcium nitrate will be
(a) 25% (b) 75% (c) 50% (d) 60%

7. Schottky defect occurs mainly in electrovalent compounds where
(a) positive ions and negative ions are of different size
(b) positive ions and negative ions are of same size
(c) positive ions are small and negative ions are big
(d) positive ions are big and negative ions are small.

8. 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) $p_A^\circ/p_B^\circ, (p_A^\circ - p_B^\circ)/p_B^\circ$ (b) $p_A^\circ/p_B^\circ, (p_B^\circ - p_A^\circ)/p_B^\circ$
(c) $p_B^\circ/p_A^\circ, (p_A^\circ - p_B^\circ)/p_B^\circ$ (d) $p_B^\circ/p_A^\circ, (p_B^\circ - p_A^\circ)/p_B^\circ$

9. If a is the length of the side of a cube, the distance between the body centred atom and one corner atom in the cube will be
(a) $\frac{2}{\sqrt{3}}a$ (b) $\frac{4}{\sqrt{3}}a$ (c) $\frac{\sqrt{3}}{4}a$ (d) $\frac{\sqrt{3}}{2}a$

10. A metal crystallises into a lattice containing a sequence of layers as $AB\,AB\,AB\ldots$. What percentage of voids are left in the lattice?
(a) 72% (b) 48% (c) 26% (d) 32%

11. Edge length of a cube is 400 pm. Its body diagonal would be
(a) 600 pm (b) 566 pm
(c) 693 pm (d) 500 pm

12. In a *fcc* arrangement of A and B atoms, where A atoms are at the corners of the unit cell and B atoms are at the face centers, two atoms are missing from two corners in each unit cell, then the simplest formula of the compound is
(a) A_7B_6 (b) A_6B_7
(c) A_7B_{24} (d) AB_4

13. Which of the following statements is false?
(a) Two sucrose solutions of same molality prepared in different solvents have same ΔT_f.
(b) Osmotic pressure, $\pi = MRT$.
(c) Osmotic pressure for 0.01 M aqueous solution; $BaCl_2 > KCl > CH_3COOH >$ Sucrose.
(d) The vapour pressure of a component over a solution is proportional to its mole fraction.

14. Azeotropic mixture of HCl and water has
(a) 84% HCl (b) 22.4% HCl
(c) 63% HCl (d) 20.4% HCl

15. The composition of a sample of wustite is $Fe_{0.93}O_{1.00}$. Percentage of iron present in the form of iron(III) is nearly
(a) 85% (b) 14% (c) 7% (d) 93%

16. An element (at. wt. = 50) crystallises in *fcc* lattice, with a = 0.50 nm. What is the density of unit cell if it contains 0.25% Schottky defects (use $N_A = 6 \times 10^{23}$)?
(a) 2.0 g/cc (b) 2.66 g/cc
(c) 3.06 g/cc (d) None of these.

17. How many 'nearest' and 'next nearest' neighbours respectively, potassium have in *bcc* lattice?
(a) 8, 8 (b) 8, 6 (c) 6, 8 (d) 8, 2

18. On mixing 10 mL of carbon tetrachloride with 10 mL of benzene the total volume of the solution is
(a) > 20 mL (b) < 20 mL
(c) = 50 mL (d) cannot be predicted.

19. An insulator oxide is
(a) CuO (b) CoO (c) Fe_2O_3 (d) all of these.

20. A 0.004 M solution of Na_2SO_4 is isotonic with a 0.01 M solution of glucose at same temperature. The apparent degree of dissociation of Na_2SO_4 is
(a) 25% (b) 50% (c) 75% (d) 85%

SECTION - II

One or More Options Correct Type

This section contains 5 multiple choice questions. Each question has four choices (a), (b), (c) and (d), out of which ONE or MORE are correct.

21. In a body-centred cubic unit cell
(a) the edge length is equal to $\frac{4r}{\sqrt{3}}$
(b) the edge length is equal to $2r^2 + 2r^2$
(c) the edge length is equal to $\frac{2d}{\sqrt{3}}$ where d is the minimum distance between two lattice points
(d) the square of the edge length is equal to $16r^2$ where 'r' is the radius of a lattice point.

22. Consider the following solutions :
I : 1 M aqueous glucose solution
II : 1 M aqueous sodium chloride solution
III : 1 M aqueous ammonium phosphate solution
IV : 1 M benzoic acid in benzene
Select the correct statements for the above solutions.
(a) All are isotonic solutions.
(b) III is hypertonic of I, II and IV.
(c) IV is hypotonic of I, II and III.
(d) II is hypotonic of III but hypertonic of I and IV.

23. Which of the following is/are correctly matched?
(a) $MgCl_2$: Molecular crystal
(b) I_2 : Covalent network crystal
(c) H_2O(ice) : Molecular crystal
(d) Diamond : Covalent network crystal

24. Which of the following conditions are correct for a binary solution, in which the solute as well as the solvent are liquid?
(a) C_6H_6 and $C_6H_5CH_3$; $\Delta H_{solution} > 0, \Delta V_{solution} = 0$
(b) CH_3COCH_3 and $CHCl_3$; $\Delta H_{solution} < 0$, $\Delta V_{solution} < 0$
(c) H_2O and HCl; $\Delta H_{solution} > 0, \Delta V_{solution} < 0$
(d) H_2O and C_2H_5OH, $\Delta H_{solution} > 0, \Delta V_{solution} > 0$

25. For the orthorhombic crystal system
(a) no two sides are equal *i.e.*, $a \neq b \neq c$
(b) all crystallographic angles are equal to 90° *i.e.*, $\alpha = \beta = \gamma = 90°$
(c) three kinds of unit cell are found, these are primitive, body centred and face centred
(d) all the four unit cells are found.

SECTION - III

Paragraph Type

This section contains 2 paragraphs each describing theory, experiment, data, etc. Six questions relate to two paragraphs with three questions on each paragraph. Each question of a paragraph has only one correct answer among the four choices (a), (b), (c) and (d).

Paragraph for Questions 26 to 28

When a solid solute is added to the solvent, some solute dissolves and its concentration increases in solution. The process is known as dissolution. Some solute particles in solution collide with the solid solute particles and get separated out of solution. This process is known as crystallisation. A stage is reached when the two processes occur at the same rate and a state of dynamic equilibrium is reached.

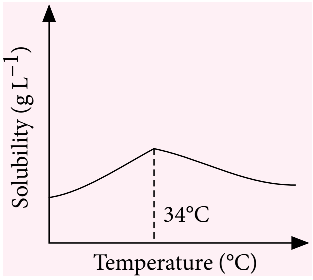
$$\text{Solute} + \text{Solvent} \rightleftharpoons \text{Solution}$$

The equilibrium being dynamic follows Le Chateliers principle. The solution which is in dynamic equilibrium with undissolved solute is the saturated solution and contains the maximum amount of solute dissolved in a given amount of solvent. Thus, the concentration of solute in such a solution is its solubility.

26. When KCl dissolves in water
(a) $\Delta H = +$ ve, $\Delta S = +$ ve, $\Delta G = +$ ve
(b) $\Delta H = +$ ve, $\Delta S = -$ ve, $\Delta G = -$ ve
(c) $\Delta H = +$ ve, $\Delta S = +$ ve, $\Delta G = -$ ve
(d) $\Delta H = -$ ve, $\Delta S = -$ ve, $\Delta G = +$ ve

27. During dissolution of a solute in a solvent, following three interactions operate.
I : Solvent—Solvent
II : Solute—Solvent
III : Solute—Solute
Which of the following take place with the absorption of heat?
(a) I, II (b) II, III (c) I, II, III (d) I, III

28. Solubility curve of $Na_2SO_4.10H_2O$ in water with temperature is given (*see* figure). Identify the correct statement.



(a) Solution process is exothermic.
(b) Solution process is exothermic till 34°C and endothermic after 34°C.
(c) Solution process is endothermic till 34°C and exothermic thereafter.
(d) Solution process is endothermic.

Paragraph for Questions 29 to 31

Spinel is the mineral in which oxide ions are arranged in *ccp* with dipositive ions occupying $\frac{1}{8}$th of the tetrahedral holes and tripositive ions occupying $\frac{1}{2}$ of the octahedral holes.

29. The formula of the spinel is
(a) $MgAl_2O_4$ (b) Mg_2AlO_4
(c) $MgO.Al_2O_3$ (d) none of these.

30. If oxide ion is replaced by $X^{-8/3}$, the number of anionic vacancies per unit cell is
(a) 1 (b) 2 (c) 3 (d) none of these.

31. In the inverse spinel structure, tripositive ions occupy
(a) tetrahedral holes (b) octahedral holes
(c) both tetrahedral and octahedral holes
(d) none of these.

SECTION - IV

Matching List Type

This section contains 3 multiple choice questions. Each question has matching lists. The codes for the lists have choices (a), (b), (c) and (d), out of which ONLY ONE is correct.

32. Match the closest packing of identical spheres given in List I with the characteristics given in List II and select the correct answer using the codes given below the lists :

	List I		List II
P.	*AAAA* packing	1.	*ccp*; CN = 12
Q.	*ABAB* packing	2.	*hcp*, CN = 12
R.	*ABCABC* packing	3.	*bcc*, CN = 8
S.	Square close packing	4.	Primitive cubic, CN = 6

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

33. Match the pair of substances given in List I with the type of forces operating between them given in List II and select the correct answer from the codes given below the lists :

	List I		List II
P.	KCl/H_2O	1.	Ion-dipole
Q.	C_6H_6/CCl_4	2.	H-bond
R.	HF/H_2O	3.	Dipole-dipole
S.	HCl/CH_3CN	4.	London dispersion

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

34. Match the substances given in List I with their magnetic properties given in List II and select the correct answer from the codes given below the lists :

	List I		List II
P.	CrO_2	1.	Anti-ferromagnetic
Q.	V_2O_5	2.	Ferromagnetic
R.	V_2O_3	3.	Paramagnetic
S.	TiO	4.	Diamagnetic

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

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :

(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** Anionic vacancies in alkali halides are produced by heating the alkali halide crystals with alkali metal vapour.
Reason : Electrons trapped in anionic vacancies are called F-centres.

36. **Assertion :** Non-ideal solutions form azeotropic mixture.
Reason : Boiling point of azeotropic mixture is always higher than boiling points of both the components.

37. **Assertion :** On heating ferromagnetic or ferrimagnetic substances, they become paramagnetic.
Reason : The electrons change their spin on heating.

38. **Assertion :** Osmotic pressure of 1 M glucose is lesser than 1 M $NaCl_{(aq)}$ but vapour pressure of 1 M glucose is higher than 1 M $NaCl_{(aq)}$.

Reason : Osmotic pressure is a colligative property but vapour pressure is not colligative property however lowering in vapour pressure is a colligative property.

39. **Assertion :** It is difficult to cook food at hills.
Reason : The boiling point of water increases at hills.

40. **Assertion :** Molecular mass of polymers cannot be calculated using boiling point or freezing point method.
Reason : Polymer solutions do not possess a constant boiling point or freezing point.

SECTION - VI

Integer Value Correct Type

This section contains 10 questions. The answer to each question is a single digit integer, ranging from 0 to 9 (both inclusive).

41. In a solution of 7.8 g benzene and 46.0 g toluene, the mole fraction of benzene is $1/y$. The value of y is

42. 18 g $C_n(H_2O)_n$ in 100 g H_2O lowers the freezing point of water by 1.86 K. Molal depression constant of water is 1.86 K kg mol^{-1}. The value of n is

43. The ratio of the value of any colligative property for KCl solution to that of sugar solution is

44. Total number of steps involved in the formation of $Na^+_{(g)}\,Cl^-_{(g)}$ lattice from $Na_{(s)}$ and $Cl_{2(g)}$ is

45. A certain mass of a substance when dissolved in 100 g of C_6H_6 lowers the freezing point by 1.28°C. The same mass of solute 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, then it produces n number of ions. n is
[K_f for H_2O and C_6H_6 are 1.86 and 5.12 K kg mol^{-1} respectively].

46. Al^{3+} ions replace Na^+ ions at the edge centres of NaCl lattice. The number of vacancies in one mole of NaCl is found to be $x \times 10^{23}$. The approximate value of x is

47. NH_4^+ and Br^- ions have ionic radii of 143 pm and 196 pm respectively. The coordination number of NH_4^+ ion in NH_4Br is

48. The molality of a sulphuric acid solution in which the mole fraction of water is 0.86, is

49. van't Hoff factor of an electrolyte A_2B_3 assuming that it ionizes 75% in the solution is

50. In hexagonal close packing, the difference in the number of tetrahedral and octahedral voids per unit cell is

SOLUTIONS

1. **(b) :** TiO_2 has tetragonal system with axial lengths $a = b \neq c$ and axial angles $\alpha = \beta = \gamma = 90°$.

2. **(b) :** The solubility of a gas in a liquid decreases with increase in temperature and increases with increase in pressure.

3. **(a)** 4. **(a)**

5. **(b) :** As the ratio of the coordination number of P to that of Q is $y : z$, P is surrounded by y atoms of Q and Q is surrounded by z atoms of P.
i.e., number of atoms of P is z and number of atoms of Q is y.
$\therefore$ the formula is P_zQ_y.

6. **(b) :** $i = \dfrac{M_{\text{calculated}}}{M_{\text{observed}}} = \dfrac{164}{65.6} = 2.5$

$$\alpha = \frac{i-1}{n-1} = \frac{2.5-1}{3-1} = 0.75 = 75\%$$

7. **(b)**

8. **(b) :** $p_A = x_A p^\circ_A,\ p_B = x_B p^\circ_B$

$$y_A = \frac{p_A}{p_A + p_B} = \frac{x_A p^\circ_A}{x_A p^\circ_A + x_B p^\circ_B} = \frac{x_A p^\circ_A}{x_A p^\circ_A + (1 - x_A) p^\circ_B}$$

$$= \frac{x_A p^\circ_A}{x_A(p^\circ_A - p^\circ_B) + p^\circ_B}$$

or $$\frac{1}{y_A} = \frac{x_A(p^\circ_A - p^\circ_B) + p^\circ_B}{x_A p^\circ_A}$$

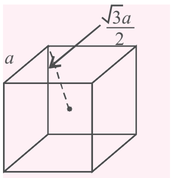
or $$\frac{1}{y_A} = \frac{p^\circ_A - p^\circ_B}{p^\circ_A} + \frac{p^\circ_B}{p^\circ_A}\frac{1}{x_A}$$

or $$\frac{1}{x_A} = \left(\frac{1}{y_A} - \frac{p^\circ_A - p^\circ_B}{p^\circ_A}\right)\frac{p^\circ_A}{p^\circ_B}$$

$$\Rightarrow \frac{1}{x_A} = \frac{p^\circ_A}{p^\circ_B}\frac{1}{y_A} + \frac{p^\circ_B - p^\circ_A}{p^\circ_B}$$

Hence, the plot of $\frac{1}{x_A}$ versus $\frac{1}{y_A}$ will be linear with slope $= p^\circ_A/p^\circ_B$ and intercept $= \frac{(p^\circ_B - p^\circ_A)}{p^\circ_B}$

9. **(d) :** The distance between the body centred atom and one corner atom is $\frac{\sqrt{3}a}{2}$ *i.e.*, half of the body diagonal.



10. **(c) :** *ABAB* packing is hexagonal close-packing in which all atoms occupy 74% of the total space. Hence, 26% of voids are left in the lattice.

11. **(c) :** $a = 400$ pm

Body diagonal $= \sqrt{3}\,a = \sqrt{3} \times 400 = 693$ pm

12. **(d) :** As two *A* atoms are missing from the corners,

No. of *A* atoms per unit cell $= \frac{1}{8} \times 6 = \frac{6}{8} = \frac{3}{4}$

No. of *B* atoms per unit cell $= \frac{1}{2} \times 6 = 3$

$\therefore$ Formula $= A_{3/4}B_3 = AB_4$

13. **(a) :** K_f is different for different solvents.

14. **(d)**

15. **(b) :** Let the sample contains 93 iron ions and 100 oxide ions.

Total negative charge on oxide ions

$= 2 \times 100 = 200$

Let the number of ions as $Fe^{3+} = x$

$\therefore$ Number of Fe^{2+} ions $= 93 - x$

$x \times 3 + (93 - x) \times 2 = 200$

$3x + 186 - 2x = 200$

$x = 200 - 186 = 14$

Percentage of iron as Fe^{3+} is 14%.

16. **(b) :** $d = \frac{Z \times M}{a^3 \times N_A}$ For *fcc*, $Z = 4$

$$d = \frac{4 \times 50}{(0.50 \times 10^{-9})^3 \times 6 \times 10^{23}} = 2.66 \times 10^6 \text{ g m}^{-3}$$

If it contains 0.25% Schottky defects, then

$$d' = 2.66 \times 10^6 \times \frac{0.25}{100} = 6.65 \times 10^3 \text{ g m}^{-3}$$

$d'' = d - d' = 2.66 \times 10^6 - 6.65 \times 10^3$ g m^{-3}

$= 2.65 \times 10^6$ g m^{-3} $= 2.65$ g cm^{-3}

17. **(b)**

18. **(a) :** Carbon tetrachloride and benzene will form non-ideal solution showing positive deviations.

Hence $\Delta V_{mix} = +$ ve

i.e. Final volume > Initial volume.

19. **(d)**

20. **(c) :** $\pi_{Na_2SO_4} = \pi_{Glucose}$

$$i = \frac{1 + (n-1)\alpha}{1}$$

where n is no. of ions produced which is 3 for Na_2SO_4.

$$i = \frac{1 + (3-1)\alpha}{1} = 1 + 2\alpha$$

$CRT(1 + 2\alpha) = CRT$

$0.004(1 + 2\alpha) = 0.01 \therefore \alpha = 0.75 = 75\%$

21. **(a, c)**

22. **(b, c, d) :** Osmotic pressure is a colligative property, depends on i factor also.

$\Rightarrow \pi_{glucose} = MRT\ \{i = 1\}$

$\pi_{NaCl_{(soln)}} = 2\ MRT\ \{i = 2\}$

$\pi_{(NH_4)_3PO_4} = 4\ MRT\ \{i = 4\}$

$\pi_{C_6H_5COOH} = \frac{1}{2}\ MRT \left\{i = \frac{1}{2}\right\}$

Hence, the order of osmotic pressures is

III > II > I > IV

23. **(c, d) :** $MgCl_2$ — Ionic crystal

I_2 — Molecular crystal

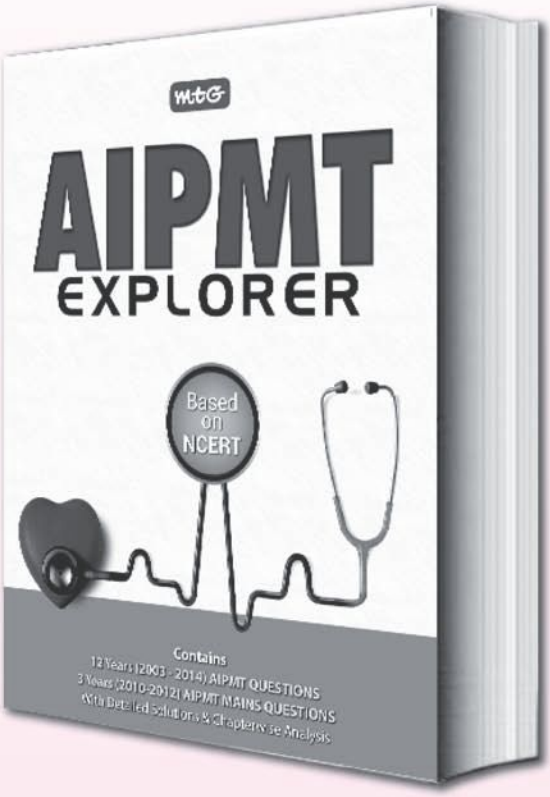
24. **(b, d) :** C_6H_6 and $C_6H_5CH_3$ forms ideal solution, $\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$.

CH_3COCH_3 and $CHCl_3$ forms non-ideal solution showing negative deviation, $\Delta H_{mix} = -$ve, $\Delta V_{mix} = -$ve.

H_2O and HCl forms non-ideal solution showing negative deviation, $\Delta H_{mix} = -$ve, $\Delta V_{mix} = -$ve.

H_2O and C_2H_5OH forms non-ideal solution showing positive deviation; $\Delta H_{mix} = +$ve, $\Delta V_{mix} = +$ve.

25. **(a, b, d) :** All the four unit cells are found *i.e.*, primitive, body centred, face centred, end centred.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26. (c)

27. (d) : Energy is used in breaking solute-solute and solvent-solvent interactions.

28. (c) : In general, if in a nearly saturated solution, the dissolution process is endothermic ($\Delta H_{sol} > 0$), the solubility should increase with rise in temperature and if it is exothermic ($\Delta H_{sol} < 0$) the solubility should decrease.

29. (a) : Let the number of oxide ions in *ccp* be *n*.

$\therefore$ No. of dipositive ions $= \frac{1}{8} \times 2n = \frac{n}{4}$

and No. of tripositive ions $= \frac{n}{2}$

$\therefore$ Formula of the spinel is $Mg_{\frac{n}{4}}Al_{\frac{n}{2}}O_n$ or $MgAl_2O_4$.

30. (a) : To balance the charge, 4 oxide ions will be replaced by $3X^{-8/3}$ ions hence, one anionic vacancy per unit cell will be created.

31. (c) **32. (a)** **33. (b)** **34. (a)**

35. (b) : When NaCl is heated in an atmosphere of Na vapour, Na atoms deposit on the surface of NaCl crystal. Cl^- ions then diffuse to the surface where they combine with the Na atoms which become ionized by losing electrons. These electrons diffuse back into the crystals and create F-centres.

36. (c) **37. (a)** **38. (b)**

39. (c) : Water boils at lower temperature due to low atmospheric pressure at hills.

40. (c) : Molecular mass of polymers cannot be calculated using boiling point or freezing point method because the changes observed in these properties are very small.

41. (6) : $x_{\text{benzene}} = \dfrac{7.8/78}{7.8/78 + 46/92} = \dfrac{1}{6}$

42. (6) : $\Delta T_f = K_f \times m$

$$\Delta T_f = \frac{K_f \times w_2 \times 1000}{M_2 \times w_1} \Rightarrow 1.86 = \frac{1.86 \times 18 \times 1000}{M \times 100}$$

$\Rightarrow M = 180\text{ g} \Rightarrow 12n + 18n = 180\text{ g} \Rightarrow n = 6$

43. (2) : For KCl *i* equal to 2 and for sugar *i* equal to 1.

$$\therefore \frac{\text{Colligative property}_{(KCl)}}{\text{Colligative property}_{(sugar)}} = 2$$

44. (5)

45. (3) : $\Delta T_f = \dfrac{1000 \times K_f \times w}{M \times W}$

For the solution in benzene,

$$1.28 = \frac{1000 \times 5.12 \times w}{M_N \times 100} \quad (M_N = \text{Normal mol. mass}) \quad ...(i)$$

For the solution in water in which solute dissociates

$$1.40 = \frac{1000 \times 1.86 \times w}{M_{exp.} \times 100} \quad ...(ii)$$

Dividing eq. (ii) by (i),

$$i = \frac{M_N}{M_{exp.}} = \frac{1.40}{1.28} \times \frac{5.12}{1.86} = 3.01 \approx 3.0$$

Now, suppose that formula of solute is

$$\begin{array}{ccccc} A_xB_y & \rightleftharpoons & xA^{y+} & + & yB^{x-} \\ 1 & & 0 & & 0 \\ (1-\alpha) & & x\alpha & & y\alpha \end{array}$$

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

$\because$ $i = 3$ and $\alpha = 1$ (Given : $\alpha = 1$)

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

46. (3) : One mole of NaCl contains one mole of Na^+ ions, *i.e.*, 6.023×10^{23} Na^+ ions.

NaCl has *fcc* arrangement of Cl^- ions and Na^+ ions are present at the edge centres and body-centre. As there are 12 edge centres and each edge centre is shared by 4 unit cells, their contribution per unit cell $= \frac{1}{4} \times 12 = 3$

Contribution of Na^+ ion at the body-centre = 1. Thus, for every 4 Na^+ ions, the ions present at the edge centres = 3. This means that Na^+ ions which have been replaced $= \frac{3}{4} \times 6.023 \times 10^{23} = 4.517 \times 10^{23}$

1 Al^{3+} ion will replace 3 Na^+ ions to maintain electrical neutrality. One vacancy will be occupied by Al^{3+} ion and the remaining 2 will be vacant. Hence, no. of vacancies in one mole of NaCl

$= \frac{2}{3} \times 4.517 \times 10^{23} = 3.01 \times 10^{23}$

47. (6) : Radius ratio lies in the range 0.414 – 0.732 hence, coordination number is 6.

48. (9) : Mole fraction of H_2SO_4 in the solution $= 1 - 0.86 = 0.14$

$$\frac{n_2}{n_1 + n_2} = 0.14$$

$\therefore$ $\dfrac{n_2}{55.55 + n_2} = 0.14$ or $n_2 = 0.14\, n_2 + 7.777$

or $0.86\, n_2 = 7.777$ or $n_2 = 9.0$

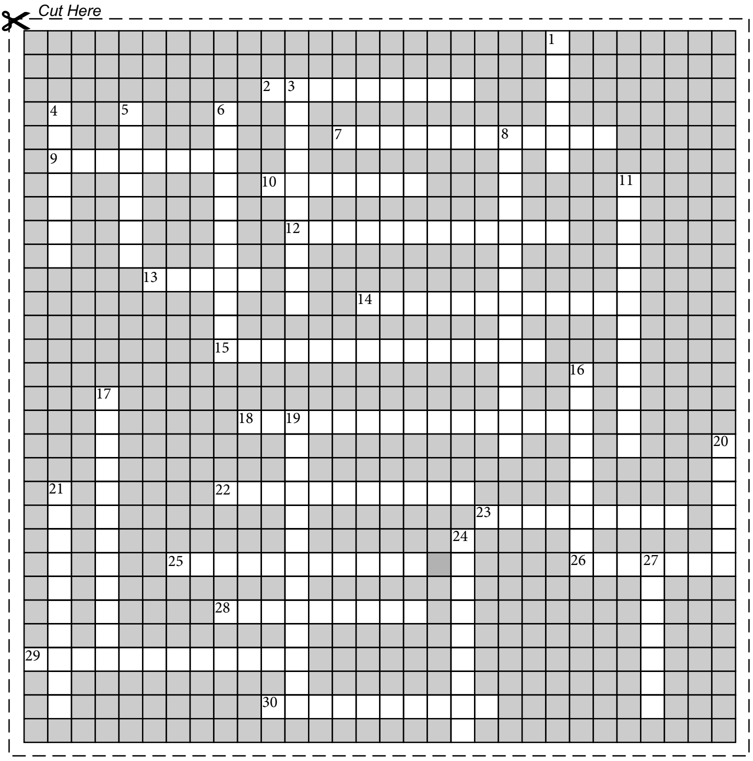
49. (4) : Total moles after dissociation $= 0.25 + 1.5 + 2.25 = 4 \therefore i = 4$

50. (6)

◆◆

CROSS WORD

Readers can send their answer with complete address before 15th of every month to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.



ACROSS

2. Gas used for artificial ripening of fruits. (9)
7. A plant extract that has a distinctive odour or flavour. (12)
9. The process of coating a photographic plate with a colloidal solution of AgBr. (8)
10. Crystalline form of boron nitride which is harder than diamond. (7)
12. The instrument used for measuring radioactivity. (12)
13. Gas used to create inert atmosphere in chemical reactions. (5)
14. A basic carbonate of magnesium. (12)
15. Vitamin which occurs only in animals. (14)
18. Fraction of volume in a crystal structure that is occupied by constituent particles. (15)
22. Reaction used to convert an α-haloester to β-hydroxy ester using zinc metal followed by mild hydrolysis. (11)
23. Fertilizer containing about 38% N and P_2O_5. (9)
25. Super alloys, highly resistant to oxidation at high temperature. (11)
26. Two peaks or bands of about equal intensity appearing close together on a spectrogram. (7)
28. A soap like emulsifier that contains a sulphate or a phosphate group instead of a carboxylate group. (9)
29. A household bleach. (12)
30. Globular proteins which protect us from diseases. (10)

DOWN

1. The term used for isotopic mixture of H^+, D^+ and T^+. (6)
3. The quantitative application of Faraday's law to the analysis of materials. (10)
4. Species containing an electrically neutral univalent carbon atom with three non bonding electrons. (7)
5. Compounds formed between urea and acetylating agents. (7)
6. Substances which absorb moisture from air without changing their state. (11)
8. The tendency of more electronegative substituent to form bond with the hybrid orbital having less *s*-character. (14)
11. Substances whose solutions can pass through filter paper as well as animal membrane. (12)
16. Colourless form of phenolphthalein in acidic medium. (9)
17. Indicator prepared by coupling diazonium salt of sulphanilic acid with *N*, *N*-dimethylaniline. (12)
19. Building block of zeolite. (13)
20. The phenomenon of adding broken glass pieces during glass making. (6)
21. The material in a distillation apparatus that is collected in the receiver. (10)
24. SI derived unit of radioactivity which equates to one decay per second. (9)
27. The heaviest stable element. (7)

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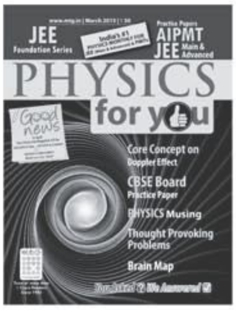

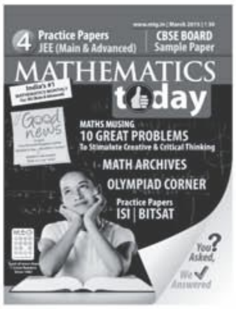

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