

The Solid State

EXERCISES

ELEMENTARY

- Q.1** (2)
 NaCl is a ionic solid in which constituent particles are positive (Na^+) and negative (Cl^-) ions.
- Q.2** (4)
 (4) Amorphous solids have short range order but no sharp in melting point.
- Q.3** (3)
 Iodine crystals are molecular crystals, in which constituent particles are molecules having interparticle forces are Vander Waal's forces.
- Q.4** (4)
 Sugar is a crystalline solid while glass, rubber and plastic are amorphous solids.
- Q.5** (1)
 Amorphous solids neither have ordered arrangement (*i.e.* no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquids. It is therefore they are regarded as super-cooled liquids.
- Q.6** (4)
 Amorphous solids neither have ordered arrangement (*i.e.* no definite shape) nor have sharp melting point like crystals, but when heated, they become pliable until they assume the properties usually related to liquids. It is therefore they are regarded as super-cooled liquids.
- Q.7** (3)
- Q.8** (4)
 Due to free electrons.
- Q.9** (2)
 A crystal system is hexagonal if its unit cell having $a = b \neq c$ axial ratio and $\alpha = \beta = 90^\circ$, $\gamma = 120^\circ$ axial angles.
- Q.10** (3)
 (3) Rhombohedral crystal system
 $a = b = c$, $\alpha = \beta = \gamma \neq 90^\circ$
 ex - NaNO_3 , CaSO_4 , calcite CaCO_3 , HgS
- Q.11** (2)
 (2) Tetragonal system has the unit cell dimension $a = b \neq c$, $\alpha = \beta = \gamma = 90^\circ$.
- Q.12** (3)
 Each unit cell of NaCl contains 4 NaCl units.
- Q.13** (1)
 Face-centred cubic lattice found in KCl and NaCl .
- Q.14** (3)
 (3) $ABAB \dots$ is hexagonal close packing.
- Q.15** (2)
 Co-ordination number in $\text{HCP} = 12$
 Co-ordination number in Mg is also = 12
- Q.16** (2)
 Distance between K^+ and $\text{F}^- = \frac{1}{2} \times$ length of the edge
- Q.17** (3)
 $58.5 \text{ g NaCl} = 1 \text{ mole} = 6.02 \times 10^{23} \text{ Na}^+ \text{Cl}^- \text{ units}$.
 One unit cell contains 4 $\text{Na}^+ \text{Cl}^-$ units. Hence number of unit cell present

$$= \frac{6.02 \times 10^{23}}{4} = 1.5 \times 10^{23}$$
- Q.18** (4)
 For bcc , $d = \frac{\sqrt{3}}{2} a$ or

$$a = \frac{2d}{\sqrt{3}} = \frac{2 \times 4.52}{1.732} = 5.219 \text{ \AA} = 522 \text{ pm}$$

$$\rho = \frac{Z \times M}{a^3 \times N_0 \times 10^{-30}} = \frac{2 \times 39}{(522)^3 \times (6.023 \times 10^{23}) \times 10^{-30}}$$

$$= 0.91 \text{ g/cm}^3 = 910 \text{ kg m}^{-3}$$
- Q.19** (1)
 $4r = \sqrt{3} a$ $r = \frac{\sqrt{3}}{4} a$
- Q.20** (2)
 The system $ABCABC \dots$ is also referred to as face-centred cubic or fcc .

- Q.21** (1)
BCC has a coordination number of 8.
- Q.22** (1)
For body centred cubic arrangement co-ordination number is 8 and radius ratio (r_+/r_-) is $0.732 - 1.000$.
- Q.23** (4)
Number of octahedral sites = Number of sphere in the packing.
- Q.24** (2)
In ZnS structure, sulphide ions occupy all FCC lattice points while Zn^{2+} ions are present in alternate tetrahedral voids.
- Q.25** (2)
Every constituent has two tetrahedral voids. In *ccp* lattice atoms

$$= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$$
 \therefore Tetrahedral void = $4 \times 2 = 8$,
 Thus ratio = $4 : 8 :: 1 : 2$.
- Q.26** (1)

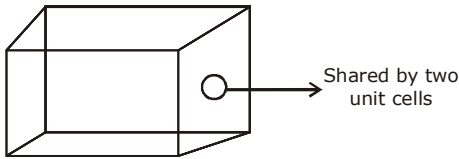
$$r = \frac{a}{2\sqrt{2}}; \quad r = \frac{620}{2\sqrt{2}} = 219.25 \text{ pm}$$
- Q.27** (2)
In $NaCl$ crystal Na^+ ions has coordination number 6.
- Q.28** (2)

$$r_+/r_- = \frac{180}{187} = 0.962$$
 which lies in the range of $0.732 - 1.000$, hence co-ordination number = 8 *i.e.* the structure is $CsCl$ type.
- Q.29** (1)
- Q.30** (1)
As each Sr^{2+} ion introduces one cation vacancy, therefore concentration of cation vacancies = mol % of $SrCl_2$ added.
- Q.2** (4)
Rubber, P lastics and glass, all are amorphous solids so
- Q.3** (1)
Zns is ionic crystal
- Q.4** (1)
LiF is an ionic crystal
- Q.5** (1)
A solid having no definite shape is called Amorphous
- Q.6** (1)
In Bravais lattices, each point has identical surroundings.
- Q.7** (1)
Refer Theory.
- Q.8** (1)
Since half of the atom is inside the unit cell.
- Q.9** (1)
In B.C.C

$$4r = a\sqrt{3}$$

$$2r = 1.73a$$

$$2 \times 1.73a = a\sqrt{3}$$

$$Q = 200 \times 10^{-12} \text{ m} = 200 \text{ pm}$$
- Q.10** (2)

- Q.11** (2)

$$4r = a\sqrt{2}$$

$$a = \frac{4r}{\sqrt{2}} = \frac{4 \times 1.28}{\sqrt{2}} \text{ \AA} = 3.62 \text{ \AA}$$
- Q.12** (2)
Close packing is maximum in either face centred or in hexagonal
- Q.13** (C)
The arrangement of sphere is shown by body diagonal plane.

JEE-MAIN**OBJECTIVE QUESTIONS**

- Q.1** (C)
KCl & $BaCl_2 \cdot 2H_2O$ are ionic solids and not pseudo solids (amorphous solids).

Q.14 (1)
It is a fact.

Q.15 (1)
In a bcc an atom will be shared by only one unit cell.

Q.16 (3)
In a face centred cubic lattice the number of nearest neighbour for a given lattice point 12.

Q.17 (2)

$$w = \frac{1}{8} \times 8 = 1$$

$$Na = 1$$

$$O = 12 \times 1/4 = 3$$

$$\Rightarrow Na_2O_3$$

Q.18 (B)
Coordination no. 8 for both is possible only in Body central cubic crystal.

Q.19 (2)

$$r_+ + r_- = \frac{a\sqrt{3}}{2} = \frac{480 \times \sqrt{3}}{2}$$

$$r_+ + 225 = 240\sqrt{3}$$

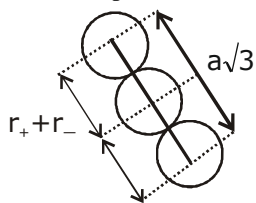
$$r_+ = 240 \times 1.732 - 225$$

$$r_+ = 190.68 \text{ pm}$$

Q.20 (1)

$$r_+ + r_- = \frac{a\sqrt{3}}{2} = \frac{387}{2}\sqrt{3}$$

$$= 335.15 \text{ pm}$$



Q.21 (1)
 for X, $8 \times \frac{1}{8} = 1$
 for Y, $6 \times \frac{1}{2}$
 so AB_3

Q.22 (4)
Total body diagonal = 4
two atoms in each body diagonal

so total number of atoms = $4 \times 2 = 8$
and 8 atom on each corner, So its contribution will be

$$= \frac{1}{8} \times 8 = 1$$

so total number of atoms = $8 + 1 = 9$

Q.23 (3)
 $\rightarrow Cu \rightarrow ccp$ so 4 atoms
 $\rightarrow Ag$ is at edge centre

each edge has its contribution $\frac{1}{4}$ so, total number of silver.

$$= \frac{1}{4} \times 12 = 3$$

$\rightarrow Au$ is present at the body so its contribution will be 1.

so formula will be Cu_4Ag_3Au .

Q.24 (3)
There are 7 atoms at the corner.

so contribution by 7 atoms form corner will be $\frac{7}{8}$

$$\text{thus } A = \frac{7}{8}$$

B will be at face so total contribution by it will be 3.

$$= \frac{A_7}{8} B_3$$

$$= A_7 B_{24}$$

Q.25 (3)
for X, $6 \times \frac{1}{8} = \frac{3}{4}$

$$\text{for Y, } 6 \times \frac{1}{2} = 3$$

so $X_{3/4} Y_3$ or $X_3 Y_{12}$ or XY_4

Q.26 (D)
for X, $8 \times \frac{1}{8} = 1$

$$\text{for Y, } 6 \times \frac{1}{2} = 3$$

so, XY_3

Q.27 (1)

$$\text{No. of X atom per unit cell} = 7 \times \frac{1}{8} = \frac{7}{8}$$

$$\text{No. of Y atom per unit cell} = 6 \times \frac{1}{2} = 3$$

$$\therefore \text{Formula} = X_{7/8} Y_3 \text{ or } X_7 Y_{24}$$

Q.28 (2)

$$X = 7 \times \frac{1}{8} = \frac{7}{8}; Y = \frac{1}{2} \times 6 = 3; Z = \frac{1}{8} \Rightarrow X_{7/8} Y_3 Z_{1/8}$$

$$8 = X_7 Y_{24} Z$$

Q.29 (B)

$$N_a = 1 \times 1 = 1$$

$$W = 8 \times \frac{1}{8} = 1 \Rightarrow \text{NaWO}_3$$

$$O = 12 \times \frac{1}{4} = 3.$$

Q.30 (1)

$$\text{Density} = z \times \frac{M}{N_a a^3}$$

$$1.9893 = \frac{4 \times 74.5}{N_a \times (6.2908 \times 10^{-8})^3}$$

$$N_o = 6.03 \times 10^{23}$$

Q.31 (1)

$$P = Z \times \frac{N}{N_a a^3}$$

$$= \frac{2 \times 23}{6.02 \times 10^{23} \times 4.24 \times 4.24 \times 4.24 \times 10^{-24}}$$

$$= \frac{0.1002}{10^{-1}} = 1.002 \text{ g cm}^{-3}$$

Q.32 (2)Simple cubic lattice \rightarrow B.C.C

So the Z will increase

so density will increase

Q.33 (2)

$$6 \text{ face centred atom contribution} = 6 \times \frac{1}{2} = 3 \text{ atom}$$

and 3 atom

and 3 atoms are enclosed

so total number of enclosed atom in the unit cell

$$= 3 + 3 = 6 \text{ atom}$$

Q.34 (3)

$$a = 2\sqrt{2} r$$

$$\therefore v = a^3 = 16\sqrt{2} r^3 = 16 \times \sqrt{2} \times (2 \times 10^{-8})^3 = 1.8 \times 10^{-22} \text{ cm}^3$$

Q.35 (3)

Z is ccp so its total number 4.

X atom occupy tetrahedral void so its

total number will be 8

$$X_8 Z_4 = X_2 Z$$

Q.36 (3)In ABB AABBA, there is no close packing as there are repeated planes adjacent to each other.**Q.37** (3)

For N spheres, the number of tetrahedral holes is 2N

Q.38 (3)

I & II represent octahedral holes.

Q.39 (1)

Only force (4) tetrahedral holes are occupied in diamond.

Q.40 (3)

No. of A atoms = 6.

$$\text{No. of C atoms} = 6 \times \frac{2}{3} = 4.$$

$$\therefore \text{Formula} = C_4 A_6 \text{ or } C_2 A_3.$$

Q.41 (1)No. of octahedral holes = No. of close packed atoms & No. of Tetrahedral holes = 2 \times No. of close packed atoms.**Q.42** (A)**Q.42** (1)

O is in ccp so total number of atom 4

$$A \text{ is occupied in } \frac{1}{6} \text{ of T.V. so } \frac{8}{6}$$

$$B \text{ is occupied in } \frac{1}{3} \text{ of O.V so } \frac{4}{3}$$

$$A_{\frac{8}{6}} B_{\frac{4}{3}} O_4$$

$$= A_{\frac{4}{3}} B_{\frac{4}{3}} O_4$$

or ABO_3

Q.44 (4)
No. of octahedral holes = No. of spheres forming close packed array.

Q.45 (1)
Refer theory.

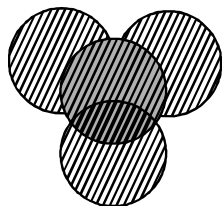
Q.46 (3)
Ionic solid having C.N. = 6 cation in octahedral holes.

$$\text{Hence, } 0.414 < \left(\frac{r_+}{r_-}\right) < 0.732.$$

Q.47 (3)
 $\frac{r_+}{r_-} = \frac{126}{216} = 0.58$, octahedral voids so C.N. = 6.

Q.48 (3)
Centre of edge is octahedral void so

Q.49 (3)
By the formation of tetrahedral void



Q.50 (2)
 $r_a + r_b = a\sqrt{3}/4$

$$4r_a = a\sqrt{2}$$

$$\Rightarrow \frac{r_a + r_b}{r_a} = \sqrt{3}/2$$

$$\Rightarrow r_b = (\sqrt{1.5} - 1)r_a$$

$$r_b = 0.225 r_a$$

Q.51 (2)
 $r_{Zn^{2+}} = 0.225 r_{S^{2-}}$
(from 12th questions)

$$r_{S^{2-}} = \frac{r_{Zn^{2+}}}{0.225} = \frac{22.5}{0.225} = 100 \text{ pm}$$

Q.52 (2)
NaCl has octahedral structure
 $2r_+ + 2r_- = a$

$$r_+ + r_- = \frac{a}{2}$$

if Fcc touches

$$\text{then } 4r_- = a\sqrt{2}$$

$$2r_- = \frac{a}{\sqrt{2}}$$

$$2r_+ = a - 2r_- = a \left(1 - \frac{1}{\sqrt{2}}\right)$$

$$2r_+ = \frac{a(\sqrt{2} - 1)}{\sqrt{2}} \quad 2r_- = \frac{a}{\sqrt{2}}$$

$$\frac{r_+}{r_-} = \sqrt{2} - 1, \quad \frac{r_+}{r_-} = 0.414$$

$$\text{so, } \frac{100}{r_-} = 0.414 \quad \text{so } r_- = 241.5$$

Q.53 (1)
 $a = 5.14 \text{ \AA}$
structure is like NaCl

$$\text{so, } 4r_- = a\sqrt{2}$$

$$r_- = \frac{5.14 \times 1.414}{4}$$

$$r_- = 1.815 \text{ \AA}$$

Q.54 (4)
 $\frac{r_+}{r_-} = 0.414$
putting the value we get 180 pm

Q.55 (3)
Zns - Zinc blende structure
 B^- ions consisting the lattice so 4
A here will be 2
 $A_2B_4 = AB_2$.

Q.56 (3)
CsCl has b.c.c. structure
 CS^+ will be at the centre of the cube and 8
 Cl^- will occupy at the corner which contribution will
be $\frac{1}{8} \times 8 = 1 \text{ } Cl^-$
thus, 1 CS^+ & 1 Cl^-
Ans (3)

Q.57 (2)
It will have the coordination number 6

Q.58 (1)
12 Na^+ will find at centre of the edge and one will at centre of body
so 13 Na atoms.
Ans (1)

Q.59 (1)
 $\therefore 2(r_+ + r_-) = a$

- Q.60** (2)
C.N. of cation & anion is six in rock salt structure.
- Q.61** (1)
It is fluorite (CaF_2) structure. Since formula is AB_2
 \Rightarrow No. of B atoms is twice the no. of A atoms. Hence B occupies all the tetrahedral voids (100%).
 AB_2 is (8 : 4) compound (Fluorite Structure Compound)

$$\begin{array}{cc} \downarrow & \downarrow \\ \text{C.N. of A} & \text{C.N. of B.} \end{array}$$
- Q.62** (C)
On increasing pressure, C.N. increases.
 \Rightarrow 6 : 6 changes to 8 : 8 .
- Q.63** (3)

$$\rho = \frac{zM}{N_A \cdot a^3} \Rightarrow 3.18 = \frac{4 \times 78}{N_A \cdot a^3}$$

$$\Rightarrow a^3 = 16.3 \times 10^{-23}$$

$$\Rightarrow a = 5.46 \times 10^{-8} \text{ cm}$$

$$= 546 \times 10^{-10} \text{ cm}$$

$$a = 546 \times 10^{-12} \text{ m}$$

$$= 546 \text{ pm}$$
- Q.64** (3)
 CaF_2 = For cation = 8
Anion = 4
 CsCl = for cation = 8
Anion = 8
- Q.65** (B)
On increasing temp^r C.N. decreases.
 \therefore CsCl (8 : 8) structure changes into (6 : 6) NaCl type structure.
- Q.66** (2)
Radius Ratio $\frac{r_{\text{Rb}^+}}{r_{\text{I}^-}} = \frac{1.46}{2.16} = 0.68 \Rightarrow$ between 0.414 & 0.732
Hence Rock salt (NaCl) structure.
- Q.67** (4)
In rock salt structure Na^+ occupy octahedral void & tetrahedral voids are vacant
- Q.68** (4)
Four corner atoms & Eight other face central atoms = 12 for face atom & 12 (all for face) w.r.to corner
- Q.69** (2)
 SrCl_2 is AB_2 type in which cation is of large size.
- Q.70** (4)
There are 12 next nearest neighbour of Na^+ each for each center octahedral void
- Q.71** (4)
for comparable size of anion 8 cation
 $r_{\text{Cs}^+} \cong r_{\text{Cl}^-}$
- Q.72** (4)
(II) $\frac{r_+}{r_-} = \frac{0.2}{0.95} = 0.21$
coordination no. = 3
(I) True (II) False
(III) True (IV) False
- Q.73** (4)
Schottky defect noticed in all
- Q.74** (2)
The structure of sodium chloride crystal is F.C.C.
- Q.75** (B)
Equal no. of Na^+ & Cl^- are missing completely,
 \Rightarrow Schottky defect.
- Q.76** (2)
See Sol. E-8.
- Q.77** (1)
Refer theory.
- Q.78** (2)
Since Ag^+ (cation) is smaller than Cl^- (anion) & hence cation is present in voids.
In CaF_2 , F_{anion}^- is smaller.
- Q.79** (1)
Ions are displaced from one place to another.

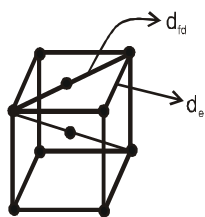
JEE-ADVANCED OBJECTIVE QUESTIONS

Q.1 (C)
Grey Cast Iron is metallic solid.

Q.2 (B)

$$P = \frac{8 \times \frac{4}{3} \pi R^3}{(4R)^3} = \frac{8 \times 4 \times \pi R^3}{3 \times 64 \times R^3} = \frac{\pi}{6} = \frac{22}{7 \times 6} = \frac{11}{21}$$

Q.3 (C)



$$d_e = a$$

$$d_{fd} = \sqrt{2}a$$

$$d_{bd} = \frac{\sqrt{3}a}{2}$$

$$\therefore d_{fd} > d_e > d_{bd}$$

Q.4 (B)

$$d_{1-2} = \frac{\sqrt{2}a}{2} = \frac{a}{\sqrt{2}}; d_{2-3} = \sqrt{\left(\frac{a}{2}\right)^2 + \left(\frac{a}{2}\right)^2} = \frac{a}{\sqrt{2}}$$

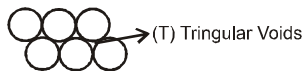
$$\text{Hence } d_{1-2} = d_{2-3}$$

Q.5 (D)

$$\text{Common Volume} = \left(\frac{a}{2}\right)^3 = \frac{a^3}{8}$$

[\therefore Common vol is a cube of edge length $\frac{a}{2}$]

Q.6 (A)



2 Square Voids (4)

Q.7 (C)



& body center.

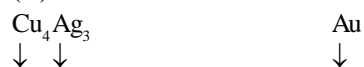
\oplus \rightarrow Tetrahedral voids on body diagonal.

Q.8 (A)

$$\text{No. of tetrahedral voids} = 8 \times \frac{1}{8} = 1$$

No. of Octahedral voids = $1 \times 1 = 1$ (at body center).

Q.9 (B)



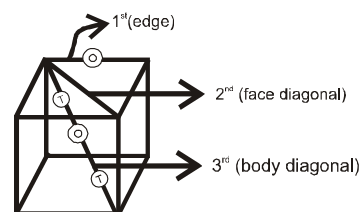
Froms c.c.p. , $\frac{3}{8}$ th of tetrahedral voids , $\frac{1}{4}$ of

Octahedral voids [\therefore No. of O- voids = 4]

$$z = 4$$

[\therefore No. of T- voids = 8].

Q.10 (A)



Q.11 (A)

Refer theory octahedral & tetrahedral voids about positions of ...

Q.12 (B)

Only tetrahedral, Since there is one tetrahedral voids just above the atom & one just below the atom.

Q.13 (D)

Total positive charge = Charge on Mg^{2+} + Charge on Al^{3+}

$$= \frac{1}{8} \times 8 \times 2 + \frac{1}{2} \times 4 \times 3 = 8 \text{ electronic charge.}$$

Q.14 (D)

Coordination no. of cation = 6

coordination no of anion = 6

Q.15 (A)

Refer NaCl (Rock salt structure).

Q.16 (C)

$$Z = 4, M = 60$$

$$60 \times 4 \text{ gram}$$

$$\text{--- } 6.023 \times 10^{23} \text{ unit cells}$$

$$1 \text{ gram}$$

$$\text{--- } \frac{6.02 \times 10^{23}}{60 \times 4} = 2.5 \times 10^{21}$$

Q.17 (C)

Some of O^{2-} combine with each other forming O_2 gas which is liberated leaving behind electrons at the site vacated by oxide ions.

Q.18 (D)

$$2(1-x)/(3x-2)$$

$$\begin{array}{ccc} & \curvearrowright M_x \curvearrowleft & \\ M^{2+} & & M^{3+} \\ \text{(Let } y) & & = x-y \end{array}$$

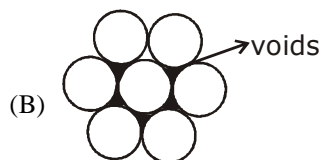
\Rightarrow Applying charge balance, $2y + 3(x-y) - 2 = 0$
 $\Rightarrow y = 3x - 2$

$$\therefore \frac{M^{3+}}{M^{2+}} = \frac{x-y}{y} = \frac{x-(3x-2)}{3x-2}$$

$$= \frac{-2x+2}{3x-2} = \frac{2(1-x)}{3x-2}$$

**JEE-ADVANCED
MCQ/COMPREHENSION/MATCHING**

Q.1 (A,B,C,D)
(A) 6 Cs^+ ion second nearest neighbour



(C) $\frac{r_+}{r_-} = 0.75$ (BCC) 8 : coordination no. (D) True

Q.2 (A,C,D)
 $r_+ + r_- = a/2$
 $(95 + 181) = a/2$
 $\Rightarrow a = 276 \times 2$
 $a = 552$ pm

Q.3 (A,C)
 $M^{+2} \longrightarrow Fe_2O_4^{-2}$
it will be ferrite and ferrimagnetic substance

Q.4 (A,B,C)
These are facts.

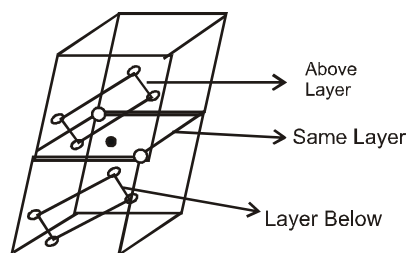
Q.5 (A,B,C)
 Na^+ & F^- are isoelectronic hence they will have same screening const (s) but not the effective nuclear charge.
and $r_{Na^+} + r_{F^-} = 2.31 \text{ \AA}$ and $r_{F^-} = 1.36 \text{ \AA}$
 $\therefore r_{Na^+}/r_{F^-} \approx 0.7$ (coordination = 6, rock salt structure)

Q.6 (A,B,C)
These are facts.

Q.7 (A,B,D)
Schottky defect is only observed in ionic compound.

Q.8 (A,B,C)
Randomness (entropy) in amorphous solids is more than that in crystalline solids.

Q.9 (B,C)
Fcc can be viewed in two following ways -
(i) Planes along the faces (and parallel to it) of the unit cell.
 \Rightarrow Each atom touches 4 in same layer, 4 in layer above and 4 in layer below it.
(ii) Planes along closest packed spheres \rightarrow each atom touches 6 atom in same layer, 3 in layer above and 3 in layer below it.



Comprehension # 1 (Q. No. 10 to 25)

Q.10 (B)
Q.11 (A)
Q.12 (C)
10 In FCC lattice each edge center act as octahedral void.
11 No. of X = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4 \Rightarrow 4$ XY unit per cell.
No. of Y = $1 + 12 \times \frac{1}{4} = 4$
12 At edge center, there is octahedral void in f.c.c. lattice.
 \Rightarrow C.N. of Y = 6
(6 : 6) C.N. \Rightarrow NaCl Structure.

Comprehension # 2 (Q. No. 13 to 16)

Q.13 (D)

Q.14 (C)

Q.15 (D)

Q.16 (D)

13 H C P

Packing efficiency = 74%

empty space = 100 - 74%

ES=26%

14 In any structure if number of atom is Z

so no. of tetrahedral voids = 2 Z

in ccp Z=4

so tetrahedral void = 8

$$\text{so ratio} = \frac{4}{8} = \frac{1}{2} = \frac{0.5}{1}$$

15 For B.C.C.

$$\frac{r_+}{r_-} = 0.732-1$$

for octahedral.

$$\frac{r_+}{r_-} = 0.414-0.732$$

for tetrahedral

$$\frac{r_+}{r_-} = 0.225-0.414$$

so, cubic > octahedral > tetrahedral

16 M— H.C.P= 6

$$\text{O}^{-2} \text{ at octahedral void} = \frac{2}{3} \times 6 = 4$$

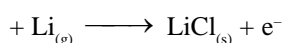
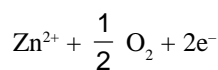
**Comprehension # 3 (Q. No. 17 to 20)**

Q.17 (C)

Q.18 (B)

Q.19 (A)

Q.20 (C)

17 Some Cl⁻ ions leave the lattice and combine with Li vapour to release electron, which is trapped into the anion vacancy giving rise to metal excess defect Cl⁻18 On heating, ZnO_(s) dissociates reversibly as ZnO \rightleftharpoons Zn²⁺ ions occupy certain interstitial sites whereas the electrons released are present at the neighbouring sites, which act as F-centers.19 In the crystallization, some Ag⁺ ions will get replaced by as many half of Cd²⁺ ions. Thus the cation vacancies will be the same as the number of Cd²⁺ ions incorporated.

20 AgBr can show both shottky and frenkel defect.

Comprehension # 4 (Q. No. 21 to 24)

Q.21 (B)

Q.22 (C)

Q.23 (A)

Q.24 (D)

21 Number of defects per mole of NaCl = (6.02 × 10²³ formula units) = $\frac{1 \times 6.02 \times 10^{23}}{10^{15}} = 6.02 \times 10^8$

22 Refer theory

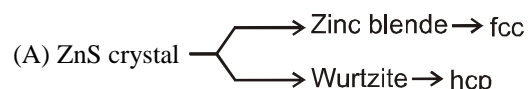
23 $3x + (0.93 - x) \times 2 = 2$
x = 0.14

$$\% \text{ of Fe as Fe (III)} = \frac{0.14}{0.93} \times 100 = 15 \%$$

24 At room temperature, thermal energy causes some electrons of the Si-Si bonds to leave. The electron deficient bond becomes a positive hole. Both the positive holes and electrons released account for the conduction of electricity.

Q.25 (i) - (e) ; (ii) - (b) ; (iii) - (c) ; (iv) - (a) ; (v) - (d)
Refer theoryQ.26 (A)- s, r ; (B) - s, r ; (C) - p ; (D) - q
Refer theory

Q.27 (A)-p,q,r,s ;(B)-p,r,s ;(C)-p,s; (D)-p,r,s

S²⁻ ion are present in fcc lattice & Zn²⁺ ion occupy all

the tetrahedral voids distance of tetrahedral voids

$$\text{from corner} = \frac{\sqrt{3}a}{4}$$

(B) $\text{CaF}_2 \rightarrow$ Fluorite structure

Ca^{2+} ion are present in ccp lattice & F^- ion are present in all tetrahedral voids.

(C) $\text{NaCl} \rightarrow$ Rock salt Type structure

Cl^- ion are present in ccp lattice & Na^+ ion occupy all the octahedral voids.

(D) Diamond crystal \rightarrow C atom present in fcc lattice in which alternate tetrahedral voids are occupied by C atom.

NUMERICAL VALUE BASED

Q.1 [2]

$$8 \times \frac{1}{8} + 2 \times \frac{1}{2} = 2$$

Q.2 [6]

Q.3 [4]

fcc arrangement

Q.4 [6]

Q.5 [4]

$$n = \frac{d \times N_A \times a^3}{A} = \frac{10.6 \times 6.023 \times 10^{23} \times (408 \times 10^{-10})^3}{108} = 4$$

Q.6 [2]

Effective number of atoms of

$$X = 4 - 4 \times \frac{1}{8} = 3.5$$

Effective number of atoms of Y = 4 - 1 = 3

Effective number of atoms of Z = 8 - 4 = 4

$$\text{Ans : } \frac{3+4}{7/2} = 2$$

Q.7 [8]

Q.8 [0125]

Q.9 [6]

$$\frac{r^+}{r^-} = \frac{88}{200} = 0.44$$

so CN is 6.

KVPY

PREVIOUS YEAR'S

Q.1 (C)

From Bragg's equation

$$n\lambda = 2d \sin \theta$$

$$d = \lambda, n = 1$$

$$1 \times \lambda = 2 \times \lambda \sin \theta$$

$$\sin \theta = \frac{1}{2}$$

$$\theta = 30^\circ$$

Q.2 (2)

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

$$= \frac{450}{\sqrt{4+4+1}} = \frac{450}{\sqrt{9}} = 150 \text{ pm}$$

Q.3 (C)

Q.4 (B)

Z (effective no. of atoms/unit cell)

$$Y \quad 4$$

$$M \quad 2$$

then formula of ionic compound is MY_2

Q.5 (C)

$$r_{\text{K}^+} + r_{\text{Cr}^-} = \frac{a}{2}$$

$$133 + 181 = \frac{a}{2}$$

$$a = 2(133 + 181)$$

$$a = 628 \text{ pm}$$

$$\text{or } a = 628 \times 10^{-10} \text{ cm}$$

and

$$\text{volume} = a^3 = (6.28 \times 10^{-8})^3 \text{ cm}^3$$

$$= 2.4767 \times 10^{-22} \text{ cm}^3$$

$$\approx 2.48 \times 10^{-22} \text{ cm}^3$$

Q.6 (A)

$$\text{Corner} \Rightarrow \frac{1}{8}$$

$$\text{Face} \Rightarrow \frac{1}{2}$$

Q.7 (A)

By definition

Q.8 (A)

	FCC	BCC	SC
η	74%	68%	52.4%

order FCC > BCC > SC

- Q.9** (D)
No. of F^- will be equal to eight since for one Ca^{+2} there should be two F^- ion.

- Q.10** (C)

$$d = \frac{N \times M}{N_A \times a^3}$$

$$8.93 = \frac{4 \times 63.5}{6.023 \times 10^{23} \times a^3}$$

$$a^3 = 4.72 \times 10^{-23}$$

$$a = (47.2 \times 10^{-24})^{1/3}$$

$$= 3.61 \times 10^{-8} \text{ cm}$$

$$= 3.61 \times 10^{-10} \text{ m}$$

$$= 361 \text{ pm}$$

$$a = 2\sqrt{2} r$$

$$r = \frac{a}{2\sqrt{2}} = 127.8$$

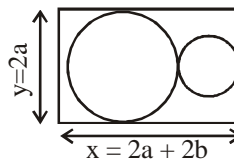
- Q.11** (B)
 No. of O^{2-} per unit cell = $8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$
 No. of Al^{3+} per unit cell = $4 \times \frac{1}{2} = 2$
 No. of Mn^{2+} per unit cell = $8 \times \frac{1}{8} = 1$
 $MnAl_2O_4$

- Q.12** (A)
 The unit cell of the above pattern will consist of 8 white square and 1 black square i.e. it will form centre unit cell.
 \therefore No. of white square $Y = 8$
 No. of black square $X = 1$
 \therefore Formula XY_8

- Q.13** (C)
 $Z = 6$ [in hcp packing]
 $X = 12$ [in tetra hedral void]
 So formula X_2Z

- Q.14** (B)
 Ionic solid is an insulator in solid state but conducts electricity in molten state.

- Q.15** (A)



$$\begin{aligned} \text{Area of rectangle} &= xy \\ &= 2a(2a+2b) \\ &= 4a(a+b) \\ \text{Area covered by circles} &= \pi a^2 + \pi b^2 = \pi(a^2+b^2) \end{aligned}$$

$$\text{Packing fraction (P.F.)} = \frac{\pi(a^2 + b^2)}{4(a^2 + ab)}$$

$$= \frac{\pi a^2 \left(1 + \frac{b^2}{a^2}\right)}{4a^2 \left(1 + \frac{b}{a}\right)}$$

$$\text{Putting } r = \left(\frac{b}{a}\right)$$

$$\text{P.F.} = \frac{\pi(1+r^2)}{4(1+r)}$$

$$\text{For minimum P.F., } \frac{d(\text{P.F.})}{dr} = 0$$

$$\text{or } \frac{\pi}{4} \left[\frac{2r(1+r) - (1+r^2)}{(1+r)^2} \right] = 0$$

$$\Rightarrow r^2 + 2r - 1 = 0$$

$$\text{or } r = \frac{-2 + \sqrt{4+4}}{2} = \sqrt{2} - 1 = 0.414$$

Answer is option (A)

- Q.16** (B)
 Number of atoms of element 'N' per unit cell = 6

$$\text{Number of atoms of element M per unit cell} = \frac{2}{3}$$

(Number of octahedral voids per unit cell)

$$= \frac{2}{3} \times 6 = 4$$

$$M : N = 4 : 6 = 2 : 3$$

Formula is M_2N_3

JEE-MAIN

PREVIOUS YEAR'S

Q.1 [8]

$$d = \frac{Z \times \text{At. Mass}}{a^3 \times N_A} = \frac{4 \times 63.54}{(3.69 \times 10^{-8})^3 \times 6.022 \times 10^{23}}$$

$$= 8.4 \text{ g / cm}^3$$

Q.2 [1]

Effective number of octahedral void in FCC lattice = 4

Effective number of lattice point in FCC = 4

Q.3 [8]

Theory

Q.4 (4)

Covalent or network solid have very high melting point and they are insulators in their solid and molten form.

Q.5 (2)

$$M_{12 \times \frac{2}{3} A_6}$$

$$M_8 A_6$$

$$M_4 A_3$$

Q.6 [5]

1 mole KBr (= 119 gm) have moles SrBr₂ and hence, 10⁻⁷ moles cation vacancy

(as 1 Sr²⁺ will result 1 cation vacancy)

∴ Required number of cation vacancies

$$= 5 \times 10^{14}$$

Q.7 [15]

HCP structure : Per atom, there will be one octahedral void (OV) and two tetrahedral voids (TV).

Therefore total three voids per atom are present in HCP structure.

→ therefore total no of atoms of Ga will be-

$$\frac{\text{Mass}}{\text{Molar Mass}} \times N_A = \frac{0.581 \text{g}}{70 \text{g / mol}} \times 6.023 \times 10^{23}$$

→ Now, total Number of voids = 3 × total no. of atoms

$$= 3 \frac{0.581}{70} 6.023 \times 10^{23} = 14.99 \times 10^{21}$$

$$\approx 15 \times 10^{21}$$

Q.8 [33]

For BCC $\sqrt{3} a = 4r$

$$\text{so } r = \frac{\sqrt{3}}{4} \times 27$$

$$\text{for FCC } a = 2\sqrt{2} r$$

$$= 2 \times \sqrt{2} \times \frac{\sqrt{3}}{4} \times 27$$

$$= \frac{\sqrt{3}}{\sqrt{2}} \times 27 = 33$$

Q.9 (4)

Q.10 (3)

Q.11 [106]

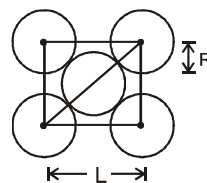
Q.12 [8]

Q.13 (3)

Q.14 [1]

JEE-ADVANCED
PREVIOUS YEAR'S

Q.1 [D]



$$4R = L\sqrt{2}$$

$$\text{so, } L = 2\sqrt{2} R$$

$$\text{Area of square unit cell} = (2\sqrt{2} R)^2 = 8R^2$$

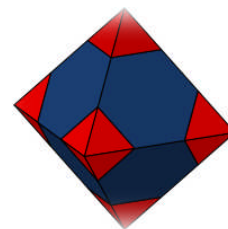
$$\text{Area of atoms present in one unit cell} = \pi R^2 +$$

$$4 \left(\frac{\pi R^2}{4} \right) = 2\pi R^2$$

$$\text{so, packing efficiency} = \frac{2\pi R^2}{8R^2} \times 100 = \frac{\pi}{4} \times 100 =$$

78.54%

Q.2 [8]



Q.3 (B)

$$\text{No. of M atoms} = \frac{1}{4} \times 4 + 1 = 1 + 1 = 2$$

$$\text{No. of X atoms} = \frac{1}{2} \times 6 + \frac{1}{8} \times 8 = 3 + 1 = 4$$

so formula = $M_2X_4 = MX_2$

Q.4

(A)

The given arrangement is octahedral void arrangement.

$$\rightarrow \frac{r_A^+}{r_{X^-}} \geq 0.414 \Rightarrow r_A^+ \geq 0.414 \times 250$$

$$r_A^+ \geq 103.5 \text{ pm.}$$

$$\& \frac{r_A^+}{r_A^-} < 0.732 \Rightarrow r_A^+ < 183 \text{ pm}$$

So, we have to choose from 104 pm and 125 pm. As no other information is given, we consider exact fit, and hence 104 pm is considered as answer.

Q.5

(A)

In ccp, O^{2-} ions are 4.

Hence total negative charge = -8

Let Al^{3+} ions be x, and Mg^{2+} ions be y.

Total positive charge = $3x + 2y$

$$\Rightarrow 3x + 2y = 8$$

This relation is satisfied only by $x = 2$ and $y = 1$.

Hence number of $Al^{3+} = 2$.

and number of $Mg^{2+} = 1$.

$\Rightarrow n =$ fraction of octahedral holes occupied by Al^{3+}

$$= \frac{2}{4} = \frac{1}{2}$$

and m = fraction of tetrahedral holes occupied by Mg^{2+}

$$= \frac{1}{8}$$

Hence, answer is (A)

Q.6

(BCD)

Q.7

[2]

$$d = \frac{Z \times \frac{M_0}{N_A}}{a^3} \quad (d = \text{density})$$

$$8 = \frac{4 \times \frac{M_0}{6 \times 10^{23}}}{(4 \times 10^{-10})^3}$$

$$M_0 = \frac{1}{8 \times 6 \times 1.6}$$

$$\text{Number of moles in } 256 \text{ g} = \frac{256}{8 \times 6 \times 1.6} = \frac{10}{3}$$

$$\text{Number of atoms} = \frac{10}{3} \times 6 \times 10^{23} = 2 \times 10^{24}$$

Q.8

(3)

$X^- \Rightarrow$ O.V.

$M^+ \Rightarrow$ FCC

M^+	X^-
(i) 4	1
(ii) 4-3	3+1
(iii) 4-3-1	3+1
(iv) 1	3

$$Z = \frac{3}{1} = 3$$

Q.9

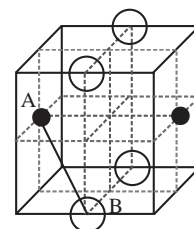
(A,C)

$$(A) Z_M = 2 \times \frac{1}{2} = 1$$

$$Z_X = 4 \times \frac{1}{4} = 1$$

\therefore Empirical formula is MX

(B) Coordinate numbers of both M and X is 8.



(C) Bond length of M-X bond

$$= AB = \sqrt{3} \cdot \frac{a}{2} = 0.866ba$$

$$(D) r_M : r_X = (\sqrt{3} - 1) : 1 = 0.732 : 1.000$$

Q.10

(B)

$$\text{Packing fraction (P.E.)} = \frac{1 \times \frac{4}{3} \pi r_-^3 + 3 \times \frac{4}{3} \pi r_+^3}{a^3}$$

$$\frac{r_+}{r_-} = 0.414 \text{ (square planar void), } a = 2r_-$$

$$\text{We get, P.E.} = \frac{\frac{4}{3} \pi (r_-^3 + 3r_+^3)}{8r_-^3}$$

$$= \left[\frac{\pi}{6} (1 + 3(0.414)^3) \right] = 0.63$$

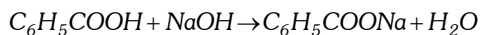
Solutions

EXERCISES

ELEMENTARY

Q.1 (2)

Q.2 (2)



$$\frac{w}{40} = \frac{12.2}{122} = 4 \text{ gms.}$$

Q.3 (2)

$$\frac{X}{X + \frac{1000}{78}} = 0.2$$

Q.4 (1)

Q.5 (3)

Q.6 (3)

Q.7 (3)

Q.8 (4)

Q.9 (3)

Q.10 (3)

Q.11 (4)

Q.12 (1)

For the ideal solution ΔH_{mix} and $\Delta V_{mix} = 0$.

Q.13 (3)

Q.14 (1)

$K_4[Fe(CN)_6]$ dissociates as $4K^+ + [Fe(CN)_6]^{4-}$, thus 1 molecule dissociates into five particles in the similar way $Al_2(SO_4)_3$ also gives five particles per molecule.

Q.15 (2)

Q.16 (2)

Q.17 (2)

Q.18 (1)

Q.19 (4)

14

$$m = \frac{K_b \times w \times 1000}{\Delta T_b \times W} = \frac{2.16 \times 0.15 \times 1000}{0.216 \times 15} = 100.$$

Q.20 (2)

Q.21 (1)

$$\Delta T_f = 1.86 \times \left(\frac{342}{342} \right) = 1.86^\circ; \therefore T_f = -1.86^\circ C.$$

Q.22 (1)

$$\text{By using, } m = \frac{K_f \times 1000 \times w}{\Delta T_f \times W_{\text{Solvent}} (\text{gm})} = \frac{5.12 \times 1000 \times 1}{0.40 \times 50} \\ = 256 \text{ gm/mol}$$

Hence, molecular mass of the solute = 256 gmol^{-1}

Q.23 (2)

$$\text{Isotonic solution} = \frac{w_1}{m_1 V_1} = \frac{w_2}{m_2 V_2}$$

$$= \frac{w_1}{342 \times 1} = \frac{6}{60 \times 1} = \frac{342 \times 6}{60} = 34.2.$$

Q.24 (4)

$$P = CRT \text{ or } \frac{P}{C} = RT$$

Q.25 (3)

$$\pi = CRT = 0.2 \times 0.0821 \times 293 = 4.81 \text{ atm.}$$

Q.26 (2)

Equal osmotic pressure only applicable of non-electrolytes solution at low concentration.

Q.27 (3)

Vapour pressure is not colligative property.

Q.28 (1)

Q.29 (3)

$BaCl_2$ gives maximum ion. Hence, it shows highest boiling point.

Q.30 (1)

$NaCl$ contain highest boiling point than other's compound.

Q.31 (1)

**JEE-MAIN
OBJECTIVE QUESTIONS**
Q.1 (3)

$$\text{Mole of H}_2\text{O} = \frac{36}{18} = 2$$

$$\text{Mole of glycerine} = \frac{46}{92} = 0.5$$

$$\text{total mole} = 2 + 0.5 = 2.5$$

$$\text{Mole fractions of glycerine} = \frac{n_1}{n_1 + n_2} = \frac{0.5}{2.5}$$

$$X_0 = 0.2 \text{ Ans.}$$

Q.2 (3)

Osmosis is a process in which solvent (water in this case) flows from low concⁿ solⁿ to high concentration through SPM.

Q.3 (2)
Q.4 (D)

18 gm of glucose means 0.1mole of glucose as it present in 1000 gm of solvent
so it is 0.1 mole

Q.5 (3)

As we know

$$\text{molarity} = \frac{10 \times d}{\text{molmt}}$$

x is % by wt.

d is the density

by putting their value we get

$$18.4 \text{ M}$$

Q.6 (4)

Molality of $\text{BaCl}_2 = 0.1 \times 0.25 = 0.025$
by calculation we get the values of (D)

Q.7 (3)

$$\text{Mole of HCl} = 25 \times 3 + 75 \times 0.05 = 75 + 3.75 = 78.75$$

$$M = \frac{78.75}{100} = .7875$$

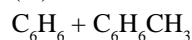
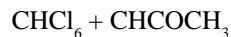
Q.8 (2)

$$[\text{Cl}^-] = 0.2 + \frac{0.2 + 0.1 \times 2}{0.5} = 0.8$$

Q.9 (2)

$$\frac{5.0 \text{ gm}}{10^6 \text{ gm}} \text{ of solutions}$$

so concentration of solution = 5 ppm

Q.10 (D)

Q.11 (A)

Q.12 (A)
Q.13 (B)
Q.14 (3)

$$P = 120 - 75 \times B$$

If

$$X_B = 1$$

$$P_B^0 = 120 - 70 = 45 \text{ mm Hg}$$

$$\text{If } X_B = 120 - 75 = 45 \text{ mmHg}$$

$$\text{if } X_B = 0 \text{ Ps} = P_A^0$$

$$P_A^0 = 120 \text{ mm Hg}$$

thus answer will be (3)

Q.15 (3)

V.P. depends on temperature.

Q.16 (2)

Non volatile substance has no V.P.

Q.17 (4)

$$P_{\text{N}_2} + P_{\text{H}_2\text{O}(v)} = 1 \text{ atm}, \quad \therefore P_{\text{H}_2\text{O}} = 0.3 \text{ atm}$$

$$\therefore P_{\text{N}_2} = 0.7 \text{ atm}$$

Now new pressure of N_2 in another vessel of volume $V/3$ at same T is given by :

$$P_{\text{N}_2} \times \frac{V_1}{3} = 0.70 \times V_1$$

$$\therefore P_{\text{N}_2} = 2.1 \text{ atm}$$

Since aqueous tension remains constant, and thus total pressure in new vessel.

$$= P_{\text{N}_2} + P_{\text{H}_2\text{O}} = 2.1 + 0.3 = 2.4 \text{ atm.}$$

Q.18 (C)

$$\text{Pressure of air} = 750 - 100 = 650 \text{ mm of Hg}$$

$$\text{on compressing } P_f = \text{Hg } 650 \times 3 \text{ mm of Hg}$$

$$= 1950 \text{ mm of Hg}$$

$$\text{so } P_T = (1950 + 100) = 2050 \text{ mm of Hg}$$

Q.19 (3)

$$\frac{p^0 - P_s}{p^0} = 0.2$$

As we know relative lowering of v.p. is equal to the mole fraction of the solute so (I) is correct it doesn't depend upon the number of moles so (II) is wrong mole fraction of solvent will be 0.8 so number of moles of solvent will be 4 so (III) will be correct,

(IV) will be also wrong so I & III will be correct so answer (3)

Q.20 (2)

Acc. of Raoult's law $P = P_A + P_B$
for non volatile solute $= P_B = 0$

$$\begin{aligned} P_s &= P_A \\ P_s &= P_A^0 X_A & X_A &= \text{mole fractions of} \\ \text{solvent} &= N_1 & & \\ \text{so } P &= P_0 N_1 & P_A^0 &= P_0 \end{aligned}$$

Q.21 (C)

$$y_A > x_A \Rightarrow \frac{1}{y_A} < \frac{1}{x_A}$$

$$\frac{y_A + y_B}{y_A} < \frac{x_A + x_B}{x_A}$$

$$\Rightarrow \frac{y_B}{y_A} < \frac{x_B}{x_A} \Rightarrow \frac{y_A}{y_B} > \frac{x_A}{x_B}$$

Q.22 (3)

$$= 40 + 120 = 160$$

$$P_A = y_A P = y_A \times 160$$

$$\Rightarrow 40 = y_A \times 160 \Rightarrow y_A = 1/4$$

Q.23 (2)

$$x_A = \frac{1}{4} : x_B = \frac{3}{4}$$

$$P_s = \frac{1}{4} \times 100 + \frac{3}{4} \times 80 = 85$$

$$y_A = \frac{P_A}{P_s} = \frac{100 \times \frac{1}{4}}{85} = \frac{25}{85} = x_A^1$$

$$y_B = \frac{60}{85} = x_B^1$$

$$\begin{aligned} P_{\text{distillate}} &= \frac{25}{85} \times 100 + \frac{60}{85} \times 80 \\ &= 85.88 \text{ mm Hg} \end{aligned}$$

Q.24 (C)

$$\text{Pure A: } X_B = 0$$

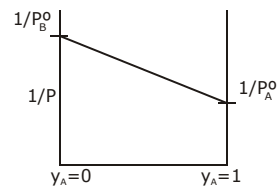
$$= P_T = P_A^0 = 120$$

$$\text{Pure B: } X_B = 1$$

$$= P_T = P_B^0 = 120 - 75 = 45$$

Q.25 (C)

$$\frac{1}{P} = \frac{1}{P_B^0} + y_A \left(\frac{1}{P_A^0} - \frac{1}{P_B^0} \right)$$



Q.26 (4)

$$P_T = 200X_A + 100X_B$$

$$X_A = X_B = 1/2 \text{ (given)}$$

$$\Rightarrow P_T = 150$$

If all the liquid become vapour then P_T can be calculated by

$$\frac{1}{P_T} = \frac{1}{P_B^0} + y_A \left(\frac{1}{P_A^0} - \frac{1}{P_B^0} \right)$$

$$\Rightarrow P_T = 133.3$$

then pressure at which half of liquid converted into vapour must be in the range of $133.3 < P < 150$

Q.27 (3)

$$P = X_A P_A^0 + X_B P_B^0 = (P_A^0 - P_B^0) X_A + P_B^0$$

$$\text{So } P_B^0 = 254$$

$$P_A^0 - P_B^0 = -119 P_A^0 = 135$$

Q.28 (1)

$$P = P_B^0 X_B + P_T^0 X_T$$

$$120 = 150(X_B) + 50(1 - X_B)$$

$$100 X_B = 70$$

$$X_B = 0.7$$

$$Y_B = \frac{X_B P_B^0}{P} = \frac{0.7 \times 150}{120} = 0.075 \frac{Y_B}{Y_T} = \frac{7}{1} Y_T = 1 -$$

$$0.875 = 0.125$$

Q.29 (3)

As $X_A \longrightarrow 1$. Then we will have pure methanol so

$$P_T = 120 X_A + 140 = 120 + 140 = 260 \text{ mm of Hg.}$$

Q.30 (B)

$$P'_A = P_A^0 X_A \text{ and } P'_B = P_B^0 X_B$$

$$P'_A = P_M \cdot Y_A \text{ and } P'_B = P_M \cdot Y_B$$

$$\therefore \frac{P'_A}{Y_A} = \frac{P'_B}{Y_B}$$

$$\text{or } \frac{P_A^0 X_A}{Y_A} = \frac{P_B^0 X_B}{Y_B} = \frac{P_B^0 (1 - X_A)}{(1 - Y_A)}$$

$$\text{or } \frac{P_A^0 X_A}{Y_A} (1 - Y_A) = P_B^0 - P_B^0 X_A$$

$$\text{or } \frac{P_B^{\circ}}{X_A} = \frac{P_A^{\circ}}{Y_A} + (P_B^{\circ} - P_A^{\circ})$$

$$\text{or } \frac{1}{X_A} = \frac{1}{Y_A} \cdot \frac{P_A^{\circ}}{P_B^{\circ}} + \frac{(P_B^{\circ} - P_A^{\circ})}{P_B^{\circ}}$$

$$\text{or } y = mx + C \therefore \text{Slope} = m = \frac{P_A^{\circ}}{P_B^{\circ}} \text{ and intercept}$$

$$C = \frac{(P_B^{\circ} - P_A^{\circ})}{P_B^{\circ}}$$

Q.31 (4)

$$P = 100 \times \frac{2}{5} + 300 \times \frac{3}{5}$$

$$= 40 + 180 = 220$$

Q.32 (3)

Initially A = 3 mole ; B = 2 mole

$$600 = \frac{3}{5}P_A^{\circ} + \frac{2}{5}P_B^{\circ} \dots\dots 1$$

finally A = 4.5 mole ; B = 2 mole and c = 0.5 mole

$$630 = \frac{4.5}{7}P_A^{\circ} + \frac{2}{7}P_B^{\circ}$$

$$P_A^{\circ} = 940$$

$$P_B^{\circ} = 90$$

Q.33 (1)

Entropy of solvent is less than that of solution.

Q.34 (C)

For ideal solution

$$\Delta H_{\text{mix}} = 0$$

$$\Delta G_{\text{mix}} < 0$$

$$\Delta S_{\text{mix}} > 0$$

Q.35 (4)

Q.36 (3)

for a ideal solution $\Delta G_{\text{mix}} < 0$.

Q.37 (2)

According to Raoult's law

$$P_T = (0.08 \times 300 + 0.92 \times 800) \text{ torr} = (24 + 736) \text{ torr} = 760$$

$$\text{torr} = 1 \text{ atm}$$

$$P_{\text{exp.}} = 0.95 \text{ atm} < 1 \text{ atm}$$

Hence solution shows -ve deviation

$$\text{so } \Delta H_{\text{mix}} < 0, \text{ and } \Delta V_{\text{mix}} < 0.$$

Q.38 (1)

(1) as in case of negative deviation.

(2) ΔG_{mix} is generally positive.

(3) Ideal mixture follows Raoult's law at all compositions, so can not form a constant boiling mixture.

(4) It is theoretically impossible to obtain an ideal solution.

Q.39 (1)

It shows negative deviation from Raoult's law

$$p_s (\text{actual}) = 580 \text{ torr}$$

$$p_s (\text{Raoult}) = 0.4 \times 300 + 0.6 \times 800 = 600 \text{ torr.}$$

Q.40 (1)

An azeotropic mixture boil at perticular temperature without changing its composition.

Q.41 (B)

V.P. does not depends on surface area of liquid. (it depends on temperature).

Q.42 (2)

$$B.P._{\text{Toluene}} > B.P._{\text{Benzene}}$$

$$V.P._{\text{Toluene}} < V.P._{\text{Benzene}}$$

Benzene is more volatile (By graph)

$$x_{\text{Benzene}} < y_{\text{Benzene}}$$

$$(A) \text{ If } x_B = 0.5 \Rightarrow y_t = 0.2, y_B = 0.8$$

$$(B) \text{ } x_t = 0.3, \Rightarrow x_B = 0.7 \Rightarrow y_B = 0.6 \text{ not possible}$$

$$(C) \text{ } x_B = 0.3 \text{ and } y_t = 0.4$$

$$\Rightarrow y_B = 0.6 \text{ correct}$$

$$(D) \text{ } x_B = 0.7, y_B > 0.7 \text{ (should be)}$$

$$\text{Given } y_t < 0.3 \Rightarrow y_B > 0.7 \text{ correct}$$

Q.43 (2)

$$\pi = iCRT$$

$$K_3[\text{Fe}(\text{CN})_6] = 3k^+ + [\text{Fe}(\text{CN})_6]^{3-}$$

$$(1-\alpha) 3\alpha \qquad \qquad \qquad \alpha$$

$$i = (1 + 3\alpha)$$

$$3.94 = (1 + 3\alpha) \times \frac{1}{10} \times 0.0821 \times 300$$

$$\alpha = 0.2$$

so 20%

Q.44 (2)

$\pi \propto$ No. of partial/ion.

$$\text{BaCl}_2 = 3, \text{ NaCl} = 2 \qquad \text{glucose} = 1$$

So. order of $\pi = \text{BaCl}_2 > \text{NaCl} > \text{glucose}$.

Q.45 (4)

As benzoic acid dimerises so number of moles decreases so osmotic pressure of benzoic acid is less than benzene.

so answer (4)

Q.46 (2)**Q.47** (1)

Higher the number of particles higher will be osmotic pressure so (A) will be answer in case of (D) precipitation will take place so number of particles will decrease.

Q.48 (2)

In option (2) oxidation state of platinum is (iv)

$$x - 6 = -2$$

$$x = +4$$

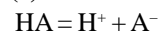
Q.49 (3)

$$i = 1 + \alpha$$

$$10^{-4} = C\alpha^2$$

$$\alpha = \sqrt{0.01} = 0.1$$

$$i = 1 + 2 = 1 + 0.1 = 1.1$$

Q.50 (4)

$$(1 - \alpha)\alpha \quad \alpha$$

$$PH = 2 = [H^+] : 10^{-2} = C^2$$

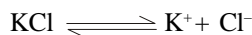
$$\alpha = 0.1$$

$$i = 1 + \alpha = 1 + 0.1 = 1.01$$

Q.51 (3)

(1) As we know

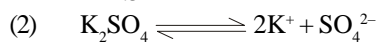
$$i = 1 + \alpha$$



$$(1 - \alpha) \quad \alpha \quad \alpha$$

$$i = 1 + \alpha = 50\% \text{ dissociation}$$

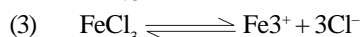
$$i = 1.5$$



$$(1 - \alpha) \quad 2\alpha \quad \alpha$$

$$1 + 2\alpha, \alpha = .4$$

$$i = 1.8$$



$$(1 - \alpha) \quad \alpha \quad 3\alpha$$

$$1 + 3\alpha$$

$$i = 1.9$$



$$(1 - \alpha) \quad \alpha \quad 4\alpha$$

$$1 + 4\alpha$$

$$i = 1.8$$

Q.52 (4)

$$\frac{P^0 - P}{P^0} = 0.05 = X_B$$

Where X_B = mole fraction of solute.

$$\text{Molality} = \frac{1000 \times X_B}{(X_A \times M_A)} = 1000 \times 0.05 / 0.95 \times 18 =$$

$$2.92 \approx 3.0$$

Q.53 (1)

$$\frac{\Delta P}{P} = \frac{ni}{ni + N}$$

$$0.5 = \frac{2i}{2i + 3}$$

$$i + 1.5 = 2i$$

$$i = 1.5$$

$$i = 1 + (y - 1)\alpha$$

$$1.5 = 1 + (2 - 1)\alpha$$

$$\alpha = 0.5$$

$$\text{mole of } Cl^- = 1.0$$

$$\text{mole of AgCl ppt.} = 1.0$$

Q.54 (2)

Glucose does not dissociate $\Rightarrow i = 1$

Q.55 (2)

$$i = \frac{\text{actual mole of solute (Experiment)}}{\text{theoretical mole of solute}}$$

$$i = \frac{M_T}{M_{\text{exp.}}}$$

$$i = 1 + \alpha(n - 1) = 1 + \alpha(3 - 1)$$

$$\Rightarrow i = 1 + 2\alpha \Rightarrow i > 1$$

$$\Rightarrow \frac{M_T}{M_{\text{exp}}} > 1$$

$$\Rightarrow M_T > M_{\text{exp}}$$

$$\Rightarrow M_{\text{exp}} < 111$$

Q.56 (2)

$$(a) \text{ Acc. to R.L. V.P. } \Rightarrow \frac{\Delta P}{P_0} = X_B$$

$$X_B = \frac{0.80 - 0.60}{0.80} = \frac{0.20}{0.80} = 0.25.$$

Q.57 (2)

$$\text{R.L.V.P.: } \frac{P_A^0 - P_s}{P_A^0} = X_B$$

$$X_B = \frac{10 - 9}{10} = \frac{1}{10}$$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{n_B}{n_A + n_B} = \frac{\frac{W_B}{M_B}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}}$$

$$M_B = \frac{900}{10} = 90.$$

Q.58 (2)

According to question $P_s = 0.95 P_0$
 according Raoult's law $P_s = P_0 X_A$ given $M_A = 0.3 M_B$

$$0.95 P_0 = P_0 \left(\frac{\frac{W_A}{M_A}}{\frac{W_A}{M_A} + \frac{W_B}{M_B}} \right) M_A = \text{molecular wt. of}$$

solvent

 $M_B =$ molecular wt. of solute

$$0.95 = \frac{\frac{W_A}{0.3 M_B}}{\frac{W_A}{0.3 M_B} + \frac{W_B}{M_B}} W_A = \text{gram wt. of solvent}$$

 $W_B =$ gram wt. of soluteon solving $\frac{W_A}{W_B} = 5.7$.**Q.59** (3)

Lowering of V.P. is colligative property

thus, $i K_2SO_4 = 1 + (y-1)x = 1 + 2x = 3$

$$\therefore \text{ If } \frac{\Delta p}{p^\circ} = \frac{n_1 i}{n_1 + n_2}$$

$$\frac{10}{50} = \frac{3n_1}{3n_1 + 12} = \frac{n_1}{n_1 + 4}$$

$$n_1 = 1$$

Q.60 (4)

$$\frac{\Delta P}{P_0} = X_B \text{ So } X_B = \frac{760 - 750}{760} = \frac{1}{76} \text{ Ans.}$$

Q.61 (3)

More is the value of Vant Hoff factor, more will be RLVP.

Q.62 (3)

$$\frac{P^0 - P}{P} = \frac{n_{\text{solute}}}{n_{\text{solvent}}} = \frac{n}{N}$$

$$\frac{P^0 - P}{P^0} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

Q.63 (1)

less no of particle of solute means maximum vapour pressure.

Q.64 (2)

$$P = 0.95 P^0$$

$$X_{\text{solvent}} = 0.95, X_{\text{solute}} = 0.005$$

$$\frac{P^0 - P}{P^0} = \frac{n}{N + n} = \frac{(W_{\text{solute}} / M_{\text{solute}})}{\frac{W_{\text{solute}}}{M_{\text{solute}}} + \frac{W_{\text{solvent}}}{M_{\text{solvent}}}}$$

$$M_{\text{solute}} = M \Rightarrow M_{\text{solvent}} = 0.3M$$

$$\Rightarrow 0.05 = \frac{(W_{\text{solute}} / M)}{\left(\frac{W_{\text{solute}}}{M} \right) + \left(\frac{W_{\text{solvent}}}{0.3M} \right)}$$

$$\Rightarrow \frac{W_{\text{solvent}}}{W_{\text{solute}}} = 5.7$$

Q.65 (3)

$$\frac{P^0 - P}{P^0} = X_{\text{solute}}$$

$$P^0 - P \propto X_{\text{solute}}$$

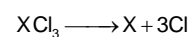
$$\frac{10}{20} = \frac{0.2}{X_{\text{solute}}}$$

$$\Rightarrow X_{\text{solute}} = 0.4 \Rightarrow X_{\text{solvent}} = 0.6$$

Q.66 (1)

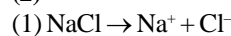
$$\frac{P^0 - P}{P} = \frac{1000}{M_{\text{solvent}}} = m$$

$$m = \frac{17.25 - 17.20}{17.20} \times \frac{1000}{18} = 0.1615$$

If $m = M = 0.1615$ 

$$M_{\text{total}} = S + 3S = 4S = 0.1615$$

$$S = 0.040375 = 4.037 \times 10^{-2}$$

Q.67 (2)

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

$$\Delta T_b = 2K_b \times m$$

elevation of b.p. will be double in case of NaCl not b.p.

(2) Will be correct because b.p. elevation will be double here in comparison to glucose.

(3) Elevation of b.p. is colligative property not b.p. so answer (2).

Q.68 (D)

$$\Delta T_f = 2K_f \times \frac{w}{W \times M} \times 1000$$

$$0.01 = 0.1 \times \frac{2.56}{100 \times M} \times 1000$$

$$M = 256$$

$$M = 8 \times 32$$

Thus atomicity = 8

Answer (D)

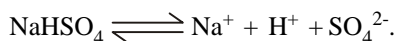
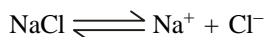
- Q.69** (3)
B.P. of water is elevated.

- Q.70** (B)
Atmospheric pressure is low.

Q.71 (2)

$$\Delta T = \frac{1000 \times K_b \times Y}{250 \times M} = \frac{4K_b Y}{M}$$

- Q.72** (2)
As $m \rightarrow 0$ (infinite dilution) both electrolytes will be completely dissociated so



$$\frac{\Delta T_b}{\Delta T_b'} = \frac{mK_b i_{\text{NaHSO}_4}}{mK_b i_{\text{NaCl}}} = \frac{3}{2} = 1.5$$

- Q.73** (4)
 $\text{AlPO}_4 \rightleftharpoons \text{Al}^{3+} + \text{PO}_4^{3-}$
 $i = 1 + x = 2$
 $\Delta T_b = \text{molality } K_b i \quad \therefore$

$$\frac{\Delta T_b}{K_b} = 0.02.$$

- Q.74** (2)
 $x_3 y_2 \rightleftharpoons 3x^{2+} + 2y^{3-}$ for complete ionization.
 $1 - \alpha \quad n\alpha \quad m\alpha$
 $i = 1 + (m + n - 1)\alpha$
 $i = 1 + (2 + 3 - 1) \times 0.25 = 1 + 1 = 2$
 $\Delta T_b = i \times k_b \times m = 2 \times 0.52 \times 1 = 1.04$
B.P. of solution (T_b) = $\Delta T_b + T_b^\circ = 1.04 + 373 = 374.04 \text{ K}$
Ans.

- Q.75** (B).
- $$\Delta T_b = m K_b = \frac{w}{M} \times \frac{1000}{W} \times K_b$$
- $$\Delta T_b = 47.98 - 46.3 = 1.68$$
- $$1.68 = \frac{28}{M} \times \frac{1000}{315} \times 2.38$$
- $$M = \frac{28 \times 1000 \times 2.38}{315 \times 1.68} = 125.92$$

$$\text{Atomicity} = \frac{\text{Mol. wt.}}{\text{At. wt.}} = \frac{125.92}{31} = 4.02$$

So. Molecule is = P_4 .

- Q.76** (B)
 $\text{AlCl}_3 = \text{no. of particle} = 4$
 $\text{CaCl}_2 = \text{no. of particle} = 3$
(vapour pressure of AlCl_3) < (vapour pressure of CaCl_2 solution)
 $T_{\text{B.P.}}(\text{AlCl}_3) > T_{\text{B.P.}}(\text{CaCl}_2)$
 $T_1 > T_2$

- Q.77** (3)
100% dissociation
 $\Delta T_f = (0.0054) = i K_f m$
 $= i \times 1.86 \times 0.001$
 $= i = 3$
 $= 3 \text{ particles } [\text{MA}_6] \text{A}_2$

- Q.78** (1)
Higher freezing point \Rightarrow lesser $\Delta T_f \Rightarrow$ lesser molality
 \Rightarrow lesser number of particles

- Q.79** (1)
 $\text{Ba}_3(\text{PO}_4)_2 \rightleftharpoons 3 \text{Ba}^{2+} + 2 \text{PO}_4^{3-}$
value of $i = 5$ (100% ionised)
so $\Delta T_f = i k_f m$
so $m = \frac{\Delta T_f}{i k_f} = \frac{0.05}{5} = 0.01$

- Q.80** (1)
 $\Delta T_f = 0.2 \times 1.2 \times 1.86 = 0.45$
therefore freezing point = -0.45°C .

- Q.81** (1)
 $\Delta T_b = i k_b m$
so $i = \frac{2.08}{0.52 \times 1} = 4$
so the complex is $\text{K}_3 [\text{Fe}(\text{CN})_6]$
 $\text{K}_3 [\text{Fe}(\text{CN})_6] \rightleftharpoons 3 \text{K}^+ + [\text{Fe}(\text{CN})_6]^{3-}$

- Q.82** (1)
 $\Delta T_f = i \cdot k_b \cdot m$
 $0.69 = i \times \frac{5.12 \times 20 \times 1000}{94 \times 1000}$
 $i = 0.63$
for dimerization $i = 1 - \alpha/2$
 $0.63 = 1 - \alpha/2$
 $\alpha = 0.74$.

- Q.83** (A)
 $1.24 = 34.3 \left[\frac{0.849/M}{0.05} \right] \Rightarrow M = 469.68$
 \therefore as Hg_2Cl_2 molecules.

Q.84 (2)

(i) $\Delta T_f = m \times K_f$

$$0.2 = \frac{X \times 1000}{100} \times 1.86 \quad X = \frac{0.2}{10 \times 1.86}$$

after freezing

$$\Delta T_f = m \times K_f$$

$$\Delta T_f = \frac{X \times 1000}{(100 - y)} \times 1.86 \quad \Delta T_f = 0.25$$

On solving, Amount of ice $y = 20$ g ice**Q.85 (C)** $T_1 =$ Tripal point temp, $T_2 =$ Critical point temp., $T_3 =$ M.P. $T_4 =$ B.P.**Q.86 (1)**

(1) $i = 1 + 0.90(5 - 1) = 1 + 3.6 = 4.6$

(2) $i = 1 + 0.90(3 - 1) = 2.8$

(3) $i = 1 + 0.9(3 - 1) = 2.8$

(4) $i = 2.8$

Ans is (A) Higher the value of i means Boiling point will be higher.**Q.87 (4)**

$M = 1 \quad d = 1.2 \quad \text{Mol mass} = 180$

$$m = \frac{1000 \times M}{1000d - M \times 180}$$

$$= \frac{1000}{1200 - 180} = \frac{1000}{1020}$$

$$\Delta T_b = \frac{1000}{1020} K_b = 0.98 K_b$$

Q.88 (B)

$$20 \text{ mole } C_6H_6, 10 \text{ mole } C_6H_5Cl \Rightarrow X_B = \frac{2}{3}, X_C = \frac{1}{3}$$

$$\text{at } t = 100^\circ C \Rightarrow p_s = 300 \times \frac{1}{3} + 1350 \times \frac{2}{3} = 100 + 900$$

(=1000).

Q.89 (2)

$0.20 = 1.8 \times M \times i$

$$i = \frac{0.20}{0.1 \times 1.8} = \frac{20}{18} = \frac{10}{9} \quad Hx \rightleftharpoons H^+ + x^-$$

$$i = \frac{10}{9} \text{ and } i = 1 + \alpha(2 - 1) = 1 + \alpha$$

$$\Rightarrow \alpha = \frac{1}{9}$$

$$K = \frac{0.1 \alpha^2}{1 - \alpha} = \frac{\left(0.1 \times \frac{1}{81}\right)}{1 - \frac{1}{9}} = 1.38 \times 10^{-3}$$

Q.90 (1)

$1.04 = 0.52 \times m$

$\Rightarrow m = 2$

$$2 = \frac{P^0 - 750}{750} \times \frac{1000}{18}$$

$\Rightarrow P^0 = 777 = P_{\text{atm}}$

 $P^0 = P_{\text{atm}}$ (because at T water boils)So at T : $P^0 = P_{\text{atm}}$

because when water boils V.P. become equals to atmospheric pressure

Q.91 (1)

$\pi = CRT \quad 7.40 = n \times 0.0821 \times 300$

$$\pi = \frac{n}{V} RT \quad n = \frac{7.4}{0.0821 \times 300} = 0.3.$$

Q.92 (3)

Isotonic solution has same conc.

$$\pi_1 = \pi_2 \quad C_1 = C_2 \quad n_1 = n_2 \quad \boxed{\frac{W_1}{M_1} = \frac{W_2}{M_2}}$$

$$\text{So, } \frac{x}{180} = \frac{4}{60} \Rightarrow x = 12 \text{ g Ans.}$$

Q.93 (4)For isotonic solution $\pi_1 = \pi_2$; $C_1 = C_2$; $n_1 = n_2$

$$\frac{W_1}{M_1} = \frac{W_2}{M_2} \Rightarrow \frac{10.5}{M} = \frac{180}{30} \Rightarrow M = \frac{10.5 \times 180}{30} = 63$$

Ans.

Q.94 (3)

$\pi_f V_f = \pi_1 V_1 + \pi_2 V_2$

$$\pi_f = \frac{1.2V + 2.5V}{2V} = \frac{3.7V}{2V}$$

$\pi_f = 1.85 \text{ atm.}$

Q.95 (1)

(1) All solutions are not isotonic because all solution are not at equal concentration so (A) is incorrect

(2) As benzoic acid dimerises so III is hypotonic of I, II, IV

(3) Is also correct as I, II & IV are hypertonic of III

(4) As ammonium sulphate has maximum number of particale so it will be hypertonic of I, II, III

so answer (1)

Q.96 (3)

As number of moles is maximum in case
urea > glucose > sucrose

$$\pi = CRT$$

It depends on number of moles
so osmotic pressure

$$P_2 > P_1 > P_3$$

i.e.,

Q.97 (4)

All solution have same No. of particle and also have
same value of π . $n_1 = n_2$; $\pi_1 = \pi_2$ (Isotonic).

Q.98 (4)

Isotonic means equal osmotic pressure so,

$$\pi_1 = \pi_2$$

$$i_1 C_1 RT = i_2 C_2 RT$$

$$\text{so } i_1 C_1 = i_2 C_2$$

In case of (4) both the volume of (i) & (3) are equal.
so Answer (D)

Q.99 (4)

Only solvent molecules can go through SPM, not the
solute particles hence no blue colour formation

Q.100 (4)

As, we know that

$$P_s = \frac{1}{4} \times 100 + \frac{3}{4} \times 60$$

$$= 25 + 45 \text{ mm Hg}$$

$$= 70 \text{ mm Hg}$$

To mm Hg < 75 mm Hg thus there is positive deviation
from Raoult's law,

so

(A) is correct

(B) If v.p. is increasing boiling point will be lowered in
that case

(C) is correct that force of attraction between A & B is
smaller than that between A and A or between B and B.

So All statement are correct

Q.101 (1)

Higher the Van't hof factor higher will be the elavation
in b. p. so

$$y < x < z$$

$$0.8 < 1.8 < 2.5$$

Q.102 (4)

$$i = 1 + \alpha (5 - 1)$$

$$= 1 + 0.6(D) = 3.4$$

$$\Delta T_b = 3.4 \times 0.52 \times 1$$

$$= 1.768$$

$$T_b^1 = 373 + 1.768$$

$$= 374.76$$

JEE-ADVANCED**OBJECTIVE QUESTIONS****Q.1** (A)

Let volumes takne by 'x' & 'y' litres, so $\frac{0.1x + 0.4y}{x + y}$

$$= 0.34 \text{ \& } V_g = (x + y) \text{ (to be maximised)}$$

so $y = 4x$ so for maximum volume

$$y = 2L \text{ \& } x = \frac{1}{2}L$$

Q.2 (B)

$$\pi = CRT$$

$$C = (0.34 + \frac{0.1 \times 0.5}{2.5} + \frac{0.2 \times 2}{2.5}) = 0.34 + 0.02 + 0.16 =$$

$$0.52$$

$$\text{so } \pi = 0.52 \times 0.082 \times 300 \text{ atm} = 12.792 \text{ atm}$$

Q.3 (A)**Q.4** (B)**Q.5** (D)

Possible vapor pressures are

$$\frac{75 + 22}{2}, \frac{75 + 10}{2}, \frac{22 + 10}{2} \text{ and } \frac{75 + 22 + 10}{3}$$

$$= 48 \frac{1}{2}, 42 \frac{1}{2}, 16, 35 \frac{2}{3}.$$

Q.6 (A)

$$760 = 300 X_A + 800 (1 - X_A)$$

$$\Rightarrow 760 = 800 - 500 X_A$$

$$\Rightarrow 500 X_A = 40$$

$$\therefore X_A = \frac{40}{500} = 0.08.$$

Q.7 (D)

$$\frac{P_A^0}{4} + \frac{3P_B^0}{4} = 1 \text{ atm}$$

$$\Rightarrow P_A^0 + P_B^0 = 2 \text{ atm}$$

$$\frac{P_A^0}{4} + \frac{3P_B^0}{4} > 1 \text{ atm}$$

$$\Rightarrow P_A^0 + 3P_B^0 > 4 \text{ atm}$$

$$\& \frac{P_A^0}{8} + \frac{3P_B^0}{8} + \frac{4P_C^0}{8} = 1 \text{ atm}$$

$$\Rightarrow P_A^0 + 3P_B^0 + 4P_C^0 = 8 \text{ atm}$$

$$\text{so } P_A^0 + 3P_B^0 = (8 - 4 \times 0.8) \text{ atm} = 4.8 \text{ atm}$$

$$\text{Hence } P_B^0 = 1.4 \text{ atm}$$

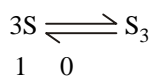
$$P_A^0 = 0.6 \text{ atm}$$

Q.8 (C)

$$P_{\text{Total}} = 0.4 \times 80 + 0.6 \times 120 = 104 > 100 \text{ mm of Hg.}$$

Q.9 (A)

Q.10 (A)



$$1 \quad 0$$

$$1 - \alpha \qquad \frac{\alpha}{3} \Rightarrow i = 1 - \frac{2\alpha}{3}$$

$$\text{Now } 0.1 \left(1 - \frac{2\alpha}{3} \right) = 0.08$$

$$\Rightarrow \alpha = 0.3. \text{ Hence } 30\% \text{ trimerization.}$$

Q.11 (B)

$$i = 1 + \alpha(n - 1) \text{ or } 4 = 1 + 0.75(n - 1)$$

$$\therefore n = 5, \text{ so complex will be } Ba_3 [Co(CN)_5]_2.$$

Q.12 (B)

$$\text{Mole of solute in first beaker} = \frac{0.05 \times 20}{1000} = 0.001$$

$$\text{mole of solute } (Na^+ \& Cl^-) \text{ in other beaker} =$$

$$\frac{2 \times 0.03 \times 20}{1000} = 0.0012$$

conc. of IInd beaker is higher than Ist beaker so water flows from Ist beaker to IInd beaker till both beaker achieved equal conc. let v volume of water flows from Ist to IInd beaker

$$\text{so } \frac{0.001}{20 - v} = \frac{0.0012}{20 + v}$$

$$v = 1.8 \text{ ml}$$

$$\text{volume of Ist beaker} = 20 - 1.8 = 18.2 \text{ ml}$$

$$\text{volume of IInd beaker} = 20 + 1.8 = 21.8 \text{ ml.}$$

Q.13 (B)

Q.14 (D)

Q.15 (B)

Wt gain means

weight loss means

$$V.P_{\text{incoming}} > V.P_{\text{outgoing}}$$

$$V.P_{\text{incoming}} < V.P_{\text{outgoing}}$$

$$\text{So } p_1 > p_2 < p_3 \qquad \text{and}$$

$$c_1 < c_2 > c_3$$

Q.16 (A)

Q.17 (D)

$$\Delta T_f = \frac{1000 k_f \times w}{m.w.}$$

$$\text{for } AB_2 = 3.2 = \frac{1000 \times k_f \times 1}{M_1 \times 20}$$

$$\text{for } AB_4 = 1.3 = \frac{1000 k_f \times 1}{M_2 \times 20}$$

$$M_1 = 110.67, M_2 = 196.15$$

$$\text{for } AB_2 = a + 2b = 110.87 \dots\dots (i)$$

$$\text{for } AB_4 = a + 4b = 196.15 \dots\dots (ii)$$

By solving eq (i) and (ii)

$$a = 25.59$$

$$b = 42.64$$

Q.18 (C)

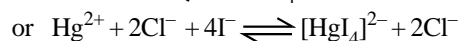
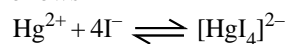
$$\Delta T_f = i \times m \times k_f$$

$$i = \frac{3.72}{1.86 \times 1} = 2$$

So salt is $(Pt(H_2O)_3 Cl_3) Cl \cdot 3H_2O$.

Q.19 (B)

Due to this addition a complex $[HgI_4]^{2-}$ will get formed as follows



on adding we can see that $4I^-$ ions are consumed but resultant number of particles are three.

Hence boiling point gets decreased.

freezing point gets increased.

Q.20 (B)

$$0.0558 = i \times 1.86 \times \frac{0.01}{1}$$

$$\Rightarrow i = 3$$

\Rightarrow fully ionized

$$0.0744 = i \times 1.86 \times \frac{21.68}{271}$$

$\Rightarrow i = 1$
 \Rightarrow fully unionized

Q.21 (C)

$$\Delta T_f = i \cdot m \cdot K_f$$

$$\Delta T_f = i_1 m_1 K_f + i_2 m_2 K_f + i_3 m_3 K_f = (m_1 + 2m_2 + m_3) K_f$$

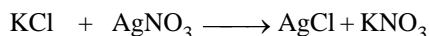
$$\Delta T_f = \frac{3}{60} + \frac{7.45 \times 2}{74.5} + \frac{9}{180} \times 1000 \times 1.86$$

$$\Delta T_f = 3 \times 1.86$$

$$= 5.58$$

$$T_f \text{ of solution} = 273 - 5.58 = 267.42 \text{ K Ans.}$$

Q.22 (B)



$$0.8 \times 25 \quad 1 \times 20 \quad \quad \quad 0 \quad 0$$

(mili mole) (mili mole) 002020

$$\text{Mole of KNO}_3 \text{ in solutions} = \frac{20}{45}$$

$$\Delta T_f = i \times m \times K_f$$

$$\Delta T_f = 2 \times \frac{20}{45} \times 2 = \frac{80}{45}$$

Q.23 (D)

$$\text{Boiling point of solution} = \text{boiling point} + \Delta T_b = 100 + \Delta T_b$$

$$\text{Freezing point of solution} = \text{freezing point} - \Delta T_f = 0 - \Delta T_f$$

$$\text{Difference in temperature (given)} = 100 + \Delta T_b - (-\Delta T_f)$$

$$104 = 100 + \Delta T_b + \Delta T_f = 100 + \text{molality} \times K_b + \text{molality} \times K_f$$

$$= 100 + \text{molality} (0.52 + 1.86)$$

$$\therefore \text{Molality} = \frac{104 - 100}{2.38} = \frac{4}{2.38} = 1.68 \text{ m}$$

$$\text{and} \quad \quad \quad \text{molality} \quad \quad \quad =$$

$$\frac{\text{moles} \times 1000}{W_{\text{gm (solvent)}}$$

$$1.68 = \frac{\text{moles} \times 1000}{500}$$

$$\therefore \text{Moles of solute} = \frac{1.68 \times 500}{1000} = 0.84 \text{ moles.}$$

Q.24 (A)

$$x + y = 0.1$$

$$x / y = 0.37$$

$$\Delta T_f = \frac{x + x + y + 2y}{1000} \times 1000 \times 1.85$$

$$\Delta T_f = \frac{0.2 + y}{1000} \times 1000 \times 1.85$$

$$\Delta T_f = (0.2 + 0.0729927) \times 1.85 = 0.505$$

Q.25 (A)

Q.26 (B)

Q.27 (D)

Semipermeable membrane allows the solvent particles only to pass through it.

Q.28 (A)

$$\pi_I = 2R \times 300 \times \left(1 + \left(\frac{1}{2} - 1 \right) \right) = 300R$$

$$\pi_{II} = 0.5R \times 300 \times 2 = 300R$$

Q.29 (B)

JEE-ADVANCED

MCQ/COMPREHENSION/MATCHING

Q.1 (AB)

$$P_T = P_A + P_B \neq P_A^0 + P_B^0$$

boiling point of the solution will be in between the boiling point of two liquids.

Q.2 (ACD)

Q.3 (A, B, C)

For - ve deviation

$$A - - B > A - - A$$

$$A - - B > B - - B$$

- ve deviation solution are non ideal solution.

Q.4 (A, B, C, D)

CHCl_3 + Acetone : Negative deviation from Raoult's law.

$$\text{So, } P_{\text{actual}} < P_{\text{Raoult}}$$

Q.5 (A, C)

polar - polar \rightarrow -ve deviation

Q.6 (ACD)

Q.7 (A, B, C)

For ideal solution $\Delta H = 0$, $\Delta V = 0$, $\Delta S_{\text{mix}} \neq 0$.

Obeys Raoult's law.

Q.8 (A,B,C)
 $C_6H_6 + C_6H_6CH_3$: ideal solution,
 Non-ideal solution : A, B, C.

Q.9 (B,D)
 Number of particles from $K_4 [Fe(CN)_6] = 5$
 number of particles from $FeSO_4 (NH_4)_2 SO_4 \cdot 6H_2O = 5$
 number of particles from $KCl \cdot MgCl_2 \cdot 8H_2O = 5$

Q.10 (D)
 $K_2SO_4 + BaCl_2 \longrightarrow BaSO_4 + 2KCl$

0.02	0.02
0	0
0	0
0.02	0.04

$$\Delta T_b = m K_b i$$

$$(\Delta T_b)_i = (0.02 \times 2 + 0.02) \times K_b = 0.06 K_b$$

$$(\Delta T_b)_{final} = 0.04 \times 2 \times K_b = 0.08 K_b$$

$\Delta T_b \uparrow$ So B.P. \uparrow

$$(\Delta T_f)_i = -0.06 K_f ; (\Delta T_f)_f = 0.08 K_f$$

$\Delta T_f \uparrow$ So F.P. \downarrow

$$\frac{dP}{P} = X_{solute} ; X_{solute} \uparrow \text{ So } dP \downarrow$$

VP \downarrow

$$\pi_{initial} = MRT i = 0.06 RT$$

$$\pi_{final} = 0.08 RT$$

So, $\pi \uparrow$

Q.11 (B, D)
Solute **y**
 $x \quad i = [1 + (y - 1) x]$

(A) KCl	2
0.5 1.5	
(B) K_2SO_4	3
0.4 1.8	
(C) $FeCl_3$	4
0.3 1.9	
(D) $SnCl_4$	5
0.2 1.8	

Q.12 (A, B, C)
 $A_x B_y \rightleftharpoons xA^{m+} + yB^{n+}$
 Initial molesnoo

At eq b.n(1- α) n x α nya

$$i = \frac{\text{Total mol at equilibrium}}{\text{Initial mol}} = \frac{n[(1-\alpha) + x\alpha + y\alpha]}{n}$$

$$i = (1-\alpha) + x\alpha + y\alpha$$

It can also be seen that all other expressions imply the same thing.

$$(A) \alpha = \frac{i-1}{x+y-1} \quad (B) i = (1-\alpha) + x\alpha + y\alpha.$$

$$(C) \frac{1-i}{1-x-y}$$

Q.13 (AB)

Q.14 (A, C)
 $i = 1 + (y - 1) \alpha$
 $i = 1 + y - 1 = y.$

y	i
Na ₂ SO ₄	33
MgCl ₂	33
Al(NO ₃) ₃	44
C ₆ H ₁₂ O ₆	-1

$$\Delta T_b = m K_b i$$

$$i_{Na_2SO_4} = i_{MgCl_2}$$

$$(\Delta T_b)_{Na_2SO_4} = (\Delta T_b)_{MgCl_2}$$

$$(B.P.)_{Na_2SO_4} = (B.P.)_{MgCl_2}$$

Q.15 (BCD)

A There will be movement of solvent

$$B \quad i_{Ba_3(PO_4)_2} > i_{MgSO_4} \quad \pi_{Ba_3(PO_4)_2} > \pi_{MgSO_4}$$

C Solvent flow from right ($MgSO_4$) to left ($Ba_3(PO_4)_2$)

D No flow of solute

\Rightarrow no ppt formation

Comprehension # 1 (Q. No. 16 to 18)

Q.16 (C)

Q.17 (C)

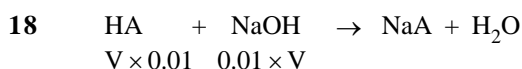
Q.18 (A)

16 $\pi = iCRT$

$$0.369 = i \times \frac{1.8}{180} \times 0.0821 \times 300$$

$$i = 1.5$$

$$17 \quad i = \frac{M_{\text{theoretical}}}{M_{\text{observed}}} = \frac{180}{1.5} = 120 \text{ gm}$$



$$00 \quad \frac{0.01 V}{2V} = 0.005$$

$$\pi = 2 \times 0.005 \times 0.082 \times 300 = 0.246 \text{ atm}$$

Comprehension # 2 (Q. No. 19 to 21)

Q.19 (B)

Q.20 (A)

Q.21 (B)

$$19 \quad \frac{P^0 - P_s}{P_s} = \frac{n_A}{n_B}$$

$$m = \frac{P^0 - P_s}{P_s} \times \frac{1000}{M_B}$$

$$P^0 = \frac{640 \times 600}{600} \times \frac{1000}{78} = 0.86$$

$$20 \quad P_s = X_A P_A^0 + X_B P_B^0$$

$$300 = \frac{1}{4} \times P_A^0 + \frac{3}{4} P_B^0$$

after adding 1 mole

$$290 = \frac{2}{5} P_A^0 + \frac{3}{5} P_B^0$$

$$P^0 = 250$$

$$21 \quad \frac{P^0 - P_s}{P_s} = \frac{n_A}{n_B}$$

$$\frac{P^0 - \frac{4}{5} P_0}{\frac{4}{5} P_0} = \frac{w}{\frac{180}{18}}$$

$$w = 150 \text{ gm}$$

Comprehension # 3 (Q. No. 22 to 24)

Q.22 (A)

Q.23 (B)

Q.24 (B)

22 The composition of the vapour (y_A)

$$= \frac{\text{partial pressure (A)}}{\text{total pressure (p)}}$$

$$= \frac{p_A}{p} = \frac{x_A P_A^0}{p_B^0 + (p_A^0 - p_B^0) x_A} \dots(1)$$

$$\text{and } y_B = \frac{p_B}{p} = 1 - y_A = \frac{x_B P_B^0}{p_A^0 + (p_B^0 - p_A^0) x_A} \dots(2)$$

To express the total vapour pressure in terms of composition of the vapour phase, rearrange equation (1)

$$x_A = \frac{y_A P_B^0}{p_A^0 + (p_B^0 - p_A^0) y_A}$$

...(3)

the total pressure over the solution is given by

$$p = p_B^0 + (p_A^0 - p_B^0) x_A$$

Substitute x_A in the above equation

$$p = p_B^0 + (p_A^0 - p_B^0) \frac{y_A P_B^0}{p_A^0 + (p_B^0 - p_A^0) y_A}$$

$$\text{i.e., } p = \frac{p_B^0 P_A^0}{p_A^0 + (p_B^0 - p_A^0) y_A} \dots(4)$$

The plot of p versus y_A for a solution in which $p_A^0 > p_B^0$ is (A), i.e., as the composition of y_A increases, the total pressure decreases.

23 From above question, we have

$$\frac{1}{p} = \frac{p_A^0 + (p_B^0 - p_A^0) y_A}{p_B^0 P_A^0}$$

$$\frac{1}{p} = \frac{1}{p_B^0} + \left(\frac{1}{p_A^0} - \frac{1}{p_B^0} \right) y_A$$

Thus a plot of $\frac{1}{p}$ vs y_A gives a linear plot with slope =

$$\left(\frac{1}{p_A^0} - \frac{1}{p_B^0} \right)$$

24 Given $x_A = 0.70$; $y_A = 0.35$; $p = 600$ torr
 $P_A^0 = ?$ $P_B^0 = ?$

$$y_A = \frac{p_A}{p} = \frac{x_A P_A^0}{p}$$

$$\therefore P_A^0 = \frac{y_A P}{x_A} = \frac{0.35 \times 600}{0.70} = 300 \text{ torr}$$

$$\text{similarly } P_B^0 = \frac{y_B P}{x_B} = \frac{0.65 \times 600}{0.30} = 1300 \text{ torr}$$

Comprehension # 4 (Q. No. 25 to 30)

Q.25 (B)

Q.26 (A)

Q.27 (C)

Q.28 (A)

Q.29 (C)

Q.30 (C)

25 Benzene is more volatile than toluene.

26 from fig. $p_{\text{toluene}}^0(25^\circ\text{C}) = 30 \text{ mm of Hg.}$

27 For boiling at 25°C vapour pressure of solution = pressure above the solution.

$$\begin{aligned} &= X_T P_T^\circ + X_B P_B^\circ = 0.6(30) + 0.4 \times 100 \\ &= 18 + 40 = 58 \text{ torr} \end{aligned}$$

from graph $\approx 60 \text{ torr.}$

28 Vapour contains equal no. of moles of benzene and volume. So $X_T' = X_B'$

$$\text{Now } \frac{1}{P_{\text{Total}}} = \frac{X_T'}{P_T^\circ} + \frac{X_B'}{P_B^\circ} =$$

$$\frac{1}{2} \left\{ \frac{1}{30} + \frac{1}{100} \right\} = \frac{1}{2} \left\{ \frac{100 + 30}{300} \right\}$$

$$\begin{aligned} P_{\text{Total}} &= \frac{6000}{130} = X_T P_T^\circ + (1 - X_T) P_B^\circ \\ &= P_B^\circ + X_T (P_T^\circ - P_B^\circ) \\ &= 100 + X_T (30 - 100) = 100 - 70 X_T \\ &\Rightarrow X_T = 0.77 \end{aligned}$$

29 $P_{\text{Total}} = X_T P_T^\circ + (1 - X_T) P_B^\circ$ & $P_{\text{Total}} = P_B^\circ + P_T^\circ$
 $= (1 - X_B) P_T^\circ + X_B P_B^\circ$
 both will be valid if $X_T = 0$
 or $X_B = 0$.

30 The above equations are consequences of both these laws.

Q.31 (A) - q, s ; (B) - q, s ; (C) - q, s ; (D) - q, s
 No of particles \downarrow , so vapour pressure \uparrow , $i \downarrow$
 $\Delta T_f = mK_f i$
 $\Delta T_f \downarrow$, freezing point \uparrow .

Q.32 (A) - Q, (B) - P, (C) - R
P \rightarrow Q

where solute-solvent interaction solute-solvent interaction. then ideal solution.

B- solute-solvent interaction are weaker than solute-solvent so it shows positive deviation.

C- solute-solvent interactions stronger than solute-solvent interaction it will show negative deviation.

Q.33 (A) - p, r, s ; (B) - q, r ; (C) - q, r ; (D) - r
 (A) Positive deviation : $\Delta H > 0, \Delta S > 0$

$$(P_T)_{\text{calculate}} <$$

$$(P_T)_{\text{observed}}$$

(B) Maximum boiling azeotrope = Negative deviation : $\Delta S > 0$.

$$(C) P_{\text{calculate}} : 100 \times 0.5 + 200 \times 0.5 = 150.$$

$$(P_T)_{\text{calculate}} >$$

$$(P_T)_{\text{observed}}$$

Negative deviation : $\Delta S > 0$.

(D) Ideal solution : $\Delta S > 0$.

Q.34 (A) - r, (B) - t, (C) - s, (D) - p, (E) - q

Q.35 (A) - (p, s, r); (B) - (p, q, t); (C) - (p); (D) - (p, q, t)
 (A) Acetone + CHCl_3 -ve deviation from Raoult's law
 $\Delta S > 0, \Delta H < 0, \Delta V < 0$

Maximum Boiling Azeotropes.

(B) Ethanol + Water +ve Deviation from Raoult's law
 $\Delta S > 0, \Delta H > 0, \Delta V > 0$ Minimum Boiling Azeotropes

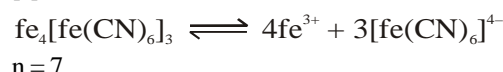
(C) $\text{C}_2\text{H}_5\text{Br} + \text{C}_2\text{H}_5\text{I}$ Ideal solution No Azeotropes $\Delta H = 0, \Delta V = 0$

(D) Acetone + Benzene +ve Deviation from Raoult's law
 $\Delta H > 0, \Delta V > 0, \Delta S > 0$ Minimum Boiling Azeotropes.

NUMERICAL VALUE BASED

Q.1 [8]

Q.2 [3]



$$n = 7$$

$$l = 1 + (n-1) a = 1 + 6a$$

$$l = 1 + 6 \times 1 = 7$$

$$P = 7 \times 2 \times 0.08 \times 300 = 326$$

$$112 n = 336$$

$$X = 3$$

Q.3 [5]

Q.4 [3]

$$\Delta T_f = (1.86) \left[(n_{\text{urea}} + n_{\text{glucose}}) 10 \right] \hat{e}$$

∴ Solution has 5% by weight urea and 10% by weight glucose

$$\therefore \% \text{ by weight} = \frac{\text{weight of solute}}{\text{weight of solution}} \times 100$$

∴ wt. of water = 85g; wt. of urea = 5g; wt. of glucose = 10g

$$\Delta T_f = \Delta T_{\text{urea}} + \Delta T_{\text{glucose}}$$

Q.5 [3]

$$\pi = CRT x_i$$

$$\pi = \frac{n}{V} RT x_i$$

$$\therefore 0.75 = \frac{n}{2.5} \times 0.0821 \times 300 \times 2.47$$

$$n = \frac{0.75 \times 2.5}{0.0821 \times 300 \times 2.47}$$

$$n = 0.03 \text{ mole} = 3 \times 10^{-2}$$

Q.6 [6]

Q.7 [2]

Q.8 [2]

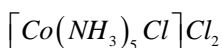
Q.9 [5]

$$\Delta T_f = i \times k_f \times m$$

$$0.558 = i \times 1.86 \times 0.1$$

$$i = 3, \alpha = 1$$

$$\alpha = \frac{i-1}{n-1}, n = 3$$



$$x = 5$$

KVPPY

PREVIOUS YEAR'S

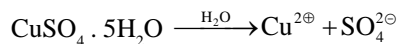
Q.1 (A)

$$P_{\text{total}} = \chi_B (P_B^0) + \chi_T (P_T^0) = \chi_B (P_B^0) + (1 - \chi_B) (P_T^0)$$

Comparing it with $y = mx + c$

$$\frac{P_{\text{total}}}{y} = \frac{\chi_B}{x} \left(\frac{P_B^0 - P_T^0}{m} \right) + \frac{P_T^0}{c}$$

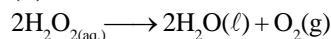
Q.2 (C)



$$\Delta T_b = i K_b \cdot m = 2 \times 0.512 \times 0.1 = 0.1024$$

$$T_b = T_b^0 + \Delta T_b = 100 + 0.1024 = 100.10$$

Q.3 (C)



It is a common trend that n-factor (H_2O_2) is taken as '2'

By the definition of volume strength of H_2O_2 if we consume 1 l of 1N H_2O_2 in the above equation we are using 1 gram equivalent of $H_2O_2 \equiv 0.5$ moles of H_2O_2 (by using n-factor = 2)

This will produce $\frac{1}{4}$ moles of O_2 gas at N.T.P.

$$\equiv \frac{1}{4} \times 22.4 = 5.6 \text{ l of } O_2 \text{ gas}$$

i.e. 1 l, 1N H_2O_2 solution gives 5.6 l O_2 at N.T.P.

Hence 1N \equiv 5.6 'vol'. H_2O_2 solution

In the given question it is 1.76 N H_2O_2 solution

Hence volume strength = $5.6 \times 1.76 \approx 10$ volumes

Q.4 (C)

$$\text{Mass of solution} = d \times v = 1.9 \times 250 = 475 \text{ gram}$$

$$\text{Mass of solvent} = (475 - 3) = 472 \text{ gram}$$

$$\text{Molality} = \frac{3 \times 1000}{126 \times 472} = 0.05$$

$$\text{Normality} = \frac{3 \times 1000}{63 \times 250} = 0.19$$

Q.5 (A)

$$\Delta T_b = i k_b m$$

So order of boiling point is dependent on (im) so order of BP $\Rightarrow CH_3COOH < NaCl < Na_2SO_4 < K_3PO_4$.

Q.6 (C)

Higher the value of K_H of gas lower will be its solubility.

So order of solubility $\Rightarrow CH_4 > CO_2 > O_2 > Ar$

**JEE-MAIN
PREVIOUS YEAR'S**
Q.1 [2]

$$\Delta T_f = i \times K_f \times m$$

$$0.93 = i \times 1.86 \times 1 \quad \therefore i = \frac{1}{2}$$

$$\therefore \frac{1}{2} = 1 + \left(\frac{1}{n} - 1\right) \quad \therefore n = 2$$

Q.2 [6]

 meq. of NaOH = meq. of $H_2C_2O_4$

$$M \times 1 \times 4.4 = 1.25 \times 2 \times 10$$

$$M = 5.68 \text{ M}$$

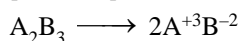
Q.3 [2.747]

$$\Delta T_b = i m K_b$$

$$2.5 = (1 + (2-1) \times 0.75) \times m \times 0.52$$

$$2.5 = 1.75 \times m \times 0.52$$

$$m = \frac{2.5}{1.75 \times 0.52} = 2.747$$

Q.4 [101.768]


$$\text{No. of Ions} = 2 + 3 = 5$$

$$i = 1 + (n-1)\alpha = 1 + (5-1) \times .6$$

$$= 1 + 4 \times .6 = 1 + 2.4 = 3.4$$

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

$$= 0.52 \times 1 \times 3.4 = 1.768^\circ\text{C}$$

$$\Delta T_b = (T_b)_{\text{Solution}} - (T_b)_{\text{H}_2\text{O}} \Big|_{\text{Solvent}}$$

$$1.768 = (T_b)_{\text{Solution}} - 100$$

$$(T_b)_{\text{Solution}} = 101.768^\circ\text{C}$$

Q.5 [35]

Q.6 [0.2]

$$M = \frac{n}{V} = \frac{4.5/90}{2.50/1000} = 0.2$$

Q.7 [1.09]

$$\Delta T_f = k_f \times m$$

$$= 5.12 \times \frac{10}{58} \times \frac{1000}{200} = 4.41^\circ\text{C}$$

$$\Delta T_f = (T_f)_{\text{Solvent}} - (T_f)_{\text{Solvent}}$$

$$= 4.41^\circ\text{C} = 5.5 - (T_f)_{\text{Solvent}}$$

$$(T_f)_{\text{Solvent}} = 5.5 - 4.41 = 1.09^\circ\text{C}$$

Q.8 [100]

$$\Delta T_b = T_b - T_b^0$$

$$100.52 - 100$$

$$= 0.52^\circ\text{C}$$

$$i = \left(1 - \frac{\alpha}{2}\right)$$

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

$$0.52 = \left(1 - \frac{\alpha}{2}\right) \times 0.52 \times 2$$

$$\alpha = 1$$

So, percentage association = 100%.

Q.9 [50]

$$\Delta T_f = (1 + \alpha) K_f m$$

$$\alpha = 0.05 = 50 \times 10^{-3}$$

Q.10 [1389]

$$P = K_H \cdot x$$

$$\text{or, } 20 \times 10^3 = (8 \times 10^4 \times 10^3) \times \frac{n_{O_2}}{n_{O_2} + n_{\text{water}}}$$

$$\text{or, } \frac{1}{4000} = \frac{n_{O_2}}{n_{O_2} + n_{\text{water}}} = \frac{n_{O_2}}{n_{\text{water}}}$$

Means 1 mole water (= 18 gm = 18 ml) dissolves

 $\frac{1}{4000}$ moles O_2 . Hence, molar solubility

$$= \left(\frac{1}{4000}\right) \times 1000 = \frac{1}{72} \text{ mol dm}^{-3}$$

$$= 1388.89 \times 10^{-5} \text{ mol dm}^{-3} \approx 1389 \text{ mol dm}^{-3}$$

Q.11 [64]

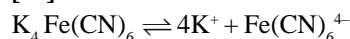
100 molal aqueous solution means there is 100 mole solute in 1 kg = 1000 gm water.

Now,

$$\text{mole-fraction of solute} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$= \frac{100}{100 + \frac{1000}{18}} = \frac{1800}{2800} = 0.6428$$

$$= 64.28 \times 10^2$$

Q.12 [85]


$$\text{Initial conc. } 1 \text{ m } \quad \quad \quad 0$$

$$\begin{array}{l} \text{Final conc.} \quad (1 - 0.4)m \quad 4 \times 0.4 \quad 0.4m \\ \quad \quad \quad = 0.6m \quad \quad = 1.6m \end{array}$$

$$\text{Effective molality} = 0.6 + 1.6 + 0.4 = 2.6m$$

For same boiling point, the molality of another solution should also be 2.6 m.

Now, 18.1 weight percent solution means 18.1 gm solute is present in 100 gm solution and hence, (100 - 18.1 =) 81.9 gm water.

$$\text{Now, } 2.6 = \frac{18.1 / M}{81.9 / 1000}$$

Q.13 [19]

$$\text{Given} = P_A^0 = 21\text{kPa} \quad \Rightarrow P_B^0 = 18\text{kPa}$$

→ An Ideal solution is prepared by mixing 1 mol A and 2 mol B.

$$\rightarrow X_A = \frac{1}{3} \text{ and } X_B = \frac{2}{3}$$

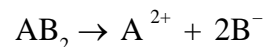
→ Acc to Raoult's law

$$P_T = X_A P_A^0 + X_B P_B^0$$

$$\Rightarrow P_T = \left(\frac{1}{3} \times 21 \right) + \left(\frac{2}{3} \times 18 \right)$$

$$\Rightarrow P_T = 7 + 12 = 19 \text{ KPa}$$

Q.14 [106]



$$t = 0 \quad a \quad 0 \quad 0$$

$$t = t \quad a - a\alpha \quad a\alpha \quad 2a\alpha$$

$$n_T = a - a\alpha + a\alpha + 2a\alpha$$

$$= a(1 + 2\alpha)$$

$$\text{so } i = 1 + 2\alpha$$

$$\text{Now } \Delta T_b = i \times m \times K_b$$

$$\Delta T_b = (1 + 2\alpha) \times m \times K_b$$

$$\alpha = 0.1 \quad m = 10 \quad K = 0.5$$

$$\Delta T_b = 1.2 \times 10 \times 0.5$$

$$= 6$$

So boiling point = 106

Q.15 [9]

Q.16 [125]

Q.17 [1575]

Q.18 [15]

Q.19 [5]

Q.20 [250]

Q.21 [18]

Q.22 [25]

Q.23 [4]

Q.24 [1]

Q.25 [78]

Q.26 [50]

Q.27 [269]

Q.28 [4]

Q.29 [3]

Q.30 [271]

Q.31 [310]

Q.32 [518]

Q.33 [20]

Q.34 (4)

Q.35 [13]

Q.36 [13]

Q.37 [64]

JEE-ADVANCED PREVIOUS YEAR'S

Q.1 (A)

$$\Delta T_f = i \times K_f \times m$$

$$= 4 \times 1.86 \times \frac{0.1}{329 \times 0.1} = 2.3 \times 10^{-2}$$

$$\Rightarrow T_f = 0 - 2.3 \times 10^{-2} = -2.3 \times 10^{-2} \text{ } ^\circ\text{C.}$$

Q.2 (A)

$$\Delta T_b = 2^\circ\text{C}; m_a = 2.5 \text{ g}$$

$$m_{\text{solvent}} = 100 \text{ g}$$

$$K_b = 0.76 \text{ K. kg. mol}^{-1}$$

$$P_{\text{solution}} = ?$$

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

$$2 = 0.76 \times m$$

$$\therefore m = \frac{2}{0.76}$$

$$\frac{P^0 - P}{P} = m \times MM \times 10^{-3} \quad \therefore \frac{760 - P}{P} = \frac{2}{0.76} \times$$

$$18 \times 10^{-3}$$

$$760 - P = \frac{36}{760}P \quad \therefore 760 = \frac{796}{760}P$$

$$\therefore P = 760 \left(\frac{796}{760} \right) \text{ torr} = 725.6 \text{ torr} \approx 724 \text{ torr}$$

Q.3 (D)

$\Delta G = -ve$,

$\Delta S_{\text{system}} = +ve$ Always for solution formation.

$\Delta S_{\text{surr.}} = 0$

No heat exchange between solution and surrounding.

$\Delta H = 0$ For ideal solution.

Q.4 (2)



$$m_0(1-\alpha) \qquad m_0\alpha$$

$$2m_0\alpha; m = m_0(1+2\alpha)$$

$$\therefore m = m_0(1+2 \times 0.5) = 2m_0 \text{ (as given)}$$

$$\frac{(-\Delta T_f)_{\text{observed}}}{(-\Delta T_f)_{\text{undissociated}}} = i = \frac{m}{m_0} = 2$$

Q.5 [1]

$$\Delta T_f = K_f \times i \times m$$

$$0.0558 = 1.86 \times i \times 0.01$$

$$i = 3$$

Given complex behaves as a strong electrolyte

$$\alpha = 100\%$$

$n = 3$ (no. of particles given by complex)

\therefore complex is $[\text{Co}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$

no. of Cl^- ions in the co-ordination sphere of the complex = 1

$$\Delta T_f = K_f \times i \times m$$

$$0.0558 = 1.86 \times i \times 0.01$$

$$i = 3$$

Q.6 (A, B)

Q.7 (A)

As T increase, V.P. increases. So C & D options get rejected.

$$\Delta T_f = K_f \times m$$

$$273 - T_f = 2 \times \frac{34.5/46}{0.5}$$

$$\therefore T_f = 270 \text{ K}$$

Q.8 (BD)

For a mixture of two liquids L and M,

For ideal solution obey Raoult's law

$$P_L = (1 - X_M)P_L^\circ = P_L^\circ - X_M P_L^\circ$$

Graph between P_L & X_M has intercept = P_L° & slope = $-ve$

But graph representing +ve deviation from Raoult's law therefore $M-L < M-M$ or $L-L$ Point Z represents intercept which is P_L° when $X_L \rightarrow 1$

Q.9 [19]

$$45 = P_A^\circ \times \frac{1}{2} + P_B^\circ \times \frac{1}{2}$$

$$P_A^\circ + P_B^\circ = 90 \dots\dots (i)$$

given $P_A^\circ = 20 \text{ torr}$

$$P_B^\circ = 70 \text{ torr}$$

$$\Rightarrow 22.5 \text{ torr} = 20x_A + 70(1 - x_A)$$

$$= 70 - 50x_A$$

$$x_A = 0.05$$

$$\text{So } \frac{x_A}{x_B} = \frac{0.95}{0.05} = 19$$

Q.10 [0.05]

From graph

For solvent X' $\Delta T_{\text{bx}} = 2$

$$\Delta T_{\text{bx}} = m_{\text{NaCl}} \times K_{\text{b(x)}} \dots\dots (1)$$

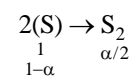
For solvent 'Y' $\Delta T_{\text{by}} = 1$

$$\Delta T_{\text{b(y)}} = m_{\text{NaCl}} \times K_{\text{b(y)}} \dots\dots (2)$$

Equation (1)/(2)

$$\Rightarrow \frac{K_{\text{b(x)}}}{K_{\text{b(y)}}} = 2$$

for solute S



$$i = (1 - \alpha/2)$$

$$\Delta T_{\text{b(x)(s)}} = \left(1 - \frac{\alpha_1}{2}\right) K_{\text{b(x)}}$$

$$\Delta T_{\text{b(y)(s)}} = \left(1 - \frac{\alpha_2}{2}\right) K_{\text{b(y)}}$$

$$\text{Given } \Delta T = \Delta T_{\text{b(x)(s)}} = 3\Delta T_{\text{b(y)(s)}}$$

$$\left(1 - \frac{\alpha_1}{2}\right) K_{b(x)} = 3 \times \left(1 - \frac{\alpha_2}{2}\right) \times k_{b(y)}$$

$$2\left(1 - \frac{\alpha_1}{2}\right) = 3\left(1 - \frac{\alpha_2}{2}\right)$$

$$\alpha_2 = 0.7$$

$$\text{so } \alpha_1 = 0.05$$

Q.11 [1.02 or 1.03]

$$\frac{P^\circ - P_s}{P^\circ} = \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}}$$

$$\frac{650 - 640}{650} = \frac{n_{\text{solute}}}{n_{\text{solute}} + 0.5}$$

$$n_{\text{solute}} = \left(\frac{5}{640}\right)$$

$$\text{Molality} = \frac{5 \times 1000}{640 \times 39}$$

$$\Delta T_f = m \times K_b$$

$$= \frac{5.12 \times 5 \times 1000}{640 \times 39}$$

$$\Delta T_f \approx 1.0256$$

Q.12 [0.20]

$$P_T = P_A^0 X_A + P_B^0 X_B$$

$$0.3 = P_A^0 \times 0.25 + P_B^0 \times 0.75 \quad \dots(i)$$

$$0.4 = P_A^0 \times 0.5 + P_B^0 \times 0.5$$

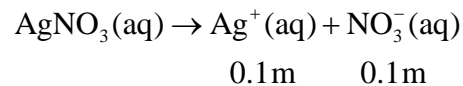
$$0.8 = P_A^0 + P_B^0 \quad \dots(ii)$$

on solving eqⁿ (i) & (ii)

$$P_A^0 = 0.6, P_B^0 = 0.2$$

Question Stem for Question Nos. 13 and 14

Q.13 [100.10]



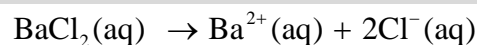
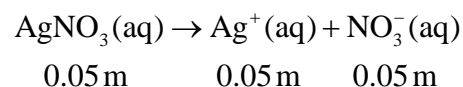
$$\Delta T_b = 0.2 \times 0.5$$

$$= 0.1^\circ\text{C} = 0.1 \text{ K}$$

Boiling point of solution = 100.1 °C

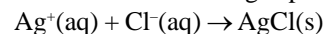
$$= X$$

Q.14 [2.50]



$$0.05 \text{ m} \quad 0.05 \text{ m} \quad 0.1 \text{ m}$$

Ag⁺ and Cl⁻ combine to form AgCl precipitate



$$t = 0 \quad 0.05 \text{ m} \quad 0.1 \text{ m}$$

$$t = \infty \quad 0 \quad 0.05 \text{ m}$$

In final solution total concentration of all ions :

$$[\text{Cl}^-] + [\text{NO}_3^-] + [\text{Ba}^{2+}] = 0.05 + 0.05 + 0.05$$

$$= 0.15 \text{ m}$$

$$\Delta T_b = 0.5 \times 0.15$$

$$= 0.075^\circ\text{C}$$

B.P. of solution 'B' = 100.075°C

B.P. of solution 'A' = 100.1°C

$$|V| = 100.1 - 100.075$$

$$= 0.025 = 2.5 \times 10^{-2}$$

Electrochemistry

EXERCISES

Elementary

- Q.1** (3)
In the electrolytic cell electrical energy change into chemical energy.
- Q.2** (3)
Velocities of both K^+ and NO_3^- are nearly the same in KNO_3 so it is used to make salt-bridge.
- Q.3** (3)
 $E^\circ = E^\circ_{Ag^+/Ag} + E^\circ_{Cu/Cu^{2+}} = 0.80 - 0.34 = +0.46V$.
- Q.4** (4)
 $Cu + FeSO_4 \rightarrow$ No reaction Because Cu has $E^\circ_{Cu^{2+}/Cu} = 0.34$ volt and Fe has $E^\circ_{Fe^{2+}/Fe} = -0.44$ volt.
- Q.5** (1)
More negative is the reduction potential, higher will be the reducing property, *i.e.* the power to give up electrons.
- Q.6** (4)
- Q.7** (2)
- Q.8** (4)
 $\Delta G^\circ = -nFE^\circ$
 $\Delta G^\circ = -2.303RT \log K$; $nFE^\circ = 2.303RT \log K$
 $\log K = \frac{nFE^\circ}{2.303RT} = \frac{2 \times 96500 \times 0.295}{2.303 \times 8.314 \times 298}$
 $\log K = 9.97 = K = 1 \times 10^{10}$.
- Q.9** (2)
 $E^\circ_{cell} = \frac{2.303 RT}{nF} \log K = \frac{0.0591}{n} \log K_c$ at 298K.
- Q.10** (1)
- Q.11** (3)
(3) In between dilute H_2SO_4 and platinum electrode
- O_2 gas evolve at anode.
- Q.12** (1)
In fused $NaCl$ chloride ions are oxidized at anode and it is called oxidation.
- Q.13** (1)
When platinum electrodes are dipped in dilute solution H_2SO_4 than H_2 is evolved at cathode.
- Q.14** (1)
(1) Wt. of Ag deposited = Eq. wt of Ag = 108 gm
Wt. of Ni deposited = Eq. wt. of Ni = 29.5 gm
Wt. of Cr deposited = Eq. wt. of Cr = 17.3 gm.
- Q.15** (4)
 $Pb + PbO_2 + 2H_2SO_4 \xrightleftharpoons[Recharge]{Discharge} 2PbSO_4 + 2H_2O$.
Sulphuric acid is consumed on discharging.
- Q.16** (4)
(4) Fuel cells are more efficient, free from pollution and they function till reactants are active.
- Q.17** (2)
- Q.18** (4)
Rusting of iron is catalysed by $[H^+]$.
- Q.19** (2)
- Q.20** (2)
Strong electrolyte ionise completely at all concentrations and the number of ions does not increase on dilution. A small increase in \wedge_m with volume on dilution is due to the weakening of electrostatic attraction between the ions on dilution.

JEE-MAIN OBJECTIVE QUESTIONS

- Q.1** (1)
In galvanic cell/electro chemical cell electrical energy is produced due to some chemical reaction.

- Q.2** (1)
Reduction and electronation take place at cathode electrode, so it become positive electrode.
- Q.3** (3)
Salt bridge complete the electrical circuit and minimises the liquid - liquid junction potential.
- Q.4** (4)
Agar-Agar is a gelatin, it used in salt bridge along with KCl electrolyte.
- Q.5** (3)
KCl can make precipitate with AgNO_3 , $\text{Pb}(\text{NO}_3)_2$ so can't be used along these electrolyte.
- Q.6** (3)
In format of anode || cathode.
- Q.7** (3)
$$E_{\text{cell}} = E^\circ_{\text{Ni}/\text{Ni}^{2+}} + E^\circ_{\text{Ag}^+/\text{Ag}}$$
$$= 0.25 + 0.80 = \mathbf{1.05 \text{ Volt}}$$
- Q.8** (3)
Lowest S.R.P., highest reducing power.
- Q.9** (4)
$$E^\circ_{\text{Cu}^{2+}/\text{Cu}} = 0.34 \quad E^\circ_{\text{Fe}^{2+}/\text{Fe}} = -0.44 \text{ volt}$$

So Cu can't displace Fe^{2+} .
- Q.10** (4)
Cu can't displace Al^{3+} ion from aluminium nitrate.
- Q.11** (1)
Lower S.R.P. containing ion can displace higher S.R.P. containing ion.
- Q.12** (3)
Lower S.R.P. containing ion can displace higher S.R.P. containing ion.
- Q.13** (1)
Lowest S.R.P., highest reducing power.
- Q.14** (1)
$$E^\circ_{\text{Fe}^{2+}/\text{Fe}} > E^\circ_{\text{H}^+/\text{H}_2}$$
; So, Fe oxidised into Fe^{2+}
$$\text{Fe} + 2\text{H}^+ \longrightarrow \text{Fe}^{2+} + \text{H}_2 \quad E_{\text{Cell}} = +\text{ve.}$$
- Q.15** (2)
- Q.16** (1)
 E° is intensive property and it do not depend on mass of F_2 taking part.
- Q.17** (4)
$$\text{Fe}^{3+} + 3\text{e}^- \longrightarrow \text{Fe}, -0.036 \text{ volt}$$

$$\text{Fe} \longrightarrow \text{Fe}^{2+} + 2\text{e}^-, 0.44 \text{ volt}$$
$$\text{Fe}^{3+} + \text{e}^- \longrightarrow \text{Fe}^{2+} + 3 \times 0.036f - 2 \times 0.44 \times f = -1 \times E^\circ \times f$$

$$E^\circ = \mathbf{0.772 \text{ Volt}}$$
- Q.18** (4)
$$\text{Cu} + \text{e}^- \longrightarrow \text{Cu}, E^\circ = x_1 \text{ Volt}$$
$$\text{Cu}^{2+} + 2\text{e}^- \longrightarrow \text{Cu}, x_2 \text{ Volt}$$
$$\text{Cu} \longrightarrow \text{Cu} + \text{e}^- - x_1 \text{ Volt}$$
$$\text{Cu}^{2+} + \text{e}^- \longrightarrow \text{Cu}^+$$
$$-2 \times x_2 \times f + 1 \times x_1 \times f = -1 \times E^\circ \times f$$

$$E^\circ = \mathbf{2x_2 - x_1}$$
- Q.19** (4)
For spontaneous reaction in every condition
 $E_{\text{cell}} > 0$, $\Delta G < 0$ and Q (reaction quotient) $< K$ (equilibrium constant).
- Q.20** (3)
$$\text{Zn} \longrightarrow \text{Zn}_{(\text{C}_1)}^{2+} + 2\text{e}^-$$
$$\text{Zn}_{(\text{C}_2)}^{2+} + 2\text{e}^- \longrightarrow \text{Zn}$$
$$\text{Zn}_{(\text{C}_2)}^{2+} \rightleftharpoons \text{Zn}_{(\text{C}_1)}^{2+}$$
$$E = 0 - \frac{0.0591}{2} \log \frac{C_1}{C_2}$$

 $E \rightarrow +\text{ve}$ When $C_1 < C_2$
- Q.21** (3)
$$\text{Hg}_2^{2+} + 2\text{e}^- \longrightarrow 2\text{Hg}, 0.789 \text{ Volt}$$
$$\text{Hg} \longrightarrow \text{Hg}^{2+} + 2\text{e}^-, -0.854 \text{ Volt}$$
$$\text{Hg}_2^{2+} \longrightarrow \text{Hg} + \text{Hg}^{2+}, -0.065 \text{ Volt}$$
$$\Delta G = -2 \times (-0.065) \times 96500 = -8.314 \times 298 \ln K_{\text{eq}}$$

$$K_{\text{eq}} = \mathbf{6.3 \times 10^{-3}}$$
- Q.22** (2)
Molar ratio
All have the same equivalent
& mole = $\frac{\text{equiv.}}{\text{nf.}}$

$$\Rightarrow \text{ratio} : \frac{1}{1} ; \frac{1}{2} : \frac{1}{3}$$

$$\Rightarrow 6 : 3 : 2$$

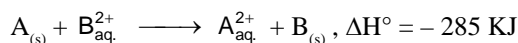
Q.23 (2)

$$\frac{2.1}{7} x = \frac{2.7}{27} \times y = \frac{7.2}{48} \times z$$

$$\Rightarrow \text{ratio } x = \frac{y}{3} = \frac{z}{2}$$

$$\text{If } x = 1 \Rightarrow y = 3, z = 2$$

Q.24 (4)



$$\text{Assuming } \Delta S \text{ to negligible, } \Delta G^\circ = \Delta H^\circ = -285 \times 10^3 \times 0.84 = -2 \times E^\circ \times 96500$$

$$E^\circ = 1.24 \text{ Volt}$$

Q.25 (3)

$$E_{298}^\circ = 1.1028 - 0.641 \times 10^{-3} \times 25 + 0.72 \times 10^{-5} \times$$

$$(25)^2 = 1.091275 \text{ Volt}$$

$$= -8.314 \times 298 \ln K = -2 \times 1.091275 \times 96500$$

$$K = 10^{36.91} = 8.128 \times 10^{36}$$

Q.26 (4)

$$\frac{d\varepsilon}{dt} = -0.00065 \text{ Vol deg}^{-1}$$

$$\Delta S_{298} = n.F. \frac{dE}{dT} = 2 \times 96500 \times (-0.00065) = -125.5 \text{ J/K.}$$

Q.27 (4)

$$\frac{dE}{dT} = \frac{(0.6753 - 0.6915)}{(25 - 0)} = -6.48 \times 10^{-4} \text{ V deg}^{-1}$$

$$\Delta H_{298} = -neF + nFT \frac{dE}{dT} = -2 \times 0.6753 \times 96500 + 2 \times 96500 \times 298 \times (-6.48 \times 10^{-4})$$

$$= 2 \times 96500 (-0.6753 - 0.1931) = -167.6 \text{ KJ.}$$

Q.28 (4)

$$E^\circ = 1.1028 - 0.641 \times 10^{-3} T + 0.72 \times 10^{-5} T^2$$

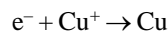
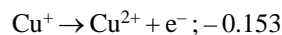
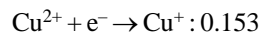
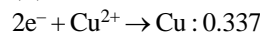
$$\left(\frac{dE^\circ}{dT} \right)_{25} = -0.641 \times 10^{-3} + 2 \times 0.72 \times 10^{-5} T = (-0.641 +$$

$$0.36) \times 10^{-3} = -0.281 \times 10^{-3}$$

$$\Delta S^\circ = nF \frac{dE^\circ}{dT} = 2 \times 96500 \times (-0.281 \times 10^{-3}) = -54.23$$

EU

Q.29 (3)



$$E_{\text{Cu}^+/\text{Cu}} = \frac{2 \times 0.337 - 1 \times 0.153}{1}$$

$$= 0.674 - 0.153$$

$$= 0.521 \text{ V}$$

Q.30 (1)

$$\wedge = \frac{1000 \times K}{M}$$

On decreasing the value of M will increase but increase will be hyperbolic.

Q.31 (1)

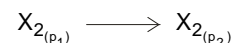
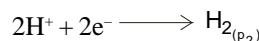
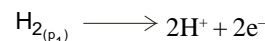
$$E = E^\circ - \frac{0.0591}{n} \log \frac{[\text{Product}]}{[\text{Reactant}]}$$

$$\text{if } \frac{[\text{Product}]}{[\text{Reactant}]} = 1 \text{ then } E = E^\circ.$$

Q.32 (1)

$$E = 1.1 - \frac{0.0591}{2} \log \frac{0.1}{0.1} \Rightarrow E = 1.10 \text{ Volt}$$

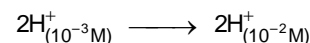
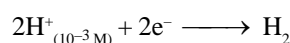
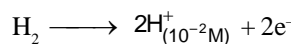
Q.33 (2)



$$E = 0 - \frac{0.0591}{2} \log \frac{p_2}{p_1}$$

$$P_2 < P_1 \text{ for } E \rightarrow +ve$$

Q.34 (2)



$$E = 0 - \frac{0.0591}{2} \log \left(\frac{10^{-1}}{10^{-2}} \right)^2$$

$$E \rightarrow -ve \text{ (Non spontaneous).}$$

Q.35 (3)

$$0 = (-0.151 - 0) - \frac{0.0591}{1} \log [\text{H}^+]$$

$$0.0591 \times \log [\text{H}^+] = -0.151$$

$$\text{pH} = \frac{0.151}{0.0591} = \mathbf{2.56}$$

Q.36 (2)

$$E_{\text{Ag}|\text{AgI}|\text{I}^-}^0 = E_{\text{Ag}^+|\text{Ag}}^0 - \frac{0.0591}{1} \log \frac{1}{K_{\text{SP}}}$$

$$-0.151 = 0.799 - \frac{0.0591}{1} \log \frac{1}{K_{\text{sp}}}$$

$$0.0591 \log K_{\text{sp}} = -0.151 - 0.799$$

$$\log K_{\text{sp}} = -16.074$$

$$K_{\text{sp}} = \mathbf{8.43 \times 10^{-17}}$$

Q.37 (4)

$$E_{\text{Ag}|\text{AgI}|\text{I}^-} = 0.8 - \frac{0.0591}{1} \log \frac{1}{K_{\text{sp}}}$$

$$= 0.8 + 0.0591 \times \log 8.3 \times 10^{-17}$$

$$= \mathbf{-0.15 \text{ Volt}}$$

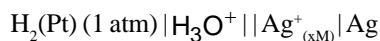
or

$$E_{\text{Ag}|\text{AgI}|\text{I}^-}^0 = E_{\text{Ag}^+|\text{Ag}}^0 + \frac{RT}{F} \cdot \ln \frac{1}{K_{\text{sp}}}$$

$$= -0.8 - \frac{8.31 \times 298 \times 2.303}{96500} \log k_{\text{sp}}$$

$$= -0.8 - 0.0591 \cdot \log 8.3 \times 10^{-17}$$

$$= -0.8 + 0.095 = 0.15 \text{ V.}$$

Q.38 (1)

$$1.0 = (0 + 0.8) - \frac{0.06}{1} \log \frac{[\text{H}^+]}{x}$$

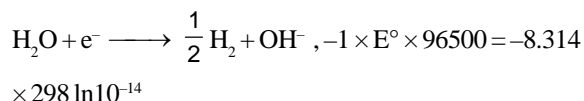
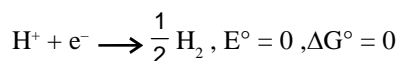
$$-\frac{0.2}{0.06} = \log \frac{[\text{H}^+]}{x}$$

$$\frac{10}{3} = \text{pH} + \log x$$

$$\log x = -1.7$$

$$\frac{10^{-5.5}}{x} = 1.62 \times 10^{-4}$$

$$x = \mathbf{2 \times 10^{-2} \text{ M}}$$

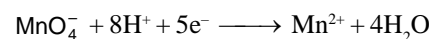
Q.39 (1)

$$E^\circ = \mathbf{-0.828 \text{ Volt.}}$$

Q.40 (3)

$$E = 0 - \frac{0.0591}{2} \log \frac{16}{4} = -\frac{0.0591}{2} \times 2 \log 2 = -$$

$$0.0591 \times 0.301 = \mathbf{-0.0178 \text{ Volt.}}$$

If connected in reverse direction, $E = 0.0178 \text{ volt.}$ **Q.41** (1)

$$E_1 = E^\circ - \frac{0.0591}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] \times 1^8}$$

$$E_2 = E^\circ - \frac{0.0591}{5} \log \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-] \times (10^{-4})^8} = -\frac{0.0591}{5} \times$$

$$32 = -0.37824$$

$$E_1 - E_2 = \mathbf{0.38 \text{ Volt.}}$$

Q.42 (1)

$$0 = (-0.771 + 0.7991) - \frac{0.0591}{1} \log \frac{1}{x}$$

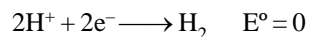
$$\Rightarrow 0 = 0.0281 + 0.0591 \log X$$

$$\log X = -\frac{0.0281}{0.0591}$$

$$\Rightarrow \mathbf{X = 0.335 \text{ M}}$$

Q.43 (1)

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{n} \log Q_{\text{eq}}$$



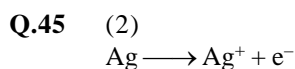
$$Q_{\text{eq}} = \frac{P_{\text{H}_2}}{(\text{H}^+)^2}, E_{\text{cell}} \frac{-0.0591}{2} \log 100 = -0.0591$$

$$\Delta E_{\text{cell}} = 0.0591$$

Q.44 (1)

$$E_{\text{cell}}^0 = \frac{0.0591}{2} \log \frac{\text{Sr}^{2+}}{\text{Mg}^{2+}} = \frac{0.0591}{2} \log (2.69 \times$$

$$10^{+12}) = 0.3667$$



$$E^\circ = -0.799 \quad E_{\text{cell}}^\circ = -0.25$$

$$E_{\text{cell}} = -0.25 \quad E_{\text{cell}}^\circ = -0.799$$

$$\Rightarrow E_{\text{cell}} = E_{\text{cell}}^\circ - \frac{0.0591}{1} \log(\text{Ag}^+)$$

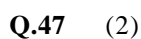
$$-0.25 + 0.799 = -0.0591 \log(\text{Ag}^+)$$

$$\log(\text{Ag}^+) = \frac{-0.799 + 0.25}{0.0591}$$

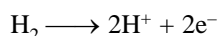
$$(\text{Ag}^+) = 5.13 \times 10^{-10}$$

$$K_{\text{sp}} = (\text{Ag}^+)(\text{Cl}^-) = 5.13 \times 10^{-10} \times 0.1$$

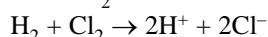
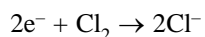
$$= 5.13 \times 10^{-11}$$



Anode



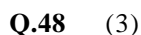
Cathode



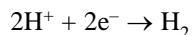
$$[(\text{H}^+)^2 (\text{Cl}^-)^2] = K_{\text{eq.}}$$

$$E_{\text{cell}} = E^\circ - \frac{0.0591}{2} \log(\text{H}^+)^2 (\text{Cl}^-)^2$$

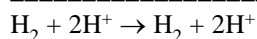
$$= E^\circ - 0.0591 \log[\text{H}^+][\text{Cl}^-]$$



$$0.4 \text{ atm} \quad 10^{-1}$$

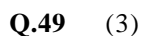


$$10^{-2} \quad 0.1 \text{ atm}$$



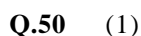
$$0.4 \quad 0.01 \quad 0.1 \quad 0.1 \quad E^\circ = 0$$

$$E_{\text{cell}} = -\frac{0.0591}{2} \log \left(\frac{(0.1)^2 (0.1)}{(0.01)^2 (0.4)} \right) = -0.041$$



In this Cl^- will oxidise to give Cl_2 , Na^+ reduction potential has lower potential than water reduction potential so water will reduce to give H_2 .

(C) NaCl



As electron flows from anode to a cathode and so current flows from cathode to anode in outer circuit

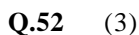


Water oxidation at anode can be represented and SO_4^{2-} can't be discharged

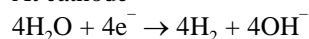
so



so ion which will be discharged at anode will be OH^-



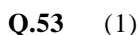
At cathode



At anode



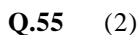
Thus at cathode we will get H_2 whereas at anode we will get O_2 .



In electrolysis of a fused salt, the weight deposited on electrode will not depend on temperature.



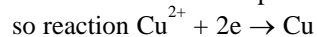
In this Cl^- will oxidise to give Cl_2 , Na^+ water reduction potential has higher potential than that of water reduction potential, so water will reduce to give H_2 .



Cation loses charge at cathode as it gave electron.



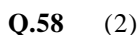
As reduction will take place at cathode



Will take place at cathode



If mercury is used as cathode in the electrolysis of aqueous NaCl solution then the metal is discharged at mercury to form amalgam.



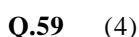
$$\text{Volume} : 10 \times 10 \times 10^{-2} = 1 \text{ cm}^3$$

$$\text{mass of Cu} = 8.94 \text{ g}$$

$$\text{mole of Cu} = \frac{8.94}{63.5}$$

$$\text{EQuivalent of Cu} = \frac{8.94}{63.5} \times 2$$

$$\text{Charge} = \frac{8.94}{63.5} \times 2 \times 96500 \text{ C} = 27172 \text{ C}$$



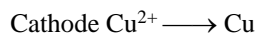
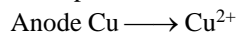
Equivalent of H_2 = Equivalent of O_2

$$= \frac{2.4}{22.4} \times 4 \Rightarrow \text{Mole of } \text{H}_2 = \frac{2.4}{22.4} \times 4 \times \frac{1}{2}$$

$$\text{Volume of H}_2 = \frac{2.4 \times 2}{22.4} \times 22.4$$

$$= 4.8 \text{ L}$$

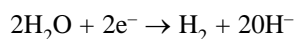
Q.60 (4)
At both electrodes oxidation of Cu & reduction of Cu takes place



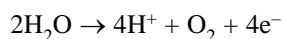
So If 2.5 g deposited at cathode \Rightarrow 2.5 of Cu mass decreased from anode

Q.61 (1)

Cathode



Anode

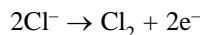
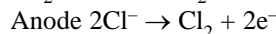
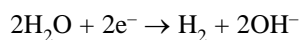


Q.62 (1)

LiCl

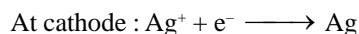
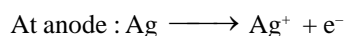
(According to S.R.P.)

Cathode



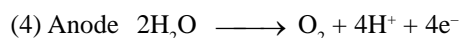
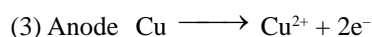
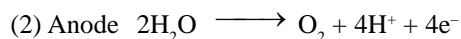
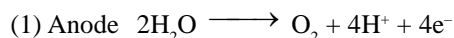
At cathode $(\text{OH}^-) \uparrow$ pH \downarrow and pH \uparrow

Q.63 (3)



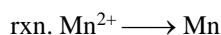
So conc. of Ag^+ will remain same .

Q.64 (4)



Q.65 (3)

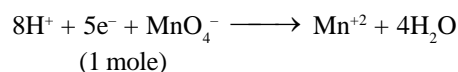
$$\frac{1.81 \times 10^{22}}{6.02 \times 10^{23}} = \frac{1}{\text{At. mass}} \times 2$$



$$n_f = 2$$

$$\text{At mass} = \frac{2 \times 6.022 \times 10^{23}}{1.81 \times 10^{22}} = 66.7$$

Q.66 (4)



5 mole e^- = 5 Faraday.

Q.67 (2)

$$\text{Mole of Fe deposited} = \frac{1}{2} \times 3 = 1.5 \text{ mole}$$

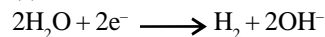
$$W_{\text{Fe}} = 1.5 \times 56 = \mathbf{84 \text{ gm.}}$$

Q.78 (3)

$$W = \frac{63.5}{2 \times 96500} \times 2 \times 60 \times 60 = 2.37 \text{ gm}$$

$$\% \text{ of efficiency} = \frac{3}{2.37} \times 100.$$

Q.69 (2)



$$\text{No. of Faraday passed} = \frac{9.65 \times 1000}{96500} = 0.1 \text{ F}$$

$$n_{\text{OH}^-} \text{ formed} = 0.1 \text{ mol}$$

$$n_{\text{NaOH}} = 0.1 \text{ mol} \equiv \mathbf{4 \text{ gm.}}$$

Q.70 (1)

Since to deposit 1 mole of aluminium 3 coulomb of electricity is required, as the valency of silver is +1 so 3 mole of silver will be deposited by 3C of electricity

Q.71 (2)

gm eq. of H_2 = gm eq. of Cu

$$\frac{0.504}{2} \times 2 = \frac{w}{63.5} \times 2$$

$$W = \frac{63.5 \times 0.504}{2} = 16.0 \text{ gm}$$

Q.72 (3)

$$\text{No. of F} = \frac{it}{96500} = \text{gm eq of Cu}$$

$$\text{moles of Cu} = \frac{\text{gm eq. of Cu}}{2}$$

$$\text{moles of Cu} = \frac{2.6 \times 380}{96500 \times 2}$$

$$\text{wt. of Cu} = \frac{2.6 \times 380}{96500 \times 2} \times 63.5$$

$$= 0.325 \text{ gm}$$

- Q.73** (2)
gm equivalent of Al = gm eq. of Cu = gm eq. of Na
 $3 = 3 = 3$
 $3/3 = 3/2 = 1$
 $1 : 1.5 : 3$
- Q.74** (3)
gm equivalent = $\frac{8}{96500}$
 $0.01 = \frac{8}{96500} = 965 \text{ C}$
- Q.75** (2)
 $Z = w/it$
w in gm
it in columb.
so $z = \text{gm/columb}$
- Q.76** (4)
Since KCl has the n-factor of 1 so 1 faraday of electricity will liberate one mole of metal from a solution.
- Q.77** (2)
Since magnesium has the n-factor 2 so the number of faraday required to generate 1 mole of Mg will be 2.
- Q.78** (3)
equivalence of $\text{H}_2 = \text{equivalence of } \text{O}_2$
 $\frac{0.224}{22.4} \times 2 = \frac{\text{volume of } \text{O}_2}{22.4} \times 4$
 $0.112 \text{ litre} = \text{volume of } \text{O}_2$.
- Q.79** (3)
 $\text{Na}^+ + \text{e}^- \longrightarrow \text{Na(s)}$
1mole 1 Faraday
 $\text{Al}^{3+} + 3\text{e}^- \longrightarrow \text{Al(s)}$
1 Faraday
No. of mole of Al = $\frac{1}{3}$ mole.
- Q.80** (2)
Discharging reaction
 $\text{Pb(s)} + \text{PbO}_2\text{(s)} + 2\text{H}_2\text{SO}_4 \longrightarrow 2\text{PbSO}_4 + 2\text{H}_2\text{O}$.
- Q.81** (1)
 $\text{H}_2\text{-O}_2$ fuel cell
At anode : $2\text{OH}^- + \text{H}_2 \longrightarrow 2\text{H}_2\text{O} + 2\text{e}^-$
At cathode : $2\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \longrightarrow 4\text{OH}^-$
- Q.82** (2)
 $K = 0.3568 \Omega \text{ cm}^{-1}$
conductance = $0.0268 \Omega^{-1}$
 $K = G \times l/A$
 $0.3568 = 0.0268 \times l/9$
 13.31 cm^{-1}
- Q.83** (2)
 $K = G L/A$
 $10^{-3} \times 2.768 = 1/R \times L/A$
 $L/A = 228.08 \times 10^{-3}$
 $= 0.2281 \text{ cm}^{-1}$
- Q.84** (3)
Higher the dilution higher will be the equivalent conductance
- Q.85** (3)
 $K = G \frac{L}{A}$
 $K = \frac{1}{R} \times \frac{L}{A}$
 $\frac{1}{100} \times 1, K = 10^{-2} \Omega^{-1} \text{ cm}^{-1}$
- Q.86** (4)
 $\lambda_m = \frac{K \times 1000}{M}$
 $\lambda_m = \frac{0.0110 \times 1000}{0.05}$
 $= 220 \text{ S cm}^2 \text{ mol}^{-1}$
- Q.87** (2)
That electrolyte will be the best electrolyte which has maximum number of ions.
- Q.88** (3)
 $\alpha = \frac{10}{200} = \frac{1}{20}$
 $[\text{H}^+] = C\alpha = 0.1 \times \frac{1}{20} = \frac{1}{200}$
 $\text{pH} = -\log \frac{1}{200} = \log 200 = 2.3$
- Q.89** (3)
 $K = \frac{1}{x}$
 $\wedge = k \frac{1000}{M} = \frac{1}{\lambda} \times \frac{1000}{y} = \frac{1000}{xy}$

Q.90 (2)

$$380 \times 10^{-4} \times 10^4 \frac{\text{Scm}^2}{\text{mole}} = k \times \frac{1000}{\text{M}}$$

↓

Molarity of ion

$$1.6 \times 10^{-5} = \frac{x^2}{0.01 - x} \Rightarrow 16 \times 10^{-8}$$

$$16 \times 10^{-8} = x^2 \\ x = 4 \times 10^{-4}$$

$$K = \frac{380 \times \text{M}}{1000} = \frac{380 \times 4 \times 10^{-4}}{1000}$$

$$= 152 \times 10^{-6} \text{Scm}^{-1}$$

$$= 1.52 \times 10^{-2} \text{Sm}^{-1}$$

Q.91 (3)

$$K_a = 25 \times 10^{-6} \wedge_{\text{eq}} = 19.6 \text{Scm}^2 \text{eq}^{-1}, C = 0.01$$

$$K_a = 0.01 \times \alpha^2 \Rightarrow \alpha = \sqrt{\frac{25 \times 10^{-6}}{10^{-2}}} = 5$$

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

$$\alpha = 5 \times 10^{-2} = \frac{19.6}{\wedge_{\text{eq}}} \Rightarrow \wedge_{\text{eq}} = \frac{19.6}{5 \times 10^{-2}} =$$

$$392 \text{Scm}^2 \text{eq}^{-1}.$$

Q.92 (4)

Molar conductivity \propto no. of ions per mole of electrolyte.

Q.93 (4)

$$\wedge_{\text{m}, \text{BaSO}_4} = (x_1 + x_2 - 2x_3) \Rightarrow \wedge_{\text{eq}, \text{BaSO}_4} =$$

$$\frac{\wedge_{\text{eq}, \text{BaSO}_4}}{\text{n-factor}}$$

$$\wedge_{\text{eq}, \text{BaSO}_4} = \frac{(x_1 + x_2 - 2x_3)}{2}$$

Q.94 (1)

$$1.5 \times 10^{-4} \times 10^4 = 9 \times 10^{-8} \times \frac{1000}{\text{N}}$$

$$\Rightarrow \text{N} = 6 \times 10^{-5}$$

$$\Rightarrow \text{M} = \frac{6 \times 10^{-5}}{3} = 2 \times 10^{-5}$$

$$K_{\text{sp}} = (3\text{S})^2 (\text{S}) = 27\text{S}^3 = 27 \times 16 \times 10^{-20} \\ = 432 \times 10^{-20} = 4.32 \times 10^{-18}$$

Q.95 (4)

$$1.53 = \frac{1000 \times 3.06 \times 10^{-6}}{\text{Normality}}$$

$$\text{Normality} = 2 \times 10^{-3} \text{M}$$

$$\text{Molarity} = \frac{2 \times 10^{-3}}{2} = 10^{-3} \text{M}$$

$$K_{\text{sp}} = 10^{-6} \text{M}$$

Q.96 (4)

$$K_a = C\alpha^2 = 0.1 \times \left(\frac{7}{380.8}\right)^2 = 3.38 \times 10^{-5}$$

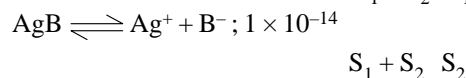
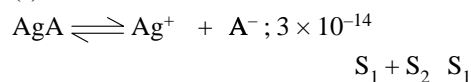
Q.97 (3)

$$K = 1.382 \times 10^{-6} \text{s cm}^{-1}$$

$$\wedge_{\text{AgCl}} = 61.9 + 76.3 = 138.2 = \frac{1000 \times 1.382 \times 10^{-6}}{\text{S}}$$

$$\text{S} = 10^{-5} \text{M}.$$

Q.98 (3)



$$S_1 + S_2 = 2 \times 10^{-7}; S_1 = 1.5 \times 10^{-7}$$

$$S_2 = 0.5 \times 10^{-7}$$

$$375 \times 10^{-10} = K_{\text{Ag}^+} + K_{\text{A}^-} + K_{\text{B}^-}$$

$$= \frac{(\wedge_{\text{Ag}^+})(\text{M}_{\text{Ag}^+})}{1000} + \frac{(\wedge_{\text{A}^-})(\text{M}_{\text{A}^-})}{1000} + \frac{(\wedge_{\text{B}^-})(\text{M}_{\text{B}^-})}{1000}$$

$$= 60(S_1 + S_2) + 80S_1 + \wedge_{\text{B}^-} S_2$$

After putting value of S_1 & S_2

$$\wedge_{\text{B}^-} = 270$$

Q.99 (3)

$$C = \frac{1}{50}; \frac{\ell}{a} = \frac{2.2}{4.4} = \frac{1}{2}$$

$$K = \frac{C\ell}{a} = \frac{1}{50} \times \frac{1}{2} = 10^{-2}$$

$$\lambda_{\text{m}} = k \times \frac{1000}{\text{M}}$$

$$= 10^{-2} \times \frac{1000}{0.5} = 20 \text{S cm}^2 \text{mol}^{-1}$$

$$= 20 \times 10^{-4} \text{Sm}^2/\text{mol}$$

$$= 0.002 \text{ Sm}^2/\text{mol}^{-1}$$

- Q.100** (1)
For strong electrolyte

$$\lambda_M^c = \lambda_M^\infty - b\sqrt{C}$$

**JEE-ADVANCED
OBJECTIVE QUESTIONS**

- Q.1** (D)

$$E_{\text{cell}} = (0.77 - 0.0713) - \frac{0.059}{1} \log \frac{0.02}{0.1 \times 0.34} = 0.713$$

volt.

- Q.2** (B)

$$E_{\text{cell}} = 0.059 \log \frac{C_1}{C_2}$$

For E_{cell} to be +ve and maximum

$$\frac{C_1}{C_2} < 1 \text{ or } C_1 < C_2 \quad \text{Give } C_2 = 1M.$$

$\therefore C_1$ should be the minimum conc. of H^+ .

\therefore (B) is the right answer.

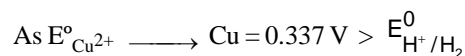
- Q.3** (B)

$$E_{\text{cell}}^\circ = 0.8 - (-0.76) = \mathbf{1.56 \text{ V}}$$

- Q.4** (A)

$$E_{\text{cell}} = 0.77 - \frac{0.059}{1} \log \frac{1.5}{0.015} = \mathbf{0.652 \text{ V}}$$

- Q.5** (A)



$\therefore \text{Cu}^{2+}$ can be reduced by H_2 .

- Q.6** (C)

M is more reactive than carbon and B is more reactive than A. Also both B and A are less reactive than C.

- Q.7** (B)

Higher the std. reduction potential, higher is the oxidising power.

- Q.8** (A)

$Z > Y > X$ (Non metals like $\text{F}_2 > \text{Cl}_2 > \text{Br}_2$)

So, Y will oxidise X^- but not Z^-

Z will oxidise both X^- and Y^-

X can't oxidise Y^- or Z^- .

- Q.9** (C)

Lower standard reduction potential related metal ions can displace higher standard reduction potential related metal ions.

- Q.10** (A)

$$E_{\text{MnO}_4^-/\text{MnO}_2}^\circ = \frac{5 \times 1.5 - 2 \times 1.23}{3} = 1.7 \text{ volt}$$

- Q.11** (A)

$$\Delta S = \frac{nF dE_{\text{cell}}}{dt} \text{ or } \frac{dE_{\text{cell}}}{dt} = \frac{\Delta S}{nF}$$

- Q.12** (B)

$$E_{\text{cell}} = 0.29 - \frac{0.059}{2} \log \frac{0.01 \times (0.01)^2}{(0.01)^2 \times 1} \text{ or } E_{\text{cell}} =$$

0.35 volt

- Q.13** (B)

$$E_1 = E^\circ - \frac{RT}{nF} \ln 2$$

$$E_2 = E^\circ - \frac{R \times 2T}{nF} \ln 1 = E^\circ$$

$\therefore E_2 > E_1$

- Q.14** (B)

$$E_{\text{cell}} = \frac{0 - 0.059}{1} \log \sqrt{\frac{10^{-5}}{10^{-3}}} = \mathbf{0.059 \text{ V}}$$

- Q.15** (C)

$$-0.413 = 0 - 0.059 \log \frac{1}{[\text{H}^+]} \text{ or } \frac{0.414}{0.059} = -\log \text{H}^+ =$$

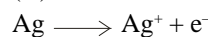
pH or $\text{pH} = 7$

- Q.16** (B)

$$1.1591 = 1.1 - \frac{0.059}{2} \log \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} \text{ or } \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]} = 10^{-2} =$$

0.01

- Q.17** (A)



$$E_1 = E_{\text{oxid}} + E_{\text{calomel}}$$

$$= E' - \frac{0.0591}{1} \log K_{\text{sp1}} + E_{\text{calomel}}$$

$$E_2 = E' - \frac{0.0591}{1} \log K_{\text{sp2}} + E_{\text{calomel}}$$

$$E_2 - E_1 = 0.177 = 0.0591 \log \frac{K_{sp1}}{K_{sp2}}$$

$$\frac{K_{sp1}}{K_{sp2}} = 10^3$$

Q.18 (C)

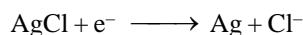
Only anode or cathode can't work alone so absolute value of reduction potential can't be determined.

Q.19 (C)

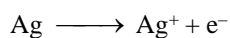
$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.059}{2} \log \frac{[\text{Sn}^{2+}]}{[\text{Ag}^+]^2}$$

Ag⁺ increase, E_{cell} increase.

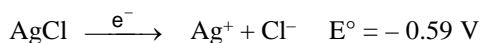
Q.20 (B)



$$E^{\circ} = 0.2 \text{ V}$$



$$E^{\circ} = -0.79 \text{ V}$$



$$E^{\circ} = \frac{0.059}{n} \log K \Rightarrow -0.59 = \frac{0.059}{1} \log K_{sp}$$

$$\Rightarrow K_{sp} = 10^{-10}$$

Now solubility of AgCl in 0.1 M AgNO₃

$$S(S + 0.1) = 10^{-10} \Rightarrow S = 10^{-9} \text{ mol/L}$$

Hence 1 mole dissolves in 10⁹ L solution

hence in 10⁶ L amount that dissolves in 1 m mol.

Q.21 (B)

$$\frac{1000 \times 2}{(55 + 32)} = \frac{27 \times 24 \times 3600 \times \eta}{96500} \text{ or } \eta = 0.951 = 95.1\%$$

Q.22 (B)

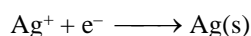
$$\frac{9.72}{22.4} \times 2 = \frac{2.35}{22.4} \times 4 + \frac{W}{194} \times 2 \text{ or } W = 43.47 \text{ g}$$

Q.23 (D)

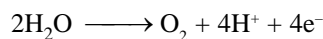
Impure Cu will oxidise from anode along with Zn but only Cu²⁺ will reduce on cathode in purification of Cu²⁺.

Q.24 (D)

AgNO₃ **At cathod :**

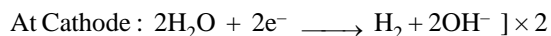


At anode :



∴ At cathode pH will increase.

Q.26 (C)



H₂ = 2 mole

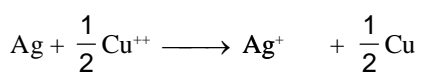
O₂ = 1 mole

Total volume = 3 × 22.4 = **67.2 L.**

Q.27 (A)

$$Q = 10 \times 4825 = 48250 \text{ C}$$

$$\text{no. of faraday} = \frac{48250}{96500} = 0.5$$



$$\frac{2.00}{2-0.25} \quad \frac{2.00}{2+0.50}$$

$$E_{\text{cell}} = E_{\text{cell}}^{\circ} - \frac{0.0591}{1} \log \frac{[\text{Ag}^+]}{[\text{Cu}^{++}]^{1/2}}$$

$$E_1 = E_{\text{cell}}^{\circ} - \frac{0.0591}{1} \log \frac{2.00}{(2.00)^{1/2}}$$

$$E_2 = E_{\text{cell}}^{\circ} - \frac{0.0591}{1} \log \frac{2.50}{(1.75)^{1/2}}$$

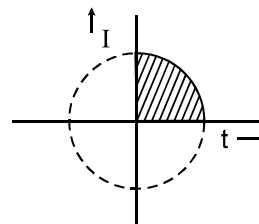
$$\Delta E = E_2 - E_1 = \frac{0.0591}{1} \left[\log \sqrt{2} - \log \frac{2.50}{\sqrt{1.75}} \right] =$$

$$\frac{0.0591}{1} [\log 1.41 - \log 1.88]$$

$$= \frac{0.0591}{1} [0.1492 - 0.2742]$$

$$= - \frac{0.0591}{1} \times 0.125 = -0.00738 \text{ V.}$$

Q.28 (A)



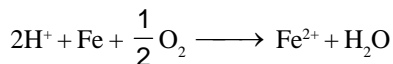
$$Q = \frac{\pi(25)}{4} C = \frac{\pi \times 25}{4 \times 96500} \text{ F}$$

$$\therefore m = \frac{108}{1} \times \frac{\pi \times 25}{4 \times 96500} \text{ g} = 0.02197 \text{ g}$$

$$= 21.97 \text{ mg} \approx 22 \text{ mg}$$

Q.29 (B)

Rusting reaction of Fe is -



Q.30 (A)

$$\frac{i \times 15 \times 60}{96500} = \frac{6.72}{22.4} \times 2 \Rightarrow i = \mathbf{64.3 \text{ amp.}}$$

Q.31 (A)

$$\frac{\lambda_{\text{Cl}^-}^\circ}{\lambda_{\text{K}^+}^\circ + \lambda_{\text{Cl}^-}^\circ} = 0.505 \text{ or } \lambda_{\text{Cl}^-}^\circ = 0.505 \times 130$$

$$= 65.65 \text{ Scm}^2 \text{ eq}^{-1}.$$

$$\lambda_{\text{K}^+}^\circ = F \times U_{\text{K}^+} \text{ or}$$

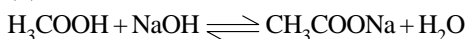
$$U_{\text{K}^+} = \frac{(130 - 65.65)}{96500} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}.$$

$$= \mathbf{6.67 \times 10^{-4} \text{ cm}^2 \text{ volt}^{-1} \text{ sec}^{-1}}.$$

Q.32 (A)

$\text{H}^+ + \text{Cl}^- + \text{NaOH} \longrightarrow \text{Na}^+ + \text{Cl}^- + \text{H}_2\text{O}$ to conductance Ist decreases since no. of ions decreases after end point it increases.

Q.33 (B)



$$0.015 \text{ V} \quad 0.015 \text{ V} \quad 0.015 \text{ V}$$

mole mole mole

$$\text{molarity } (\text{CH}_3\text{COONa}) = \frac{0.015 \text{ V}}{2 \text{ V}} = \frac{0.015}{2}$$

$$\Lambda_m^\circ = 6.3 \times 10^{-4} \times \frac{1000}{\left(\frac{0.015}{2}\right)} = \frac{6.3 \times 2}{0.15} = 84$$

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MCQ/COMPREHENSION/MATCHING

Q.1 (ABC)

Reduction Potential of Ce is higher than that of Zn.

Q.2 (BC)

(a) SOP (SO_4^{2-}) = -2.00

SOP (Cl^-) = -1.36

oxidation of SO_4^{2-} will not take place

(b) SOP (Cl^-) = -13.6

SOP (I^-) = -0.54

SOP (Br^-) = -1.09

(c) Similarly as (b) option

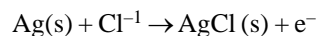
(d) Br^- can't be reduced further.

Q.3

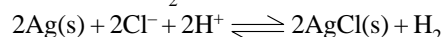
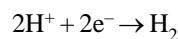
(AD)

Cell reaction

Anode



Cathode



$$E = E^\circ - \frac{0.0591}{2} \log \left\{ \frac{P_{\text{H}_2}}{[\text{Cl}^-]^2 [\text{H}^+]^2} \right\}$$

$$0.22 = E^\circ - \frac{0.0591}{2} \log \left[\frac{1}{1 \times 1} \right]$$

$$\Rightarrow E^\circ = 0.22 \text{ V}$$

$$E_{\text{cell}} = 0.22 - \frac{0.0591}{2} \log \left\{ \frac{P_{\text{H}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right\}$$

$$\text{(a) } P_{\text{H}_2} = 2 \Rightarrow E_{\text{cell}} < 0.22$$

$$\text{(b) } [\text{Cl}^-] \uparrow \Rightarrow \log \left\{ \frac{P_{\text{H}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right\} = -\text{ve value}$$

$$\Rightarrow E_{\text{cell}} > 0.22$$

$$\text{(c) } [\text{H}^+] \uparrow \Rightarrow E_{\text{cell}} > 0.22$$

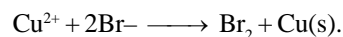
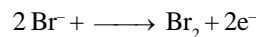
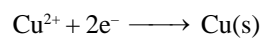
$$\text{(d) } \text{KCl conc}^n \downarrow \Rightarrow [\text{Cl}^-] \downarrow$$

$$\Rightarrow \log \left\{ \frac{P_{\text{H}_2}}{[\text{H}^+]^2 [\text{Cl}^-]^2} \right\} > 0 \Rightarrow E_{\text{cell}} < 0.22$$

Q.4

(AB)

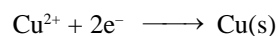
At Cathode :



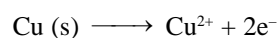
Q.5

(AB)

At Cathode :



At Anode

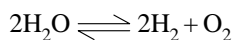


Increase in mass of cathode = decrease in mass of

$$\text{Anode} = \frac{2.68 \times 3600}{96500} \times \frac{63.5}{2} = \mathbf{3.174 \text{ g.}}$$

Q.6 (ACD)because $E_{\text{Cu}^{2+}/\text{Cu}}^{\circ} > E_{\text{Fe}^{2+}/\text{Fe}}^{\circ}$.**Q.7** (AB)

Cell reaction



$$270 \text{ g H}_2\text{O} = \frac{270}{18} \text{ mole} = 15 \text{ mole}$$

equivalent = $15 \times 2 = 30$ equivalent

$$\begin{aligned} \text{(a) O}_2 \text{ evolved} &= \frac{15}{2} = 7.5 \text{ mole} = 7.5 \times 22.4 \text{ L} \\ &= 168 \text{ L} \end{aligned}$$

$$\text{(b) Total mole of gas} = 15 \times \frac{3}{2} = \frac{45}{2}$$

Total volume of gas produced

$$= 22.4 \times \frac{45}{2} = 504 \text{ L}$$

$$\text{(c) H}_2 \text{ produced} = 30 \times 22.4 = 336 \text{ L}$$

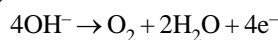
at cathode current efficiency = 75%

(d) for 30 F electricity consumed

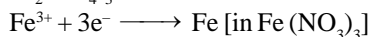
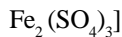
$$\text{will be} = 30 \times \frac{100}{75} = 40 \text{ F}$$

Q.8 (BCD)(A) At anode oxidation of Cu produce Cu^{2+} (B) At both electrode oxidation or reduction of hydrogen or H^+

(C) At anode

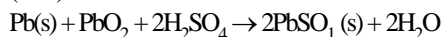


(D) Anode

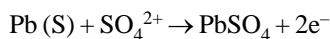
**Q.9** (BCD)

$$\text{Amount of Fe deposited in FeSO}_4 = \frac{Q}{96500} \times \frac{56}{2}$$

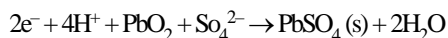
$$\text{Amount of Fe deposited in Fe}_2(\text{SO}_4)_3 = \frac{Q}{96500} \times \frac{56}{3}$$

Q.10 (CD) H_2SO_4 : consumed H_2O : produced (volume increases and density decreases)

Anode



Cathode

**Q.11** (ACD)

Resistance of cell is not due to vibrations of ion but actually it is due to collisions of ions.

Q.12 (ACD)

On dilution specific conductance decreases while molar conductivity increases.

Comprehension # 1 (Q. No. 13 to 17)**Q.13** (A)**Q.14** (C)**Q.15** (A)**Q.16** (A)**Q.17** (B)

$$\begin{aligned} \mathbf{13} \quad \Delta W &= -nFE \\ 82700 &= -3 \times 96500 \end{aligned}$$

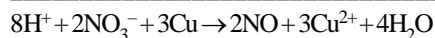
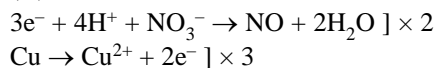
$$\begin{aligned} \mathbf{14} \quad E &= \varepsilon^{\circ} - \frac{0.591}{n} \log Q. \\ \text{ef } KC &= Q \\ E &= O \\ \text{Ans. (C)} \end{aligned}$$

$$\begin{aligned} \mathbf{15} \quad \varepsilon &= \varepsilon^{\circ} - \frac{0.591}{n} \log Q. \\ \text{(A) i.e. straight line} \end{aligned}$$

$$\begin{aligned} \mathbf{16} \quad \varepsilon^{\circ} &= \frac{0.591}{n} \log V_e. \\ \text{here } n &= 2 \end{aligned}$$

$$\begin{aligned} 0.46 &= \frac{0.591}{n} \log K_e \\ \mathbf{17} \quad \varepsilon^{\circ} &= \frac{0.591}{2} \log V_e \end{aligned}$$

$$1.10 = \frac{0.591}{2} \log K_e$$

Comprehension # 2 (Q. No. 18 to 19)**Q.18** (B)**Q.19** (C)

$$E^{\circ}_{\text{cell}} = 0.96 - 0.34 = 0.62$$

$$E_{\text{cell}} = 0.62 - \frac{0.06}{6} \log \frac{(P_{\text{NO}})^2 (\text{Cu}^{2+})^3}{(\text{NO}_3^-)^2 (\text{H}^+)^8}$$

$$= 0.62 - 0.01 \log \frac{10^{-6} \times 10^{-3}}{(1)^2 (1)^8}$$

$$= 0.62 + 0.01 \times 9 = 0.62 + 0.09 = 0.71 \text{ V}$$

Comprehension # 3 (Q. No. 20 to 22)

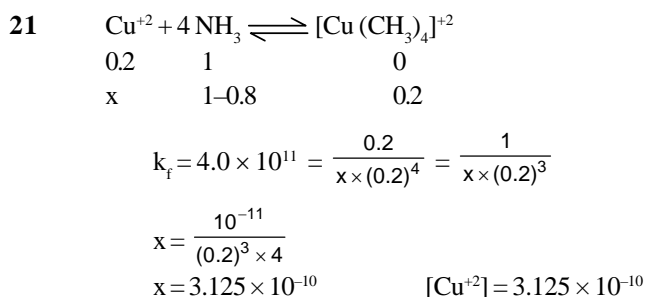
Q.20 (B)

Q.21 (A)

Q.22 (A)

20
$$E_{\text{cell}} = E^{\circ}_{\text{cell}} - \frac{2.303RT}{nF} \log \frac{(\text{Zn}^{+2})}{(\text{Cu}^{+2})}$$

$$= 0.76 + 0.34 - \frac{2.303 \times 8.31 \times 200}{2 \times 96500} \log \frac{2}{0.2} = 1.08 \text{ volt.}$$



$$E_{\text{cell}} = 0.75 + 0.34 - \frac{0.0591}{2} \log \frac{2}{3.125 \times 10^{-10}}$$

$$= 1.1 - \frac{0.0591}{2} (10 - 0.194) = 1.1 - 0.29 = 0.81 \text{ volt}$$

22
$$E_{\text{cell}} = 1.1 - \frac{0.0591}{2} \log \frac{[2]}{[\text{Cu}^{+2}]} = 0$$

$$\log \frac{[2]}{[\text{Cu}^{+2}]} = \frac{1.1 \times 2}{0.0591} = 37.23$$

$$\frac{2}{[\text{Cu}^{+2}]} = 1.68 \times 10^{37} \quad [\text{Cu}^{+2}] = 1.19 \times 10^{-37}$$

Comprehension # 4 (Q. No. 23 to 27)

Q.23 (D)

Q.24 (C)

Q.25 (B)

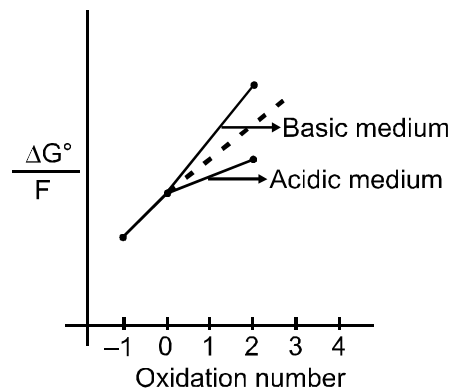
Q.26 (D)

Q.27 (A)

23 From given Latimer diagrams, $\text{Cl}_2 - \text{Cl}^-$ is independent of H^+ concentration.

24
$$\Delta G^{\circ} = \Delta G_1^{\circ} + \Delta G_2^{\circ}$$
, using this $E^{\circ} = \frac{0.42 + 1.36}{2} \text{ V} = 0.89 \text{ V}$

25



26 As $\frac{\Delta G^{\circ}}{F}$ is low, stability is higher.

27 As $\frac{\Delta G^{\circ}}{F}$ is low, stability is higher so, +2 and 0 state is more stable than +1.

Comprehension # 5 (Q. No. 28 to 32)

Q.28 (B)

Q.29 (D)

Q.30 (C)

Q.31 (A)

Q.32 (A)

28
$$560 \text{ mL of H}_2 \text{ gas} = \frac{560}{22400} \text{ moles of H}_2 \text{ gas} = \frac{1}{4} \times 10^{-1}$$

$$\text{moles of H}_2 \text{ gas} = \frac{1}{2} \times 10^{-1} \text{ moles of electrons}$$

$$= \frac{1}{2} \times 10^{-1} \times 96500 \text{ C of electrical charge} = 4825 \text{ C}$$

$$\text{So, electrical current} = \frac{4825}{600} = 8.04 \text{ A}$$

29
$$\Delta G^{\circ} = -nFE^{\circ}_{\text{cell}} = -2 \times 96500 \times 1.2288 \text{ J/mole}$$

$$= -237.1584 \text{ kJ/mole}$$

So, thermodynamic efficiency = $\frac{237.1584}{285} = 0.83$.

30 as per passage

31 as per passage

32 as per passage

Comprehension # 6 (Q. No. 33 to 35)

Q.33 (B)

Q.34 (C)

Q.35 (A)

33 $200 = k \times \frac{1000}{0.02}$ for KCl
 $k = 4 \times 10^{-3}$

$$\text{for KCl } k = C \frac{\ell}{A}$$

$$\Rightarrow 4 \times 10^{-3} = \frac{1}{100} \times \frac{\ell}{A}$$

$$\frac{\ell}{A} = 0.4$$

34 Conductance of $\text{H}_2\text{O} = \frac{1}{10000} = C$

$$k = C \frac{\ell}{A} = \frac{1}{10000} \times 0.4$$

$$k = 4 \times 10^{-5}$$

35 For NaCl $125 = k \times \frac{1000}{M}$

$$k = C \frac{\ell}{A};$$

$$\text{For C}$$

$$C_{\text{NaCl}} + C_{\text{water}} = C_{\text{NaCl(solution)}}$$

$$C + \frac{1}{10000} = \frac{1}{8000}$$

$$C = \frac{1}{8000} - \frac{1}{10000} = \frac{1}{40000}$$

$$\Rightarrow k = \frac{1}{40000} \times 0.4 = 1 \times 10^{-5}$$

$$\Rightarrow 125 = 1 \times 10^{-5} \times \frac{1000}{M} \Rightarrow M = 8 \times 10^{-5}$$

$$\text{Mole of NaCl} = \frac{585}{58.5} = 10 \text{ mole}$$

$$\Rightarrow \text{Volume} = \frac{10}{8 \times 10^{-5}} = 125000 \text{ L}$$

Comprehension # 7 (Q. No. 36 to 38)

Q.36 (C)

Q.37 (D)

46

Q.38 (D)

$$36 \quad \lambda_m^C = \lambda_m^\infty - b\sqrt{C}$$

$$\text{when } C_1 = 4 \times 10^{-4} \quad \lambda_m^C = 107$$

$$\text{and when } C_2 = 9 \times 10^{-4} \quad \lambda_m = 97$$

$$\text{so } 107 = \lambda_m^\infty - b \times 2 \times 10^{-2} \quad \dots (1)$$

$$97 = \lambda_m^\infty - b \times 3 \times 10^{-2} \quad \dots (2)$$

$$b = 1000$$

$$\lambda_m = \lambda_m^\infty - b\sqrt{C}$$

$$\lambda_m^\infty = \lambda_m + b\sqrt{C}$$

$$= 107 + 10^3 \times 2 \times 10^{-2}$$

$$\lambda_m^\infty = 127 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

37 For 25×10^{-4} (M) NaCl solution

$$\lambda_m = \lambda_m^\infty - b\sqrt{C}$$

$$\lambda_m = 127 - 10^3 (25 \times 10^{-4})^{1/2}$$

$$\lambda_m = 127 - 10^3 \times 5 \times 10^{-2}$$

$$\lambda_m = 77$$

$$\text{But } \lambda_m = \frac{K \times 1000}{M}, K = \left(\frac{\ell}{a}\right) \times \frac{1}{R}$$

$$\lambda_m = \left(\frac{\ell}{a}\right) \times \frac{1}{R} \times \frac{1000}{M}$$

$$\lambda_m = [\text{Cell constant}] \times \frac{1000}{R \times M}$$

$$\Rightarrow 77 = [\text{Cell constant}] \times \frac{1000}{1000 \times 25 \times 10^{-4}}$$

$$\text{Cell constant} = 77 \times 25 \times 10^{-4} = 0.1925 \text{ cm}^{-1}$$

38 For Na_2SO_4 solution

$$K = \left(\frac{\ell}{a}\right) \times \frac{1}{R} = \frac{0.1925}{400} = 4.81 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$$

$$\lambda_m = \frac{K \times 1000}{M} = \frac{4.81 \times 10^{-4} \times 1000}{\frac{5}{2} \times 10^{-3}}$$

$$\lambda_m (\text{Na}_2\text{SO}_4) = 192.4 \text{ ohm}^{-1} \text{ cm}^2 \text{ mole}^{-1}$$

Comprehension # 8 (Q. No. 39 to 41)

Q.39 (A)

Q.40 (C)

Q.41 (B)

39 First conductance decreases due to neutralisation of free H^+ ions of weak acid, then it increases due to formation of salt and after equivalence point it increases more fastly due to increasing of OH^- ions.

40 First conductance decreases due to neutralisation of strong acid H^+ ion then after it increases due to neutralisation of weak acid and after equivalence point it increases more fastly.

41 At the equivalence point the concentrations will be $[Br^-] = 100 \text{ m}^3$, $[Na^+] = 100 \text{ m}^3$

Therefore $k_{\text{total}} = k_{Br^-} + k_{Na^+} = 1.2 \text{ Sm}^{-1} = 12 \times 10^{-1} \text{ Sm}^{-1}$.

NUMERICAL VALUE BASED

Q.1 [9]

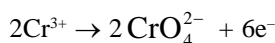
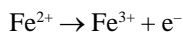
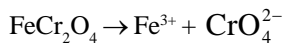
Mole ratio of $O_2 : Cl_2 = 2 : 1$

Charge ratio = 4 : 1

$$[OH^-]_{\text{left}} = \frac{1}{5} \times \frac{4.825}{96500} \text{ mol L}^{-1} = 10^{-5} \text{ M}$$

$$p^{OH} = 5 \Rightarrow pH = 14 - 5 = 9$$

Q.2 [8]



n-factor = 7

Theoretical requirement = 7F

$$x \times \frac{87.5}{100} = 7$$

$$x = \frac{700}{87.5} = 8F$$

Q.3 [4]

Since $Pd^{n+} + ne^- \rightarrow Pd$

$$\text{For Pd, } \frac{W}{E} = \frac{i \times t}{96500}$$

$$\frac{2.977}{106.4/n} = \frac{3 \times 1 \times 60 \times 60}{96500} \quad n = 4$$

Q.4 [0]

Q.5 [1]

Q.6 [6]

Q.7 [9]

Q.8 [4]

Q.9 [3]

$$m = \frac{EQ}{96500}$$

$$3.283 \text{ g} = \frac{197/x \times 4825}{96500}$$

x = valency of metal

Q.10 [5]

KVPY

PREVIOUS YEAR'S

Q.1 (A)

$$0 = 1.1 - \frac{0.0591}{2} \log \frac{Zn^{+2}}{Cu^{+2}}$$

$$1.1 = \frac{0.0591}{2} \log \frac{Zn^{+2}}{Cu^{+2}}$$

$$\log \frac{Zn^{+2}}{Cu^{+2}} = 37.3$$

Q.2 (B)

SRP ↓ Reducing power ↑

Q.3 (A)

Since conductance of H^+ is highest so molar conductivity of HCl will be highest and after that conductance of CH_3COOH will come
∴ order $HCl > CH_3COOH > NaCl > CH_3COONa$

Q.4 (B)

Q.5 (A)

$$\lambda = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda} = \frac{6.62 \times 10^{-34}}{720 \times 10^{-3} \times 11 \times 10^{-10}}$$

Q.6 (B)

$$\Delta G^\circ = -2.303 \times 8.314 \times 298 \log (3.8 \times 10^{-3}) \text{ J}$$

$$= 13809.3876 \text{ J} = 13.809 \text{ KJ}$$

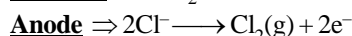
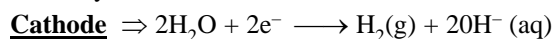
$$\Delta G^\circ = nFE^\circ$$

$$13809.387 = -2 \times 96500 \times E^\circ$$

$$E^\circ_{\text{cell}} = .071$$

Q.7 (A)

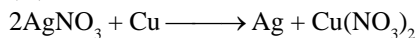
Electrolysis of can centrated NaCl.



Duet to formation of OH^- at cathode pH of solution

increases.

Q.8 (D)



Metal can reduce that metal cation which is placed below it in reactivity series.

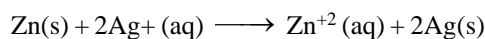
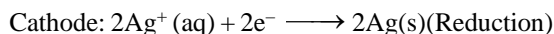
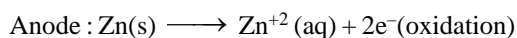
JEE-MAIN

PREVIOUS YEAR'S

Q.1 [147]

$$E_{\text{Cell}}^{\circ} = \left[E_{\text{Ag}^+/\text{Ag}}^{\circ} \right]_{\text{cathode}} - \left[E_{\text{Zn}^{2+}/\text{Zn}}^{\circ} \right]_{\text{anode}}$$

$$= 0.8 + 0.76 = 1.56 \text{ V}$$



$$E_{\text{cell}} = E_{\text{Cell}}^{\circ} - \frac{0.0591}{2} \log_{10} \left[\frac{[\text{Zn}^{2+}]}{[\text{Ag}^+]^2} \right]$$

$$= 1.56 - \frac{0.0591}{2} \log_{10} \left[\frac{0.1}{10^{-4}} \right]$$

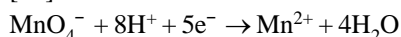
$$= 1.56 - \frac{0.0591}{2} \times 3$$

$$= 1.56 - 0.088 = 1.472 \text{ V}$$

$$= 147 \times 10^{-2} \text{ C}$$

$$X = 147$$

Q.2 [25]

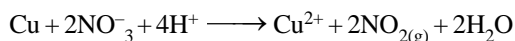


1 mole of MnO_4^- require 5 Faraday charge

5 moles of MnO_4^- will require 25 Faraday

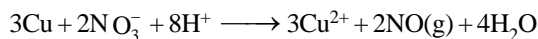
Q.3 (1)

Q.4 [144.54]



$$E_{\text{NO}_3^-/\text{NO}_2/\text{H}^+} = E_1^{\circ} - \frac{0.059}{2} \log \frac{1}{x^2(x)^4}$$

$$= 0.79 + 0.059 \times 3 \log(x) \quad \dots(i)$$



$$E_{\text{NO}_3^-/\text{NO}_2/\text{H}^+} = E_2^{\circ} - \frac{0.059}{6} \log \frac{1}{x^2(x)^8}$$

$$= 0.96 + \frac{0.059}{6} \times 10 \log(x) \quad \dots(ii)$$

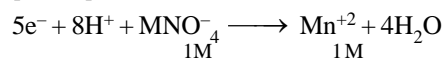
From (i) & (ii) $0.79 + 0.059 \times 3 \log x$

$$= 0.96 + \frac{0.059}{6} \times 10 \log(x)$$

$$0.059 \times \frac{8}{9} \log(x) = 0.17$$

$$\log_{10} x \cdot 2.16 \Rightarrow x \cdot 10^{2.16} = 144.54$$

Q.5 [0.3776]



$$E_1 = E^{\circ} - \frac{0.59}{5} \log_{10} \left[\frac{1}{[\text{H}^+]^8} \times \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-]} \right]$$

$$= E^{\circ} - \frac{0.059}{5} \log_{10} \left[\frac{1}{(1)^8} \right] = E^{\circ}$$

$$E_2 = E^{\circ} - \frac{0.059}{5} \log_{10} \left[\frac{1}{(10^{-4})^8} \times \frac{[\text{Mn}^{2+}]}{[\text{MnO}_4^-]} \right]$$

$$= E^{\circ} - \frac{0.059}{5} \log_{10} [10^{32}]$$

$$= E^{\circ} - \frac{0.059}{5} \times 32$$

$$E_1 - E_2 = E^{\circ} - E^{\circ} + \frac{0.059}{5} \times 32$$

$$= 0.3776 \text{ V}$$

Q.6 [288]

From Kohlrausch's law

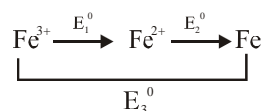
$$\Lambda_m^{\infty}(\text{BaSO}_4) = \lambda_m^{\infty}(\text{Ba}^{2+}) + \lambda_m^{\infty}(\text{SO}_4^{2-})$$

$$\Lambda_m^{\infty}(\text{BaSO}_4) = \Lambda_m^{\infty}(\text{BaCl}_2) + \Lambda_m^{\infty}(\text{H}_2\text{SO}_4) - 2 \Lambda_m^{\infty}(\text{HCl})$$

$$= 280 + 860 - 2(426)$$

$$= 288 \text{ Scm}^2\text{mol}^{-1}$$

Q.7 [45]



$$E_1^{\circ} + 2E_2^{\circ} = 3E_3^{\circ}$$

$$E_1^{\circ} = 3E_3^{\circ} - 2E_2^{\circ}$$

$$= 3(-0.036) - 2(-0.44)$$

$$= +0.772 \text{ V}$$

$$E_{\text{cell}}^{\circ} = E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^{\circ} + E_{\text{I}^-/\text{I}_2}^{\circ} = 0.233$$

$$\Delta_r G^{\circ} = -2 \times 96.5 \times 0.233 = -45 \text{ kJ}$$

Q.8 [143]

$$\text{Given conc}^n \text{ of KCl} = \frac{\text{m.mol}}{\text{L}}$$

: Conductance (G) = 0.55 mS

$$\text{: Cell constant} \left(\frac{\ell}{A} \right) = 1.3 \text{ cm}^{-1}$$

To Calculate : Molar conductivity (λ_m) of sol.

$$\rightarrow \text{Since } \lambda_m = \frac{1}{1000} \times \frac{k}{m} \quad \dots\dots(1)$$

$$\rightarrow \text{Molarity} = 5 \times 10^{-3} \frac{\text{mol}}{\text{L}}$$

$$\rightarrow \text{Conductivity} = G \times \left(\frac{\ell}{A} \right) = 0.55 \text{ mS} \times \frac{1.3}{1} \text{ m}^{-1}$$

$$= 55 \times 1.3 \quad \text{mSm}^{-1}$$

$$\text{eq}^n (1) \quad \lambda_m = \frac{1}{1000} \times \frac{55 \times 1.3}{\left(\frac{5}{1000} \right)} \frac{\text{mSm}^2}{\text{mol}}$$

$$\Rightarrow \lambda_m = 14.3 \frac{\text{mSm}^2}{\text{mol}}$$

Q.9 (4)

The E° value for $\text{Ce}^{4+}/\text{Ce}^{3+}$ is +1.74 V because the most stable oxidation state of lanthanide series elements is +3.

It means Ce^{3+} is more stable than Ce^{4+} .

Q.10 [57]

$$\kappa = \frac{1}{R} \cdot G^*$$

For same conductivity cell, G^* is constant and hence $\kappa \cdot R = \text{constant}$.

$$\therefore 0.14 \times 4.19 = \kappa \times 1.03$$

$$\text{or, } \kappa \text{ of HCl solution} = \frac{0.14 \times 4.19}{1.03}$$

$$= 0.5695 \text{ Sm}^{-1}$$

$$= 56.95 \times 10^{-2} \text{ Sm}^{-1} \approx 57 \times 10^{-2} \text{ Sm}^{-1}$$

Q.11 (1)

Q.12 [28]

Q.13 [12]

Q.14 [24]

Q.15 [3]

Q.16 [1]

Q.17 [109]

Q.18 (4)

Q.19 [760]

Q.20 [25]

Q.21 (1)

$$\text{Cell constant} = \left(\frac{\ell}{A} \right) \Rightarrow \text{Units} = \text{m}^{-1}$$

$$\text{Molar conductivity} (\Lambda_m) \Rightarrow \text{Units} = \text{Sm}^2 \text{ mole}^{-1}$$

$$\text{Conductivity (K)} \Rightarrow \text{Units} = \text{S m}^{-1}$$

Degree of dissociation (α) \rightarrow Dimensionless

\therefore (a) - (iii)

(b) - (i)

(c) - (iv)

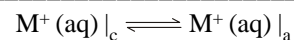
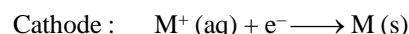
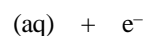
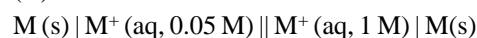
(d) - (ii)

Q.22 [26]

JEE-ADVANCED PREVIOUS YEAR'S

Comprehension # 1 (Q.1 & Q.2)

Q.1 (B)



$$E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{1} \log \frac{\text{M}^+(\text{aq}) |_{\text{a}}}{\text{M}^+(\text{aq}) |_{\text{c}}}$$

$$= 0 - \frac{0.0591}{1} \log \left\{ \frac{0.05}{1} \right\}$$

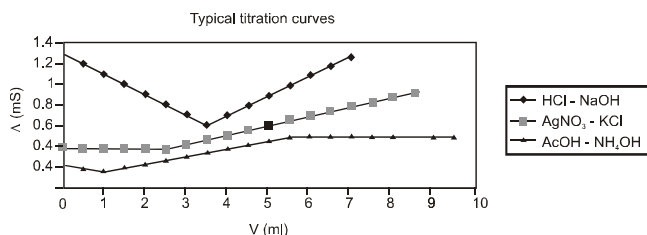
$$= +ve = 70 \text{ mV and hence } \Delta G = -nFE_{\text{cell}} = -ve.$$

Q.2 (C)

$$E_{\text{cell}} = \frac{-0.0591}{1} \log \left\{ \frac{0.0025}{1} \right\} = -\frac{0.0591}{1} \log \left\{ \frac{0.05}{20} \right\}$$

$$= 70 \text{ mV} + \frac{0.0591}{1} \log 20 = 140 \text{ mV}.$$

Q.3 (D)



Q.4 (D)

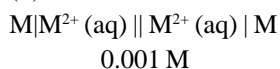
$$E = E^\circ - \frac{0.059}{4} \log \frac{[\text{Fe}^{2+}]^2}{[\text{H}^+]^4 \text{P}_{\text{O}_2}}$$

$$= 1.67 - \frac{0.06}{4} \log \frac{(10^{-3})^2}{(10^{-3})^4 \times 0.1} = 1.67 - \frac{0.03}{2} \log 10^7$$

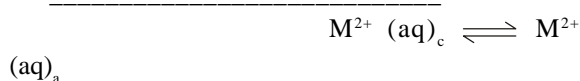
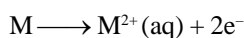
$$= 1.67 - \frac{0.03}{2} \times 7 = 1.67 - 0.105 = 1.565 = 1.57 \text{ V.}$$

Comprehension # 2 (Q.5 & Q.6)

Q.5 (B)



Anode :



$$E_{\text{cell}} = 0 - \frac{0.059}{2} \log \left\{ \frac{\text{M}^{2+}(\text{aq})_{\text{a}}}{10^{-3}} \right\}$$

$$0.059 = -\frac{0.059}{2} \log \left\{ \frac{\text{M}^{2+}(\text{aq})_{\text{a}}}{10^{-3}} \right\}$$

$$-2 = \log \left\{ \frac{\text{M}^{2+}(\text{aq})_{\text{a}}}{10^{-3}} \right\}$$

$$10^{-2} \times 10^{-3} = \text{M}^{2+}(\text{aq})_{\text{a}} = \text{solubility} = s$$

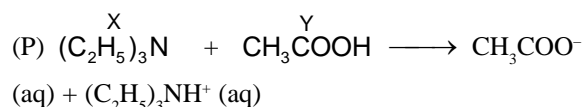
$$K_{\text{sp}} = 4s^3 = 4 \times (10^{-5})^3 = 4 \times 10^{-15}$$

Q.6 (D)

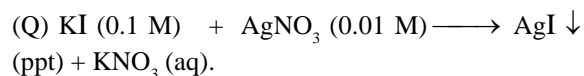
$$\Delta G = -nFE_{\text{cell}} = -2 \times 96500 \times 0.059 \times 10^{-3} \text{ kJ/mole}$$

$$= -11.4 \text{ kJ/mole.}$$

Q.7 (A)

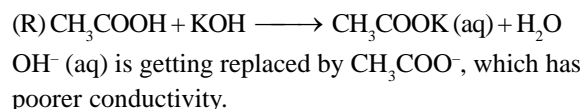


As CH_3COOH is a weak acid, its conductivity is already less. On addition of weak base, acid-base reaction takes place and new ions are created. So conductivity increases.

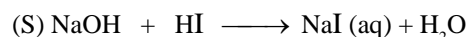


As the only reaction taking place is precipitation of AgI and in place of

Ag^+ , K^+ is coming in the solution, conductivity remain nearly constant and then increases.



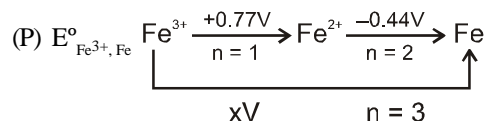
So conductivity decreases and then after the end point, due to common ion effect, no further creation of ions take place. So, conductivity remain nearly same.



As H^+ is getting replaced by Na^+ conductivity decreases and after end point, due to OH^- , it increases.

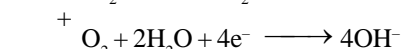
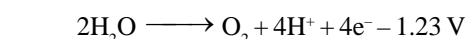
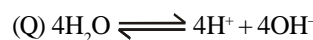
So answer of 39 is : (P) – (3) ; (Q) – (4) ; (R) – (2) ; (S) – (1). Answer is (D).

Q.8 (D)



$$\Rightarrow 1 \times 0.77 + 2 \times (-0.44) = 3 \times x$$

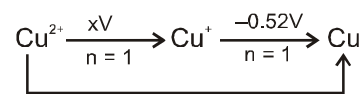
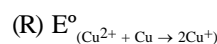
$$\Rightarrow x = -\frac{0.11}{3} \text{ V} \approx -0.04 \text{ V.}$$



$$+0.4 \text{ V}$$



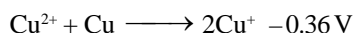
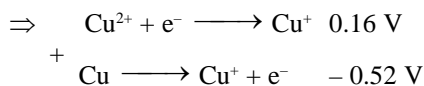
$$-0.83 \text{ V}$$



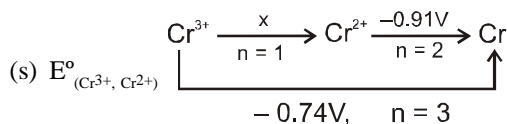
$$+0.34 \text{ V, } n=2$$

$$x \times 1 + 0.52 \times 1 = 0.34 \times 2$$

$$x = 0.16 \text{ V.}$$



However, in the given option, -0.18 V is printed.



$$x \times 1 + 2 \times (-0.91) = 3 \times (-0.74)$$

$$x - 1.82 = -2.22 \Rightarrow x = -0.4 \text{ V}$$

Hence, most appropriate is (D).

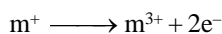
(P) - (3); (Q) - (4); (R) - (1); (S) - 2.

Q.9 (A)

Salt bridge is introduced to keep the solutions of two electrodes separate, such that the ions in electrode do not mix freely with each other. But it cannot stop the process of diffusion.

It does not participate in the chemical reaction. However, it is not necessary for occurrence of cell reaction, as we know that designs like lead accumulator, there was no salt bridge, but still reactions takes place.

Q.10 [4]



$$\Delta G^0 = -nFE^0 \text{ For 1 mole of } m^+$$

$$\Delta G^0 = -2 \times 96500 \times (-0.25) \text{ J}$$

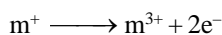
$$= +48250 \text{ J/mole} = 48.25 \text{ KJ/mole}$$

Energy released by conversion of 1 mole of



Hence mole of m^+ convert

$$\frac{193}{48.25} = 4$$



$$\Delta G^0 = -nFE^0 \text{ } m^+$$

$$\Delta G^0 = -2 \times 96500 \times (-0.25) \text{ J}$$

$$= +48250 \text{ J/mole} = 48.25 \text{ KJ/mole}$$



$$\frac{193}{48.25} = 4$$

Q.11 [3]

$$\lambda_{X^-}^\circ \approx \lambda_{Y^-}^\circ$$

$$\Rightarrow \lambda_{H^+}^\circ + \lambda_{X^-}^\circ \approx \lambda_{H^+}^\circ + \lambda_{Y^-}^\circ$$

$$\Rightarrow \lambda_{HX}^\circ \approx \lambda_{HY}^\circ \quad (1)$$

$$\text{Also } \frac{\lambda_m^\circ}{\lambda_m^\circ} = \alpha, \text{ So } \lambda_m^\circ(\text{HX}) = \lambda_m^\circ \alpha_1$$

$$\text{and } \lambda_m^\circ(\text{HY}) = \lambda_m^\circ \alpha_2$$

(Where α_1 and α_2 are degrees of dissociation of HX and HY respectively.)

Now, Given that

$$\lambda_m^\circ(\text{HY}) = 10 \lambda_m^\circ(\text{HX}).$$

$$\Rightarrow \lambda_m^\circ \alpha_2 = 10 \times \lambda_m^\circ \alpha_1$$

$$\alpha_2 = 10 \alpha_1 \quad (2)$$

$$K_a = \frac{C\alpha^2}{1-\alpha}, \text{ but } \alpha \ll 1,$$

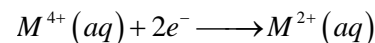
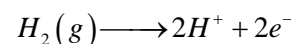
$$\text{therefore } K_a = C\alpha^2.$$

$$\Rightarrow \frac{K_a(\text{HX})}{K_a(\text{HY})} = \frac{0.01\alpha_1^2}{0.1\alpha_2^2} = \frac{0.01}{0.1} \times \left(\frac{1}{10}\right)^2 = \frac{1}{1000}.$$

$$\Rightarrow \log(K_a(\text{HX})) - \log(K_a(\text{HY})) = -3.$$

$$\Rightarrow \text{p}K_a(\text{HX}) - \text{p}K_a(\text{HY}) = 3.$$

Q.12 (D)



$$E_{cell} = E_{cell}^0 - \frac{0.0591}{2} \log 10^x \times \frac{1^2}{1}$$

$$0.092 = 0.151 - \frac{0.0591}{2} \log^x$$

$$x = 2$$

Q.13 (C)

$$\Delta G = \Delta G^0 + 2.303 RT \log_{10} Q; Q = \frac{[\text{Zn}^{2+}]}{[\text{Cu}^{2+}]}$$

$$= -2F(1.1) + 2.303 RT \log_{10} 10$$

$$= 2.303 RT - 2.2 F$$

Q.14 [6]

$$C = 0.0015 \text{ M}$$

$$\ell = 120 \text{ cm}$$

$$G = 5 \times 10^{-7} \text{ s}$$

$$a = 1 \text{ cm}^2$$

$$G = \kappa \times \frac{a}{\ell}$$

$$5 \times 10^{-7} = \kappa \times \frac{1}{120}$$

$$\kappa = 6 \times 10^{-5} \text{ s cm}^{-1}$$

$$\Lambda_m^c = \frac{\kappa \times 1000}{M} = \frac{6 \times 10^{-5} \times 1000}{0.0015}$$

$$\text{pH} = 4$$

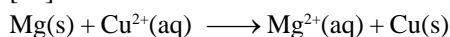
$$[\text{H}^+] = 10^{-4} = c \alpha = 0.0015 \alpha$$

$$\alpha = \frac{10^{-4}}{0.0015}$$

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^o} \Rightarrow \frac{10^{-4}}{0.0015} = \frac{6 \times 10^{-5} \times 1000}{\Lambda_m^o}$$

$$\Lambda_m^o = 6 \times 10^2 \text{ s cm}^2 \text{ mole}^{-1}$$

Q.15 [10]



$$E_{\text{cell}}^o = 2.70 \quad E_{\text{cell}} = 2.67 \quad \begin{array}{l} \text{Mg}^{2+} = x \text{ M} \\ \text{Cu}^{2+} = 1 \text{ M} \end{array}$$

$$E_{\text{cell}} = E_{\text{cell}}^o - \frac{RT}{nF} \ln x$$

$$2.67 = 2.70 - \frac{RT}{2F} \ln x$$

$$-0.03 = -\frac{R \times 300}{2F} \times \ln x$$

$$\ln x = \frac{0.03 \times 2}{300} \times \frac{F}{R} = \frac{0.03 \times 2 \times 11500}{300 \times 1}$$

$$\ln x = 2.30 = \ln(10)$$

$$x = 10$$

Q.16 (3)

Q.17 [13.32]

$$E_{\text{cell}}^o = 1.23 - 0.00 = 1.23 \text{ V}$$

$$\Delta G_{\text{cell}}^o = -nFE_{\text{cell}}^o = -2 \times 96500 \times 1.23 \text{ J}$$

\therefore Work derived from this fuel cell

$$= \frac{70}{100} \times (-\Delta G_{\text{cell}}^o) \times 10^{-3} = x \text{ J}$$

Since insulated vessel, hence $q=0$

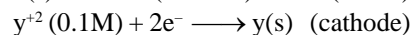
From equation, for monoatomic gas,

$$w = \Delta U \Rightarrow x = nC_{V,m} \Delta T \left\{ C_{V,m} = \frac{3R}{2} \right\}$$

$$\text{or, } \frac{70}{100} \times (2 \times 96500 \times 1.23) \times 10^{-3} = 1 \times \frac{3}{2} \times 8.314 \times \Delta T$$

$$\therefore \Delta T = 13.32$$

Q.18 (A, B, C)



$$E_{\text{cell}} = E_{\text{cell}}^o - \frac{0.06}{2} \log \frac{x^{+2}}{y^{+2}}$$

$$E_{\text{cell}} = E_{\text{cell}}^o + 0.06$$

$$\text{(A) Cd and Ni } E_{\text{cell}}^o = +0.4 - 0.24; E_{\text{cell}} = 0.22$$

$$\text{(B) Cd and Fe } E_{\text{cell}}^o = -0.04; E_{\text{cell}} = 0.02$$

$$\text{(C) Ni and Pb } E_{\text{cell}}^o = 0.11; E_{\text{cell}} = 0.17$$

$$\text{(D) Ni and Fe } E_{\text{cell}}^o = -0.2; E_{\text{cell}} = -0.14$$

since in (A) (B) (C) E_{cell} is positive hence answer is

(A) (B) (C).

Question Stem for Question Nos. 19 and 20

Q.19 [0.21 or 0.22]

$$K_a = \frac{\Lambda_m^2 C}{\Lambda_m^o (\Lambda_m^o - \Lambda_m)}$$

$$K_a = \frac{(y \times 10^2)^2 \times C}{4 \times 10^2 (4 \times 10^2 - y \times 10^2)} =$$

$$\frac{(3y \times 10^2)^2 \times \frac{C}{20}}{4 \times 10^2 (4 \times 10^2 - 3y \times 10^2)}$$

$$\Rightarrow \frac{1}{(4-y)} = \frac{9}{20(4-3y)} \Rightarrow y = \frac{44}{51}$$

$$\alpha = \frac{\frac{44}{51} \times 10}{4 \times 10^2}$$

$$\alpha = 0.2156 (\alpha = 0.22 \text{ or } 0.21)$$

$$y = 0.86$$

Q.20 [0.86]

Surface Chemistry

EXERCISES

ELEMENTARY

Q.1 (4)
Chemical adsorption is irreversible due to formation of new bonds and compounds.

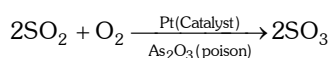
Q.2 (2)

Q.3 (4)

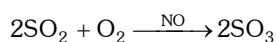
Q.4 (3)

Q.5 (4)
Chemisorption first increases and then decreases with temperature.

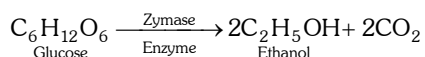
Q.6 (2)



Q.7 (2)

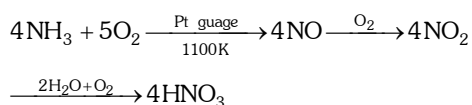


Q.8 (1)

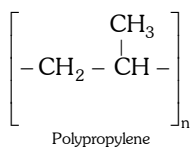
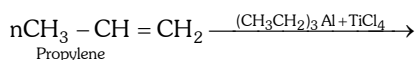


Q.9 (3)

Q.10 (4)



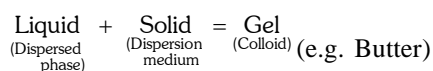
Q.11 (2)



Q.12 (4)

Q.13 (2)

Q.14 (3)

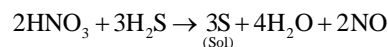


Q.15 (2)

Lyophilic possesses solvent loving nature and thus a thin layer of dispersed phase is formed round sol particles

Q.16 (4)

Q.17 (2)



Q.18 (1)

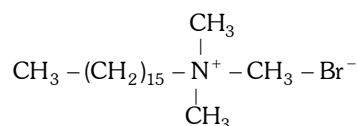
Colloidal particles range between 10^{-7} to 10^{-9} m or 10^{-5} to 10^{-7} cm.

Q.19 (1)

Q.20 (1)

Q.21 (2)

Surfactant are those which have charge on their tail e.g., cetyltrimethyl ammonium bromide.

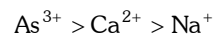


Surfactants are those, which dissociate in water to yield positively charged ion.

Q.22 (2)

Q.23 (1)

Negatively charged As_2S_3 sol coagulated most effectively by AlCl_3 . This is because oppositely charged Al^{+++} ions have maximum charge.



Q.24 (4)

$\text{K}_3[\text{Fe}(\text{CN})_6]$ is most effective in coagulating a ferric hydroxide sol.

Q.25 (3)

KBr is least effective in causing flocculation of ferric hydroxide sol due to minimum charge at $(\text{KBr}) \text{Br}^-$

Q.26 (3)

According to Hardy-Schulze rule.

Q.27 (3)

According to Hardy schulze rule the ions having opposite charge to sol particle cause coagulation and greater the valency of oppositely charged ion more is the coagulating power ($\text{PO}_4^{3-} > \text{SO}_4^{2-} > \text{NO}_3^-$).

Q.28 (2)

Q.29 (4)

Q.30 (2)

$$\text{Protective power} \propto \frac{1}{\text{Gold number}}$$

Hence, the correct order of protective power is
 $B > A > C > D$.

Q.31 (4)

The ability of an ion to bring about coagulation of a given colloid depends upon both the magnitude and sign of its charge.

Q.32 (2)

Q.33 (2)

JEE-MAIN OBJECTIVE QUESTIONS

Q.1 (4)

Activation energy is required for chemical adsorption.

Q.2 (2)

Adsorption is dependent on temperature.

Q.3 (2)

As temperature increases, physical adsorption decreases because physical adsorption is exothermic and reversible process.

Q.4 (2)

A gas with high critical temperature has high van der Waals force due to which they are more easily liquefiable & hence more easily adsorb as adsorption decreases their energy

Q.5 (4)

Extent of adsorption increases with increase in critical temperature

Q.6 (3)

Extent of adsorption & intermolecular force \propto van der Waals const. (1) $\text{NH}_3 > \text{CO}_2 > \text{CH}_4$

Q.7 (2)

Refer theory

Q.8 (1)

Accumulation substance on the surface of the other substance is known as adsorption.

Q.9 (2)

The volume of N_2 at STP required to cover the iron surface with monolayer = 8.15 ml gm^{-1}
 Area occupied by single molecule = $16 \times 10^{-18} \text{ cm}^2$

22400 ml of N_2 at STP contains = N_A molecule of N_2

$$\therefore 8.15 \dots\dots\dots = \frac{8.15 \times N_A}{22400} = 2.19 \times 10^{20}$$

molecule of N_2

Area occupied by 2.19×10^{20} molecule of $\text{N}_2 = 2.19 \times 10^{20} \times 16 \times 10^{-18} \text{ cm}^2 = 35.06 \times 10^2 \text{ cm}^2$

surface area of the iron adsorbed = $0.35 \text{ m}^2 \text{ gm}^{-1}$

In short $A =$

$$\frac{\text{Volume covered by the } \text{N}_2 \text{ molecule} \times N_A \times \text{Area occupied by single molecule}}{22400}$$

Q.10 (1)

Physical adsorption decreases as temperature increases.

Q.11 (2)

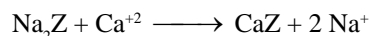
On increasing pressure more molecules will come into contact with the surface of solid adsorbent.

Q.12 (4)

Van der Waals force is responsible for adsorption.

Q.13 (1)

Softening of hard water : Ion exchange resins used for softening of hard water is based upon selective and competitive adsorption of ions on resins.



The organic polymers containing groups like $-\text{COOH}$, $-\text{SO}_3\text{H}$ and $-\text{NH}_2$ etc. possess the property of selective adsorption of ions from solution. These are quite useful in the softening of water.

Q.14 (3)

Chemical adsorption is irreversible.

Q.15 (3)

$$\text{Total surface area of eight cubes} = 8 \times 6 \times \left(\frac{1}{2} \times \frac{1}{2}\right)$$

Apply the formula

$$\text{Surface area on } n \text{ split of a cube} = 8^n \times 6 \times \left(\frac{1}{2}\right)^{2n}$$

$$6291456 = 8^n \times 6 \times \left(\frac{1}{2}\right)^{2n}$$

Q.16 (2)

Colloidal range of particle is 1nm-1000 nm

Q.17 (4)

Finely divided iron is used as catalyst in manufacture of NH_3 .

Q.18 (3)

Catalyst provides new path to the chemical reaction which has lower value of activation energy. Reactant

- and product will not be affected, so there will not be any change in state parameter like enthalpy and internal energy.
- Q.19** (2)
For eg. Mn^{2+} auto catalyses $\text{H}_2\text{C}_2\text{O}_4 + \text{HMnO}_4 + \text{H}^+ \rightarrow \text{Cr} + \text{Mn}^{2+} + \text{CO}_2 + \text{H}_2\text{O}$
- Q.20** (4)
Milk is emulsion
- Q.21** (2)
colloids are heterogeneous in nature & hence consist of two phase.
- Q.22** (2)
Emulsion :- ($\ell + \ell$) dispersed phase & dispersion medium both are liquid
- Q.23** (2)
Gelation, starch & gum are organic in nature & hence lyophilic in nature but S_8 is inorganic in nature & hence lyophobic in nature
- Q.24** (2)
Tyndall effect is due to scattering of light
- Q.25** (1)
Milk is emulsion (butter fat dispersed in water).
- Q.26** (4)
- Q.27** (2)
Fog (liquid + gas) dispersed phase Dispersion medium.
- Q.28** (2)
- Q.29** (1)
Ultra-microscope is based on tyndall effect which is based on scattering of light.
- Q.30** (1)
Molecular size for colloidal range in 1nm–1000 nm.
- Q.31** (3)
Lyophilic colloids do not move in presence of electric field due to uncharged nature.
- Q.32** (2)
 As_2S_3 colloid can be represented as $\text{As}_2\text{S}_3 \cdot \text{s}^{2-}$ so it is negatively charged.
- Q.33** (3)
Crystalloid & colloids differ in particle size & due to smaller size of crystalloid.
- Q.34** (4)
Ethanol is alcohol to the colloidal system is called alcosols.
- Q.35** (1)
Physical adsorption is multi-layered.
- Q.36** (3)
It is the property of colloidal solution.
- Q.37** (4)
- Q.38** (2)
Due to charge on colloidal particle they move under the influence of electric field.
- Q.39** (1)
Refer theory
- Q.40** (2)
Neutralization of charge on colloid as per hardy shulze rule.
- Q.41** (3)
As per Hardy shulze rule coagulation power $\propto +ve$ charge which is maximum in Al^{3+} .
- Q.42** (1)
Different colloidal particle will provide different colour to the sol.
- Q.43** (3)
Alums due to the charged nature of colloidal particle & hence coagular impurities in muddy water as per shulze rule.
- Q.44** (4)
- Q.45** (2)
Process by which precipitate is converted into colloid is known as peptisation.
- Q.46** (3)
Blood is a colloidal solution containing a -ve charge colloidal particle (Albuminoid), bleeding can be stopped by use of alum or FeCl_3 solution. The addition of Al^{3+} or Fe^{3+} causes coagulation of blood, so bleeding stops.
- Q.47** (3)
Gold number $\propto \frac{1}{\text{Protecting power}}$
- Q.48** (1)
Their protective action is because of their lyophilic nature.

- Q.49** (3)
10 ml of 1 M NaCl contains NaCl = $10 \times 1 = 10$ milli mole
200 ml of As_2S_3 required NaCl for the coagulation = 10 milli mole
 \therefore 1000 ml of As_2S_3 required NaCl for the coagulation = $10 \times 1000/200 = 50$ milli mole
- Q.50** (3)
Effectiveness of ion in coagulation \propto charge on coagulating ion.
- Q.51** (4)
Ferric hydroxide is a positive sol.
- Q.52** (3)
Micelle is a associated form of colloid
- Q.53** (2)
Liquid in liquid is known as emulsion.
- Q.54** (3)
AT (CMC) critical micellization concentration, the surfactant molecules associate to form micelles. For soap CMC is 10^{-3} mol/litre
- Q.55** (1)
Loss of water from gel is known as syneresis.
- JEE-ADVANCED**
OBJECTIVE QUESTIONS
- Q.1** (C)
$$V_2 = \frac{P_1 V_1}{P_2} = \frac{720 \times 1000}{480} = 1500 \text{ ml}$$

Volume of gas in the flask = 1000 – volume of charcoal
$$= 1000 - \frac{5}{1.25} = 996 \text{ ml}$$

Total volume of gas adsorbed by charcoal = 1500 – 996 = 504 ml
Volume of gas adsorbed by per gram of charcoal = $\frac{504}{5} = 100.08 \text{ ml}$
- Q.2** (B)
Physical adsorption is reversible in nature.
- Q.3** (C)
Adsorption is a bulk phenomena.
- Q.4** (B)
As in adsorption $\Delta S = -ve$
 $\Delta G = -ve$
 $\Delta H = -ve$
- Q.5** (D)
All are facts to remember.
- Q.6** (A)
Reddish brown sol is prepared by adding FeCl_3 in $\text{Fe}(\text{OH})_3$ precipitate.
- Q.7** (A)
Lyophobic colloid are solvent hating.
- Q.8** (D)
Lyophilic solution is easily solvated and quite stable in solvent.
- Q.9** (B)
Silver sol in water is an example of lyophobic solution.
- Q.10** (A)
Colloidal particle has size range of 1 to 1000 nm.
- Q.11** (B)
Cellulose is macromolecular colloid.
- Q.12** (A)
Similar charged colloidal particles will repel each other so colloidal system will not be suspended.
- Q.13** (C)
Smoke is solid in gas dispersion.
- Q.14** (A)
Smoke is blue because of scattering of light.
- Q.15** (B)
Viscosity of lyophilic colloid is less than water.
- Q.16** (A)
Small particles has more random behave.
- Q.17** (B)
Soap + water forms micelle which is an associated colloid.
- Q.18** (C)
$$\frac{\text{coagulation power of AlCl}_3}{\text{coagulation power of NaCl}} = \frac{\text{coagulation value of NaCl}}{\text{coagulation value of AlCl}_3}$$
- Q.19** (B)
Gold sol is multimolecular colloid.
- Q.20** (D)
All three are example of coagulation.
- Q.21** (A)
Lower the gold number, higher the producing power of lyophilic colloid.

- Q.22 (C)**
 $0.03 = \text{weight of Hb in mg} \times 10 / 100$
 weight of Hb in mg = 0.30.
- Q.23 (D)**
 Higher the charge on coagulating ion, lesser the flocculation value.
- Q.24 (C)**
 Impurity destabilises the solution.
- Q.25 (D)**
 Coagulation depends on charge.
- Q.26 (D)**
 $\text{As}_2\text{S}_3/\text{S}^{2-}$ is negatively charged so cation is effective in coagulation
 $\therefore \text{Al}^{3+}$ is effective.
- Q.27 (C)**
 More the charge on cation, more the effectiveness of the electrolyte.
- Q.28 (B)**
 Potential difference between two layer is known as zeta potential.
- Q.29 (B)**
 Micelles have large molar mass so less colligative property.
- Q.30 (C)**
 Emulsion is liquid in liquid sol.
- Q.31 (D)**
 Liquid in solid sol is gel.
- Q.32 (D)**
 Sponge will be completely soaked by water, so it is absorption.
- Q.33 (A)**
 Monolayer is formed during chemisorption.
- Q.34 (A)**
 Emulsifier stabilises the emulsion.
- JEE-ADVANCED**
- MCQ/COMPREHENSION/MATCHING**
- Q.1 (A, C)**
 Physisorption is reversible and its extent increases with pressure.
- Q.2 (A,B,D)**
 Physical adsorption is due to vander waal force net by free valency.
- Q.3 (B,C)**
 This is because of absorption.
- Q.4 (A,B,D)**
 Chemisorption is monolayer phenomenon.
- Q.5 (B, D)**
 Colloidal particle diameter is 10^{-9} m to 10^{-6} m.
- Q.6 (B,C,D)**
 $\text{Fe}(\text{OH})_3$ is positive sol, remaining all three are negative sol.
- Q.7 (B, C)**
 Solid in gas is known as aerosol.
- Q.8 (A, B)**
 Gold number is the index of protective power of lyophilic colloidal for standard gold sol.
- Q.9 (A, B, C)**
 Facts to remember.
- Q.10 (A,B,D)**
- Q.11 (A,B,C)**
 Except paramagnetism all are properties of sol.
- Q.12 (A,B,D)**
 Egg albumin is lyophilic colloid.
- Q.13 (B,C,D)**
 As_2S_3 is negatively charged.
- Q.14 (B, D)**
 Gold sol and $\text{Fe}(\text{OH})_3$ sol are hydrophobic.
- Q.15 (A,B,D)**
 When liquid is dispersed in liquid it is called emulsion.
- Q.16 (A,B)**
 Refer properties of lyophilic sols.
- Q.17 (A,B,D)**
- Q.18 (A, B)**
 Positive and negative sol will precipitate each other.
- Q.19 (A,B,C)**
- Q.20 (B,C,D)**
 Organic sol. are lyophilic.

- Q.21 (A,B)**
Since gold is metal so it is prepared by bredig's arc method
 $\text{AuCl}_3 + \text{SnCl}_2 \rightarrow \text{Au} + \text{SnCl}_4$
- Q.22 (A,B,C,D)**
- Q.23 (A, C)**
Egg albumin is macromolecular colloid and soap solution is associated colloid.
- Q.24 (A, C)**
Delta formation is because of coagulation.
- Q.25 (A,C,D)**
Sulphur being inorganic in nature so, it is lyophobic & rest are organic in nature.
- Q.26 (A,D)**
 $\text{AgI} + \text{AgNO}_3 \rightarrow \text{AgI}/\text{Ag}^+ + \text{ve charge colloidal particle}$
& hence - ve charge is effective in coagulation.
- Comprehension # 1 (Q. No. 27 to 29)**
- Q.27 (C)**
Co can displace remaining gas as CO involve dipole-dipole interaction but O_2 , N_2 , H_2 involves london force which is weakest in nature & hence CO as more tendency as adsorption.
- Q.28 (B)**
As per Le chatelier principle increase in temperature causes deadsorption.
- Q.29 (A)**
Activated charcoal is more porous & hence adsorbs gases quantitatively.
- Comprehension # 2 (Q. No. 30 to 32)**
- Q.30 (A)**
Silica gel is used to adsorb water.
- Q.31 (A)**
The process of imbibing water when elastic gel are placed in water is called as imbibation.
- Q.32 (B)**
Interconversion of sol and gel is known as thixotropy.
- Comprehension # 3 (Q. No. 33 to 35)**
- Q.33 (A)**
$$\text{AgNO}_3 \text{ (excess)} + \text{KI} \longrightarrow \text{AgI} + \text{AgNO}_3 \text{ (remaining)}$$
- Q.34 (C)**
AgI coagulates mist hanging in air.
- Q.35 (A)**
Smoke screen is cloud of smoke. It consists of fine particles of TiO_2 .
- Comprehension # 4 (Q. No. 36 to 38)**
- Q.36 (A)**
AgI adsorbs Ag^+ ion from excess AgNO_3 & forms AgI/Ag^+ +ve charge colloidal particle.
- Q.37 (A)**
Clouds are colloidal solution due to presence of liquid in gas.
- Q.38 (B)**
Electrical chimneys are based on the principle of charged nature of smoke.
- Comprehension # 5 (Q. No. 39 to 41)**
- Q.39 (D)**
Gold no. = $0.025 \times 10^3 = 25$
It is the weight of starch in Mg required for protection.
- Q.40 (B,D)**
Gold no. \propto protective power
- Q.41 (A)**
Gold no. measures protective power of colloids.
- Comprehension # 6 (Q. No. 42 to 65)**
- Q.42 (D)**
 ΔS for micelles formations positive in nature as hydration energy released in hydration is more than the energy required for micelles formation.
- Q.43 (C)**
 $\text{RCOO}^- \text{Na}^+$ soap.
- Q.44 (A)**
Organic part i.e., RCOO^- dissolves grease
- Q.45 (B)**
Refer theory
- Q.46 (A)**
grease (Like dissolves)
- Q.47 (A)-(P); (B)-(Q,R,S) ; (C)-(P,S) ; (D)-(P,Q)**
- Q.48 (A)-(S) ; (B)-(R) ; (C)-(Q) ; (D)-(P)**
(A) Coagulation is known as accumulation of collidal sols.

- (B) Dialysis is purification of colloids.
- (C) Peptization is formation of colloidal solution from precipitates.
- (D) Tyndall effect is scattering of light by colloidal particle

Q.49 (A)-(S);(B)-(R) ; (C)-(P) ;(D)-(Q)

Q.50 (A)-(R) ; (B)-(P) ; (C)-(S) ; (D)-(Q)

- (A) Mechanical property of colloid particle is known as Brownian movement.
- (B) Purification of colloids is done by dialysis.

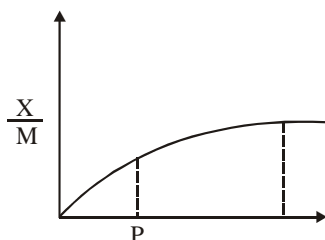
(C) Gold number $\propto \frac{1}{\text{protection power}}$

(D) Formation of a sol is done by peptization.

Q.51 (A)-(S); (B)-(P); (C)-(R); (D)-(Q)

NUMERICAL VALUE BASED

Q.1 [1]
At very low pressure



$$\frac{x}{m} \propto P; \quad \frac{x}{m} = KP$$

so $r = 1$

Q.2 [0]

Q.3 [1]

Q.4 [2]

Gold number is the mg of the protective colloid to be added to 10 ml of a standard gold sol which just prevents its coagulation when 1 ml of 10% NaCl solution is added to it. Coagulation of 250 ml is prevented by 0.05 g = 50 mg. Coagulation of 10 ml will be prevented by $50/250 \times 10 \text{ mg} = 2 \text{ mg}$. Hence the gold number is 2.

Q.5 [5]

millimoles of CH_3COOH in 100 ml = $100 \times 0.5 = 50$

millimoles of CH_3COOH after adsorption = $0.49 \times 100 = 49$

so millimoles of acetic acid adsorbed = 1

number of molecules of acetic acid adsorbed

$$= 1 \times 10^{-3} \times 6.02 \times 10^{23} \\ = 6.02 \times 10^{20}$$

Total surface area of charcoal = $3.01 \times 10^2 \text{ m}^2$

Surface area adsorbed by each molecule of

$$\text{acetic acid} = \frac{3.01 \times 10^2}{6.01 \times 10^{20}} \\ = 5 \times 10^{-19} \text{ m}^2$$

Hence answer is 5

Q.6 [50.0]

Flocculation value of NaCl = 5×1

= 5 millimole for 100

ml

So for 1 litre value is 50 millimole.

Q.7 [25.0]

For 10 ml, 1 ml 10% NaCl is required so for 100 ml, 10 ml 10% NaCl will be required.

So gold number is 250.

Q.8 [5]

Let there are total n pores, then

$$\text{Vol. of pores} : n \left(\frac{1}{4} \pi d^2 \ell \right) = 0.1 \text{ C.C}$$

$$\Rightarrow n \left(\frac{\pi d^2 \ell}{4} \right) = 10^{-7} \text{ m}^3 \dots\dots(i)$$

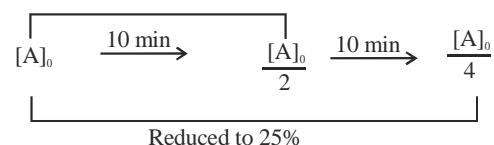
$$\text{Area of pores} : n (\pi d \ell) = 800 \text{ m}^2 \dots\dots(ii)$$

By dividing equation (i) by (ii) we get -

$$d = \frac{4 \times 10^{-7}}{800} \text{ m} = 5 \text{ \AA}$$

Q.9 [20]

It takes two half-lives to reduce the concentration of reactant to 25% of its original concentration.



Hence, total time taken = 10 + 10
= 20 minutes

KVPY

PREVIOUS YEAR'S

Q.1 (B)

$$\frac{\text{Surface area}}{\text{Volume}} = \frac{\pi d^2}{\frac{\pi d^3}{6}} = \frac{6}{d}$$

$$d_1 = 30 \text{ nm} \quad d_2 = 10 \text{ nm}$$

$$\left(\frac{\text{Surface area}}{\text{Volume}} \right)_2 = \frac{6}{d_2} = \frac{d_1}{d_2} = \frac{30}{10} = 3$$

$$\left(\frac{\text{Surface area}}{\text{Volume}} \right)_1 = \frac{6}{d_1}$$

Q.2 (D)

According to Lagmuir curve

$$x = \frac{ap}{1 + bp}$$

$$p \rightarrow \infty \quad x = \frac{a}{b}$$

$$p \rightarrow 0 \quad x \propto p$$

Q.3 (C)

Factually incorrect.

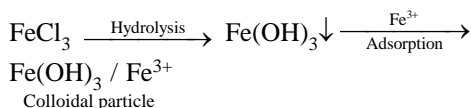
The initially adsorbed layer cannot act as a substrate for further adsorption.

Q.4 (B)

JEE-MAIN

PREVIOUS YEAR'S

Q.1 (1)



Q.2 (1)

$$\frac{x}{m} = kp^{1/n}$$

Q.3 (2)

$$\text{Moles of O}_2 = \frac{3.12}{32} = 0.0975$$

$$\text{Volume of O}_2 = \frac{nRT}{P} = \frac{0.0975 \times 0.082 \times 300}{1} =$$

$$2.3985 \text{ litres} \simeq 2.4 \text{ litres}$$

$$\text{Volume of O}_2 \text{ adsorbed per gm of Pt} = \frac{2.4}{1.2} = 2$$

Q.4 (1)

The viscosity of the hydrophilic sols are much higher than that of the dispersion medium.

Q.5 (3)

Q.6 (1)

$$\text{Slope} = \frac{1}{n} \quad (0 \text{ to } 1)$$

Q.7 (2)

Blood is a negative charged Sol. Therefore according hardy-Schulz rule Fe^{+3} cation have highest coagulation power. Therefore FeCl_3 can be used for clotting of blood efficiently.

Q.8 (2)

To coagulate negative sol, cation with higher charge has higher coagulation value.

Q.9 (3)

Colloid of gas dispersed in solid is called solid sol.

Q.10 (2)

- * Colloidal solution exhibits colligative properties
- * An ordinary filter can not stop the flow of colloidal particles.
- * Flocculating power increases with increase the opposite charge of electrolyte.
- * Colloidal particles show brownian motion.

Q.11 (4)

CdS sol \rightarrow -ve solTiO₂ sol \rightarrow +ve sol

Q.12 [17]

Q.13 (4)

Q.14 (1)

Q.15 (Bonus)

Q.16 (1)

Q.17 (1)

Q.18 (3)

Q.19 (4)

Q.20 (3)

Q.21 (4)

Q.22 [128]

JEE-ADVANCED

PREVIOUS YEAR'S

Q.1 (A,B,D)

(A) $\Delta H = -ve$ for adsorption

(B) fact

(D) chemical bonds are stronger than vander waal's forces so chemical adsorption is more exothermic.

Q.2 (A,D)

(A) due to preferential adsorption of common ions

(C) due to repulsion not due to attraction

(D) The layer of oppositely charged particles around any colloidal particles will decrease the potential energy of system as a whole.

Q.3 (A,C)

In physisorption on increasing temperature at constant pressure, adsorption decreases while in chemical adsorption on increasing temperature due to requirement of activation energy adsorption will increase at same pressure. So, I is physisorption while II is chemisorption.

III is physical adsorption as on increasing temperature, extent of adsorption is decreasing .

IV is representing enthalpy change (which is high) during chemical adsorption (due to bond formation) So, is valid for chemical adsorption. So, answer is (A) and (C)

Q.4 (B)

As the adsorption of methylene blue over activated characoal is physisorption (Reference : NCERT), it is accompanied by decrease in enthalpy.

Q.5 (B,C,D)

(A) As electron transfer is involved, so chemisorption is taking place.

(B) Adsorption is exothermic process.

(C) The π^* orbitals of O_2 accommodate the incoming electron as they are partially filled.

(D) As electron enters antibonding MO, bond length increases.

So, answer is (B,C,D).

Q.6 (D)

Higher the water solubility, higher will be its surface tension.

Q.7 (A,C)

 \Rightarrow Higher the critical temperature, higher will be extent of adsorption. \Rightarrow Cloud is an aerosol, emulsions are liquid-liquid colloidal system. \Rightarrow For adsorption $\Delta H \Rightarrow$ negative : $\Delta S \Rightarrow$ negative \Rightarrow Brownian movement of colloidal particles depends on size of particles.

Q.8 (B, C)

(A) Process of precipitating colloidal solution is called coagulation. Hence false.

(B) For colloidal solutions concentration is very small due to very large molar mass and hence their colligative properties are very small as compared to true solutions

 $\therefore T_f$ is lesser for colloidal solution. Hence true.

(C) At CMC surfactant form micelles. Hence true

(D) Micelles and macromolecular colloids are two different types of colloids. Hence false.

Chemical Kinetics

EXERCISES

ELEMENTARY

Q.1 (2) $R = k[RCl]$, if $[RCl] = 1/2$, then rate = $R/2$.

Q.2 (3) $k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}$;

$$t = 2 \times 10^2, a = 800, a - x = 50$$

$$\begin{aligned} k &= \frac{2.303}{2 \times 10^2} \log_{10} \frac{800}{50} = \frac{2.303}{2 \times 10^2} \log_{10} 16 \\ &= \frac{2.303}{2 \times 10^2} \log_{10} 2^4 = \frac{2.303}{2 \times 10^4} \times 4 \times 0.301 \\ &= 1.38 \times 10^{-2} \text{ s}^{-1} \end{aligned}$$

Q.3 (4) Increase in the rate of reaction is determined by the increase in the number of effective collisions.

Q.4 (1)

Q.5 (1)

Q.6 (4)

Q.7 (4)

Q.8 (2)

Q.9 (1)

Q.10 (3)

Q.11 (2)

Q.12 (3)

Q.13 (1)

Q.14 (1)

Q.15 (1)

Q.16 (1)

Q.17 (3)

Q.18 (2)

Q.19 (1)

Q.20 (3)

Q.21 (1)

Q.22 (2)

Q.23 (4)

Q.24 (1)

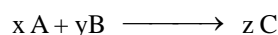
Q.25 (4)

Q.26 (1)

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OBJECTIVE QUESTIONS

Q.1 (3)



$$\frac{-d}{dt} [A] = \frac{-d}{dt} [B] = 1.5 \frac{-d}{dt} [C]$$

$$\Rightarrow \frac{-1}{3} \frac{-d}{dt} [A] = \frac{-1}{3} \frac{-d}{dt} [B] = \frac{1}{2} \frac{-d}{dt} [C]$$

$$x = 3 \quad y = 3 \quad z = 2$$

Q.2 (2)



$$\frac{-1}{x} \frac{d}{dt} [A] = \frac{1}{y} \frac{d}{dt} [B]$$

$$\Rightarrow \frac{-d}{dt} [A] = \frac{x}{y} \frac{d}{dt} [B]$$

$$\log \left(\frac{-d[A]}{dt} \right) = \log \left(\frac{x}{y} \right) + \log \left(\frac{+d[B]}{dt} \right)$$

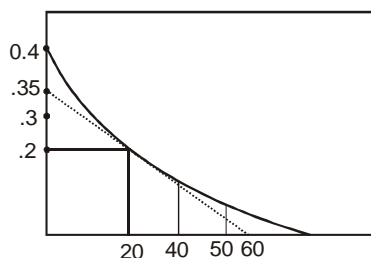
$$\Rightarrow \log \frac{-d}{dt} [A] = \log \frac{d}{dt} [B] + \log \left(\frac{x}{y} \right)$$

$$\log \left(\frac{x}{y} \right) = 0.3$$

$$\Rightarrow \frac{x}{y} = \frac{2}{1}$$

$$\Rightarrow x : y = 2 : 1$$

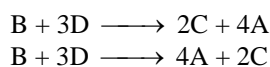
Q.3 (4)



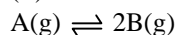
$$\text{slope of graph at } 20 \text{ sec} = \frac{dy}{dx} = \frac{0.35}{50} = 7 \times 10^{-3}$$

Q.4 (2)

$$-\frac{1}{3} \frac{d[D]}{dt} = -\frac{d[B]}{dt} = \frac{1}{2} \frac{d[C]}{dt} = \frac{1}{4} \frac{d[A]}{dt}$$



Q.5 (4)



$$K_f = 1.5 \times 10^{-3} \text{ s}^{-1}$$

At eq.^m, $R_f = R_b$

$$K_f [A] = K_b [B]^2$$

$$\text{On solving : } K_b = 1.5 \times 10^{-11}$$

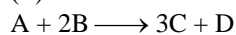
Q.6 (2)

From the above data, it is clear that on doubling the concentration of B, the rate is doubled hence order w.r.t. B is 1

Similarly, Order w.r.t. A = 2

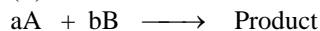
$$\Rightarrow \text{rate} = K[A]^2[B]$$

Q.7 (4)



$$-\frac{d[A]}{dt} = -\frac{1}{2} \frac{d[B]}{dt} = \frac{1}{3} \frac{d[C]}{dt} = \frac{d[D]}{dt}$$

Q.8 (2)



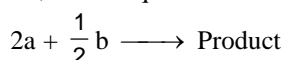
$$\frac{dx}{dt} = k[A]^a [B]^b$$

(i) As on doubling concentration of A rate become four time so $a = 2$.

(ii) On four time concentration of B rate become

$$\text{double so } b = \frac{1}{2}.$$

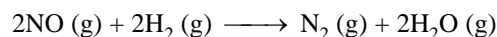
So, Given equation :



$$-\frac{1}{2} \frac{d[A]}{dt} = -2 \frac{d[B]}{dt}$$

$$-\frac{d[A]}{dt} = -4 \frac{d[B]}{dt}$$

Q.9 (2)



$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NO}]}{dt} = -\frac{1}{2} \frac{d[\text{H}_2]}{dt} = \frac{d[\text{N}_2]}{dt} =$$

$$\frac{1}{2} \frac{d[\text{H}_2\text{O}]}{dt} = K_1 [\text{NO}] [\text{H}_2]$$

$$(1) \frac{d[\text{H}_2\text{O}]}{dt} = 2K_1 [\text{NO}] [\text{H}_2] = K [\text{NO}] [\text{H}_2]$$

$$\text{So } k = 2k_1$$

$$(2) -\frac{d[\text{NO}]}{dt} = 2k_1 [\text{NO}] [\text{H}_2] = K_1' [\text{NO}] [\text{H}_2]$$

$$k_1' = 2k_1$$

$$(3) -\frac{d[\text{H}_2]}{dt} = 2k_1 [\text{NO}] [\text{H}_2] = K_1'' [\text{NO}] [\text{H}_2]$$

$$k_1'' = 2K_1$$

Rate law for

Q.10 (3)

Order have no relation with stoichiometric coefficient.

Q.11 (4)

By definition of order.

Q.12 (4)

Rate law for Ist order IInd order IIIrd order

$$\text{Rate} = K[A]^1 \quad R_2 = K[A]^2$$

$$R_3 = K[A]^3$$

than we can say $[A] = 1$

$$r_1 = r_2 = r_3$$

$$[A] < 1$$

then $r_1 > r_2 > r_3$

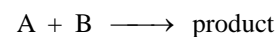
y $[A] > 1$ then $r_3 > r_2 > r_1$

Q.13 (4)

$$-\frac{d[\text{BrO}_3^-]}{dt} = k[\text{BrO}_3^-] [\text{Br}^-] [\text{H}^+]^2$$

So, on doubling the concentration of H^+ ion will increase the reaction rate by 4 times.

Q.14 (1)



$$r = K [A]^1 [B]^2$$

$$r_1 = K [1]^1 [1]^2 = 1 \times 10^{-2} \quad (K = 1 \times 10^{-2})$$

$$r_1 = K \left[\frac{1}{2} \right] \left[\frac{1}{2} \right]^2 = 1 \times 10^{-2} \times \frac{1}{8} = 1.25 \times 10^{-3}$$

Q.15 (2)

$$\text{Rate} \propto \frac{1}{\text{time}}$$

Since,

Rate becomes four times by doubling the concentration of A

⇒ Order w.r.t A is 2

Also, by doubling the concentration of B, the rate becomes double

⇒ Order w.r.t B is 1.

Q.16 (2)

$$-\frac{1}{3} \frac{d[\text{H}_2]}{dt} = \frac{1}{2} \frac{d[\text{NH}_3]}{dt}$$

$$\Rightarrow -\frac{d[\text{H}_2]}{dt} = \frac{3}{2} \frac{d[\text{NH}_3]}{dt}$$

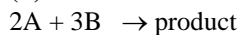
$$= \frac{3}{2} \times 3.4 = 5.1 \text{ Kgmin}^{-1}$$

Q.17 (4)

Given $\frac{dx}{dt} = k [\text{A}]^a [\text{B}]^b$ and if $\frac{dx}{dt} = k$

then $a + b = 0$ i.e. zero order reaction.

Q.18 (4)



A in Excess then Rate law

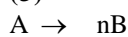
$$\text{Rate} = K[\text{B}]^n \text{ given } \text{Rate}_1 = K[0.1]^n$$

$$\text{given } \text{Rate}_2 = 2\text{Rate}_1 = K[0.4]^n$$

$$\text{From (1) and (2) } n = \frac{1}{2}$$

$$\text{then Rate law } \frac{dx}{dt} = K [\text{B}]^{\frac{1}{2}}$$

Q.19 (3)



$$\text{A}_0 \quad 0$$

$$\text{A}_0 - x \quad nx$$

$$nx = \text{A}_0 - x$$

$$x = \frac{\text{A}_0}{n+1}$$

$$\therefore [\text{B}] = nx = \frac{n\text{A}_0}{n+1}$$

Q.20 (4)

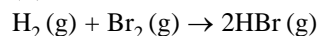
Complex reaction order of reaction depends on rate determining step (RDS) x y are not related to a & b.

Q.21 (2)

$$\frac{dc}{dt} = \left(\frac{dn}{dt} \right) \times \frac{1}{V}$$

$$c = \frac{n}{V} = \frac{P}{RT}$$

Q.22 (3)



$$r = k[\text{H}_2][\text{Br}_2]^{1/2}$$

Molecularity → not defined.

$$\text{order} = 1 + \frac{1}{2} = \frac{3}{2}$$

Q.23 (4)

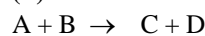
Number of molecules of CO involved in slowest step will be 0.

Q.24 (2)

$$\left(\frac{dx}{dt} \right) = k[\text{A}]^2[\text{B}]^{-1} - K_2[\text{C}]$$

net rate is $2\text{A} - \text{B} \rightleftharpoons \text{C}$.

Q.25 (2)



$$k = 2.303 \times 10^{-3} \text{ sec}^{-1}$$

$$t = \frac{2.303}{k} \log \frac{1}{0.25} = \frac{2.303}{2.303 \times 10^{-3}} \log \frac{100}{25}$$

$$= 10^3 \times (0.605) = 600 \text{ sec}$$

Q.26 (4)

$$k_1 = \frac{2.303}{t} \log \frac{100}{50} = \frac{2.303}{t} \log 2 = \frac{0.6955}{t}$$

$$k_2 = \frac{2.303}{t} 2 \log 5 = \frac{2.303}{t} \times 2 \times 0.69 = \frac{3.22}{t}$$

$$\frac{k_2}{k_1} = 4.65$$

Q.27 (1)

$$\text{sec}^{-1}, \text{Msec}^{-1}$$

Q.28 (2)

$$t = \frac{2.303}{K} \log \frac{C_0}{C_t}$$

$$\Rightarrow t = \frac{2.303}{K} [\log C_0 - \log C_t]$$

$$\frac{Kt}{2.303} = \log C_0 - \log C_t$$

$$\Rightarrow \log C_t = \left(\frac{-K}{2.303} \right) t + \log C_0$$

$$\text{So, slope} = \left(\frac{-K}{2.303} \right)$$

Q.29 (2)

Equal amount of Rxn completed in equal time property as zero order Rxn, and unit as Rate constant mole Litre⁻¹ sec⁻¹

Q.30 (2)

$$\text{No. of half life} = \frac{60}{10} = 6 \text{ half life.}$$

$$C_t = \frac{C_0}{(2)^n} = \frac{C_0}{(2)^6} = \left(\frac{C_0}{64}\right)$$

$$k = \frac{2.303}{t} \log\left(\frac{100}{100-x\%}\right)$$

$$\frac{k_1}{k_2} = \left(\frac{t_2}{t_1}\right) \frac{\log\left(\frac{100}{10}\right)}{\log\left(\frac{100}{1}\right)}$$

$$\frac{k_1}{k_2} = 2 \frac{\log 10}{2 \log 10} = 1.$$

Q.31 (2)

$$t_{1/2} = 10$$

$$\text{No. of Half life} = \frac{60}{10} = 6 \text{ half life}$$

$$C_t = \frac{C_0}{(2)^n} = \frac{C_0}{(2)^6} = \left(\frac{C_0}{64}\right)$$

Q.32 (2)

$$K = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$K = \frac{2.303}{20} \log \frac{1}{0.6}$$

Also,

$$K = \frac{2.303}{t} \log \frac{0.60}{0.36}$$

Since, Rate constant will be equal

$$\frac{2.303}{20} \log \frac{1}{0.6} = \frac{2.303}{t} \log \frac{0.60}{0.36}$$

On solving, $t = 20$ min**Q.33** (3)

For a first order reaction, the concentration of the reactant varies exponentially with time

$$(A = A_0 e^{-kt})$$

Q.34 (1)

$$K_1 = \frac{2.303}{t} \log\left(\frac{100}{10}\right) \quad \dots(1)$$

$$K_2 = \frac{2.303}{2t} \log\left(\frac{100}{1}\right) \quad \dots(2)$$

then from (1) and (2)

$$\frac{K_1}{K_2} = 1$$

Q.35 (2)

$$C_t = C_0 e^{-Kt}$$

According to question

$$C_{A,t} = C_{B,t}$$

$$C_A e^{-K_A t} = C_B e^{-K_B t}$$

$$\frac{C_A}{C_B} = \frac{e^{-K_B t}}{e^{-K_A t}} \Rightarrow \frac{C_A}{C_B} = e^{(K_A - K_B)t}$$

$$4 = e^{\left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] \times t}$$

$$\ln 4 = \left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] t$$

$$\ln(2)^2 = \left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] t$$

$$2 \ln 2 = \left[\frac{\ln 2}{5} - \frac{\ln 2}{15}\right] t$$

$$2 = \left[\frac{1}{5} - \frac{1}{15}\right] t$$

$$2 = \frac{2}{15} \times t$$

$$t = 15 \text{ minute.}$$

Q.36 (3)

$$t_1 = \frac{2.303}{K} \log\left(\frac{100}{40}\right) \quad \dots(1)$$

$$t_2 = \frac{2.303}{K} \log\left(\frac{100}{80}\right) \quad \dots(2)$$

$$\text{From (1) and (2)} \quad \frac{t_1}{t_2} = 4.11$$

Q.37 (3)

$$K_1 = \frac{1}{t} \ln\left(\frac{C_0}{a C_0}\right) = \frac{1}{t} \ln\left(\frac{1}{a}\right)$$

$$K_2 = \frac{1}{2t} \ln\left(\frac{C_0}{a^2 C_0}\right) = \frac{1}{t} \ln\left(\frac{1}{a}\right)$$

Q.38 (3)
Q.39 (3)

Reaction is zero order
hence, Option C will be correct.

Q.40 (3)

$t_{1/4}$ = time taken for $\frac{1}{4}$ th decomposition.

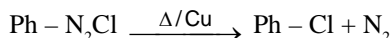
$\Rightarrow \frac{3}{4}$ will be left

$$t_{1/4} = \frac{2.303}{K} \log \frac{1}{3/4} = \frac{2.303}{K} \log \frac{4}{3}$$

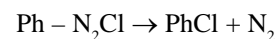
Q.41 (3)

If we calculate K, it comes constant every time
i.e. reaction is of first order.

$$\text{Also, } K = \frac{2.303}{t} \log \frac{C_0}{aC_0} = \frac{1}{t} \ln \left(\frac{1}{a} \right)$$

Q.42 (2)


Half life is independent of concentration
 \Rightarrow reaction is of first order



$$t = 0 \quad A_0 \quad 0 \quad 0$$

$$t = 30 \quad A_0 - x \quad x \quad x$$

$$t = \infty \quad 0 \quad A_0 \quad A_0$$

$$x \propto 10$$

$$A_0 \propto 50$$

$$\Rightarrow A_0 - x \propto 40$$

$$K = \frac{2.303}{t} \log \frac{A_0}{A_0 - x} = \frac{2.303}{10} \log \frac{50}{40}$$

$$= \frac{2.303}{10} \log (1.25) \text{ min}^{-1}$$

Q.43 (4)


$$t = 0 \quad C_0 \quad 2C_0 \quad 0 \quad 0$$

$$t = 30 \quad C_0 - 2x \quad 2C_0 - x \quad x \quad x$$

$$\text{given,} \quad x = \frac{C_0}{4}$$

$$\text{After 30 min, } [A] = C_0 - 2 \times \frac{C_0}{4} = \frac{C_0}{2}$$

$$[B] = 2C_0 - \frac{C_0}{4} = \frac{7C_0}{4}$$

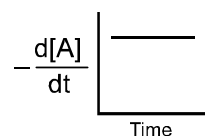
$$r = K \left[\frac{C_0}{2} \right] \left[\frac{7C_0}{4} \right]$$

$$\Rightarrow R = \frac{49kC_0^3}{32}$$

Q.44 (3)

From given graph $x = Kt$
i.e. it is a zero order reaction.

$$\therefore -\frac{d[A]}{dt} = K$$


Q.45 (3)

As $t_{50\%}$ is constant. Hence order of reaction is 1.

$$t_{50\%} = \frac{0.693}{K}$$

$$n = 1, t_{1/2} = \frac{0.693}{K}$$

Q.46 (1)

by graph we can say $\log t_{1/2} = \log a \quad t_{1/2} = a \quad \dots(1)$

$$t_{1/2} \propto a \text{ then zero order Rxn} \quad k \times t_{1/2} = \frac{a}{2} \quad \dots(2)$$

$$\text{then } k = \frac{1}{2}$$

Q.47 (3)

time Total for drop to disappears $(a_0 - a_t) = kt$
 $a_t = 0$

$$\frac{3.0 \times 10^{-6}}{(0.05 \times 10^{-3}) \times 1.0 \times 10^7} = t_{100\%}$$

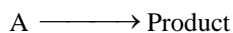
$$\Rightarrow t_{100\%} = 6 \times 10^{-9} \text{ sec}$$

Q.48 (1)

$$t_1 = \frac{2.303}{3K} \log \frac{100}{75}$$

$$t_2 = \frac{2.303}{2K} \log \frac{100}{25}$$

$$\Rightarrow \frac{t_1}{t_2} = \frac{0.311}{1} = 0.311 : 1$$

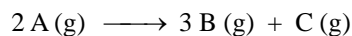
Q.49 (4)

a

a - x

Since equal interval of time equal conc. decreased then reaction zero order

$$\text{Rate} = \frac{\Delta A}{\Delta t} = \frac{20 - 12}{20} = \frac{8}{20} = 0.4 .$$

Q.50 (1)

$$t = 0 \quad P^0 \quad 0 \quad 0$$

$$t = 3 \text{ hour} \quad (P^0 - x) \quad \frac{3x}{2} \quad \left(\frac{x}{2}\right)$$

$$(P^0 + x) = 2 P^0$$

$$x = P^0$$

Reaction is completed in limited time so reaction is zero order reaction.

Q.51 (2)

$$\text{At low } C_A = \frac{-dC_A}{dt} = K_f C_A$$

Q.52 (3)**Q.53 (1)**

Rate = k (conc.) order

here k depends on temperature.

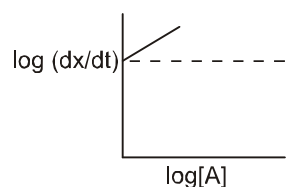
Q.54 (2)

$$\text{No. of half lives} = \frac{18}{3} = 6$$

$$\text{The mass remaining undecayed} = \frac{256}{2^6} = 4 \text{ gm}$$

Q.55 (3)

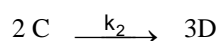
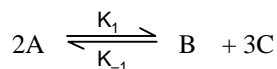
$$\frac{dx}{dt} = k [A]^2$$



$$\log\left(\frac{dx}{dt}\right) = \log k + 2 \log [A]$$

Slope = 2

Intercept = log k.

Q.56 (1)

$$\frac{1}{3} \frac{d[C]}{dt} = k_1 [A]^2 - k_{-1} [B][C]^3$$

$$\Rightarrow \frac{d[C]}{dt} = 3K_1 [A]^2 - 3K_{-1} [B][C]^3 \dots\dots\dots(I)$$

from 2nd reaction

$$-\frac{1}{2} \frac{dC}{dt} = K_2 [C]^2$$

$$\Rightarrow \frac{dC}{dt} = -2K_2 [C]^2 \dots\dots\dots(II)$$

From (I) & (II)

$$\frac{d[C]}{dt} = 3K_1 [A]^2 - 3K_{-1} [B][C]^3 - 2K_2 [C]^2$$

Q.57 (4)

$$t_{1/2} \propto \left(\frac{1}{a}\right)^{n-1}$$

$$\Rightarrow t_{1/2} \propto (1)^{1-n}$$

$$\Rightarrow \frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_1}{a_2}$$

$$\Rightarrow \frac{235}{950} = \left(\frac{500}{250}\right)^{1-n}$$

$$\Rightarrow \log 23.5 - \log 95 = (1-n) \log 2$$

$$\Rightarrow n = 3$$

Q.58 (2)

$$t_{1/2} = 20 \text{ min} \quad \text{at } 300 \text{ K}$$

$$t'_{1/2} = 5 \text{ min} \quad \text{at } 320 \text{ K}$$

$$t_{1/2} = \frac{0.693}{\frac{-E_a}{A \cdot e^{300R}}} = 20$$

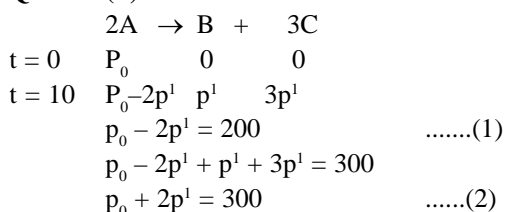
$$t'_{1/2} = \frac{0.693}{\frac{-Ea}{A \cdot e^{320R}}} = 5$$

$$\frac{t_{1/2}}{t'_{1/2}} = 4 = \frac{e^{\frac{-Ea}{320R}}}{e^{\frac{-Ea}{300R}}}$$

$$4 = e^{\frac{Ea}{R} \left(\frac{1}{300} - \frac{1}{320} \right)}$$

$$\ln 4 = \frac{Ea}{R} \left(\frac{20}{300 \times 320} \right)$$

$$\begin{aligned} \text{On solving, } Ea &= 55303.12 \text{ J} \\ &= 55.3 \text{ KJ} \end{aligned}$$

Q.59 (4)

$$(I) + (II) \quad 2p_0 = 500 \Rightarrow p_0 = 250$$

$$\begin{aligned} \text{Pressure of A After 10 min} \\ = p_0 - p^1 = 200 \end{aligned}$$

$$K = \frac{1}{2 \times 10} \ln \frac{250}{200}$$

$$K = \frac{1}{2 \times 10} \ln 1.25$$

\Rightarrow None is correct

Q.60 (4)

$$t_{1/2} = \left(\frac{2 - \sqrt{2}}{K} \right) \times C_0^{1/2}$$

$$\Rightarrow t_{1/2} \propto C_0^{1/2}$$

$$\text{Also, } t_{1/2} \propto C_0^{1-n} \text{ (where } n \text{ is the order of reaction)}$$

$$\Rightarrow 1 - n = 1/2 \Rightarrow n = 0.5$$

Q.61 (2)

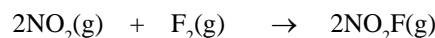
$$\text{Let } r = (1)^x (2)^y$$

$$x = \frac{\log \left(\frac{r_1}{r_2} \right)}{\log \left(\frac{a_1}{a_2} \right)} = \frac{\log \frac{0.1}{0.1}}{\log \left(\frac{0.012}{0.024} \right)} = \frac{\log \left(\frac{1}{8} \right)}{\log \left(\frac{1}{2} \right)}$$

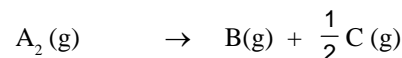
$$x = 3$$

$$y = \frac{\log \frac{r_1}{r_3}}{\log \left(\frac{b_1}{b_2} \right)} = \frac{\log \left(\frac{0.1}{0.1} \right)}{\log \left(\frac{0.035}{0.070} \right)} = \frac{\log(1)}{\log \left(\frac{1}{2} \right)}$$

$$y = 0$$

Q.62 (2)

$$\begin{array}{l} t = 0 \quad 2P_0 \quad P_0 \quad 2P_0 + P_0 = 3 \text{ atm} \\ t = 0 \quad 2 \text{ atm} \quad 1 \text{ atm} \quad 0 \quad P_0 = 1 \text{ atm} \\ t = t \quad 0 \quad 0 \quad 2 \text{ atm} \end{array}$$

Q.63 (2)

$$\begin{array}{l} t = 0 \quad 100\text{mm} \quad 0 \quad 0 \\ t = 5\text{mm} \quad (100 - x) \quad x \quad \frac{x}{2} \end{array}$$

$$\text{Total pressure} \quad 100 - x + x + \frac{x}{2} = 120 \quad (x = 40)$$

$$\text{then Rate of disappearance of } \text{A}_2 = - \frac{d[\text{A}_2]}{dt} = \frac{40}{5} =$$

$$8$$

Q.64 (3)

$$\text{Given } k_{\text{app}} = \frac{k_1 C}{1 + \alpha C} = \frac{k_1}{1/C + \alpha} \quad (C \rightarrow \infty)$$

$$\therefore k_{\text{app}} = \frac{k_1}{\alpha}$$

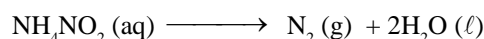
Put this value in given equation

$$\frac{k_1}{\alpha} = \frac{k_1 C}{1 + \alpha C}$$

$$\frac{k_1 \times 90}{\alpha \times 100} = \frac{k_1 C}{1 + \alpha C}$$

Put the value of α in this equation we get

$$C = 10^{-5} \text{ mole/litre.}$$

Q.65 (2)

$$K = \frac{2.303}{t} \log \left(\frac{V_\infty - V_0}{V_\infty - V_t} \right)$$

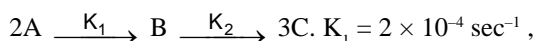
$$\Rightarrow V_0 = 0$$

$$\Rightarrow K = \frac{2.303}{20} \log \left(\frac{70-0}{70-40} \right)$$

$$= \frac{2.303}{20} \log \left(\frac{70}{30} \right)$$

$$\Rightarrow K = \frac{2.303}{1200} \log \frac{7}{3}$$

Q.66 (3)



$$K_2 = 3 \times 10^{-4} \text{ L/mol-sec.}$$

From the unit of rate constant for the given sequential reactions, it is clear that first reaction is of first order & the second reaction is of second order.

Hence, rate law is given as

$$\text{Rate} = K_1[A] - K_2[B]^2$$

Q.67 (3)

$$\text{mole/L-sec} = [K_1][M/L]^3$$

$$[K_1] = L^2M^{-2}\text{sec}^{-1}$$

$$ML^{-1}\text{sec}^{-1} = [K_2][M/L]$$

$$[K_2] = \text{sec}^{-1}$$

Q.68 (2)

$$\text{In given sequence of Rxn} \quad \frac{d[c]}{dt} = k_2[B] - K_3[C]$$

Q.69 (3)

$$N_{10} = N_0 e^{-\lambda t} = N_0 e^{-10\lambda}$$

$$N_{11} = N_0 e^{-\lambda t} = N_0 e^{-11\lambda}$$

No. of atoms decayed during eleventh day

$$= N_{10} - N_{11}$$

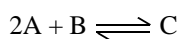
$$= 0.1 \times N_A [e^{-10\lambda} - e^{-11\lambda}]$$

$$\text{Where, } \lambda = \frac{0.693}{5} \text{ per day}$$

Q.70 (2)

$$\left(\frac{dx}{dt} \right) = k_1 [A]^2 [B]^1 - k_2 [C]$$

net rate is



Q.71 (2)



$$\left[\frac{dx}{dt} \right] = 0$$

$$k_1 [A] [B] - k_2 [C] [D] = 0$$

$$k_1 [A] [B] = k_2 [C] [D]$$

$$[A] [B] = [C] [D]$$

$$0.4 \times 0.25 = 0.2 \times 0.5$$

$$1 = 1.$$

Q.72 (2)

$$\% \text{ of B} = \frac{k_1 \times 100}{k_1 + k_2} = \frac{1.26 \times 10^{-4} \times 100}{12.6 \times 10^{-5} + 3 \times 10^{-5}} = 76.83\%.$$

$$\% \text{ of C} = \frac{k_2 \times 100}{k_1 + k_2} = \frac{3 \times 10^{-5} \times 100}{12.6 \times 10^{-5} + 3 \times 10^{-5}} = 23.18\%.$$

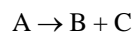
Q.73 (2)

$$\text{we know } E_a = \frac{E_{a1} \times K_1 + E_{a2} \times K_2}{(K_1 + K_2)}$$

$$= \frac{[1.0 \times 10^{-2} \times 60 + 3 \times 10^{-2} \times 70]}{[1.0 \times 10^{-2} + 3.0 \times 10^{-2}]}$$

$$E_a = 67.5 \text{ kJ/mole}$$

Q.74 (3)



$$e^{\frac{-E_a}{RT}} = \frac{3.8 \times 10^{-16}}{100}$$

$$\frac{-E_a}{RT} = 2.303 \log(3.8 \times 10^{-18})$$

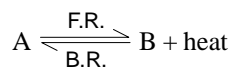
$$E_a = 100 \text{ KJ/mol}$$

Q.75 (2)

At temperature = ∞

Rate constant = Arrhenius constant.

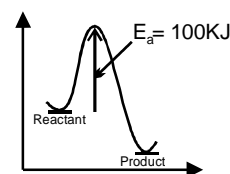
Q.76 (4)



$$E_{af} = 100 \text{ KJ/mol}$$

$$E_{ab} = ?$$

heat of reaction = ?



Only one option because

$$E_b = E_a + \Delta H.O. \text{ reaction}$$

Q.77 (1)

In a reaction, the threshold energy is equal to :
Activation energy + Normal energy of reactants.

Q.78 (1)

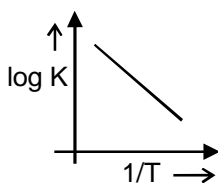
$$\log K = 15 - \frac{10^6}{T}$$

$$\log A = 15 \Rightarrow A = 10^{15}$$

$$\text{Also, } \frac{E_a}{2.303R} = 10^6$$

$$E_a = 1.9 \times 10^4 \text{ KJ}$$

Q.79 (2)



When line cuts y axis

$$\frac{1}{T} = 0$$

$$\Rightarrow \boxed{T = \infty}$$

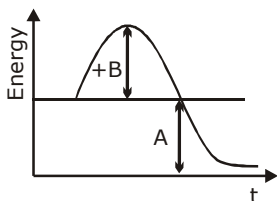
When it cut X-axis

$$\log K = 0$$

$$\Rightarrow \log A = \frac{E_a}{2.303RT}$$

$$\Rightarrow \boxed{T = \frac{E_a}{R \ln A}}$$

Q.80 (2)



$$E_a (\text{Backward}) = A + B$$

Q.81 (4)

$$R_{T+10}^I = 2R_T^I$$

$$R_{T+10}^{II} = 2R_T^{II}$$

$$\frac{K_2}{K_1} = \left(\frac{3}{2a}\right)^5 = 7.6$$

Q.82 (1)

Q.83 (1)

Rate of reaction increases with increase of temperature whether it is endothermic or exothermic.

Q.84 (2)

By using maxwell's velocity distribution curve the rise in temperature, increases the activated molecules to form the product therefore rate of reaction increases.

Q.85 (4)

$$E_a = 41570 \times R = 41570 \times 8.31 = 345612.98 \text{ J}$$

Q.86 (4)

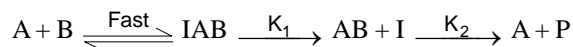
$\Delta H = E_f - E_b - 40 = 80 - E_b$ $E_b = 120 \text{ kJ/mole}$,
catalyst lower the E_f To 20 kJ/mole for forward Rxn
then $E'_f = 20 \text{ kJ/mol}$

we know catalyst decreases the Activation energy equal amount in both direction

$$E'_b = (120 - 60) = 60 \text{ kJ/mol}$$

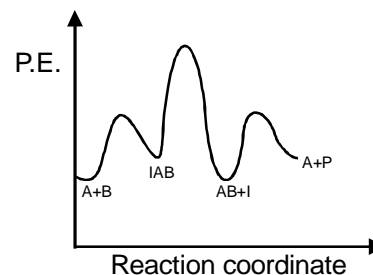
$$\frac{E_b}{E'_b} = \frac{120}{60} = 2.0$$

Q.87 (1)

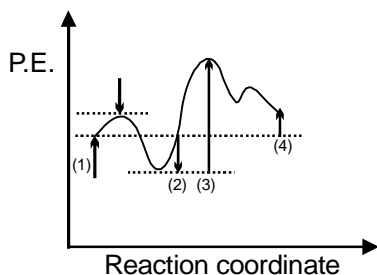


Since

$K_1 \lll K_2$ = most Imp. peak will be higher



Q.88 (2)

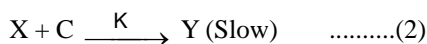
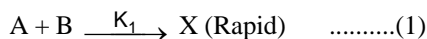
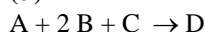
As ΔE overall = 4

So, first option is correct.

Q.89 (2)

Slowest step is rate determining step.

Q.90 (3)



Since X is not in the original reaction, hence it has to be eliminated.

$$\text{from eq}^n (1), K_1 = \frac{[X]}{[A][B]} \Rightarrow [X] = K_1[A][B]$$

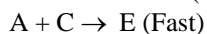
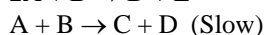
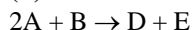
Putting this value in eqⁿ (4)

$$\text{Rate} = KK_1[A][B][C]$$

$$\text{Rate} = K' [A][B][C]$$

$$\Rightarrow \text{Order} = 3$$

Q.91 (4)



$$\Rightarrow \text{Rate} = K[A][B]$$

[As slowest step is rate determining step].

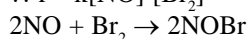
Q.92 (1)

All the reactins

$$r = k[\text{No}][\text{NOBr}_2]$$

Rate of reaction expression do not contain intermediate

$$\therefore r = k[\text{NO}]^2[\text{Br}_2]$$



Q.93 (4)

$$\text{Rate} = k_1 [M] [Z] \dots\dots(1)$$

$$\text{from equation (1)} K_{\text{eq}} = \frac{[M]}{[x][y]}$$

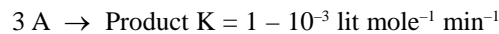
$$M = k_{\text{eq}} [x] [y] \dots\dots(2)$$

put the value of M from (2) to (1)

$$\text{Rate} = k_1 k_{\text{eq}} [x] [y] [z] \quad \text{Rate} = k [x] [y] [z]$$

JEE-ADVANCED OBJECTIVE QUESTIONS

Q.1 (C)



Reaction is second order

$$r = K [A]^2 \Rightarrow r = \left[\frac{1 \times 10^{-3}}{60} \right] (2)^2$$

$$\Rightarrow 0 = \frac{1 \times 10^{-3} \times 15}{60} = 6.67 \times 10^{-5}$$

$$r = -\frac{1}{3} \frac{d[A]}{dt} = k [A]^2 = 6.67 \times 10^{-5}$$

$$\Rightarrow \frac{-d[A]}{dt} = 2 \times 10^{-4}$$

Q.2 (D)

$$-\frac{d[\text{MnO}_4^-]}{dt} = 4.56 \times 10^{-3} \text{ Ms}^{-1}$$

$$-\frac{1}{2} \frac{d[\text{MnO}_4^-]}{dt} = +\frac{1}{5} \frac{d[\text{I}_2]}{dt}$$

$$\frac{d[\text{I}_2]}{dt} = \frac{5}{2} \left[-\frac{d[\text{MnO}_4^-]}{dt} \right]$$

$$\frac{d[\text{I}_2]}{dt} = \frac{5}{2} \times 4.56 \times 10^{-3} = 11.4 \times 10^{-2} \text{ Ms}^{-1}$$

Q.3 (D)

$$t_{1/2} = \left(\frac{2 - \sqrt{2}}{K} \right) C_0^{1/2}$$

For nth order reaction

$$t_{1/2} \propto (C_0)^{1 - \text{order}}$$

$$1 - n = \frac{1}{2}$$

So, n = 0.5.

Q.4 (A)

$$K = \frac{1}{t(n-1)} \left[\frac{1}{C^{n-1}} - \frac{1}{(C_0)^{n-1}} \right]$$

$$; t = \frac{1}{(n-1)k} \left[\frac{1}{C^{n-1}} - \frac{1}{(C_0)^{n-1}} \right]$$

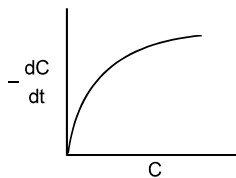
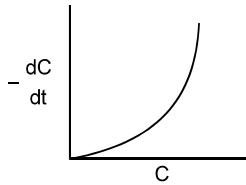
$$\frac{t_{3/4}}{t_{1/2}} = \left(\frac{4^{n-1} - 1}{2^{n-1} - 1} \right) \Rightarrow \frac{t_{3/4}}{t_{1/2}} = \frac{(2^{n-1})^2 - 1}{2^{n-1} - 1}$$

$$\frac{t_{3/4}}{t_{1/2}} = \frac{(2^{n-1})(2^{n-1} + 1)}{(2^{n-1} - 1)} \Rightarrow \frac{t_{3/4}}{t_{1/2}} = (2^{n-1} + 1)$$

Q.5 (B)

dt is parab parabolic graph

of $y = x^2$



So This the

graph of second order

$$y^2 = x$$

$$y = (x)^{\frac{1}{2}}$$

$$\frac{-dc}{dt} = K [C]^{\frac{1}{2}}$$

So reaction is $\left(\frac{1}{2}\right)$ order.

Q.6 (A)

Given $f = \left(1 - \frac{c}{c_0}\right)$ then $\frac{c}{c_0} = (1 - f)$

$$\frac{df}{dt} = \frac{1}{c_0} \frac{dc}{dt} \text{ for first order reaction } - \frac{dc}{dt} = K$$

[c]

$$\frac{df}{dt} = \frac{1}{c_0} K [c]$$

then $\frac{df}{dt} = K (1 - f)$

Q.7 (B)

$$t_1 = \frac{2.303}{k} \log \left(\frac{100}{67} \right)$$

$$t_2 = \frac{2.303}{k} \log \left(\frac{100}{33} \right)$$

$$(t_2 - t_1) = \frac{2.303}{k} \left[\log \frac{100}{33} \times \frac{67}{100} \right]$$

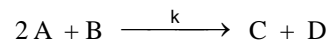
$$(t_2 - t_1) \frac{2.303}{k} \times 0.30 = 30$$

$$k = \frac{2.303}{30} \times \frac{30}{100} = 2.303 \times 10^{-2}$$

$$t = \frac{2.303}{2.303 \times 10^{-2}} \log \left(\frac{100}{75} \right)$$

$$t = 100 [\log 4 - \log 3] = 100 [0.6020 - 0.4771] = 12.49 = 12.5 \text{ minute}$$

Q.8 (D)



$$r = K [A]^1 [B]^2 \quad r_0 = K (C_0)^1 (2C_0)^2 = 4K (C_0)^3 \quad \dots\dots(1)$$



$t = 0$	C_0	$2C_0$	0	0
$(C_0 - 2x)$	$(2C_0 - x)$	x	x	

$$x = \left(\frac{C_0}{4}\right) \quad [A] = C_0 - \frac{C_0}{2} = \frac{C_0}{2}$$

$$[B] = 2C_0 - \frac{C_0}{4} = \frac{7C_0}{4}$$

$$r = K \left(\frac{C_0}{2}\right) \left(\frac{7C_0}{4}\right)^2 = \frac{49K(C_0)^3}{32}$$

Q.9 (B)

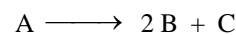
$$K = \frac{2.303}{80} \log \left(\frac{100}{6.25} \right) = 3.465 \times 10^{-2} \text{ mm}^{-1}$$

$$\text{Then } 3.465 \times 10^{-2} = \frac{2.303}{100} \log \left(\frac{0.2}{a_t} \right)$$

$$a_t = 0.00625$$

$$\text{Rate} = K \times [a_t] = 0.00625 \times 3.465 \times 10^{-2} = 2.166 \times 10^{-4} \text{ sec}^{-1}$$

Q.10 (B)



$t = 0$	P_0	0	0	P_0
---------	-------	-----	-----	-------

$$\begin{aligned}
 t = t & \quad (P_0 - x) & 2x & \quad x & \quad P_0 + 2x = 176 \\
 & 0 & 2P_0 & & P_0 \\
 & 3P_0 = 270 & & & \\
 & P_0 = 90 & & 2x = 176 - 90 = 86 & \\
 & & & x = 43 & \\
 & \text{Pressure of A after 10 minute} = 90 - 43 = 47 & & &
 \end{aligned}$$

$$\begin{aligned}
 A_0 &= 0.1 \\
 x &= \frac{0.05}{3} \\
 \frac{2}{6} &= e^{-7.5 \times 10^{-3} t} \\
 \ln(1.5) \times \frac{10^3}{7.5} &= t \\
 t &= 53.4 \text{ sec}
 \end{aligned}$$

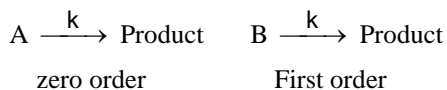
Q.11 (C)

$$K = \frac{\ln 2}{10}$$

$$K_2 = \frac{\ln 2}{K^3}$$

10 min

Q.12 (D)



$$t_{1/2} = \frac{a}{2K} \quad t_{1/2} = \frac{\ln 2}{K}$$

$$\Rightarrow \frac{a}{2K} = \frac{\ln 2}{K}$$

$$\Rightarrow a = 2 \ln_2$$

Q.13 (A)

$$t_{25} = \frac{1}{K_1} \ln \left(\frac{100}{75} \right)$$

$$\Rightarrow t_{75\%} = \frac{1}{K_2} \ln \left(\frac{100}{25} \right)$$

$$\frac{t_{25}}{t_{75}} = \frac{K_2}{K_1} \frac{\ln \frac{4}{3}}{\ln 4}$$

$$\Rightarrow \frac{t_{25}}{t_{75}} = \frac{(t_{1/2})_1}{(t_{1/2})_2} \times \frac{\left(\frac{\log 4}{3} \right)}{\log 4} = \frac{3}{2} \left[\frac{\log 4 - \log 3}{0.60} \right]$$

$$= \frac{3}{2} \left[\frac{0.60 - 0.48}{0.60} \right] = 0.311 : 1$$

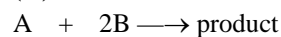
Q.14 (C)

$$A_0 - 2x + 4x + x = 0.15$$

Q.15 (D)

$$t_{3/4} = \frac{3[A_0]}{4K}$$

Q.16 (C)



$$a \quad 2a \quad \frac{-d[A]}{dt} = K(\sqrt{a-x}) \times \sqrt{2(a-x)}$$

$$(a-x) \quad 2(a-x) \quad \text{Final}$$

$$K = \frac{2.303}{\sqrt{2} \times t} \log \frac{a}{(a-x)}$$

$$t_{1/2} = \frac{0.6932}{\sqrt{2} K}$$

Q.17 (C)

$$\frac{dB}{dt} = \frac{-dA}{dt} = A_0 K e^{-kt}$$

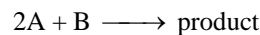
Q.18 (C)

$$\log(a_0 - x) = \log a_0 - kt \log e$$

$$k \log e = \frac{2}{10}$$

$$K = \frac{\ln 10}{5} = \frac{2.303}{5} = 0.46$$

Q.19 (A)



$$-\frac{d[A]}{dt} = K[A]$$

$$-\frac{d[A]}{dt} = K[a-x]$$

$$C_t = C_0 e^{-Kt}$$

$$C_t = C_0 e^{-K \times \frac{1}{K}}$$

$$C_t = C_0 e^{-kt}$$

$$C_t = \frac{C_0}{e}$$

Q.20 (B)

$$C_t = C_0 e^{-Kt}$$

$$\frac{1}{e^2} \times C_0 = C_0 e^{-Kt}$$

$$e^{-2} = e^{-Kt}$$

$$t = \frac{2}{K}$$

$t = 2$ natural life time.

Q.21 (C)

From the given graph it is clear that the concentration decrease linearly with time then zero order Reaction and $A \rightarrow 3B$ type.

Q.22 (A)

$$\frac{0.8}{1.5} = e^{-K \times 20}$$

$$K = \frac{\ln(15/8)}{20} = 0.03$$

Q.23 (A,B,D)

$$t_{1/2} = 100 \text{ days}$$

$$a = \text{entry} = \frac{6.93 \times 10^{-6}}{80} \text{ mol/L/day}$$

$$\frac{dx}{dt} = at - kx$$

$$\frac{0.643 \times 10^{-6}}{8} = t = \frac{643}{100} \times x$$

$$x = t \times \frac{10.4}{8}$$

Q.24 (C)

Q.25 (C)

Flask A
1 m

4 hr ↓

0.5 m

Flask B
0.62 m

4 hr ↓

0.3 m

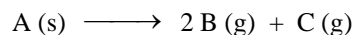
4 hr ↓
0.25 m

Q.26 (A)

$$1 - \frac{1}{100} = e^{-\frac{K}{2}}$$

$$K = 2 \ln 100 = 0.02 \text{ min}^{-1}$$

Q.27 (D)



$$K = \frac{1}{t} \ln \left(\frac{P_\infty - P_0}{P_\infty - P_t} \right) \quad P_0 = 0$$

$$P_t = 150 \quad P_\infty = 225$$

$$\frac{1}{20} \ln \left[\frac{225}{225 - 150} \right] \Rightarrow \frac{1}{20} \ln \left(\frac{225}{75} \right) = 0.05 \ln 3$$

$$\frac{1}{20} \ln \left(\frac{225}{75} \right) = \frac{1}{20} \ln \left(\frac{225}{225 \times P_{40}} \right) \Rightarrow \left(\frac{225}{75} \right)^2 = \frac{225}{225 \times P_{40}}$$

$$\frac{225}{75 \times 75} = \frac{1}{225 - P_{40}} \Rightarrow P_{40} = 200$$

Q.28 (A)

$$0.1 = e^{-\frac{K}{2}}$$

$$\ln 10 = \frac{K}{2}$$

$$K = 4.606$$

Q.29 (A)

$$\text{molarity} = \frac{16.8}{11.2} = \frac{3}{2}$$

Let new molarity = x

$$\frac{20x}{1000} \times \frac{2}{4} = \frac{37.5 \times 0.02 \times 5}{1000}$$

$$x = 0.375$$

Q.30 (C)

$$K = \frac{2.303}{(40-20)} \log \frac{(0.80-0.20)}{(0.35-0.20)} = 6.93 \times 10^{-2}$$

Q.31 (C)

$$\begin{array}{ll} \text{pH} = 5 & \text{pH} = 6 \\ [\text{H}^+] = 10^{-5} & [\text{H}^+] = 10^{-6} \end{array}$$

$$\frac{(t_{1/2})}{(t_{1/2})} = \left(\frac{10^{-5}}{10^{-6}} \right)^{1-n} = \frac{1}{10} = (10)^{1-n}$$

$$\begin{aligned} 10^{-1} &= (10)^{1-n} \\ \Rightarrow 1 - n &= -1 \\ \Rightarrow n &= 2 \end{aligned}$$

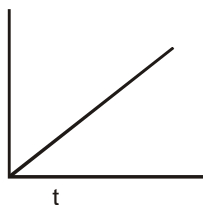
Q.32 (D)

$$\begin{aligned} (2-x_B-x_C)60^\circ - (x_B) + 42^\circ(x_C) \\ = 120^\circ - 132^\circ x_B - 18x_C \end{aligned}$$

$$\frac{x_B}{x_C} = \frac{1}{2}$$

$$\begin{aligned} &= 120^\circ - 168^\circ x_B \\ t \rightarrow \infty \quad x_B &\rightarrow 2/3 \\ A &= 0.5 \\ B &= 0.5 \\ \theta &= 36^\circ \end{aligned}$$

Q.33 (D)



$$\left[\frac{C_0 - C}{C} \right]$$

For second order reaction $\frac{1}{C} = \frac{1}{C_0} + kt$

$$\frac{1}{C} - \frac{1}{C_0} = kt \quad \left(\frac{C_0 - C}{C} \right)$$

$$\left[\frac{C_0 - C}{C} \right] = (KC_0)t \quad \text{So reaction is second order}$$

Q.34 (D)

A → B (uncatalysed reaction)

A $\xrightarrow{\text{catalyst}}$ B (catalyst reaction)

$$K = A e^{-E_a/RT}$$

$$K_{\text{cat.}} = A e^{-E_{a(\text{cat.})}/RT}$$

$$\frac{K_{\text{cat.}}}{K} = e^{(E_a - E_a') \times \frac{1}{RT}}$$

$$\frac{K_{\text{cat.}}}{K} = e^{\frac{8.314 \times 10^3}{8.314 \times 300}} = e^{3.33} = 28 \text{ times}$$

Q.35 (D)

Intermediate and product have less potential energy than activated complex.

Q.36 (A)

$$K = A e^{-\frac{E_a}{RT}}$$

$$\log k = \log A + \left(\frac{-E_a}{2.303R} \right) \times \frac{1}{T}$$

Q.37 (C)

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log 2 = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$0.3 = \frac{E_a}{2.303R} \times \frac{10}{280 \times 290}$$

$$E_a = 0.3 \times 2.303 \times 280 \times 29 \times R$$

.....(1)

Now again

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$\log \frac{k_2}{k_1} = \frac{0.3 \times 2.303 \times 280 \times 29R}{2.303R} \left[\frac{10}{290 \times 300} \right]$$

$$= 1.905.$$

JEE-ADVANCED

MCQ/COMPREHENSION/MATCHING

Q.1 (ABC)

$$\text{Rate} = K[A]^2[B]$$

⇒ rate w.r.t B = 1

Overall order of the reaction = 2 + 1 = 3

for a complex reaction the rate determining step is determined experimentally.

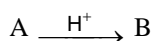
Q.2 (BD)

In SN¹ reaction, formation of carbocation takes place which is planar.

⇒ equimolar mixture of (I) and (II) will be formed in case of SN¹.

In SN^2 reaction Nucleophile will attack from the opposite to leaving group
 \Rightarrow Product (II) will be formed in case of SN^2 reaction.

Q.3 (BC)



$$\text{Rate} = K[\text{H}^+][\text{A}]$$

$$\text{Rate} = K'[\text{A}]$$

If K' has greater value for HA

$\Rightarrow [\text{H}^+]$ has to be large

\Rightarrow for that acid has to be stronger

$\Rightarrow [\text{HA}]$ is stronger than HB

Also Relative strength = 2

Q.4 (ABCD)

(A) For zero order reaction

$$t_{1/2} = \frac{a_0}{2K}$$

$\Rightarrow t_{1/2} \propto a_0$ (initial concentration)

(B) For first order reaction

Average life = $1.44 \times$ half life

(C) For II^{nd} order reaction

$$t_{1/2} = \frac{1}{KC_0} \quad (\text{Co} = \text{initial concentration})$$

$$\text{Also } Kt = \frac{1}{C} - \frac{1}{C_0}$$

$$t_{3/4} = \frac{1}{k} \left[\frac{1}{C_0/4} - \frac{1}{C_0} \right]$$

$$= \frac{1}{k} \times \frac{3}{C_0} = \frac{3}{KC_0} = 3 \times t_{1/2}$$

$$\Rightarrow t_{3/4} = 3 \times t_{1/2}$$

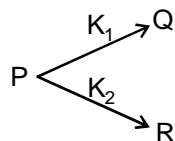
$$\text{(D)} t_{99.9} = \frac{2.303}{0.0693} \log \frac{100}{0.1}$$

$$t_{99.9} = 100 \text{ min}$$

Q.5 (ACD)

$t_{1/2}$ of (A) zero (C) second (D) third order varies with concentration.

Q.6 (AB)



Since $[\text{Q}] = [\text{R}]$ all the times,

$$[\text{P}] = P_0 e^{-(K_1+K_2)t} = P_0 \left(\frac{K_1}{K_1+K_2} \right) \left(1 - e^{-(K_1+K_2)t} \right)$$

As $K_1 = K_2$

$$\Rightarrow e^{-2K_1 t} = \frac{1}{2} - \frac{1}{2} e^{-2K_1 t}$$

$$\Rightarrow \frac{3}{2} e^{-2K_1 t} = \frac{1}{2}$$

$$\Rightarrow e^{-2K_1 t} = \frac{1}{3}$$

Taking ln of both side

$$-2K_1 t = -\ln 3$$

$$t = \frac{\ln 3}{2K_1} = \frac{2.303}{2K_1} \log_{10} 3$$

As $K_1 = K_2$

$$t = \frac{2.303}{2K_2} \log_{10} 3$$

Q.7 (ABC)

From the given data, it is clear that

(A) keeping $[\text{B}]$ constant, After doubling the concentration of $[\text{A}]$ makes the rate of reaction four times.

\Rightarrow reaction is of order two w.r.t. A.

(B) Similarly order w.r.t. B = 1

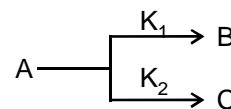
(C) Rate = $K[\text{A}]^2[\text{B}]$

$$5 \times 10^{-4} = K \times (2.5 \times 10^{-4})^2 \times 3.0 \times 10^{-5}$$

$$\Rightarrow K = 2.67 \times 10^8 \text{ L}^2 \text{mol}^{-2} \text{ s}^{-1}$$

(D) order = $2 + 1 = 3$

Q.8 (AB)



$$K_1 = 1.26 \times 10^{-4} \text{ sec}^{-1}$$

$$K_2 = 3.8 \times 10^{-5} \text{ sec}^{-1}$$

$$\% \text{ B} = \frac{K_1}{K_1 + K_2} \times 100 = 76.83 \%$$

$$\% \text{ C} = \frac{K_2}{K_1 + K_2} \times 100 = 23.17 \%$$

Q.9 (ABC)

For the given curve

(A) $a = E_B$ (B) $b = E_A$ (C) $\Delta H_A = b - d$

and $\Delta H_B = a - c$

Q.10 (BCD)

Q.11 (ABD)

From figure it is clear that $E_a(\text{forward}) = y$

$E_a(\text{backward}) = Z$

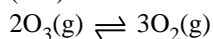
$\Delta H_r = +x$

Q.12 (AB)

- (A) $A \xrightarrow{E_a=50\text{kcal}} \Delta H = -10\text{KCal}$
 E_a (backward) = 60 KCal
- (B) $A \xrightarrow{E_a=60\text{kcal}} B$; $\Delta H = -20\text{KCal}$
 E_a (backward) = 80 KCal
- (C) $A \xrightarrow{E_a=50\text{kcal}} B$; $\Delta H = +10\text{KCal}$
 E_a (backward) = 40 KCal
- (D) $A \xrightarrow{E_a=60\text{kcal}} B$; $\Delta H = +20\text{KCal}$

Q.13 (ABCD)

Q.14 (CD)



Slowest step is rate determining step

$$\text{rate} = K[\text{O}_3][\text{O}] \dots\dots\dots(1)$$

Since, [O] is not in the original reaction hence it has to be eliminated.

From first step

$$K_1 = \frac{[\text{O}_2][\text{O}]}{[\text{O}_3]} \Rightarrow [\text{O}] = \frac{K_1[\text{O}_3]}{[\text{O}_2]} \dots\dots\dots(2)$$

Putting the value of [O] in the eq. (1)

$$\text{rate} = K_1 K [\text{O}_3] \frac{[\text{O}_3]}{[\text{O}_2]}$$

$$\text{Rate} = K[\text{O}_3]^2[\text{O}_2]^{-1}$$

Q.15 (ABC)

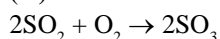
Energy of activation can never be negative

Option (D) is incorrect.

Q.16 (ACD)

Comprehension # 1

Q.17 (D)



$$\frac{d[\text{SO}_3]}{dt} = 10\text{g/sec}^{-1}$$

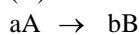
$$\frac{d[\text{SO}_3]}{dt} = \frac{1}{8} \text{ mol/sec}$$

$$\text{As } \frac{-1}{2} \frac{d[\text{SO}_2]}{dt} = -\frac{d[\text{O}_2]}{dt} = \frac{1}{2} \frac{d[\text{SO}_3]}{dt}$$

$$\Rightarrow -\frac{d[\text{O}_2]}{dt} = \frac{1}{16} \text{ mol/sec}$$

$$\Rightarrow \frac{d[\text{O}_2]}{dt} = 2\text{g sec}^{-1}$$

Q.18 (A)



$$-\frac{1}{a} \frac{d[A]}{dt} = \frac{1}{b} \frac{d[B]}{dt}$$

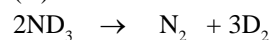
$$\left(-\frac{d[A]}{dt}\right) / \left(\frac{d[B]}{dt}\right) = \frac{a}{b}$$

$$\log\left(-\frac{d[A]}{dt}\right) = \log\left(\frac{d[B]}{dt}\right) + \log\left(\frac{a}{b}\right)$$

$$\Rightarrow \log\left(\frac{a}{b}\right) = 0.6$$

$$\Rightarrow \frac{a}{b} = 3.98$$

Q.19 (B)



$$\frac{-d[\text{ND}_3]}{2 dt} = \frac{d\text{N}_2}{dt} = \frac{1}{3} \frac{d[\text{D}_2]}{dt}$$

$$\frac{-1}{2} K_1[\text{ND}_3] = K_2[\text{ND}_3] = \frac{1}{3} \times K_3[\text{ND}_3]$$

$$\frac{k_1}{2} = k_2 = \frac{k_3}{3}$$

$$3 k_1 = 6 k_2 = 2 k_3 \text{ (by multiplying with 6)}$$

Comprehension # 2

20. (A)

$$P_B = 2p = \frac{P_0}{4} = \frac{10}{4} = 2.25 \text{ bar}$$

21. (D)

$$K = \frac{2.303}{t_1} \log \frac{P_0}{P_0 - p}$$

$$\log \frac{64}{49} = \frac{2.303}{t_1} \log \frac{10}{10 - 1.125}$$

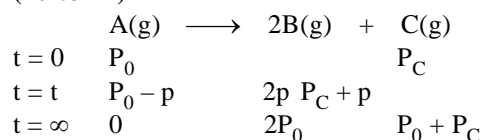
$$t_1 = 1.15 \text{ sec.}$$

22. (B)

Rate constant depends only on temperature.

$$\therefore 1 : 1 : 1$$

(20 to 22)



$$P_C = \frac{1}{3} [P_0 + P_C]$$

$$3P_C = P_0 + P_C$$

$$2P_C = P_0$$

$$P_C = \frac{P_0}{2}$$

$$P_T = P_0 - p + 2p + P_C + p$$

$$= P_0 + P_C + 2p$$

$$P_\infty = 2P_0 + P_0 + P_C$$

$$= 3P_0 + P_C$$

$$P_T = \frac{1}{2} P_\infty \text{ (given)}$$

$$P_0 + P_C + 2p = \frac{1}{2} [3P_0 + P_C]$$

$$\frac{3P_0}{2} + 2p = \frac{1}{2} \left[3P_0 + \frac{P_0}{2} \right]$$

$$\frac{3P_0}{2} + 2p = \frac{1}{2} \times \frac{1}{2} \times 7P_0$$

$$2p = \frac{7}{4} P_0 - \frac{3P_0}{2}$$

$$2p = \frac{P_0}{4}$$

$$P = \frac{P_0}{8}$$

$$P_\infty = 3P_0 + P_C = 35$$

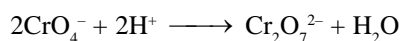
$$= 3P_0 + \frac{P_0}{2} = 35$$

$$= \frac{7P_0}{2} = 35$$

$$P_0 = 10 \text{ bar}$$

Comprehension # 3

23. (B)



Let Rate Law is

$$\text{Rate} = K[\text{MnO}_4^-]^a [\text{Cr}^{3+}]^b$$

$$\text{Rate} = - \frac{d[\text{Cr}_2\text{O}_7]}{dt} = \left[\frac{C_f - C_i}{\Delta t} \right]$$

From Exp. 1 and 2

$$\left[\frac{0.01 \times 0.1 \times 10^{-3}}{\text{V.f.}} \right] \times \frac{1}{22} = K (1 \times 25 \times 10^{-3})^a$$

$$(1 \times 25 \times 10^{-3})^b \quad \dots(1)$$

$$\left[\frac{0.01 \times 0.1 \times 10^{-3}}{\text{V.f.}} \right] \times \frac{1}{11} = K (2 \times 25 \times 10^{-3})^a$$

$$(1 \times 25 \times 10^{-3})^b \quad \dots(2)$$

$$\frac{1}{2} = \frac{1}{(2)^a}$$

⇒ So, a = 1

24. (A)

Similarly from Exp. 1 and 3

$$\left[\frac{0.01 \times 0.01 \times 10^{-3}}{\text{V.f.}} \right] \times \frac{1}{22}$$

$$\left[\frac{0.01 \times 0.1 \times 10^{-3}}{\text{V.f.}} \right] \times \frac{1}{45}$$

$$= \frac{K(1 \times 25 \times 10^{-3})^a (1 \times 25 \times 10^{-3})^b}{K(1 \times 25 \times 10^{-3})^a (0.5 \times 25 \times 10^{-3})^b}$$

$$2 = (2)^b$$

So, b = 1

25. (B)

So, order with respect to $\text{MnO}_4^- = 1$
with respect to $\text{Cr}^{3+} = 1$.

Overall order = 2.

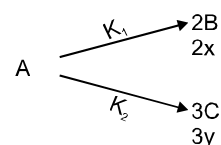
So, rate law

$$\text{Rate} = K [\text{MnO}_4^-] [\text{Cr}^{3+}]$$

So, reaction is elementary reaction.

Comprehension # 4

26. (C)



$$t = 0 \quad a$$

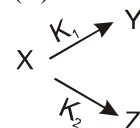
$$t - t \quad a - x - y$$

$$\therefore [A]_0 = [A]_t + \frac{[B]_t}{2} + \frac{[C]_t}{3}$$

$$a = a - x - y + \frac{2x}{2} + \frac{3y}{3}$$

$$a = a$$

27. (B)



$$\frac{[X]_t}{[Y]_t + [Z]_t} = \frac{ae^{-(k_1+k_2)t}}{\frac{k_1a}{k_1+k_2}[1-e^{-(k_1+k_2)t}] + \frac{k_2a}{(k_1+k_2)}[1-e^{-(k_1+k_2)t}]}$$

$$= \frac{ae^{-(k_1+k_2)t}}{[1-e^{-(k_1+k_2)t}] \left[\frac{k_1a+k_2a}{k_1+k_2} \right]}$$

$$= \frac{ae^{-(k_1+k_2)t}}{e^{-(k_1+k_2)t} [1-e^{-(k_1+k_2)t}]} = \frac{1}{[e^{(k_1+k_2)t} - 1]} = \frac{1}{[e^{kt} - 1]}$$

[where $k = k_1 + k_2$]

28. (B)

$$\text{Fraction of acetic acid reacting} = \frac{k_1}{k_1+k_2} = \frac{3}{3+4} = \frac{3}{7}$$

29. (A)

$$\frac{[B]_t}{[C]_t} = \frac{3k_1}{4k_2} \text{ which depends only on temperature not on time.}$$

Comprehension # 5

Q.30 (B)

$$\frac{df}{dt} = K(1-f)$$

$$K = \frac{1}{t} \ln \frac{1}{1-f}$$

$$K = \frac{1}{200} [\ln 1 - \ln(1-f)]$$

$$\Rightarrow K = \frac{3}{200}$$

$$t_{1/2} = \frac{0.693}{K} = \frac{0.693}{3/200}$$

$$t_{1/2} = 46.2 \text{ hrs}$$

Q.31 (A)

$$1-f = e^{-kt}$$

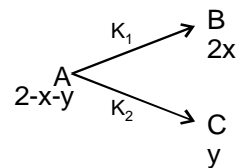
$$\Rightarrow f = 1 - e^{-kt}$$

Putting the value of k in from eqⁿ(1)

$$f = 1 - e^{-3t/200}$$

Comprehension # 6

Q.32 (B)



$$2 - x - y = 1$$

$$\Rightarrow x + y = 1 \quad \dots\dots\dots(1)$$

$$\frac{1}{2} \frac{d[B]}{dt} = K_1[A]$$

$$\frac{d[B]}{dt} = 2K_1[A]$$

$$\text{Also, } \frac{d[C]}{dt} = K_2[A]$$

$$\Rightarrow \frac{[B]}{[C]} = \frac{2K_1}{K_2} = 2 \times \frac{1}{2} \text{ (Given } K_1 : K_2 = 1 : 2 \text{)}$$

$$\Rightarrow [B] = [C]$$

$$\Rightarrow 2x = y$$

$$\dots\dots\dots(2)$$

Solving (1) and (2)

$$x = \frac{1}{3}, y = \frac{2}{3}$$

Total moles after 50 % of the reaction

$$= 2 - x - y + 2x + y$$

$$= 2 + x = 7/3$$

Q.33 (B)

No. of Moles of B = $2x$

$$= 2/3$$

$$= 0.666$$

Comprehension # 7

Q.34 (C)

$$\frac{dN}{dt} = \alpha - \lambda N$$

$$\Rightarrow \int_{N_0}^N \frac{dN}{\alpha - \lambda N} = \int_0^t dt$$

$$\Rightarrow N = \frac{1}{\lambda} [\alpha - (\alpha - \lambda N_0)e^{-\lambda t}]$$

Q.35 (C)

Put $\alpha = 2N_0\lambda$

$$\text{and } t = t_{1/2} = \frac{\ln 2}{\lambda}$$

Q.36 (B)

At steady state

$$\frac{dN}{dt} = \alpha - \lambda N = 0$$

$$N = \frac{\alpha}{\lambda} = 4 N_0$$

Comprehension # 8**Q.37 (A)** Greater is the temperature greater is the rate constant.**Q.38 (C)** Activation energy is independent on temperature.**Q.39 (A)** At higher temperature value of 'k' is more.**Comprehension # 9****Q.40 (A)**

$$\log k = \log_{10} A - \frac{E_a}{2.303RT}$$

When $E_a = 0$, $k = 3.2 \times 10^5$ & it does not depend on T**Q.41 (B)**When E_a is max,

$$\frac{k_{310}}{k_{300}} \text{ would be max}$$

Q.42 (C)

$$\log \left(\frac{K_1}{K'_1} \right) = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \dots(1)$$

$$\text{Also } \log \left(\frac{K_2}{K'_2} \right) = \frac{E'_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \dots(2)$$

eq. (1)/(2)

$$\frac{\log \left(\frac{K_1}{K'_1} \right)}{\log \left(\frac{K_2}{K'_2} \right)} = \frac{E_a}{E'_a}$$

$$\Rightarrow \frac{\log \left(\frac{K_1}{K'_1} \right)}{\log \left(\frac{K_2}{K'_2} \right)} > 1 \quad (E_a < E'_a) \quad \Rightarrow$$

$$\frac{K_1}{K'_1} > \frac{K_2}{K'_2}$$

Q.43 (A)

$$10^{15} e^{-\frac{2000}{T}} = 10^{15} e^{-\frac{2000}{T}} = 10^{14} e^{-\frac{1000}{T}}$$

$$10 = e^{-\frac{1000}{T} + \frac{2000}{T}}$$

$$10 = e^{\frac{1000}{T}}$$

$$\ln 10 = \frac{1000}{T}$$

$$T = \frac{1000}{2.303}$$

$$T = 434.22 \text{ K}$$

Comprehension # 10**Q.44 (A)**

A → B

$$\log_{10} K = 14 - \frac{1.25 \times 10^4}{T}$$

.....(1)

$$\log K = \log A - \frac{E_a}{2.303RT}$$

Comparing

$$\log A = 14$$

$$\Rightarrow A = 10^{14} \text{ sec}^{-1}$$

Also

$$\frac{E_a}{2.303RT} = \frac{1.25 \times 10^4}{T}$$

$$\Rightarrow E_a = 2.39.34 \text{ KJ}$$

Q.45 (B)

Exponential factor = 0

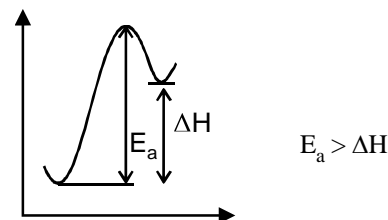
when $T = \infty$

Free radical combination

Energy of activation + Threshold energy

Q.46 (A)

For an endothermic reaction

**Comprehension # 11****Q.47 (A)**When x moles of I_3^- form per litre then decrease in concentrations of the reactants are 3x and 3x.

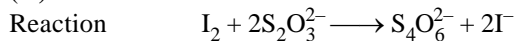
Q.48 (B)



Q.49 (B)

Rate is determined by the slow step of the mechanism.

Q.50 (B)



$$-\frac{d[\text{I}_2]}{dt} = -\frac{1}{2} \frac{d[\text{S}_2\text{O}_3^{2-}]}{dt} = \quad \text{(D)}$$

$$\frac{d[\text{S}_4\text{O}_6^{2-}]}{dt} = \frac{1}{2} \frac{d[\text{I}^-]}{dt}$$

Comprehension # 12

Q.51 (A)

$$\Delta m = (\text{At. mass of } {}^4_{10}\text{Be} - 4m_e) - (\text{At. mass of } {}^5_{10}\text{Be} - 5m_e + m_e)$$

Q.52 (D)

$$\Delta m = (\text{At. mass of } {}^8_5\text{B} - 5m_e) - (\text{At. mass of } {}^8_4\text{B} - 4m_e + m_e)$$

Q.53 **A** → p, q, r, s ; **B** → q, r, s ; **C** → p, q, r, s ; **D** → p, r, s

$$\text{(A)} \quad r = k [\text{A}] [\text{B}]$$

i.e. IInd order reactionunit of k = mol⁻¹ lt time⁻¹

$$-\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = k [\text{A}] [\text{B}]$$

$$-\frac{d[\text{A}]}{dt} = \frac{d[\text{C}]}{dt}$$

(t_{1/2})_A = (t_{1/2})_B if A and B are taken in stoichiometric ratio.

(B)



$$r = k_2 [\text{B}]^0 [\text{A}] = k_2 [\text{A}]$$

unit of k = time⁻¹ does not have concentration unit.

$$-\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = k_2 [\text{A}]$$

$$-\frac{d[\text{A}]}{dt} = \frac{d[\text{C}]}{dt}$$



$$r = k_3 [\text{A}]^0 [\text{B}]^0$$

unit of k = mole litre⁻¹ time⁻¹

$$-\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = k_3$$

$$-\frac{d[\text{A}]}{dt} = \frac{d[\text{C}]}{dt}$$



$$r = K_3 [\text{A}]^0 [\text{B}]^0$$

unit of K = mol lt⁻¹ time⁻¹

$$-\frac{1}{2} \frac{d[\text{A}]}{dt} = -\frac{1}{2} \frac{d[\text{C}]}{dt}$$

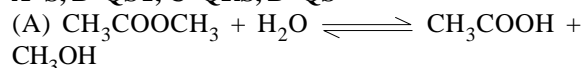
$$-\frac{d[\text{A}]}{dt} = \frac{d[\text{C}]}{dt}$$

Q.54 **(A** → r) ; **(B** → s) ; **(C** → q) ; **(D** → p)

(A) for zero order reaction C = Co - kt

(B) for first order reaction $\log C = \log \text{Co} - \frac{k}{2.303} \times t$ (C) for zero order reaction $\frac{-dc}{dt}$ vs C equal to zero(D) for first order reaction $\frac{-dc}{dt} = kc$, $\log \left(\frac{dc}{dt} \right)$

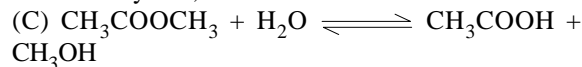
= log k + log c

Hence plot of $\log \left(\frac{-dc}{dt} \right)$ against log c (abscissa) will have slope equal to unityQ.55 **A-S, B-QST, C-QRS, D-QS**

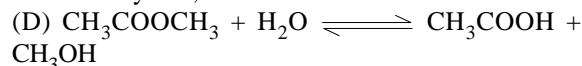
molecularity = 2; order = 1



molecularity = 2; order = 1



molecularity = 2; order = 2



order = 2

Q.56 **(A) p, q, s ; (B) p, q, s ; (C) q, r ; (D) p, q, r**(A) $2\text{N}_2\text{O}_5 \xrightarrow{\text{1st order}} 4\text{NO}_2(\text{g}) + \text{O}_2(\text{g})$
NO₂ and O₂ are paramagnetic molecules.

In N_2O_5 (g) Nitrogen atom is SP^2 hybridised.
Half life is not dependent at initial concentration.
Reaction goes back ward.

- (B) $2\text{H}_2\text{O}_2$ (aq) $\xrightarrow{\text{1st order}}$ $2\text{H}_2\text{O}$ (aq) + O_2 (g)
 O_2 (g) molecule is paramagnetic.
In H_2O_2 Oxygen atom is SP^3 hybridised.
Half life is not dependent at initial concentration.
Reaction goes back ward.

- (C) 2NH_3 $\xrightarrow{\text{Zero order}}$ N_2 (g) + 3H_2 (g)
 N_2 (g) and H_2 (g) both are diamagnetic molecules.
In $\dot{\text{N}}\text{H}_3$ Nitrogen atom is SP^3 hybridised.

$$t_{1/2} = \frac{C_0}{2k} \text{ for zero order reaction.}$$

Rate remains always constant.

- (D) $2\text{Cl}_2\text{O}_7$ (g) $\xrightarrow{\text{Zero order}}$ 4ClO_2 (g) + 3O_2 (g)
 ClO_2 (g) and O_2 (g) both are paramagnetic molecules.
In Cl_2O_7 (g) chlorine atom is SP^3 hybridised.

$$t_{1/2} = \frac{C_0}{2k} \text{ for zero order reaction.}$$

Rate remains always constant.

- Q.57** $\text{A} \rightarrow \text{S}, \text{B} \rightarrow \text{R}, \text{C} \rightarrow \text{P}, \text{D} \rightarrow \text{Q}$

- Q.58** ($\text{A} - r$; $\text{B} - s$; $\text{C} - p$; $\text{D} - q$)

$$(A) 2.303 \log_{10} \frac{K_2}{K_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\Rightarrow \frac{K_2}{K_1} = 11$$

$$T_2 = 298 \text{ K}; T_1 = 273 \text{ K}, E_a = 65000 \text{ J}, R = 8.314 \text{ J/(mol K)}$$

$$(B) \frac{2.5}{20} = \frac{1}{8} = \left(\frac{1}{2} \right)^n$$

$$\Rightarrow n = 3 \Rightarrow t = 3 \times \frac{0.693}{0.0693} = 30$$

$$(C) \text{Zero order: } t_{1/2} = \frac{a}{2K}$$

$$\text{I order: } t_{1/2} = \frac{0.693}{K}$$

$$\frac{1}{2K_1} = \frac{0.693}{K_2}$$

$$\Rightarrow \frac{K_2}{K_1} = 2 \times 0.693$$

$$(D) t_{1/2} \propto (a)^{1-n} \text{ or } (1-n) = \frac{\log t'_{1/2} - \log t''_{1/2}}{\log a' - \log a''}$$

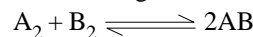
$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

$$\Rightarrow \frac{480}{240} = \left(\frac{0.0677}{0.136} \right)^{n-1} \quad n = 0$$

- Q.59** $\text{A} \rightarrow \text{P}, \text{B} \rightarrow \text{Q}, \text{S} \rightarrow \text{R}, \text{T} \rightarrow \text{D} \rightarrow \text{V}$

- Q.60** $\text{A} \rightarrow \text{R}, \text{B} \rightarrow \text{Q}, \text{C} \rightarrow \text{P}, \text{D} \rightarrow \text{S}$

From the figure it is clear that.



(A) $E_a = 40 \text{ KJ/mol}$

(B) $E_{ab} = 50 \text{ KJ/mol}$

(C) $\Delta H_r = -10 \text{ KJ/mol}$

NUMERICAL VALUE BASED

- Q.1** [5]

$$\text{order in zero } T_{50} = \frac{6.93}{2 \times 0.693}$$

- Q.2** [8]

- Q.3** [0]

For zero order reaction $t_{1/2} \propto a$

- Q.4** [2]

$t_{x\%}$ of a first order reaction is constant

- Q.5** [2]

- Q.6** [4]

$$T_1 T_2 = \frac{E_a}{0.0693 R}$$

$$T_2 - T_1 = 10$$

$$2.303 \log \frac{K_{35}}{K_{25}} = \frac{E_a}{R} \times \left[\frac{T_2 - T_1}{T_1 T_2} \right]$$

$$2.303 \log \frac{K_{35}}{K_{25}} = \frac{E_a}{R} \times \frac{10 \times R \times 0.0693}{E_a} = 0.0693$$

$$\log \frac{K_{35}}{K_{25}} = \frac{0.693}{2.303} = 0.3010$$

$$\frac{K_{35}}{K_{25}} = 2 \Rightarrow \text{So, } \frac{K_{45}}{K_{25}} = 4$$

- Q.7** [0]

Half life 500 for all concentrations of sugar.

Half life is independent of the conc. of the sugar. So

reaction is 1st order W.R.T. sugar

For H^+ conc.

$$\frac{t_1}{t_2} = \left(\frac{a_2}{a_1}\right)^{n-1}$$

$$\frac{500}{50} = \left(\frac{10^{-6}}{10^{-5}}\right)^{n-1}$$

$$\therefore n = 0$$

Q.8 [2]

No of $t_{1/2}$ of A in 2 days = 4

No of $t_{1/2}$ of B in 2 days = 3

$$A_t = \frac{1}{4}, B_t = \frac{1}{8}$$

$$A : B = 2$$

Q.9 [2]

$$t_{1/2} = 20 \text{ min}, t'_{1/2} = 10 \text{ min} \text{ \& } [A]_0 = 2[A]_0$$

$$\therefore t_{1/2} \propto \frac{1}{[A]_0^{n-1}} \Rightarrow \frac{t'_{1/2}}{t_{1/2}} = \left[\frac{[A]_0}{[A]_0'}\right]^{n-1}$$

or

$$\frac{20}{10} = \left[\frac{2 \times [A]_0^{n-1}}{[A]_0}\right]^{n-1} \rightarrow 2 = 2^{n-1} \rightarrow n-1=1 \Rightarrow n=2$$

Q.10 $T = 306 \text{ K}$

$$K_2 = \frac{0.693}{2 \times 3600} \text{ Sec}^{-1}$$

$$K_1 = 3.46 \times 10^{-5} \text{ sec}^{-1}$$

$$\text{We have } \log \frac{K_2}{K_1} = \frac{100 \times 10^3}{2.303R} \left[\frac{1}{298} - \frac{1}{T} \right]$$

$$T = 306 \text{ K}$$

KVPY

PREVIOUS YEAR'S

Q.1 (B)

$$\frac{0.693}{t_{1/2}} = \frac{2.303}{2 \times 60} \log \frac{\alpha}{\alpha/16}$$

$$t_{1/2} = 30 \text{ min}$$

Q.2 (A)

$$K = \frac{A_0 - A_t}{t}$$

$$K = \frac{A_0}{2t_{1/2}}$$

$$t_{1/2} = \frac{A_0}{2K} \text{ Zero order}$$

$t_{1/2} \propto$ initial concentration
so double times

Q.3 (B)

Q.4 (4)

$$r = K [X]^x [Y]^y$$

Total order = $n = x + y$

By exp. (1) & (2)

$$\frac{r_1}{r_2} = \frac{K[.25]^x [.25]^y}{K[.50]^x [.25]^y} = \frac{1.0 \times 10^{-6}}{4.0 \times 10^{-6}}$$

$$\frac{1}{(2)^x} = \frac{1}{4}, x = 2$$

By exp. (1) & (3)

$$\frac{r_1}{r_3} = \frac{K[.25]^x [.25]^y}{K[.25]^x [.50]^y} = \frac{1 \times 10^{-6}}{8 \times 10^{-6}}$$

$$\frac{1}{(2)^y} = \frac{1}{8}, y = 3$$

So Total order = $2 + 3 = 5$

Q.5 (4)

$$K = Ae^{-\frac{E_a}{RT}}$$

$$\ln K = \ln A - \frac{E_a}{RT}$$

Q.6 (2)

$$t_{1/2} \propto \frac{1}{a^{n-1}}$$

for zero order reaction $n = 0$

so $t_{1/2} \propto a$

so

$$\frac{(t_{1/2})_1}{(t_{1/2})_2} = \frac{a_1}{a_2}$$

$$\frac{.2}{(t_{1/2})_2} = \frac{[A_0]}{2[A]_0}$$

$$t_{1/2} = .4 \text{ sec}$$

Q.7 (D)

$$C_t = C_0 e^{-kt}$$

Q.8 (D)

$$C_t = C_0 - kt; \text{ slope} = -k$$

Q.9 (A)

For plot between $\ln k$ v/s $1/T$ y-intercept is $\ln A$

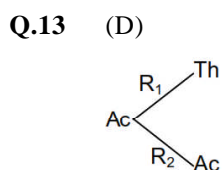
$$\text{\& slope is } \frac{-E_a}{R}$$

therefore ; $E_{II} < E_I$ and $A_I > A_{II}$

Q.10 (C)
 $K = Ae^{-E_a/RT}$
 $T \rightarrow \infty \quad k = A$

Q.11 (D)
 $t_{1/2} = 1 \text{ hr}$
 $t_{87.5} = \frac{2.303}{k} \log \frac{a}{a-x}$
 $= \frac{2.303}{0.693} \log \frac{a}{a-.875}$
 $= \frac{2.303}{0.693} \log 8$
 $= \frac{2.303}{0.693} \times 3 \times .3010$
 $= 3$

Q.12 (B)
 no. of α -particel = $\frac{232-208}{4} = 6$
 no. of β -particel = 4



$$\% \text{ Th} = \frac{R_1}{R_T} = \frac{2}{100}$$

$$\% \text{ Ac} = \frac{R_2}{R_T} = \frac{98}{100}$$

$$\therefore \frac{R_1}{R_2} = \frac{2}{98}$$

$$R_T = R_1 + R_2$$

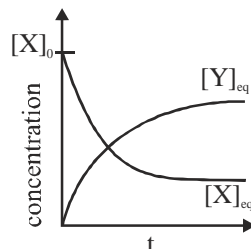
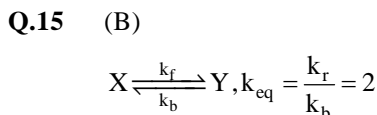
$$\frac{0.693}{22} = R_1 + \frac{98}{2} R_1$$

$$\therefore R_1 = 6.3 \times 10^4$$

Q.14 (A)
 $\log_{10} \frac{K_2}{K_1} = \frac{209 \times 10^3}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{T} \right]$

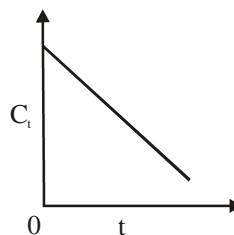
$$9.16 \times 10^{-5} = 3.33 \times 10^{-3} - \frac{1}{T}$$

$$T = 308.4 \text{ K or } 35^\circ \text{C} = X$$

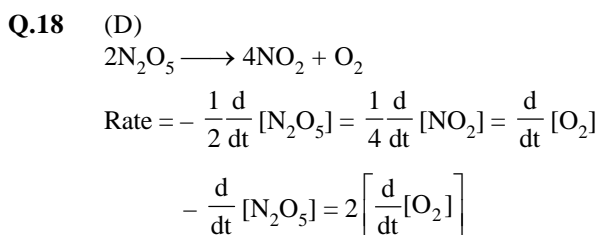


at equation concentration of $[Y] > [X] \Rightarrow [Y] = 2[X]$

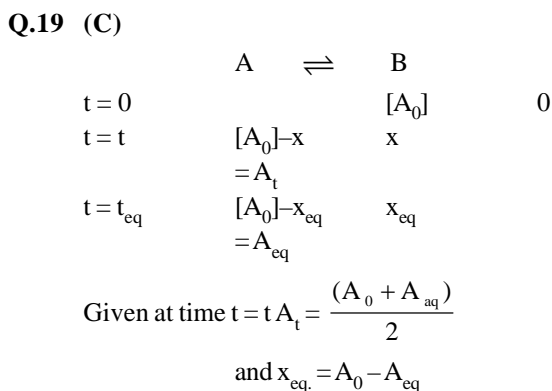
Q.16 (A)
 For zero order reaction
 $C_t = C_0 - kt$
 Graph of C_t Vs t is



Q.17 (C)
 $K = Ae^{-\frac{E_a}{RT}}$
 For 1st order reactime unit of $k = \text{time}^{-1}$ and for A unit is same as unit of K.

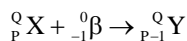


So rate of disappearance of N_2O_5 is twice the O_2 production rate.



$$\text{Now, } t = \frac{1}{k_f + k_b} \ln \left(\frac{x_e}{x_e - x} \right) = \left(\frac{\ln 2}{k_f + k_b} \right)$$

Q.20 (D)



X and Y has same mass number, hence they are isotones.

JEE-MAIN

PREVIOUS YEAR'S

Q.1 (4)

Fact Based

${}_1\text{H}^3$ (tritium) is radio active

Its $\frac{n}{p} = \frac{2}{1}$ (Higher), Hence

It emits β particle

Q.2 [14]

$$\text{Fraction (f)} = e^{-\frac{E_a}{RT}}$$

$$= e^{-\frac{80.3 \times 10^3}{8.314 \times 700}}$$

$$= e^{-13.8}$$

$$= e^{-14}$$

Q.3 [50 kJ/mole]

$$\Delta H = E_a, f - E_{a,b}$$

$$-20 = 30 - E_{a,b}$$

$$E_{a,b} = 50 \text{ kJ/mole}$$

Q.4 [51.74]

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log_{10} 5 = \frac{E_a}{2.303 \times 8.314} \left[\frac{1}{300} - \frac{1}{325} \right]$$

$$0.693 = \frac{E_a}{2.303 \times 8.314} \times \frac{25}{300 \times 325}$$

$$E_a = 51.74 \text{ kJ/mole}$$

Q.5 [526.3K]

$$\log_{10} k = \log_{10} A - \frac{E_a}{2.303RT}$$

$$\text{Slope} = \frac{-E_a}{2.303RT} = -10000$$

$$\log_{10} \frac{k_2}{k_1} = \frac{E_a}{2.303R} \times \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\log_{10} \frac{10^{-4}}{10^{-5}} = 10000 \times \left[\frac{1}{500} - \frac{1}{T} \right]$$

$$1 = 10000 \times \left[\frac{1}{500} - \frac{1}{T} \right]$$

$$\frac{1}{10000} = \frac{1}{500} - \frac{1}{T}$$

$$\frac{1}{T} = \frac{1}{500} - \frac{1}{10000}$$

$$= \frac{20 - 1}{10,000} = \frac{19}{10,000}$$

$$T = \frac{10,000}{19} = 526.3 \text{ K}$$

Q.6 [1535.3]

$$t = \frac{2.303}{K} \log \frac{100}{100 - x}$$

$$= \frac{2.303}{3.3 \times 10^{-4}} \log \frac{100}{100 - 40}$$

$$= \frac{2.303}{3.3 \times 10^{-4}} \times 0.22$$

$$= 1535.3 \text{ sec.}$$

Q.7 [81]

$$f = \frac{1}{2^n} \quad n = \frac{\text{time given}}{t_{1/2}} = \frac{9 \text{ hr}}{3.33 \text{ hr}} = 2.7$$

$$= \frac{1}{2^{2.7}}$$

$$\log \frac{1}{f} = \log 2^{2.7} = 2.7 \times 0.81$$

$$100 \times \log_{10} \left(\frac{1}{f} \right) = 100 \times 0.81 = 81$$

Ans. 81

Q.8 [10]

$$\frac{t_{99.9\%}}{t_{50\%}} = \frac{\frac{1}{K} \ln \frac{100}{0.1}}{\frac{1}{K} \ln 2}$$

$$= \frac{\ln 1000}{\ln 2} \times t_{50\%}$$

$$= \frac{3 \ln 10}{\ln 2} \times 1$$

$$= \frac{3 \times 2.3}{0.69} \times 10$$

Q.9 [3]

$$r = k[\text{NO}]^m [\text{Cl}_2]^n$$

$$= k(0.1)^m (0.1)^n \quad \dots(1)$$

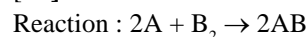
$$= k(0.1)^m (0.2)^n \quad \dots(2)$$

$$= k(0.2)^m (0.2)^n \quad \dots(3)$$

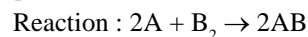
$$n = 1$$

$$m = 2$$

$$m + n = 3$$

Q.10 [27]

As the reaction is elementary, the rate of reaction is $r = k \cdot [\text{A}]^2 [\text{B}_2]$ on reducing the volume by a factor of 3, the concentrations of A and B_2 will become 3 times and hence, the rate becomes $3^2 \times 3 = 27$ times of initial rate.

Q.11 [27]

As the reaction is elementary, the rate of reaction is $r = k \cdot [\text{A}]^2 [\text{B}_2]$ on reducing the volume by a factor of 3, the concentrations of A and B_2 will become 3 times and hence, the rate becomes $3^2 \times 3 = 27$ times of initial rate.

Q.12 [2]

For 1st order reaction,

$$k = \frac{2.303}{t} \cdot \log \frac{[\text{A}_0]}{[\text{A}_t]} = \frac{2.303}{570 \text{ sec}} \cdot \log \left(\frac{100}{32} \right)$$

$$= 1.999 \times 10^{-3} \text{ sec}^{-1} \approx 2 \times 10^{-3} \text{ sec}^{-1}$$

Q.13 [108]

$$\text{Given } t_2 = 54 \text{ min} \quad T_{1/2} = 18 \text{ min}$$

$$\text{A} \quad \quad \quad \text{B}$$

$$t = 0 \text{ 'x' M} \quad t = 0 \text{ 'x' M}$$

$$\Rightarrow \text{To calculate : } [\text{A}_t] = 16 \times [\text{B}_t] \dots(1) \text{ time} = ?$$

$$\Rightarrow \text{For I order kinetic : } \boxed{[\text{A}_t] = \frac{\text{A}_0}{(2)^n}}$$

$n \rightarrow$ no of Half lives

\Rightarrow Now from the relation (1)

$$[\text{A}_t] = 16 \times [\text{B}_t]$$

$$\Rightarrow \frac{x}{(2)^{n_1}} = \frac{x}{(2)^{n_2}} \times \Rightarrow (2)^{n_2} = (2)^{n_1} \times (2)^4$$

$$\Rightarrow n_2 = n_1 + 4 \quad \Rightarrow \frac{t}{(t_{1/2})_2} = \frac{t}{(t_{1/2})_1} + 4$$

$$\Rightarrow t \left(\frac{1}{18} - \frac{1}{54} \right) = 4 \Rightarrow t = \frac{4 \times 18 \times 54}{36}$$

$$\Rightarrow \boxed{t = 108 \text{ min}}$$

Q.14 [10]

$$K_{300} = 10^{-4} \quad K_{200} = ?$$

$$E_a = 11.488 \text{ KJ/mole} \quad R = 8.314 \text{ J/mole-K}$$

$$\text{so } \ln \left(\frac{K_{300}}{K_{200}} \right) = \frac{E_a}{R} \left(\frac{1}{200} - \frac{1}{300} \right)$$

$$\ln \left(\frac{K_{300}}{K_{200}} \right) = \frac{11.488 \times 1000 \times 100}{8.314 \times 200 \times 300}$$

$$= 2.303$$

$$= \ln 10$$

$$\text{so } \frac{K_{300}}{K_{200}} = 10$$

$$K_{200} = \frac{1}{10} \times K_{300} = 10^{-4}$$

$$= 10 \times 10^{-5} \text{ sec}^{-1}$$

Q.15 [464]**Q.16** [19]**Q.17** [78]**Q.18** [68]**Q.19** [12]**Q.20** [600 to 700]**Q.21** (3)**Q.22** (4)**Q.23** (2)**Q.24** [7]**Q.25** [1]**Q.26** [106]**Q.27** [0.02]**Q.28** (1)**Q.29** [16]

Q.30 [4]

$$1 - 0.01 \quad 0.01 \quad 0.01 \\ \approx 1$$

Q.31 [2]

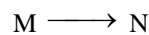
Q.32 [45]

$$K_a = \frac{0.01 \times 0.01}{1} = 10^{-4}$$

Q.33 [47]

Q.5

(3)



$$r = K [M]^x$$

as [M] is doubled, rate increases by a factor of 8.

$$\text{i.e. } 8r = K [2M]^x$$

$$\Rightarrow 8 = (2)^x$$

$$x = 3$$

Q.34 (3)

Q.35 [40]

Q.36 [7]

JEE-ADVANCED PREVIOUS YEAR'S

Q.1 (ABD)

$$C_t = C_0 e^{-Kt}$$

$$t_{1/2} \propto \frac{1}{K}, K \uparrow \text{ on increasing } T.$$

After eight half lives,

$$C = \frac{C_0}{2^8} \Rightarrow \% \text{ completion} = \frac{C_0 - \frac{C_0}{2^8}}{C_0} \times 100 = 99.6\%$$

Q.2 [9]

$$Kt_{1/8} = \ln \left\{ \frac{C_0}{C_0/8} \right\} = \ln 8$$

$$Kt_{1/10} = \ln \left\{ \frac{C_0}{C_0/10} \right\} = \ln 10$$

$$\text{then } \frac{t_{1/8}}{t_{1/10}} \times 10 = \frac{\ln 8}{\ln 10} \times 10 = \frac{\log 8}{\log 10} \times 10 = 9$$

Q.3 (D)

For P, if $t_{50\%} = x$ then $t_{75\%} = 2x$

This happens only in first order reaction. So, order with respect to P is 1.

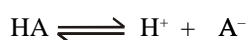
For Q, the graph shows that concentration of Q decreases linearly with time. So rate, with respect to Q, remains constant. Hence, it is zero order wrt Q. So, overall order is $0 + 1 = 1 \rightarrow$ Ans. is D

Q.4 (A)

As ester hydrolysis is first order with respect to $[H^+]$.

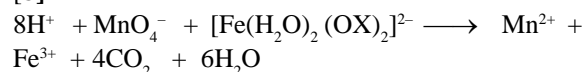
$$\frac{R_{HA}}{R_{HX}} = \frac{[H^+]_{HA}}{[H^+]_{HX}}$$

$$\frac{1}{100} = [H^+]_{HA}$$



Q.6

[8]



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

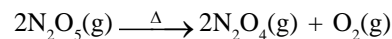
Q.7

(A,B)

(A) E_a is independent of steric factor

Q.8

[2.30]



at constant V, T

$$t = 0$$

$$1$$

$$t = y \times 10^3 \text{ sec}$$

$$(1 - 2P)$$

$$2P$$

$$P$$

$$P_T = (1+P) = 1.45$$

$$P = 0.45 \text{ atm}$$

$$(2K)t = 2.303 \log \left(\frac{1}{1 - 2P} \right)$$

$$(2 \times 5 \times 10^{-4}) \times y \times 10^3 = 2.303 \log \frac{1}{0.1}$$

$$y = 2.303 = 2.30$$

Q.9

[6.75]

$$r = K[A]^{n_1}[B]^{n_2}[C]^{n_3}$$

From table

$$n_1 = 1$$

$$n_2 = 0$$

$$n_3 = 1$$

$$r = K[A][C]$$

From Exp - 1

$$6 \times 10^{-5} = K \times 0.2 \times 0.1$$

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

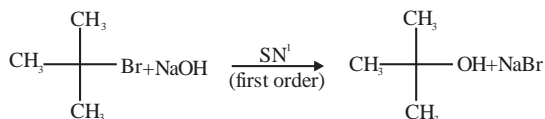
$$r = (3 \times 10^{-3}) \times 0.15 \times 0.15$$

$$= 6.75 \times 10^{-5}$$

$$Y \times 10^{-5}$$

$$Y = 6.75$$

Q.10 (A)



$$\begin{array}{l} t=0 \quad P_0 \quad 0 \\ t \quad P \quad P_0 - P \end{array}$$

$$\text{rate} = k[\text{C(CH}_3)_2\text{Br}] \quad \ln \frac{P_0}{P} = kt$$

$$t_{1/2} = \frac{0.693}{k} \quad \ln \frac{P}{P_0} = -kt$$

$$\frac{[Q]}{[P]_0} = \frac{[P_0] - [P]}{[P_0]} = 1 - \frac{[P]}{[P_0]} = 1 - e^{-kt}$$

Q.11 [1.20]

$$\text{Initial moles of } \text{U}^{238} = \frac{68 \times 10^{-6}}{238} = x$$

Moles of U^{238} decayed in three half-lives $\frac{7}{8}x$

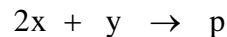
In decay from U^{238} to Pb^{206} , each U^{238} atom decays and produces 8 α -particles and hence, total number of α -particles emitted out

$$= \left(\frac{7}{8}x\right) \times 8 \times N_A$$

$$= 7 \times \frac{68 \times 10^{-6}}{238} \times 6.022 \times 10^{23}$$

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

Q.12 (B, C, D)



$$t=0 \quad 2 \quad 1$$

$$t=50 \text{ s} \quad (2-1) \quad (1-0.5) \quad 0.5$$

$$-\frac{1}{2} \frac{dx}{dt} = \frac{dp}{dt} = k[x]^{-1}$$

$$-\frac{dx}{dt} = 2k[x]^1$$

$$2k = \frac{\ln 2}{50} = 2k[x]^1 \Rightarrow k = \frac{\ln 2}{100}$$

$$\text{At } 50 \text{ sec} \quad \frac{-dx}{dt} = 2k \times (1)^1 = \frac{\ln 2}{50}$$

$$\text{At } 100 \text{ sec} \quad -\frac{1}{2} \frac{dx}{dt} = \frac{-dy}{dt}$$

$$\Rightarrow -\frac{dy}{dt} = \frac{\ln 2}{100} \times \frac{1}{2} \left\{ \frac{-dy}{dt} = k[x]^1 \right\}$$