My Success Story

2nd RANK **PARTH SHARMA AIIMS**

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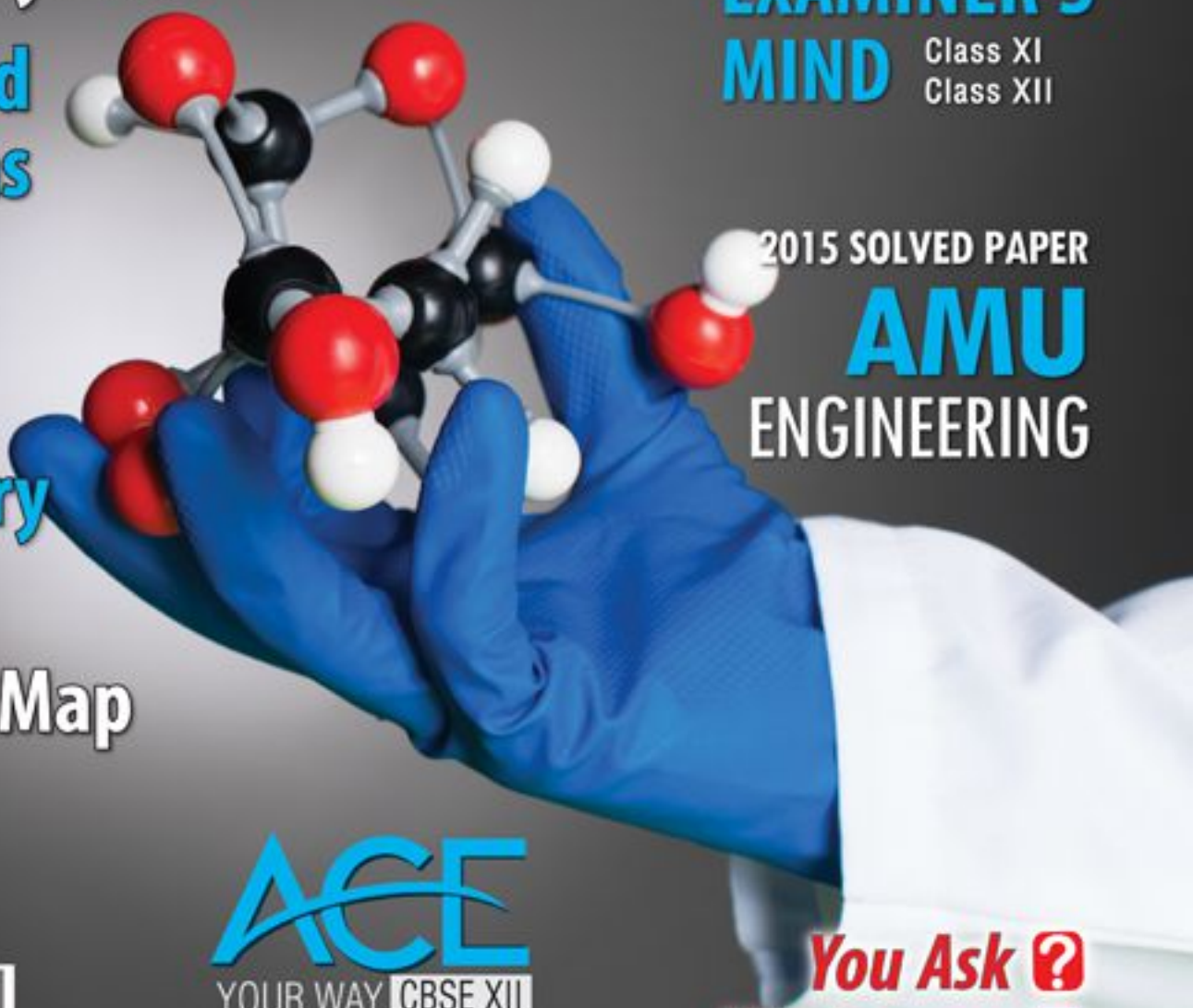**Advanced Chemistry Bloc**

Olympiad Problems

Concept Booster

Chemistry Musing

Concept Map

EXAMINER'S MIND Class XI Class XII

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CHEMISTRY today

Contents

edit**Q**rial

Chemistry is Connecting Link
Between Physics and Mathematics

In the beginning, chemistry was purely experimental. Skilled experimentalists and theoreticians built the base of chemistry analysis and production of compounds and titrations were the base.

As the physicists started analysis to a high degree of accuracy by spectrometers, chemists started supplementing wet analysis by spectroscopic analysis.

Every big chemistry laboratory started using optical spectroscopy, infra-red and ultraviolet spectroscopy. Later X-ray spectrometers and X-ray diffractometers became the common utilities in both chemistry and physics laboratories.

From the time the components of radioactive materials such as Radium were separated by Madame and Pierre Curie, radiochemistry laboratories sprang up in various centres of research. But the methods of study were the same as used by physicists. Every industry such as cement, steel, metallurgy and petroleum products were marching ahead using the same instruments.

The role of mathematics in the development of analysis of data by statistical methods became very important. To be a good physicist, one must know chemistry and higher mathematics. The role of group theoretical analysis to study data given by chemistry is well known.

The study of higher mathematics is now absolutely necessary to study any branch of science ranging from astronomy to physical chemistry.

Research has no barriers. We are back to the old days when there were scientists who were not having the labels to limit their work.

Anil Ahlawat
Editor

"MTG BOOKS & TEST SERIES **MAKE IT HAPPEN**"

2nd Rank AIIMS

PARTH SHARMA

Dedication, sincerity and hard work. I always remained self-motivated with the support of my parents and teachers .

- **MTG : Why did you appear for medical entrance exams?**
  Parth : Medical stream always attracted me , that is why I opted for it.

- **MTG : What exams you have appeared for and what is your rank in these exams?**
  Parth : I appeared for AIPMT which got cancelled and AIIMS in which I secured AIR 2.

- **MTG : Any other achievements?**
  Parth : Apart from AIIMS entrance exam, I managed to become NTSE SCHOLAR, SSTSE SCHOLAR (11th rank) and KVPY FELLOW. I also scored 95% in CBSE board.

- **MTG : How many hours in a day did you study to prepare for the exams?**
  Parth : More than 12 hours.

- **MTG : On which topic and chapters you laid more stress in each subject?**
  Parth : Physics : Modern Physics, Chemistry : Organic Chemistry, Biology : Genetics.

- **MTG : In your words, what are the components of an ideal preparation plan?**
  Parth : 2 years of constant hard work and staying

MTG questions were extraordinarily good. It proved really useful in achieving my goal. I owe a big thanks to MTG!!.

focussed will help you in achieving your desired result.

- **MTG : Any extra coaching?**
  Parth : I took coaching in AAKASH institute in 11th standard and ALLEN institute in 12th standard, both located in Jaipur. I also took MTG AIIMS Test Series (Order no. 205251).

- **MTG : Which subjects/topics you were strong/weak at?**
  Parth : I laid more stress on Biology and Organic Chemistry as these were the areas in which I faced a lot of problems.

- **MTG : Which Books/Magazines have you read?**
  Parth : Apart from institute, I followed MTG's magazines and also subscribed to MTG's AIIMS Rank INDICATOR Test Series. I scored 1st Rank in two tests there.

- **MTG : What role did your parents, teachers and school play in your success?**
  Parth : I would just say one word: HARD WORK!
  (a) Parents : They were my constant supporters and helped me in dealing stress. Apart from this they provided me the most suitable amiable environment to enhance my study and concentration.

(b) Teachers : They guided me and were always there to clear my doubts even in the middle of the night! And believe it or not, it is true that they used to reply me even after 12 in the midnight on WhatsApp and solve my problems.

(c) School : It provided me the most relaxing atmosphere. A few chit chat and little bit of fun in school always helped to maintain my cool during routine. Stress and anxiety were rare feelings I encountered in last 2 years.

- **MTG : Your family background?**
  Parth : My father G.D. Sharma is a Govt. Servant designated ACIT, Jaipur. My mother Renu Sharma is a homemaker. I also have an elder sister pursuing B.Tech from MNIT, Jaipur.

- **MTG : What mistake you think you shouldn't have made?**
  Parth : I should have been less tensed on the day of exam.

- **MTG : How have MTG magazines and books helped you in your preparation?**
  Parth : The questions were extraordinarily good. It proved really useful in achieving my goal. I owe a big thanks to MTG!!.

- **MTG : Was this your first attempt?**
  Parth : Yes, this was my first attempt.

- **MTG : Had you not been selected then what would have been your future plans?**
  Parth : I never had this second thought.

- **MTG : What do you think is the secret of your success?**
  Parth : Again I would say determination and hard work.

- **MTG : What advice would you like to give our readers who are PMT aspirants?**
  Parth : Might sound like a litany, but hard work, determination and staying focussed constantly for 2 years will lead to success! and ALL THE BEST to PMT aspirants!

◈ ◈

CHEMISTRY MUSING

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

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

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

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

PROBLEM Set 25

JEE MAIN/PMTs

1. Choose the incorrect statement from the following.
   (a) Hydrolysis of $SnCl_4$ is affected by the presence of HCl vapours.
   (b) Ammonolysis of $SnCl_4$ is not affected by the presence of NH_4Cl vapours.
   (c) Piece of Sn kept with $SnCl_2$ prevents its oxidation.
   (d) $SnCl_2$, $SnCl_4$, and $PbCl_4$ all form complex acids with conc. HCl.

2. Reduction of but-2-yne with Na and liquid NH_3 gives an alkene which upon catalytic hydrogenation with D_2/Pt gives an alkane. The alkene and alkane formed respectively are
   (a) *cis*-but-2-ene and *racemic*-2, 3-dideuterobutane
   (b) *trans*-but-2-ene and *meso*-2, 3-dideuterobutane
   (c) *trans*-but-2-ene and *racemic*-2, 3-dideuterobutane
   (d) *cis*-but-2-ene and *meso*-2, 3-dideuterobutane.

3. The total vapour pressure of a 4 mole % solution of NH_3 in water at 293 K is 50.0 torr and the vapour pressure of pure water is 17.0 torr at this temperature. Applying Henry's law and Raoult's law, the total vapour pressure for a 5 mole % solution is
   (a) 58.42 torr   (b) 33 torr
   (c) 42.1 torr   (d) 52.25 torr

4. Which of the following statements is correct for the complex $[Fe(H_2O)_5NO]SO_4$?
   (a) The colour of the complex is due to charge transfer.

   (b) The hybridization of the central atom is d^2sp^3.
   (c) It is paramagnetic with $\mu = 1.73$ B.M.
   (d) None of these.

5. Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using the Bronsted-Lowry definition?
   (a) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$
   (b) $NH_3 + CH_3COOH \rightleftharpoons NH_4^+ + CH_3COO^-$
   (c) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
   (d) $[Cu(H_2O)_4]^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$

JEE ADVANCED

6. A hydrogen like atom with atomic number 'Z' is in higher excited state of quantum number 'n'. This excited state atom can make a transition to the first excited state by successively emitting two photons of energies 10 eV and 17 eV respectively. Alternatively, the atom from the same excited state

---

### Solution Senders of Chemistry Musing

SET 24

1. Dimpi Das (Assam)
2. Sayantan Bhanja (West Bengal)
3. Subham Adak
4. Ashutosh Bhatnagar (Chandigarh)

can make a transition to the second excited state by emitting two photons of energies 4.25 eV and 5.95 eV respectively. The 'n' and 'Z' are
(a) $n = 6, Z = 3$ (b) $n = 3, Z = 6$
(c) $n = 6, Z = 6$ (d) $n = 5, Z = 5$

COMPREHENSION

Nitration of benzene or any aromatic system is done by treating it with a mixture of conc. HNO_3 and conc. H_2SO_4 called nitrating mixture. In this mixture, HNO_3 acts as base and H_2SO_4 acts as acid.

$$2H_2SO_4 + HNO_3 \longrightarrow 2HSO_4^- + H_3O^+ + \underset{\text{Nitronium ion}}{\overset{+}{N}O_2}$$
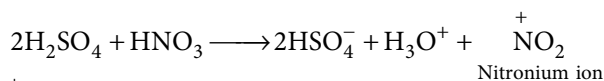
$\overset{+}{N}O_2$ ion acts as an electrophile and attacks benzene to form arenium ion as follows :
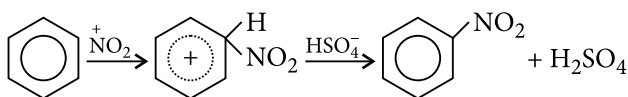
The direct nitration of aniline with nitrating mixture gives benzoquinone and *m*-nitroderivatives as unexpected products. In dinitration, the position of second group depends on the activating and deactivating power of the group present in the ring. Activating groups are *o/p*-directors while deactivating groups are *m*-directors.

7.
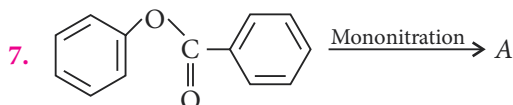
'A' will be

8. If the freezing point depression constant of solution of any solute (non-ionising) in conc. H_2SO_4 be X degree kg mol^{-1}, then freezing point depression of the nitrating mixture (conc. HNO_3 and conc. H_2SO_4) which is a molal solution of conc. HNO_3

in conc. H_2SO_4 assuming almost complete reaction that yields $\overset{+}{N}O_2$ should be almost equal to
(a) $X°$ (b) $2 X°$
(c) $4 X°$ (d) $0.5 X°$

INTEGER VALUE

9. The total number of cyclic silicates among the following is
Be_2SiO_4 (Phenacite), $ZrSiO_4$ (Zircon), Mg_2SiO_4 (Forsterite), $Zn_4Si_2O_7(OH)_2.H_2O$ (Hemimorphite), $Sc_2Si_2O_7$ (Thortveitite), $MgSiO_3$ (Enstatite), $Ca_3(Si_3O_9)$ (Wollastonite), $Be_3Al_2(SiO_3)_6$ (Beryl), $Ca_2Mg_5(Si_4O_{11})_2$ (Tremolite), $KAl_2(OH)_2(AlSi_3O_{10})$ (Mica), SiO_2 (Quartz)

10. The total number of products formed in the following reaction is

$$\xrightarrow[\text{warm}]{H_2O} \text{(Products)}$$

OLYMPIAD PROBLEMS

1. Study the given figure carefully.
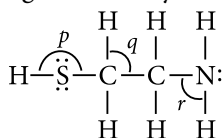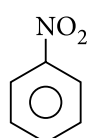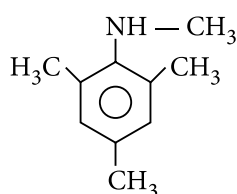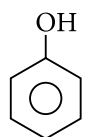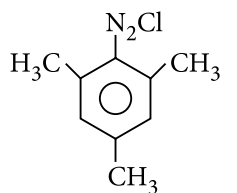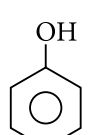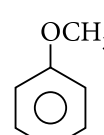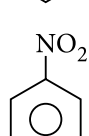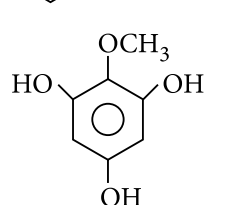
What is the decreasing order of the values of bond angles p, q and r?
(a) p, q, r (b) p, r, q
(c) q, r, p (d) r, q, p

2. At 250°C, the reaction,
$$PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$$
has an equilibrium constant, $K_c = 1.80$. If 0.100 mol of PCl_5 is added to a 5.00 L flask, the concentration of PCl_5 at this temperature will be
(a) 0.0002 M   (b) 0.0040 M
(c) 0.0200 M   (d) 0.0198 M

3. The most electron-rich carbon in the given molecule is

(a) only C_1 (b) only C_2
(c) both C_1 and C_2 (d) either C_1 or C_2.

4. Which of the following mixtures when heated liberates chlorine?
(a) $NH_4Cl + NaNO_2$
(b) $Na_2Cr_2O_7 + KCl$
(c) $K_2Cr_2O_7 + KCl + H_2SO_4$
(d) $K_2Cr_2O_7 + HCl$

5. Replacement of chlorine of C_6H_5Cl to form phenol requires drastic conditions but chlorine of 2, 4-dinitrochlorobenzene is readily replaced, because
(a) $-NO_2$ withdraws e^- from o-and p-positions
(b) $-NO_2$ withdraws e^- from m-position

(c) $-NO_2$ donates e^- to m-position
(d) $-NO_2$ donates e^- to o-and p-positions.

6. The volume of nitrogen gas at 0°C and 1.013 bar required to cover a sample of silica gel with unimolecular layer is 129 cm^3 g^{-1} of gel. Calculate the surface area per gram of the gel if each nitrogen molecule occupies 16.2×10^{-20} m^2.
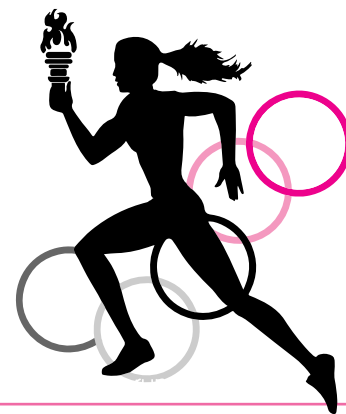(a) 586 m^2 g^{-1} (b) 568 m^2 g^{-1}
(c) 580 m^2 g^{-1} (d) 562 m^2 g^{-1}

7. Which of the following is not a biotechnology product?
(a) Interferon   (b) Human insulin hormone
(c) Vaccines   (d) Cortisone

8. Which of the following statements is not correct with reference to ferrous and ferric ions?
(a) Fe^{3+} gives brown colour with potassium ferricyanide.
(b) Fe^{2+} gives blue precipitate with potassium ferricyanide.
(c) Fe^{3+} gives red colour with potassium thiocyanate.
(d) Fe^{2+} gives brown colour with ammonium thiocyanate.

9. In dichromate ion
(a) 4Cr—O bonds are equal
(b) 6Cr—O bonds are equal
(c) all Cr—O bonds are equal
(d) all Cr—O bonds are unequal.

10. Which of the following is not the mechanistic step during chlorination of methane by Cl_2/hv?
(a) $Cl_2 \longrightarrow 2\dot{C}l$
(b) $\dot{C}l + CH_4 \longrightarrow \dot{C}H_3 + HCl$
(c) $\dot{C}l + CH_4 \longrightarrow CH_3Cl + \dot{H}$
(d) $\dot{C}l + \dot{C}H_3 \longrightarrow CH_3Cl$

11. Study the given reactions sequence carefully. The compounds X and Y are respectively
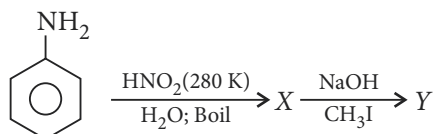
(a) ;

(b) ;

(c) ;

(d) ;

12. Which resonance form is not possible in the nucleophilic addition of OH^- ion to *p*-fluoronitro benzene?
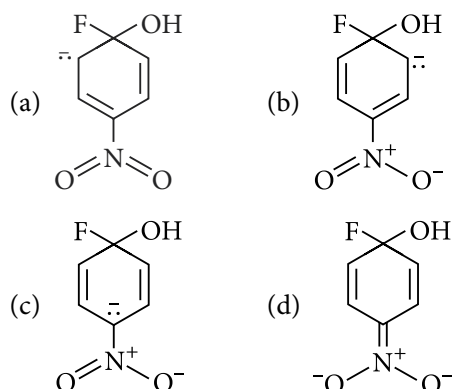
13. The pK_a value of the acids $MeC \equiv CH$ (I), $MeCOCH_2COOEt$ (II), $MeCOOEt$ (III) and PhMe (IV) decreases as
(a) I > III > IV > II
(b) II > IV > III > I
(c) IV > III > I > II
(d) I > IV > III > II

14. The covalency of nitrogen in N_2O_5 is
(a) 3
(b) 2
(c) 5
(d) 4

15. What will be formed when methyl mercaptan, CH_3SH is burnt in excess of air?
(a) CO, CO_2, H_2S
(b) CO, H_2O, SO_3
(c) CO_2, H_2O, SO_2
(d) CO_2, H_2O, SO_3

16. In the given reaction,
$$4Fe_{(s)} + 3O_{2(g)} \longrightarrow 2Fe_2O_{3(s)}; \Delta H° = -1648 \text{ kJ}$$
what is the standard enthalpy change of formation of iron (III) oxide?
(a) $-4944 \text{ kJ mol}^{-1}$
(b) -824 kJ mol^{-1}
(c) $-1648 \text{ kJ mol}^{-1}$
(d) $-3296 \text{ kJ mol}^{-1}$
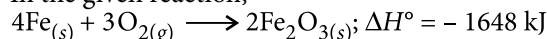
17. From the stability constants (hypothetical values) given below, predict which is the strongest ligand?
(a) $Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}; \beta = 4.5 \times 10^{11}$
(b) $Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}; \beta = 2.0 \times 10^{27}$
(c) $Cu^{2+} + 2en \rightleftharpoons [Cu(en)_2]^{2+}; \beta = 3.0 \times 10^{15}$
(d) $Cu^{2+} + 4H_2O \rightleftharpoons [Cu(H_2O)_4]^{2+}; \beta = 9.5 \times 10^8$

18. For making good quality mirrors, plates of float glass are used. These are obtained by floating molten glass over a liquid metal which does not solidify before glass. The metal used can be
(a) mercury
(b) tin
(c) sodium
(d) magnesium.

19. The solubilities of carbonates decrease down the magnesium group due to decrease in
(a) lattice energies of solids
(b) hydration energies of cations
(c) interionic attraction
(d) entropy of solution formation.

20. Which reaction sequence would best accomplish this transformation?

(a) $\xrightarrow{SOCl_2}$ $\xrightarrow{(CH_3)_2NH}$

(b) $\xrightarrow{NH_3}$ $\xrightarrow{CH_3I \text{ (excess)}}$

(c) $\xrightarrow{NaBH_4}$ $\xrightarrow{(CH_3)_2NH}$

(d) $\xrightarrow{LiN(CH_3)_2}$
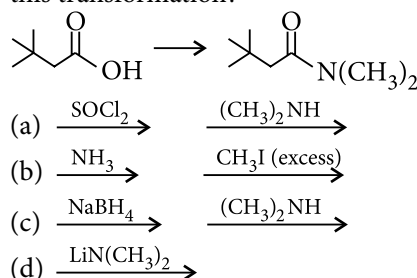
21. Pheromones are chemicals
(a) formed by fermentation process of fungi
(b) secreted by endocrine glands of man
(c) secreted outside the body of insects
(d) plant growth hormones.

22. The radius of a divalent cation A^{2+} is 94 pm and anion B^{2-} is 146 pm. The compound AB has _____ type structure.
(a) rock salt
(b) zinc blende
(c) antifluorite
(d) caesium chloride

23. An alcohol with molecular formula $C_nH_{2n+1}OH$ has a chiral carbon atom but does not react with MnO_4^-/OH^-. What is the least number of carbon atoms such an alcohol could possess?
(a) 5
(b) 6
(c) 7
(d) 8

24. For a 5% solution of H_2SO_4 by mass ($\rho = 1.01 \, g \, mL^{-1}$), match the quantities in column-I with their values in column-II.

Column-I		Column-II
P. Molarity of the solution	(i)	0.537
Q. Molality of the solution	(ii)	0.0096
R. Mole fraction of H_2SO_4	(iii)	0.05
S. Mass fraction of H_2SO_4	(iv)	0.515

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

25. Which of the following statements about the spontaneous reaction occurring in a galvanic cell is always true?
(a) $E°_{cell} > 0$, $\Delta G° > 0$ and $Q < K_{eq}$
(b) $E°_{cell} > 0$, $\Delta G° < 0$ and $Q > K_{eq}$
(c) $E°_{cell} > 0$, $\Delta G° > 0$ and $Q > K_{eq}$
(d) $E°_{cell} > 0$, $\Delta G° < 0$ and $Q < K_{eq}$

26.
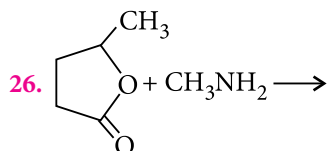
Product P is
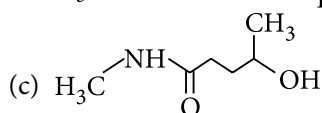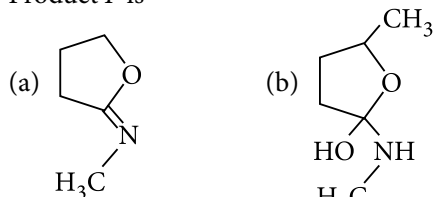
(a)
(b)
(c)
(d) none of the above.

27. Which of the following statements is true?
(a) Activation energy cannot be zero for a reaction.

(b) After five half-life periods of a first-order reaction, the fraction of reactant left will be 1/64.
(c) For a zero-order reaction, the units of rate constant and rate are not same.
(d) Half-life period of a first-order reaction is not independent of the initial concentration of reactants.

28. Select the true statement.
(a) Below 710 °C, C is better reducing agent than CO.
(b) Below 710 °C, CO is better reducing agent than C.
(c) Below 710 °C, CO is an oxidising agent.
(d) Below 710°C, CO_2 is a reducing agent.

29. Choose the incorrect relation on the basis of Bohr's theory.
(a) Velocity of an electron $\propto 1/n$
(b) Frequency of revolution $\propto 1/n^2$
(c) Radius of orbit $\propto n^2Z$
(d) None of the above.

30. Which reagent gives the same result with acetone and propan-2-ol?
(a) 2, 4-Dinitrophenylhydrazine reagent
(b) Acidified potassium dichromate (VI)
(c) Sodium
(d) Tollens' reagent

ANSWER KEYS

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

❖❖

EXAMINER'S MIND

CLASS XI

NCERT

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

CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES | CHEMICAL BONDING AND MOLECULAR STRUCTURE

SECTION - I

Only One Option Correct Type

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

1. The electronic configuration of four elements are
(i) $[Xe]5s^1$
(ii) $[Xe]4f^{14}5d^16s^2$
(iii) $[Ar]4s^24p^5$
(iv) $[Ar]3d^74s^2$
Select the incorrect match about these elements.
(a) (i) – a strong reducing agent
(b) (ii) – a d-block element
(c) (iii) – high magnitude of $\Delta_{eg}H$
(d) (iv) – exhibits variable oxidation states

2. If z-axis is the molecular axis, then π-molecular orbitals are formed by the overlap of
(a) $s + p_z$
(b) $p_x + p_y$
(c) $p_z + p_z$
(d) $p_x + p_x$

3. If $Na_{(g)} \xrightarrow{+E_1} Na^+_{(g)}$; $Mg_{(g)} \xrightarrow{+E_2} Mg^+_{(g)}$ and $Na^+_{(g)} \xrightarrow{+E_3} Na^{2+}_{(g)}$, then the correct order of absorbed energies is
(a) $E_1 > E_2 > E_3$
(b) $E_3 > E_1 > E_2$
(c) $E_2 > E_3 > E_1$
(d) $E_3 > E_2 > E_1$

4. The electronic configuration of the four elements are $P : 1s^2$; $Q : 1s^2, 2s^2, 2p^2$; $R : 1s^2, 2s^2, 2p^5$; $S : 1s^2, 2s^2, 2p^6$. The tendency to form electrovalent bond is maximum in
(a) P
(b) Q
(c) R
(d) S

5. Read the following statements carefully.
I. The physical and chemical properties of elements are a periodic function of their electronic configurations.
II. Electronegativity of fluorine is less than the electronegativity of chlorine.
III. Electropositive nature decreases from top to bottom in a group.

The correct statement(s) is (are)
(a) I, II and III
(b) only I
(c) only I and III
(d) only II and III.

6. If the electronegativity difference between two atoms A and B is 2.0, then the percentage of covalent character in the molecule is
(a) 54%
(b) 46%
(c) 23%
(d) 72%

7. The atomic numbers of elements A, B, C and D are $Z – 1$, Z, $Z + 1$ and $Z + 2$ respectively. If 'B' is a noble gas, choose the correct statements from the following.
(i) 'A' has higher electron affinity.
(ii) 'C' exists in +2 oxidation state.
(iii) 'D' is an alkaline earth metal.
(a) (i) and (ii)
(b) (ii) and (iii)
(c) (i) and (iii)
(d) (i), (ii) and (iii)

8. Which one of the following compounds has the trigonal bipyramidal geometry with three equatorial positions occupied by lone pairs of electrons?
(a) $AlCl_3$
(b) XeF_2
(c) $Pt(NH_3)_2Cl_2$
(d) CH_3MgBr

9. Identify the incorrect statement.
(a) The first ionisation potential of Al is less than the first ionisation potential of Mg.
(b) The second ionisation potential of Mg is greater than the second ionisation potential of Na.
(c) The first ionisation potential of Na is less than the first ionisation potential of Mg.
(d) The third ionisation potential of Mg is greater than that of Al.

10. An atom of an element A has three electrons in its outermost shell, and that of B has six electrons in the outermost orbit. The formula of the compound formed by these two elements will be
(a) A_3B_6
(b) A_2B
(c) A_2B_3
(d) A_3B_2

11. Which of the following statements is correct for the periodic classification of elements?
(a) Atomic size gradually increases from left to right in a period of representative elements.
(b) Across a transition series, atomic size gradually but somewhat irregularly decreases and then increases at the end of the series.
(c) Electron gain enthalpies of representative elements in third period are less negative than those of second period in respective groups.
(d) Ionisation potential gradually but irregularly decreases across a period in representative elements.

12. The enolic form of acetone contains
(a) 10 σ-bonds, 1 π-bond and 1 lone pair
(b) 8 σ-bonds, 2 π-bonds and 2 lone pairs
(c) 9 σ-bonds, 1 π-bond and 2 lone pairs
(d) 9 σ-bonds, 2 π-bonds and 1 lone pair.

13. Which of the following pairs shows reverse properties on moving along a period from left to right and from top to bottom in a group?
(a) Nuclear charge and electron affinity
(b) Ionisation energy and electron affinity
(c) Atomic radius and electron affinity
(d) None of the above.

14. If a molecule MX_3 has zero dipole moment, the sigma bonding orbital used by M is
(a) sp^3d-hybrid   (b) sp-hybrid
(c) sp^3-hybrid   (d) sp^2-hybrid.

15. The energy required to pull out the two electrons are E_1 and E_2 respectively.
$$A \rightarrow A^+ + e^-; E_1$$
$$A^+ \rightarrow A^{2+} + e^-; E_2$$
The correct relationship between the two energies would be
(a) $E_1 < E_2$ (b) $E_1 > E_2$
(c) $E_1 = E_2$ (d) cannot be predicted.

16. The correct order of bond order values among the following species is
(i) NO^- (ii) NO^+
(iii) NO (iv) NO^{2+}
(v) NO^{2-}
(a) (i) < (iv) < (iii) < (ii) < (v)
(b) (iv) = (ii) < (i) < (v) < (iii)
(c) (v) < (i) < (iv) = (iii) < (ii)
(d) (ii) < (iii) < (iv) < (i) < (v)

17. The attraction that an atom exerts on a pair of electrons being shared between this atom and another atom forming a covalent bond is referred to as
(a) electron affinity   (b) electronegativity
(c) ionisation energy   (d) valency.

18. Paramagnetism of oxygen is explained on the basis of its electronic configuration
(a) $(\pi^\star 2p_x)^1 (\pi^\star 2p_y)^1$ (b) $(\pi^\star 2p_y)^1 (\pi^\star 2p_z)^1$
(c) $(\sigma^\star 2s)^1 (\pi 2p_y)^1$ (d) $(\sigma 2s)^1 (\pi 2p_y)^1$

19. The first ionisation energy of oxygen is less than that of nitrogen. Which of the following is the correct reason for this observation?
(a) Lesser effective nuclear charge of oxygen than nitrogen.
(b) Lesser atomic size of oxygen than nitrogen.
(c) Greater interelectronic repulsion between two electrons in the same p-orbital which counterbalances the increase in effective nuclear charge on moving from nitrogen to oxygen
(d) Greater effective nuclear charge of oxygen than nitrogen.

20. The relationship between the dissociation energy of N_2 and N_2^+ is
(a) $N_2^+ > N_2$
(b) $N_2 = N_2^+$
(c) $N_2 > N_2^+$
(d) can either be lower or higher

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SECTION - II

One or More Options Correct Type

</div>

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

21. In which of the following sets of ions $\frac{Z}{e}$ decreases?
(a) I^+, I, I^- (b) Fe^{3+}, Fe^{2+}, Fe
(c) Mg^{2+}, Ne, F^- (d) F, Ne, Mg^{2+}

22. Amongst the following, the correct statement(s) is/are
(a) NO has one unpaired electron in the antibonding molecular orbital
(b) NO^+ is more stable than O_2^+
(c) OF^+ is more paramagnetic than Ne_2^+
(d) In a π-bond, the electron density is concentrated along the bond axis.

23. Which of the following is/are correct statement(s)?
(a) The electron affinity of Si is greater than that of P.
(b) Penetrating power of p-orbital is more than s-orbital.

(c) The numerical value of electronegativity of an atom depends on its ionisation potential and electron affinity.

(d) All of the above.

24. Select the incorrect statement(s) about C_2 molecule.
    (a) It exists in vapour phase.
    (b) It contains 12 electrons out of which 8 are present in bonding orbitals and 4 in antibonding orbitals.
    (c) It is paramagnetic in nature.
    (d) It contains double bonds of which both are π-bonds.

25. Which of the following is not true for the long form of periodic table?
    (a) It reflects the sequence of filling the electrons in s, p, d and f-orbitals.
    (b) It helps to predict the stable valency of elements.
    (c) It reflects trends in physical and chemical properties.
    (d) It helps to predict the relative ionic character of the bond between two elements.

SECTION - III

Paragraph Type

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

Paragraph for Questions 26 to 28

The distribution of electrons among various molecular orbitals is called the electronic configuration of the molecule. From the electronic configuration of the molecule, it is possible to get important information about the molecule like stability of molecules, bond order, nature of the bond, bond length and magnetic nature.

26. The molecule having one unpaired electron is
    (a) NO (b) CO
    (c) CN^- (d) O_2

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

28. According to molecular orbital theory, which of the following statements about the magnetic character and bond order is correct regarding O_2^+?
    (a) Paramagnetic and bond order $< O_2$
    (b) Paramagnetic and bond order $> O_2$
    (c) Diamagnetic and bond order $< O_2$
    (d) Diamagnetic and bond order $> O_2$

Paragraph for Questions 29 to 31

There are many observable patterns in the physical and chemical properties of elements like, atomic and ionic radii, ionisation enthalpy, electron gain enthalpy, electronegativity, valence and chemical reactivity as we descend in a group or move across a period in the periodic table. The periodicity is related to the electronic configuration. That is, all chemical and physical properties are a manifestation of the electronic configuration of elements.

29. Which of the following is incorrect order regarding the property indicated?
    (a) $Sc^{3+} > Cr^{3+} > Fe^{3+} > Mn^{3+}$ – Ionic radius
    (b) $Sc < Ti < Cr < Mn$ – Density
    (c) $Mn^{2+} > Ni^{2+} < Co^{2+} < Fe^{2+}$ – Ionic radius
    (d) $FeO < CaO > MnO > CuO$ – Basic nature

30. The electronic configurations of four elements are given below :
    (i) $2s^2 2p^5$ (ii) $3s^2 3p^5$
    (iii) $2s^2 2p^4$ (iv) $3s^2 3p^4$
    The correct order of the magnitude (without sign) of their electron gain enthalpy is
    (a) (i) < (ii) < (iv) < (iii)
    (b) (ii) < (i) < (iv) < (iii)
    (c) (iii) < (iv) < (ii) < (i)
    (d) (iii) < (iv) < (i) < (ii)

31. Which of the following orders regarding ionisation energy is correct ?
    (a) N > O > F (b) N < O < F
    (c) N > O < F (d) N < O > F

SECTION - IV

Matching List Type

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

32. Match the List I (hybridisation) with List II (species) and select the correct answer using the code given below the lists :

List I	List II
P. sp^3	1. ICl_4^-
Q. dsp^2	2. $TeCl_4$
R. sp^3d	3. MnO_4^-
S. sp^3d^2	4. $[Ni(CN)_4]^{2-}$

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

33. Match the List I (electronegativity scale) with List II (method of calculation) and select the correct answer using the code given below the lists :

List I		List II
P.	Pauling	1.	Electrostatic attractions proportional to Z_{eff}/r^2
Q.	Mulliken	2.	Average of EA and IE
R.	Allred and Rochow	3.	Electron densities of atoms
S.	Sanderson	4.	Bond energies

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

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

List I		List II
P.	$(CH_3)_3B$	1.	Square planar
Q.	NH_4Cl	2.	Trigonal bipyramidal
R.	ICl_4^-	3.	Tetrahedral
S.	PCl_5	4.	Trigonal

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

SECTION - V
Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** Lithium having maximum negative $E°$ value is the strongest reducing agent amongst all alkali metals in solution.
Reason : Lithium is the lightest metal in the periodic table.

36. **Assertion :** According to Fajan's rule, covalent character is favoured by small cation and large anion.
Reason : The magnitude of covalent character in the ionic bond depends upon the extent of polarisation.

37. **Assertion :** The electron gain enthalpy of inert gases is positive.
Reason : Electron affinity of inert gases is zero.

38. **Assertion :** Fluorine molecule has bond order one.
Reason : The number of electrons in the antibonding molecular orbitals is two less than that in bonding molecular orbitals.

39. **Assertion :** The size of the heavier lanthanoid ions Dy^{3+} and Ho^{3+} are similar to that of Y^{3+}.
Reason : The lanthanoid contraction reduces the radii of the last four elements in the series below that of Y^{3+} in the preceding transition series.

40. **Assertion :** N-atom in NH_3 is sp^3 hybridised and bond angle is 107°.
Reason : lp-bp repulsion decreases bond angle.

SECTION - VI
Integer Value Correct Type

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

41. The electron affinity of chlorine is 3.7 eV. The energy (in kcal) released when 2 g of chlorine is completely converted to Cl^- ion in a gaseous state is

42. The formal charge of each atom in sulphuric acid is equal to

43. The element with atomic number 26 will be found in group number

44. In NO_3^- ion, the number of bond pairs of electrons on nitrogen atom is

45. The successive ionisation energy values for an element X are given below :
1st ionisation energy = 410 kJ mol^{-1}
2nd ionisation energy = 820 kJ mol^{-1}
3rd ionisation energy = 1100 kJ mol^{-1}
4th ionisation energy = 1500 kJ mol^{-1}
5th ionisation energy = 3200 kJ mol^{-1}
The number of valence electrons for the atom X is

46. The ratio of σ to π-bonds in mesitylene is

47. If IP = 13.0 eV and EA = 4.0 eV, electronegativity value of chlorine on Mulliken's scale is

48. A diatomic molecule has a dipole moment of 1.2 D. If the bond distance is 1.0 Å, $1/x$ of an electronic charge exists on each atom. The value of x is

49. The element with maximum electronegativity belongs to period

50. The molecule ML_x is planar with six pairs of electrons around M in the valence shell. The value of x is

SOLUTIONS

1. (b): (i) Since, the last electron enters in s-orbital. Hence, it is a s-block element and s-block elements are good reducing agents.

(ii) Since, the last electron enters in f-block, so, it is a f-block element (element of $4f$-series).

(iii) Electronic configuration reveals that it contains 7 electrons in its outer shell, so it is a halogen and halogens have high magnitude of $\Delta_{eg}H$.

(iv) The last electron enters in d-orbital, so it is a d-block element which shows variable oxidation states.

2. (d)

3. (d): The outer electronic configuration of Na$^+$ is $2s^2$, $2p^6$ which is more stable than Mg($3s^2$) so, $E_3 > E_2$. Similarly, outer electronic configuration of Mg($3s^2$) is more stable than that of Na($3s^1$) so, $E_2 > E_1$,

Hence, the correct order is $E_3 > E_2 > E_1$.

4. (c) : R forms anion readily by gaining one electron only.

5. (b): Fluorine is the most electronegative element and electropositive character increases from top to bottom in a group.

6. (a) : % ionic character $= 16(\chi_A - \chi_B) + 3.5(\chi_A - \chi_B)^2$
$= 16 \times 2 + 3.5 \times (2)^2 = 46\%$
$\therefore$ % covalent character $= 100 - 46 = 54\%$

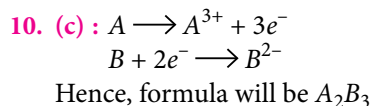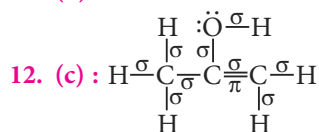**7. (c) :** A is a halogen, D is an alkaline earth metal and C is an alkali metal which exists in +1 oxidation state.

8. (b) :

Linear, sp^3d
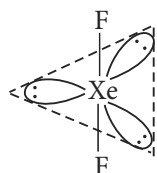
9. (b): IE_2 of Na is higher than that of Mg because in case of Na, the second electron has to be removed from the noble gas core while in case of Mg, removal of second electron gives a noble gas core.

10. (c) : $A \longrightarrow A^{3+} + 3e^-$
$B + 2e^- \longrightarrow B^{2-}$
Hence, formula will be A_2B_3

11. (b)

12. (c) :

13. (c)

14. (d): MX_3 molecule with M having sp^2 hybrid orbitals will have triangular planar geometry and hence, zero dipole moment.

15. (a): IE_2 is always greater than IE_1 as more energy is required to remove an electron from a cation as compared to its parent atom.

16. (c) : (iii) NO(15) : $KK\ \sigma 2s^2\ \sigma^\star 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2$
$$= \pi 2p_y^2, \pi^\star 2p_x^1$$

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

(iv) NO^{2+} :

Bond order $= \dfrac{1}{2}(7-2) = 2.5$

(ii) NO$^+$:

Bond order $= \dfrac{1}{2}(8-2) = 3.0$

(i) NO$^-$:

Bond order $= \dfrac{1}{2}(8-4) = 2.0$

(v) NO^{2-} :

Bond order $= \dfrac{1}{2}(8-5) = 1.5$

Hence, the correct order is
$$\underset{(v)}{NO^{2-}} < \underset{(i)}{NO^-} < \underset{(iv)}{NO^{2+}} = \underset{(iii)}{NO} < \underset{(ii)}{NO^+}$$
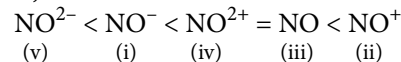
17. (b) : It is the definition of electronegativity.

18. (a) : According to MOT,
O$_2$ (16) : $KK\ \sigma 2s^2\ \sigma^\star 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2\ \pi^\star 2p_x^1$
$$= \pi^\star 2p_y^1$$
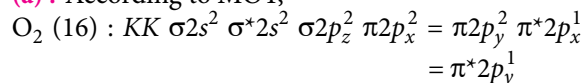
No. of unpaired electrons is two and hence, O$_2$ is paramagnetic in nature.

19. (c) : The electronic configuration of oxygen is
$_8$O $= 1s^2\ 2s^2\ 2p^4$

$2p^4$
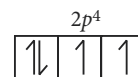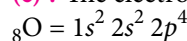
The electronic configuration of nitrogen is
$_7$N $= 1s^2\ 2s^2\ 2p^3$

$2p^3$
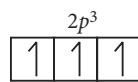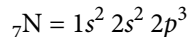
Half-filled p-orbital

Due to the presence of half-filled p-orbital, a large amount of energy is required to remove an electron from nitrogen. Hence, first ionisation energy of nitrogen is greater than that of oxygen.

Also there is greater interelectronic repulsion between the electrons present in the same p-orbital which counterbalances the increase in effective nuclear charge from nitrogen to oxygen.

20. (c) :

Species	Bond order
N_2	3.0
N_2^+	2.5

Higher the bond order, greater is the bond dissociation energy.
Thus, dissociation energy of $N_2 > N_2^+$.

21. (a, b, c) : (a) $\dfrac{Z}{e}$ for I^+, I and I^- is $\dfrac{53}{52}, \dfrac{53}{53}, \dfrac{53}{54}$ (decreases).

(b) $\dfrac{Z}{e}$ for Fe^{3+}, Fe^{2+} and Fe is $\dfrac{26}{23}, \dfrac{26}{24}, \dfrac{26}{26}$ (decreases).

(c) $\dfrac{Z}{e}$ for Mg^{2+}, Ne and F^- is $\dfrac{12}{10}, \dfrac{10}{10}, \dfrac{9}{10}$ (decreases).

(d) $\dfrac{Z}{e}$ for F, Ne and Mg^{2+} is $\dfrac{9}{9}, \dfrac{10}{10}, \dfrac{12}{10}$ which is not in decreasing order.

22. (a, b, c) : NO (15) : $KK\, (\sigma 2s)^2 (\sigma^\star 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2$
$$= (\pi 2p_y)^2 (\pi^\star 2p_x)^1$$
NO^+ (14) : $KK\, (\sigma 2s)^2 (\sigma^\star 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2$
B.O. = 3.0
O_2^+(15) : $KK\, (\sigma 2s)^2 (\sigma^\star 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2$
$$= (\pi 2p_y)^2\, (\pi^\star 2p_x)^1$$
B.O. = 2.5
OF^+ (16) : $KK\, (\sigma 2s)^2 (\sigma^\star 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2$
$$(\pi^\star 2p_x)^1 = (\pi^\star 2p_y)^1$$
Ne_2^+(19) : $KK\, (\sigma 2s)^2 (\sigma^\star 2s)^2 (\sigma 2p_z)^2 (\pi 2p_x)^2 = (\pi 2p_y)^2$
$$(\pi^\star 2p_x)^2 = (\pi^\star 2p_y)^2 (\sigma^\star 2p_z)^1$$
In a π-bond, the electron density is concentrated in the region perpendicular to the bond axis.

23. (a, c) : (a) is correct because the electronic configuration of P is exactly half-filled *i.e.,* more stable.
(b) is incorrect because s-orbital is closer to nucleus than p-orbital.
(c) is correct because, Electronegativity = (I.P. + E.A.)/2

24. (c) : C_2(12) : $KK\, \sigma 2s^2 \sigma^\star 2s^2 \pi 2p_x^2 = \pi 2p_y^2$

It exists in vapour phase and is diamagnetic in nature because it contains no unpaired electrons. Since four electrons are present in two pi-molecular orbitals so the double bond contains both π-bonds.

25. (b) : Stable valency of an element depends upon electronic configuration and not on its position in the periodic table. Statements (a), (c) and (d) are correct.

26. (a) : The molecular electronic configurations are :
NO (15) : $KK\, \sigma 2s^2\, \sigma^\star 2s^2\, \sigma 2p_z^2\, \pi 2p_x^2 = \pi 2p_y^2\, \pi^\star 2p_x^1$
CO (14) : $KK\, \sigma 2s^2\, \sigma^\star 2s^2\, \sigma 2p_z^2\, \pi 2p_x^2 = \pi 2p_y^2$
CN^- (14) : $KK\, \sigma 2s^2\, \sigma^\star 2s^2\, \pi 2p_x^2 = \pi 2p_y^2\, \sigma 2p_z^2$
O_2 (16) : $KK\, \sigma 2s^2\, \sigma^\star 2s^2\, \sigma 2p_z^2\, \pi 2p_x^2 = \pi 2p_y^2$
$$\pi^\star 2p_x^1 = \pi^\star 2p_y^1$$

Thus, NO has one unpaired electron.
CO and CN^- have no unpaired electrons while O_2 has two unpaired electrons.

27. (b) : According to molecular orbital theory, the energy levels of the given molecules are
C_2^{2-} (14) : $\sigma 1s^2\, \sigma^\star 1s^2\, \sigma 2s^2\, \sigma^\star 2s^2\, \pi 2p_x^2 = \pi 2p_y^2\, \sigma 2p_z^2$
B.O. = (10 – 4)/2 = 3.0
He_2^+ (3) : $\sigma 1s^2\, \sigma^\star 1s^1$
B.O. = (2 – 1)/2 = 0.5
NO (15) : $\sigma 1s^2\, \sigma^\star 1s^2\, \sigma 2s^2\, \sigma^\star 2s^2\, \sigma 2p_z^2$
$$\pi 2p_x^2 = \pi 2p_y^2\, \pi^\star 2p_x^1$$
B.O. = (10 – 5)/2 = 2.5
O_2^- (17) : $\sigma 1s^2\, \sigma^\star 1s^2\, \sigma 2s^2\, \sigma^\star 2s^2\, \sigma 2p_z^2\, \pi 2p_x^2 = \pi 2p_y^2$
$$\pi^\star 2p_x^2 = \pi^\star 2p_y^1$$
B.O. = (10 – 7)/2 = 1.5
So, the correct order of their increasing bond orders is $He_2^+ < O_2^- < NO < C_2^{2-}$.

28. (b) : O_2^+ has one unpaired electron hence, it is paramagnetic while O_2 is diamagnetic.
The bond order of O_2^+ is 2.5 and that of O_2 is 2. Thus, its bond order is greater than that of O_2.

29. (a) : Ionic radius (with same oxidation state) in the first transition series decreases across the period because effective nuclear charge per electron increases. So, the correct order of ionic radius is $Sc^{3+} > Cr^{3+} > Mn^{3+} > Fe^{3+}$.

30. (d) : The given configurations (i), (ii), (iii) and (iv) belong to fluorine, chlorine, oxygen and sulphur respectively. Due to small size of oxygen and fluorine atoms, there is strong interelectronic repulsion when extra electron is added to these atoms. Thus, addition of electron is not easy. Hence, electron gain enthalpy of sulphur and chlorine are more negative than that of oxygen and fluorine.

31. (c) : Electronic configurations are as follows :

$_7N : 1s^2 2s^2 2p^3$;

$_8O : 1s^2 2s^2 2p^4$

$_9F : 1s^2 2s^2 2p^5$
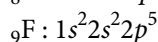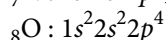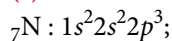
Although O and F are smaller than N but nitrogen has stable half-filled configuration. So, it will have higher ionisation energy than O.

F being smallest in size will have highest ionisation energy.

So, order is N > O < F.

32. (d) :
ICl_4^- — $sp^3 d^2$
$TeCl_4$ — $sp^3 d$
MnO_4^- — sp^2
$[Ni(CN)_4]^{2-}$ — dsp^2

33. (a)

34. (c) :
$(CH_3)_3B$ – Trigonal
NH_4Cl – Tetrahedral
ICl_4^- – Square planar
PCl_5 – Trigonal bipyramidal

35. (b) : The strength of Li metal as reducing agent depends not only on *IE* but also on heat of atomisation and heat of hydration of the ion formed. Li^+ ion has very high heat of hydration due to its small size.

36. (a)

37. (b) : Inert gases have $ns^2 np^6$ configuration, *i.e.*, no place for incoming electron. As a result, energy has to be supplied to add an additional electron. Therefore, electron gain enthalpy of inert gases is positive.

Earlier electron affinity of the noble gas was taken to be zero.

38. (a) : Electronic configuration of F_2 molecule is

$F_2(18) : KK\ \sigma 2s^2\ \sigma^\star 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2 = \pi 2p_y^2 = \pi^\star 2p_x^2$
$\pi^\star 2p_y^2$

Bond order = $\dfrac{N_b - N_a}{2} = \dfrac{8-6}{2} = 1$

39. (a)   **40. (a)**

41. (5) : $Cl + e^- \longrightarrow Cl^- + 3.7$ eV
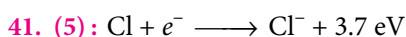
Energy released for the conversion of 35.5 g of Cl into $Cl^- = 3.7 \times 23.06$ kcal [1 eV = 23.06 kcal mol^{-1}]

Energy released for the conversion of 2 g of Cl into

$Cl^- = \dfrac{3.7 \times 23.06 \times 2}{35.5} = 4.8$ kcal ≈ 5 kcal

42. (0) :

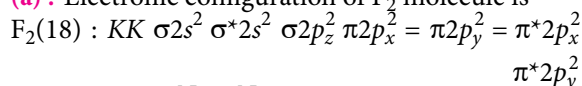$$H-\ddot{\underset{..}{O}}-\overset{\overset{:O:}{\|}}{\underset{\underset{:O:}{\|}}{S}}-\ddot{\underset{..}{O}}-H$$

$FC = 6 - 0 - 12/2 = 0$
$FC = 1 - 0 - 2/2 = 0$
$FC = 6 - 4 - 4/2 = 0$
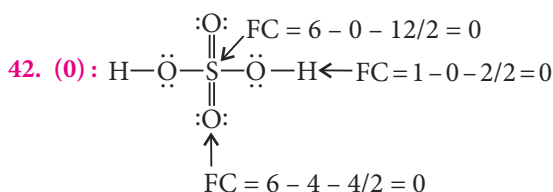
43. (8) : Electronic configuration = $[Ar]\ 3d^6 4s^2$

Group = 8th.

44. (4) : The structure of NO_3^- :

$$\left[O = N \overset{\displaystyle O}{\underset{\displaystyle O}{\big<}} \right]^-$$
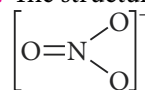
Hence, N has four bond pairs and no lone pair.

45. (4) : The ionisation energies provide an indication about the number of valence electrons in an atom. In this case, *X* has $IE_5 >> IE_4 > IE_3 > IE_2 > IE_1$. The large jump between IE_4 and IE_5 shows that it has four valence electrons.

46. (7) : The structure of mesitylene is
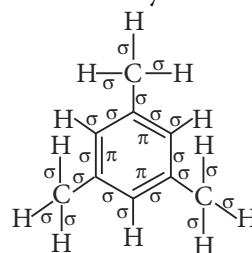
Total no. of σ-bonds = 21

Total no. of π-bonds = 3

∴ Ratio of σ to π-bonds is 21/3 = 7

47. (3) : $EN = \dfrac{IP + EA}{5.6} = \dfrac{13.0 + 4.0}{5.6} = 3.035 \approx 3$

48. (4) : Partial charge = $\dfrac{\text{Dipole moment}}{\text{Bond distance}}$

$= \dfrac{1.2 \times 10^{-18} \text{ esu. cm}}{1.0 \times 10^{-8} \text{ cm}} = 1.2 \times 10^{-10}$ esu

The fraction of an electronic charge is

$\dfrac{1.2 \times 10^{-10} \text{ esu}}{4.8 \times 10^{-10} \text{ esu}} = \dfrac{1}{4}$ ∴ Value of $x = 4$

49. (2) : Fluorine is the most electronegative element which belongs to period 2.

50. (4) : Since, the molecule has six pairs of electrons, it should have octahedral geometry. But the structure is planar, therefore it should have two lone pairs and four bond pairs. Therefore, value of x in ML_x is 4.

◈ ◈

ACE
YOUR WAY **CBSE XII**

Series 3

CHAPTERWISE PRACTICE PAPER :
SURFACE CHEMISTRY | GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

Time Allowed : 3 hours   Maximum Marks : 70

GENERAL INSTRUCTIONS

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

1. Write one condition for Tyndall effect to take place.

2. Write the reaction involved in thermite process. Name the reducing agent used.

3. What are the dispersed phase and dispersion medium in cell fluids?

4. What is the significance of Ellingham diagram?

5. Why are powdered substances more effective adsorbents than their crystalline forms?

6. Explain the principle involved in electrolytic refining of copper.

7. How does adsorption of a gas on a solid surface vary with temperature? Illustrate with the help of appropriate graphs.

OR

How does adsorption of a gas on a solid surface vary with pressure? Illustrate with the help of appropriate graphs.

8. (i) Explain the magnetic separation process for the concentration of ores.
   (ii) Give examples of ores that can be concentrated by this method.

9. (i) What is the difference between a colloidal solution and an emulsion? Give one example of each.
   (ii) What are the two types of emulsions? Give one example of each.

10. Describe the role of the following :
    (i) NaCN in the extraction of silver from a silver ore.
    (ii) Cryolite in the extraction of aluminium from alumina.

11. Give reasons for the following :
    (i) The enthalpy in case of chemisorption is usually higher than that of physisorption.
    (ii) Same substance can act both as colloid and crystalloid.
    (iii) Artificial rain is caused by spraying salt over clouds.

12. (i) Why is leaching of gold by metal cyanides carried out in the presence of oxygen?
    (ii) Give the chemical equation involved.
    (iii) Name the metal used as reducing agent in this process.

13. Show the relationship between the extent of adsorption of a gas on the surface of a solid with lower and higher ranges of pressure.

14. (i) Based on the given Ellingham diagram, indicate the temperature favourable for the reduction of metal oxide to metal.
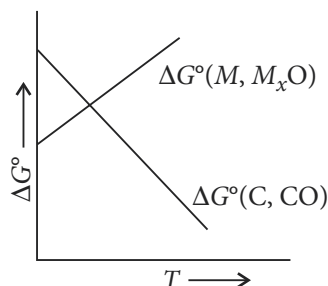
(ii) Why is the reduction of a metal easier if the metal formed is in liquid state at the temperature of reduction?

15. (i) Copper can be extracted by hydrometallurgy but not zinc. Explain.
(ii) Is it true under certain conditions Mg can reduce SiO_2 and Si can reduce MgO? What are those conditions?

OR

(i) Why is zinc and not copper used for the recovery of Ag from $[Ag(CN)_2]^-$?
(ii) Why is it advantageous to roast a sulphide ore to the oxide before reduction?

16. Explain the following terms :
(i) Peptisation
(ii) Dialysis
(iii) Hardy–Schulze rule

17. (i) Which of the following electrolytes is most effective for the coagulation of $Fe(OH)_3$ sol and why? Na_3PO_4, Na_2SO_4, NaCl
(ii) Which of the following electrolytes will be most effective in the coagulation of As_2S_3 sol and why ? $AlCl_3$, $BaCl_2$ and NaCl
(iii) Lyophilic sol is more stable than lyophobic sol. Explain.

18. Write the principles involved in the following methods :
(i) Hydraulic washing
(ii) Vapour phase refining
(iii) Froth-floatation method

19. Illustrate the following with examples :
(i) Lyophilic and lyophobic sols
(ii) Homogeneous and heterogeneous catalysis

20. Describe the role of the following :
(i) Graphite rod in the electrometallurgy of aluminium
(ii) Depressant in froth-floatation process
(iii) Silica in the metallurgy of copper

21. How is the concept of coupling reactions useful in explaining the occurrence of non-spontaneous thermochemical reactions? Explain giving an example.

22. A colloidal solution of AgI is prepared by two different methods shown below :
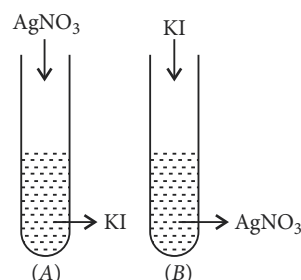
(i) What is the charge of AgI colloidal particles in the test tubes (A) and (B)? Explain.
(ii) Name the process responsible for the origin of charges.

23. Sunita noticed many people of her colony suffering from nausea, headache, vomiting, etc. She analysed the situation and came to the conclusion that her locality is near the industrial area due to which air and water around get contaminated. She suggested them to wear gas masks and use alum to purify water.
(i) What values are shown by Sunita?
(ii) What is the purpose of wearing gas mask?
(iii) How can the industrial pollution be reduced?
(iv) How can water be purified?

24. (i) Illustrate the following :
(a) Precipitation
(b) Brownian movement
(c) Electroosmosis
(ii) (a) How can colloidal solution and true solution of the same colour be distinguished from each other?
(b) List four applications of adsorption.

OR

(i) Explain what is observed
(a) when a beam of light is passed through a colloidal sol.
(b) an electrolyte, NaCl is added to hydrated ferric oxide sol.

(c) electric current is passed through a colloidal sol?

(ii) Define each of the following :
   (a) Micelles
   (b) Emulsification

25. (i) Free energies of formation ($\Delta_f G$) of $MgO_{(s)}$ and $CO_{(g)}$ at 1273 K and 2273 K are given below :
$\Delta_f G\ (MgO)_{(s)}$ = –941 kJ mol^{-1} at 1273 K
$\Delta_f G\ (MgO)_{(s)}$ = –314 kJ mol^{-1} at 2273 K
$\Delta_f G\ (CO)_{(g)}$ = –439 kJ mol^{-1} at 1273 K
$\Delta_f G\ (CO)_{(g)}$ = –628 kJ mol^{-1} at 2273 K
On the basis of above data, predict the temperature at which carbon can be used as a reducing agent for $MgO_{(s)}$.

(ii) Out of C and CO, which is a better reducing agent at 673 K ?

OR

(i) Describe how the following changes are brought about :
   (a) Pig iron into steel
   (b) Zinc oxide into metallic zinc
   (c) Impure titanium into pure titanium.

(ii) How do you differentiate the following :
   (a) Roasting and calcination?
   (b) Mineral and ore?

26. (i) How do (a) surface area of adsorbent, (b) pressure and (c) temperature influence the extent of adsorption of a gas on a solid?

(ii) List two differences between adsorption and absorption.

OR

(i) Describe the preparation of the following colloidal solutions and name the method used in each case :
   (a) Silver solution
   (b) Sulphur solution

(ii) List four differences between physisorption and chemisorption.

SOLUTIONS

1. The refractive indices of the dispersed phase and the dispersion medium should differ greatly in magnitude.

2. $2Al_{(s)} + Fe_2O_{3(s)} \xrightarrow{\Delta} Al_2O_{3(s)} + 2Fe_{(l)}$
Aluminium acts as the reducing agent.

3. Dispersed phase : Solid
Dispersion medium : Liquid

4. Ellingham diagram helps in predicting the feasibility of thermal reduction of an ore.

5. Powdered substances have large surface area which increases the extent of adsorption than their crystalline forms.

6. In electrolytic refining of copper, anode is of impure copper and pure copper strips are taken as cathode. The electrolyte is acidified solution of copper sulphate and the net result of electrolysis is the transfer of copper in pure form from the anode to the cathode.
   At anode : $Cu \longrightarrow Cu^{2+} + 2e^-$
   At cathode : $Cu^{2+} + 2e^- \longrightarrow Cu$
Impurities from the blister copper deposit as anode mud.
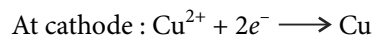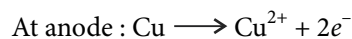
7. Physical adsorption of a gas on a solid decreases with increase in temperature while chemical adsorption first increases and then decreases with increase in temperature.
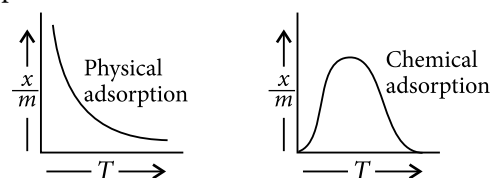
$\dfrac{x}{m}$ represents the extent of adsorption where x is the mass of adsorbate and m is the mass of adsorbent.

OR

Physical adsorption of a gas on a solid increases with increase in pressure while chemical adsorption first increases and then becomes independent of pressure with increase in pressure.
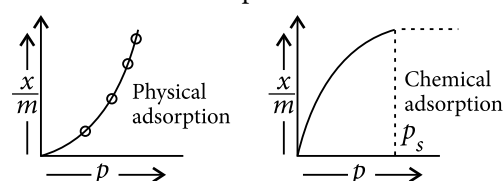
$\dfrac{x}{m}$ represents the extent of adsorption where x is the mass of adsorbate and m is the mass of adsorbent.

8. (i) Magnetic separation process is based on differences in magnetic properties of the ore components. If either the ore or the gangue is capable of being attracted by a magnetic

field, then such separations are carried out. The ground ore is carried on a conveyer belt which passes over a magnetic roller. The magnetic and non-magnetic components form separate heaps.

(ii) Chromite ($FeCr_2O_4$) and magnetite (Fe_3O_4) are separated from non-magnetic silicious gangue by this method.

9. (i) In a colloidal solution, the dispersed phase is a solid and the dispersion medium is a liquid *e.g.*, cell fluids, muddy water.
In an emulsion, both the dispersed phase and dispersion medium are liquid *e.g.,* milk, hair cream.

(ii) The two types of emulsions are :
(a) Oil in water type, in which small droplets of an oil are dispersed in water which is a dispersion medium *e.g.,* milk.
(b) Water in oil type, in which water droplets are dispersed in an oil which is a dispersion medium *e.g.,* butter.

10. (i) Leaching is used for extracting silver by converting its ore into soluble complex. NaCN combines with argentite ore of silver forming a soluble complex.

$$Ag_2S + 4NaCN \rightleftharpoons 2Na[Ag(CN)_2] + Na_2S$$
Sodium dicyanoargentate(I)
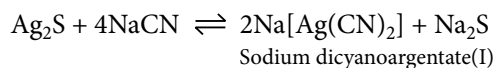
Silver is recovered from this complex by reduction or displacement method using a more electropositive zinc metal.

$$2Na[Ag(CN)_2]_{(aq)} + Zn_{(s)} \longrightarrow 2Ag_{(s)}$$
$$+ Na_2[Zn(CN)_4]_{(aq)}$$

(ii) In the extraction of aluminium from alumina, Al_2O_3 (a bad conductor of electricity), cryolite (Na_3AlF_6) and fluorspar (CaF_2) are added which not only make alumina a good conductor of electricity but also reduce the melting point of the mixture to around 1140 K.

11. (i) Chemisorption involves the formation of chemical bonds between adsorbent and adsorbate molecules which results in high energy changes while in physisorption, the molecules of adsorbate and adsorbent are held by weak van der Waals interactions.

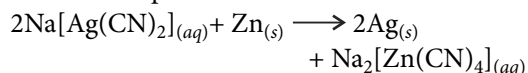(ii) Same substance can act both as colloid and crystalloid. It depends on the size of the particles. When the size of the particles lies between 1 to 1000 nm, it behaves as a colloid. If particle size is less than 1 nm, it exists as a true solution and behaves like a crystalloid.

(iii) Artificial rain is caused by spraying salt over clouds. The colloidal water particles of the clouds get neutralised by oppositely charged ions of the salt and coagulate to bigger water drops which cause artificial rain.

12. (i) In leaching of gold, the finely powdered gold is treated with dilute solution of metal cyanide with the passage of air. The presence of oxygen is necessary to convert gold, Au to oxidised state, Au^+.

(ii) $$4Au_{(s)} + 8KCN_{(aq)} + 2H_2O_{(l)} + O_{2(g)} \longrightarrow$$
$$4K[Au(CN)_2]_{(aq)} + 4KOH_{(aq)}$$
Potassium dicyanoaurate (I)
(soluble complex)

$$2K[Au(CN)_2]_{(aq)} + Zn_{(s)} \longrightarrow K_2[Zn(CN)_4]_{(aq)}$$
$$+ 2Au_{(s)}$$
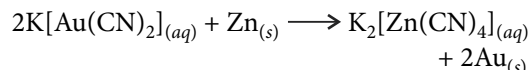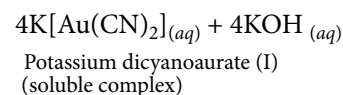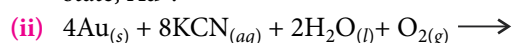
(iii) Zinc metal is used as the reducing agent.

13. The variation in the amount of gas adsorbed by the adsorbent with pressure at constant temperature is expressed by Freundlich adsorption isotherm. The relationship can be expressed by the following equation :

$$\frac{x}{m} = k.p^{1/n} \ (n > 1)$$

where x is the mass of the gas adsorbed on mass m of the adsorbent at pressure p, The factor $\frac{1}{n}$ can have values between 0 and 1.
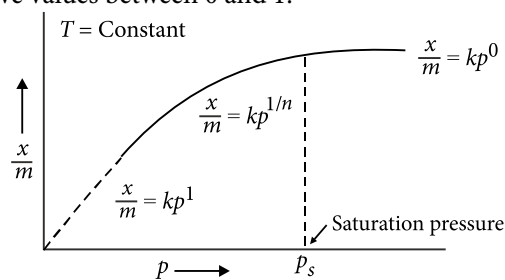
(i) At low pressure, the graph is nearly a straight and sloping line. It means $x/m \propto p$ or $x/m = kp^1$.

(ii) At high pressure, x/m becomes independent of pressure, *i.e.*, $x/m \propto p^0$ or $x/m = kp^0$.

(iii) At intermediate range of pressure, x/m varies with the power of the pressure lying between 0 and 1, *i.e.,* $x/m \propto p^{1/n}$ or $x/m = kp^{1/n}$.

14. (i) The formation of carbon monoxide from carbon can reduce the metal oxide at a temperature higher than the point of intersection of the two lines.

$$M_xO_{(s)} + C_{(s)} \longrightarrow xM_{(s)} + CO_{(g)}$$
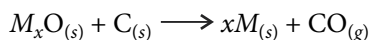
After that point, the $\Delta G°$ value becomes more negative for the combined process including the reduction of M_xO. The difference in the two $\Delta G°$ values after that point determines whether reduction of the oxide of the upper line is feasible by the element represented by the lower line. If the difference is large, the reduction is easier.

For temperatures at which the (C, CO) line lies below (M, M_xO) line, carbon can be used to reduce metal oxide which itself gets oxidised to carbon monoxide.

(ii) The entropy is higher if metal is in liquid (molten) state. This means the ΔS of reduction process is positive when the metal is in liquid state. This will make the value of ΔG more negative ($\Delta G = \Delta H - T\Delta S$), thus making reduction easier.

15. (i) Hydrometallurgy is based on the conversion of ore into soluble salts by leaching with acid or base and then subsequent reduction with other active metals.

$$CuS + H_2SO_4 \longrightarrow CuSO_4 + H_2S\uparrow$$
$$CuSO_4 + Zn \longrightarrow Cu + ZnSO_4$$
$$Zn^{2+} + 2e^- \longrightarrow Zn; \qquad E°_{Zn^{2+}/Zn} = -0.76\ V$$
$$Cu^{2+} + 2e^- \longrightarrow Cu; \qquad E°_{Cu^{2+}/Cu} = +0.34\ V$$

Zn^{2+} cannot be reduced by H_2 or other active metals. Hence, Zn is not extracted by hydrometallurgy.

(ii) $$Mg_{(s)} + \frac{1}{2}O_{2(g)} \longrightarrow MgO_{(s)}\ ; \Delta G_{Mg,\ MgO}$$

$$Si_{(s)} + O_{2(g)} \longrightarrow SiO_{2(s)}\ ; \Delta G_{Si,\ SiO_2}$$

The temperature range in which $\Delta G_{Mg,\ MgO}$ is lesser than $\Delta G_{Si,SiO_2}$, Mg can reduce SiO_2 to Si.

$$2Mg_{(s)} + SiO_{2(s)} \longrightarrow 2MgO_{(s)} + Si_{(s)}; \Delta G° = -ve$$

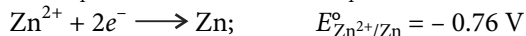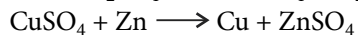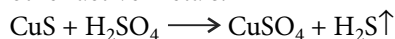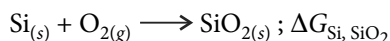whereas, the temperature range in which $\Delta G_{Si,SiO_2}$ is less than $\Delta G_{Mg,MgO}$, Si can reduce MgO to Mg.

$$Si_{(s)} + 2MgO_{(s)} \longrightarrow SiO_{2(s)} + 2Mg_{(s)}; \Delta G° = -ve$$
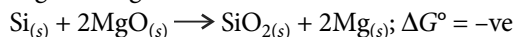
The temperature at which $\Delta_f G$ curve of these two substances intersect is 1966 K. Below this temperature, the $\Delta G°$ curve for the formation of SiO_2 lies above the $\Delta G°$ curve for the formation of MgO. Thus, at temperature less than 1966 K, Mg can reduce SiO_2 and above 1966 K, Si can reduce MgO.

OR

(i) $E°$ of Zn ($E°_{Zn^{2+}/Zn} = -0.76$ V) is lower than that of copper ($E°_{Cu^{2+}/Cu} = +0.34$ V), therefore, Zn is a stronger reducing agent than Cu. Thus, zinc reduces $[Ag(CN)_2]^-$ to give metallic Ag. Further, zinc is cheaper than copper.

(ii) $\Delta_f G°$ of most of the sulphides are more negative than those of CS_2 and H_2S. Therefore, neither carbon nor hydrogen can reduce metal sulphides to metal. In contrast, $\Delta_f G°$ of oxides are much lower than that of SO_2 and hence oxidation of metal sulphides to metal oxides is thermodynamically favourable. Furthermore, the $\Delta_f G°$ of these metal oxides is less negative than that of CO and hence carbon can easily reduce these oxides to the corresponding metals.

16. (i) Peptisation : It is the process of converting a precipitate into a colloidal solution by shaking it with dispersion medium in the presence of a small amount of electrolyte which is called peptising agent. During this, the precipitate adsorbs one of the ions of the electrolyte on its surface. This causes the development of charge on it, which ultimately breaks up into smaller particles of the size of a colloid.

(ii) Dialysis : It is the process of removing a dissolved substance from a colloidal solution by means of diffusion through a suitable membrane since particles in a true solution can pass through membrane but not the colloidal particles. A bag made of parchment paper or cellophane is filled with colloidal sol and suspended in fresh water. The impurities of electrolyte particles pass out leaving behind colloidal sol.

(iii) Hardy–Schulze rule : According to this rule :
  (a) The ions carrying charge opposite to that of the sol particles are effective in causing the coagulation of the solution.
  (b) Coagulating power of an electrolyte is directly proportional to the valency of the ions causing coagulation.

17. (i) $Fe(OH)_3$ is a positively charged sol, hence the anion having maximum charge will be more effective. Therefore, Na_3PO_4 having PO_4^{3-} ion will be most effective.

(ii) $AlCl_3$ having Al^{3+} ion is most effective in coagulation of As_2S_3 sol which is negatively charged colloid.

(iii) Lyophilic sol is more stable than lyophobic sol. If the dispersed phase is separated from the dispersion medium of lyophilic sol, the sol can be obtained again by simply remixing it with the dispersion medium. They are not easily precipitated. The stability is due to its high degree of hydration. Lyophobic sol cannot be formed directly by mixing. Special methods are employed for its formation. It can be readily precipitated. Once precipitated it does not give back the sol again, simply by addition of dispersion medium.

18. (i) Hydraulic washing : It is based on the difference in gravities of the ore and the gangue particles. In this method, when upward stream of running water is used to wash the powdered ore, lighter gangue particles are washed away and heavier ore particles are left behind.

(ii) Vapour phase refining : In this method, the impure metal is converted into its volatile compound and collected. It is then decomposed to give pure metal.

$$\underset{\text{Impure}}{Ni} + 4CO \xrightarrow{330-350 \text{ K}} Ni(CO)_4$$

$$Ni(CO)_4 \xrightarrow{450-470 \text{ K}} \underset{\text{Pure}}{Ni} + 4CO$$

(iii) Froth floatation method : This process is based on preferential wetting of ore by oil while gangue particles by water. Powdered ore is mixed with water and a little pine oil. The mixture is vigorously stirred by passing compressed air. The froth, which is produced rises to the surface and carries the ore particles along with it. The gangue particles are left behind.

19. (i) The colloidal solutions in which dispersed phase and dispersion medium attract each other are known as lyophilic sols *e.g.*, proteins, starch, rubber etc. They directly pass into the colloidal state when brought in contact with the solvent.

The colloidal solutions in which dispersed phase and dispersion medium repel each other are called lyophobic sols *e.g.*, metals, their sulphides, hydroxides, etc. They do not form colloidal solution readily when mixed with the dispersion medium. Their colloidal solution can be prepared only by special methods.

(ii) Homogeneous catalysis : The process in which the reactants and catalyst are present in the same phase, *e.g.,* lead chamber process for the manufacture of H_2SO_4.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{NO_{(g)}} 2SO_{3(g)}$$
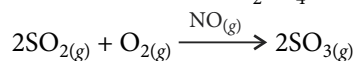
Heterogeneous catalysis : The process in which the reactants and catalyst are present in different phases, *e.g.*, contact process for the manufacture of H_2SO_4.

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{V_2O_{5(s)}} 2SO_{3(g)}$$
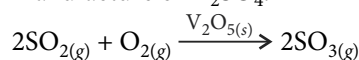
20. (i) Graphite anode is used in the electrometallurgy of aluminium from alumina, Al_2O_3. Oxygen liberated at high temperature reacts with graphite to form both CO_2 and CO gases and prevents the liberation of O_2 gas at the anode which may react with Al metal to give Al_2O_3 again.

At anode : $C_{(s)} + O^{2-}$ (melt) $\longrightarrow CO_{(g)} + 2e^-$

$C_{(s)} + 2O^{2-}$ (melt) $\longrightarrow CO_{2(g)} + 4e^-$
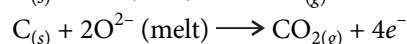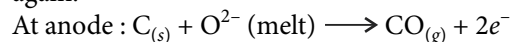
(ii) Depressants in froth floatation process are used to prevent one type of sulphide ore particles from forming the froth with air bubbles.

For example, sodium cyanide is used as a depressant to separate PbS ore from ZnS ore by preventing ZnS from coming with the froth.

(iii) During the extraction of copper from copper pyrites, $CuFeS_2$, its roasting gives FeO besides Cu_2O and SO_2.

Roasting :

$$\underset{\text{Copper pyrites}}{2CuFeS_2} + O_2 \xrightarrow{\Delta} Cu_2S + 2FeS + SO_2$$

$$2Cu_2S + 3O_2 \xrightarrow{\Delta} 2Cu_2O + 2SO_2$$

Smelting :

$$2FeS + 3O_2 \longrightarrow 2FeO + 2SO_2$$
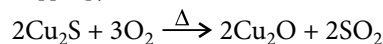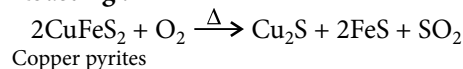
To remove FeO, SiO_2 is added to form slag.

$$\underset{\text{(Basic oxide)}}{FeO_{(s)}} + \underset{\text{(Acidic oxide)}}{SiO_{2(s)}} \longrightarrow \underset{\text{Slag}}{FeSiO_{3(l)}}$$
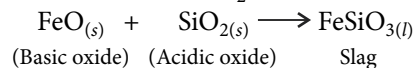
Thus, the role of silica in the metallurgy of copper is to remove ferrous oxide as ferrous silicate slag.

21. Many reactions which are non-spontaneous (ΔG is positive) can be made to occur spontaneously if these are coupled with reactions having negative

free energy. For example, decomposition of Fe_2O_3 into iron is a non-spontaneous reaction ($\Delta G = +1487\,kJ\,mol^{-1}$). However, this decomposition can take place spontaneously if carbon monoxide is simultaneously burnt in oxygen ($\Delta G = -514.4\,kJ\,mol^{-1}$).

$$2Fe_2O_{3(s)} \longrightarrow 4Fe_{(s)} + 3O_{2(g)}; \qquad \text{...(i)}$$
$$\Delta G° = +1487.0\,kJ\,mol^{-1}$$
$$2CO_{(g)} + O_{2(g)} \longrightarrow 2CO_{2(g)}; \qquad \text{...(ii)}$$
$$\Delta G° = -514.4\,kJ\,mol^{-1}$$
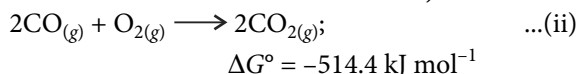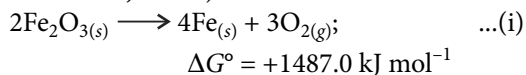
Multiplying equation (ii) by 3 and then adding to equation (i), we get

$$6CO_{(g)} + 3O_{2(g)} \longrightarrow 6CO_{2(g)};$$
$$\Delta G° = -1543.2\,kJ\,mol^{-1}$$
$$2Fe_2O_{3(s)} \longrightarrow 4Fe_{(s)} + 3O_{2(s)};$$
$$\Delta G° = +1487.0\,kJ\,mol^{-1}$$

$$\overline{2Fe_2O_{3(s)} + 6CO_{(g)} \longrightarrow 4Fe_{(s)} + 6CO_2;}$$
$$\Delta G° = -56.2\,kJ\,mol^{-1}$$

Since $\Delta G°$ in the reduction of Fe_2O_3 with CO is negative, therefore the reaction is feasible and spontaneous.

22. **(i)** In test tube (*A*), when $AgNO_3$ is added in excess to KI solution, AgI is precipitated and the common Ag^+ ions are adsorbed from the excess of $AgNO_3$. While in test tube (*B*) on adding KI to $AgNO_3$ solution in excess, AgI is precipitated and the common I^- ions are adsorbed from the excess of KI. Thus, test tube (*A*) has positively charged and test tube (*B*) has negatively charged AgI sol.

   (ii) It is the preferential adsoption of common ions of the electrolyte present in excess on the colloidal particles.

23. **(i)** Caring nature and social responsibility.
   (ii) Gas masks contain charcoal which is a good adsorbent and therefore adsorbs many poisonous gases.
   (iii) The nuisance of smoke in big industrial cities can be avoided by the use of Cottrell precipitator which allows smoke and many poisonous gases to get precipitated before coming out through the chimneys.
   (iv) The precipitation of colloidal impurities present in water can be done by adding certain electrolytes like alum, etc. Impurities get coagulated and settle down and pure water can be decanted off.

24. **(i)** (a) Precipitation is a process of aggregating together the colloidal particles so as to

change them into large sized particles which ultimately settle down as a precipitate under the force of gravity. It is generally brought about by the addition of electrolytes. When an el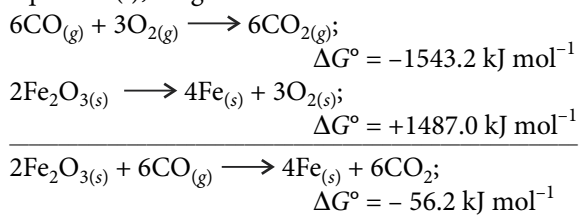ectrolyte is added to a colloidal solution, the particles of the sol adsorb the ions which are oppositely charged and thus get neutralised and start accumulating to form large sized particles.

   (b) When colloidal solutions are viewed under a powerful ultramicroscope, the colloidal particles appear to be in a state of continuous zig-zag motion all over the field of view. This motion is known as Brownian movement. Smaller the size and lesser the viscosity, faster is the motion of the particles. It is due to the unbalanced bombardment of the colloidal particles with the molecules of the dispersion medium. It is responsible for the stability of sols.

   (c) All the colloidal particles in a given sol carry the same charge and the dispersion medium has an opposite and equal charge; the system as a whole being electrically neutral. On placing a colloidal solution under the influence of an electric field, the particles of the dispersion medium move towards oppositely charged electrode, provided the colloidal particles are not allowed to move. This phenomenon is called electroosmosis.

(ii) (a) The path of light becomes visible when passed through the colloidal solution due the scattering of light by colloidal particles while it is not visible in case of true solution.

   (b) Applications of adsorption :
      1. Activated charcoal is used in gas masks to remove poisonous gases such as CH_4, CO, etc.
      2. Animal charcoal is used as decolouriser in the manufacture of sugar.
      3. Silica is used for removing moisture.
      4. The ion exchange resins are used for removing hardness of water.

OR

(i) (a) When a beam of light is passed through a colloidal sol, its path becomes clearly visible

(Tyndall effect). It is due to scattering of light by colloidal particles. The bright cone of the light is called Tyndall cone.

(b) When NaCl is added to hydrated ferric oxide sol coagulation takes place. Since ferric oxide is a positive sol, it is coagulated by the negative chloride ions.

(c) When electric current is passed through a colloidal sol, the colloidal particles move towards one or the other electrode. This is called electrophoresis. Since all the colloidal particles in a given colloidal solution carry the same charge, the particles move to one or the other electrode depending on the charge.

(ii) (a) **Micelles :** There are some substances which at low concentrations behave as normal, strong electrolytes but at higher concentrations exhibit colloidal behaviour due to the formation of aggregated particles. The aggregated particles thus formed are called micelles. The formation of micelles take place only above a particular temperature called Kraft temperature and above a particular concentration called Critical Micelle Concentration (CMC). Surface active agents such as soap and synthetic detergents belong to this class.
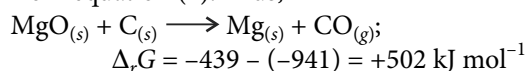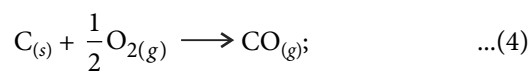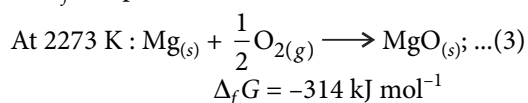
(b) **Emulsification :** An emulsion is prepared by shaking vigorously the mixture of two liquids. The emulsion thus obtained usually unstable therefore, certain substances such as gum, proteins, neutral and synthetic soaps called emulsifiers are added. The process of making an emulsion is known as emulsification.

25. (i) At 1273 K : $Mg_{(s)} + \dfrac{1}{2}O_{2(g)} \longrightarrow MgO_{(s)}$; ...(1)
$$\Delta_f G = -941 \text{ kJ mol}^{-1}$$

$$C_{(s)} + \dfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}; \qquad \qquad ...(2)$$
$$\Delta_f G = -439 \text{ kJ mol}^{-1}$$
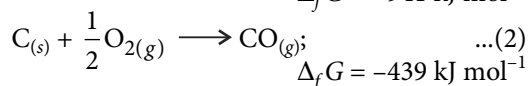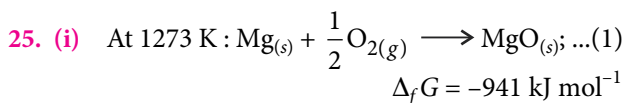
Redox reaction for reduction of $MgO_{(s)}$ by C can be obtained by subtracting equation (1) from equation (2). Thus,
$MgO_{(s)} + C_{(s)} \longrightarrow Mg_{(s)} + CO_{(g)}$;
$$\Delta_r G = -439 - (-941) = +502 \text{ kJ mol}^{-1}$$
As $\Delta_f G$ is positive, reaction is not feasible.

At 2273 K : $Mg_{(s)} + \dfrac{1}{2}O_{2(g)} \longrightarrow MgO_{(s)}$; ...(3)
$$\Delta_f G = -314 \text{ kJ mol}^{-1}$$

$$C_{(s)} + \dfrac{1}{2}O_{2(g)} \longrightarrow CO_{(g)}; \qquad \qquad ...(4)$$
$$\Delta_f G = -628 \text{ kJ mol}^{-1}$$

As above, the redox reaction for reduction of $MgO_{(s)}$ by $C_{(s)}$ is obtained by subtracting equation (3) from equation (4). Thus,
$MgO_{(s)} + C_{(s)} \longrightarrow Mg_{(s)} + CO_{(g)}$;
$$\Delta_r G = -628 - (-314) = -314 \text{ kJ mol}^{-1}$$
As $\Delta_r G$ for the reaction is negative, the reaction is feasible. Therefore, $C_{(s)}$ will reduce $MgO_{(s)}$ to $Mg_{(s)}$ at or above 2273 K.
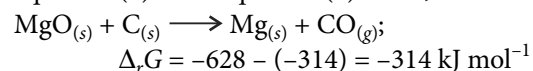
(ii) At 673 K (low temperature), the $\Delta G°$(CO, CO_2) line lies below $\Delta G°$(C, CO_2) line in the Ellingham diagram. Therefore, at 673 K, CO is a better reducing agent. On the other hand, at higher temperature, $\Delta G°$(C, CO_2) line lies below $\Delta G°$(CO, CO_2) line and hence at a higher temperature carbon is better reducing agent than CO.

OR

(i) (a) Pig iron is mixed with scrap iron and heated in a furnace. After removal of impurities, required quantity of spiegel is added to make steel.

(b) Zinc oxide is mixed with coke and clay and brickettes are made. The brickettes are heated at 1673 K to give metallic zinc.

$$ZnO_{(s)} + C_{(s)} \xrightarrow{\text{1673 K}} Zn_{(s)} + CO_{(g)}$$
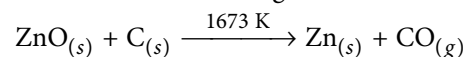
(c) Impure titanium is heated with iodine to form volatile complex TiI_4 which on further heating at higher temperature decomposes to give pure titanium.

$$\underset{\text{Impure}}{Ti_{(s)}} + 2I_{2(s)} \rightarrow TiI_4 \xrightarrow{\Delta} \underset{\text{Pure}}{Ti_{(s)}} + 2I_2$$
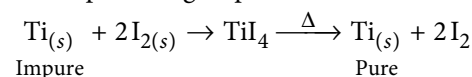
(ii) (a) The process of converting carbonate and hydroxide ores of metals to their respective oxides by heating them strongly below their melting points either in absence or limited supply of air is called calcination.

$$\underset{\text{Calamine}}{ZnCO_3} \xrightarrow{\text{Heat}} ZnO + CO_2\uparrow$$
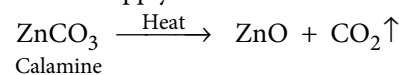
The process of converting a sulphide ore into its metallic oxide by heating strongly below its melting point in excess of air is called roasting.

$$\underset{\text{Zinc blende}}{2ZnS} + 3O_2 \rightarrow \underset{\text{Zinc oxide}}{2ZnO} + 2SO_2\uparrow$$
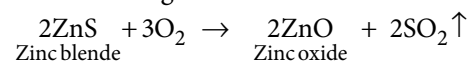
(b) The naturally occurring chemical substances in the form of which metals occur in the earth's crust alongwith impurities are called minerals.

The mineral from which the metal can be extracted conveniently and profitably is called an ore. *e.g.*, aluminium occurs in earth's crust in the form of two minerals, *i.e.*, bauxite ($Al_2O_3 \cdot xH_2O$) and clay ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$). Out of these two minerals, Al can be conveniently and economically extracted from bauxite. Therefore, bauxite is the ore of aluminium.

26. (i) (a) Greater the surface area of the solid available for adsorption per gram of adsorbent, greater would be its adsorbing power. That is why porous or finely divided forms of adsorbents adsorb more strongly.

(b) At constant temperature, the adsorption of a gas increases with increase of pressure. It is observed that at low temperature, the adsorption of a gas increases very rapidly as the pressure is increased from small values.

(c) Adsorption being exothermic decreases with increase in temperature. This is true for physical adsorption. However, in chemical adsorption the extent of adsorption first increases and then decreases with the increase in temperature.

(ii)

	Adsorption	Absorption
1.	It is a surface phenomenon. It takes place on the surface of adsorbent and not in the bulk of adsorbent.	It is a bulk phenomenon. The substance is distributed uniformly throughout the body of the material.
2.	The concentration of adsorbed substance (adsorbate) on the surface of adsorbent is higher than in the bulk.	The concentration is same throughout the material.

OR

(i) (a) **By reduction :** Silver sol is obtained by reduction of dilute silver chloride solution with stanous chloride.

$$2AgCl + SnCl_2 \longrightarrow 2Ag + SnCl_4$$
$$\text{(Silver sol)}$$
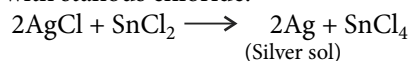
(b) **By oxidation :** Sulphur sol is obtained by passing H_2S gas through an oxidising agent like bromine water.

$$H_2S + Br_{2(aq)} \longrightarrow S + 2HBr$$
$$\text{(Sulphur sol)}$$
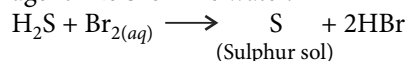
(ii)

	Physisorption	Chemisorption
1.	It arises due to van der Waals forces.	It is caused by chemical bond formation.
2.	It is not specific in nature.	It is highly specific in nature.
3.	It is reversible in nature.	It is irreversible.
4.	It does not require any activation energy.	It requires activation energy.

◈◈

Class XI-XII
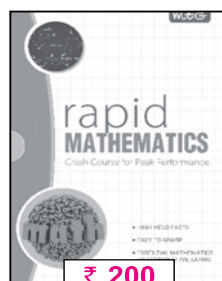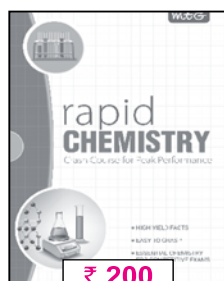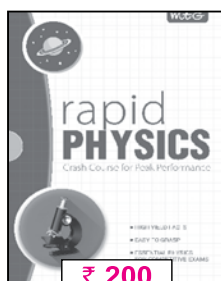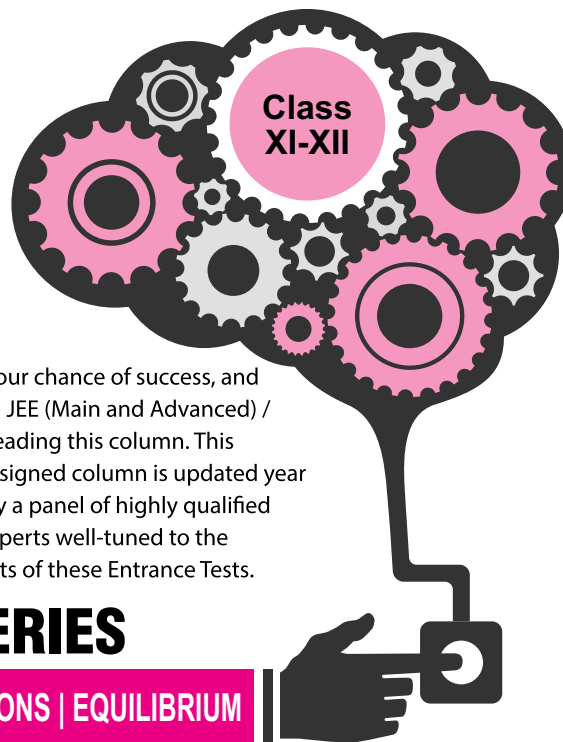
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Unit ❷ CHEMICAL THERMODYNAMICS | SOLUTIONS | EQUILIBRIUM

CHEMICAL THERMODYNAMICS

- Introduction
- Fundamentals of Thermodynamics
- First Law of Thermodynamics
- Second Law of Thermodynamics

TIPS TO REMEMBER

- ❑ *Thermodynamics* includes the study of all energy correlations and energy transformations, most commonly heat into work and *vice versa*.

- ❑ The branch of thermodynamics which deals with the study of chemical changes and chemical substances only is called *chemical thermodynamics*.

Fundamentals of Thermodynamics

- ❑ **System :** It is the part of universe under investigation where energy changes can be regulated and studied.

- ❑ **Surroundings :** Rest part of the universe which can interact with the system or can influence the properties of the system is called *surroundings*.

- ❑ **Boundary :** A real or imaginary surface that separates the system from the surroundings is known as *boundary*.
  - ○ A boundary can be rigid or non-rigid (movable), permeable or impermeable, adiabatic (non-conductor of heat) or diathermic (conductor of heat).

- ❑ **Types of system**
  - ○ *Open system :* A system which can exchange mass as well as energy with the surroundings.
  - ○ *Closed system :* A system which can exchange energy but not mass with the surroundings.
  - ○ *Isolated system :* A system which can neither exchange energy nor mass with the surroundings.

- ❑ **Extensive properties :** Properties which depend on the quantity of the matter contained in the system are called extensive properties. *e.g.*, mass, volume, enthalpy, internal energy, entropy, Gibbs free energy etc.

- ❑ **Intensive properties :** Properties which do not depend on the amount of the matter present in the system but on its nature are called intensive properties. *e.g.*, temperature, pressure, density, refractive index, equilibrium constant, molar entropy etc.

- ❑ **State functions :** Properties which are used to define a particular thermodynamic state and are independent of the path by which the state is attained are called state functions. *e.g.*, pressure, mass composition, volume, temperature, internal energy, entropy, Gibbs free energy etc.

- ❑ **Path functions :** Variables whose values depend upon the path followed by the system in attaining that state are known as path functions.

KEY POINT

- Extensive properties are additive while intensive properties are non-additive.
- An extensive property becomes an intensive property if defined for a definite value of another extensive property *e.g.*, molar volume.
- Ratio of two extensive properties is always intensive.

Types of Thermodynamic Processes

- **Isothermal process :** Temperature of the system remains constant ($\Delta T = 0$).

- **Isobaric process :** Pressure of the system remains constant ($\Delta P = 0$).

- **Isochoric process :** Volume of the system remains constant ($\Delta V = 0$).

- **Adiabatic process :** The system does not exchange heat with the surroundings ($q = 0$).
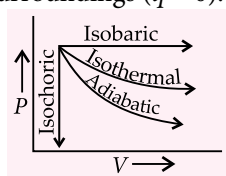
- **Reversible process :** Direction may be reversed at any stage.

- **Irreversible process :** Proceeds only in one direction and cannot be reversed.

- **Cyclic process :** System returns to its original state after a number of steps. For such a process $\Delta U = 0$ and $\Delta H = 0$.

- **Exothermic process :** Accompanied by the evolution of heat.

- **Endothermic process :** Accompanied by the absorption of heat.

First Law of Thermodynamics

Work and heat are the two important ways by which a system can exchange energy with the surroundings.

- **Heat :** It is the mode of transfer of energy due to difference in temperature during a non-mechanical process.
  - Heat evolved or absorbed, $\Delta q = ms\Delta t$
    where, m is the mass of substance, s is the specific heat and Δt is the temperature difference.
  - q is +ve when heat is absorbed by the system and –ve when heat is evolved from the system.

- **Work :** It is another mode of transfer of energy which is expressed as product of two factors, intensity factor (measures driving force responsible for the process) and capacity factor (extent to which process occurs).

  - *Different forms of work :*

    Work
    - → Expansion work ($-P\Delta V$)
    - → Mechanical work ($F \times d$)
    - → Gravitational work (mgh)
    - → Electrical work (nFE)
    - → Extension work ($T \times \Delta l$)
      where, T = tension; Δl = change in length
    - → Surface expansion work ($\gamma \times \Delta A$)
      where, γ = surface tension;
      ΔA = change in area
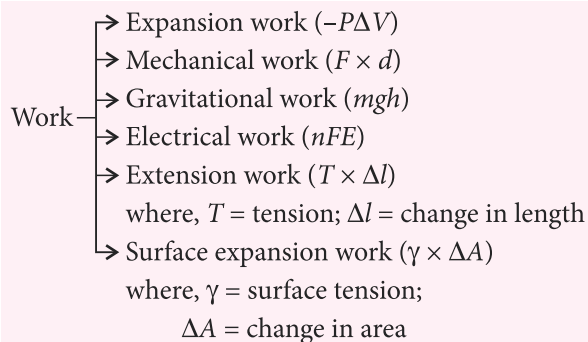
  - Work done on the system is +ve while the work done by the system is –ve.

  - Work done against constant external pressure (isothermal irreversible expansion),
    $w = - p_{ext} \Delta V$

  - Work done in an isothermal reversible expansion or compression of an ideal gas,
    $$w = -2.303 \, nRT \log \frac{V_2}{V_1}$$

SELF CHECK

1. A piston filled with 0.04 mol of an ideal gas expands reversibly from 50.0 mL to 375 mL at a constant temperature of 37.0°C. As it does so, it absorbs 208 J of heat. The values of q and w for the process will be (R = 8.314 J/mol K) (ln 7.5 = 2.01)
   (a) $q = + 208$ J, $w = + 208$ J
   (b) $q = + 208$ J, $w = - 208$ J
   (c) $q = - 208$ J, $w = - 208$ J
   (d) $q = - 208$ J, $w = + 208$ J   (JEE Main 2013)

- **Internal energy :** It is the sum of different forms of energy stored in atoms or molecules.
  $$U = E_{trans} + E_{rot} + E_{vib} + E_{bonding} + E_{electronic} + E_{nuclear}$$

  - $\Delta U = U_2 - U_1$, ΔU is + ve when $U_2 > U_1$ and –ve when $U_1 > U_2$

  - For a cyclic process, $\Delta U = 0$.

  - $\Delta U = q_v$, at constant volume.

- ΔU is calculated in a bomb calorimeter using the relation,

  $\Delta U = Q \times \Delta t \times \dfrac{M}{m}$ where, Q is the heat capacity of the calorimeter, Δt is rise in temperature, m is the mass of the substance taken and M is the molecular mass of the substance.

- **First law of thermodynamics** (proposed by Helmholtz) is the most general statement for the law of conservation of energy.

  According to this law :

  - Energy can neither be created nor destroyed however, may be transformed from one form into other.

  - The total mass and energy of an isolated system remain constant.

  - Whenever an energy of a particular type appears, equivalent amount of other type of energy disappears.

  - Mathematically, if q amount of heat is supplied to the system and w amount of work is done on the system then

    $\Delta U = q + w$

- **Enthalpy :** It is the total heat content within the body which is available for conversion at constant pressure.

  $\Delta H = \Delta U + P\Delta V$

  $\Delta H = q_p$, at constant pressure

  - In case of solids and liquids participating in a reaction, $\Delta H \approx \Delta U$ as $P\Delta V \approx 0$.

  - In case of gases, $\Delta H = \Delta U + \Delta nRT$

    where, $\Delta n = n_{g\,(\text{products})} - n_{g\,(\text{reactants})}$.

✓ SELF CHECK

2. For complete combustion of ethanol,

   $C_2H_5OH_{(l)} + 3O_{2(g)} \longrightarrow 2CO_{2(g)} + 3H_2O_{(l)}$,

   the amount of heat produced as measured in bomb calorimeter, is 1364.47 kJ mol^{-1} at 25 °C. Assuming ideality the enthalpy of combustion, $\Delta_c H$, for the reaction will be ($R = 8.314$ J K^{-1} mol^{-1})

   (a) – 1350.50 kJ mol^{-1} (b) – 1366.95 kJ mol^{-1}
   (c) – 1361.95 kJ mol^{-1} (d) – 1460.50 kJ mol^{-1}

   (JEE Main 2014)

Heat Capacity, Specific Heat Capacity and Molar Heat Capacity

- Heat capacity, $C = \dfrac{q}{\Delta T}$ where, q is the energy given as heat and ΔT is the change in temperature.

- *Heat capacity at constant volume,*

  $C_v = \left(\dfrac{dq}{dT}\right)_v = \left(\dfrac{dU}{dT}\right)_v$

- *Heat capacity at constant pressure,*

  $C_p = \left(\dfrac{dq}{dT}\right)_p = \left(\dfrac{dH}{dT}\right)_p$

- Specific heat capacity, $C_s = \dfrac{C}{m}$ in J K^{-1} g^{-1}

- Molar heat capacity, $C_m = \dfrac{C}{n}$ in J K^{-1} mol^{-1}

- **Relation between C_p and C_v :**

Nature of the gas	Monatomic (He, Ar)	Diatomic (H_2, O_2, CO)	Triatomic (CO_2, H_2S)
$\gamma = \dfrac{C_p}{C_v}$	$\dfrac{(5/2)R}{(3/2)R}$ $=\dfrac{5}{3}=1.66$	$\dfrac{(7/2)R}{(5/2)R}$ $=\dfrac{7}{5}=1.40$	$\dfrac{4R}{3R}$ $=\dfrac{4}{3}=1.33$

Hess's Law of Constant Heat Summation

- The total amount of heat change in a chemical reaction is same whether the reaction takes place in one step or in number of steps.

  - The total amount of heat change in a reaction depends only upon the nature of the initial reactants and final products and is independent of the path by which this change is brought about.

  $Q = q_1 + q_2 + q_3$
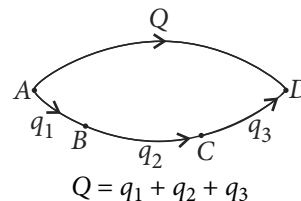
- **Applications of Hess's law :** The most important application of Hess's law is in the calculation of heat changes for those reactions for which experimental determination is not possible.

  - The thermochemical equations can be treated as algebraic equations which can be added, subtracted, multiplied or divided.

Different Types of Enthalpies of Reactions

- **Enthalpy of reaction ($\Delta_r H$) :** It is a general term used for the heat change (enthalpy change) accompanying any reaction.

  - Amount of heat change when the number of moles of reactants given in a balanced chemical

equation have completely reacted to give the products is known as enthalpy of reaction,

$$\Delta_r H = \Sigma a_i H_{(products)} - \Sigma b_i H_{(reactants)}$$

where, a_i and b_i represent the coefficients of the products and reactants respectively.

Depending upon the nature of the reaction, the enthalpy of reaction is named accordingly :

○ *Enthalpy of formation ($\Delta_f H$) :* It is the amount of heat change when one mole of the substance is formed from its elements in their most stable form.

○ *Enthalpy of combustion ($\Delta_c H$) :* It is the amount of heat change (usually the heat evolved) during the complete combustion of one mole of substance in the presence of oxygen or in excess of air.

○ *Enthalpy of dissolution ($\Delta_{diss} H$) :* It is the amount of heat change when one mole of substance is dissolved in excess of solvent.

○ *Enthalpy of hydration ($\Delta_{hyd} H$) :* It is the amount of heat change when one mole of anhydrous substance combines with the required number of moles of water to convert into hydrated compound.

○ *Enthalpy of phase transitions :*
— *Enthalpy of fusion ($\Delta_{fus} H$) :* It is the amount of heat required to change one mole of a solid substance completely into its liquid state at its melting point.
— *Enthalpy of vaporisation ($\Delta_{vap} H$) :* It is the amount of heat required to change one mole of a liquid substance into its vapour state at its boiling point.
— *Enthalpy of sublimation ($\Delta_{sub} H$) :* It is the amount of heat required to change one mole of a solid substance directly into its vapour form at a given temperature below its melting point.

○ *Enthalpy of neutralisation ($\Delta_{neut} H$) :* It is the amount of heat change (usually the heat released) when one gram equivalent of an acid is completely neutralised by one gram equivalent of a base in a dilute solution.

○ *Enthalpy of transition :* It is the enthalpy change when one mole of substance undergoes transition from one allotropic form to another.

○ *Enthalpy of solution ($\Delta_{sol} H$) :* It is the enthalpy change when one mole of the substance is dissolved in a specified amount of the solvent.

$$\Delta_{sol} H = \Delta_{lattice} H + \Delta_{hyd} H$$

— $\Delta_{lattice} H$ is calculated using Born–Haber cycle,

$$\Delta_f H = \Delta_{sub} H + IE + \frac{1}{2}\Delta_d H + \Delta_{eg} H + \Delta_{lattice} H$$

where, $\Delta_f H$ = Enthalpy of formation,
$\Delta_{sub} H$ = Enthalpy of sublimation,
IE = Ionisation energy,
$\Delta_d H$ = Enthalpy of dissociation,
$\Delta_{eg} H$ = Electron gain enthalpy
and $\Delta_{lattice} H$ = Lattice energy.

❑ **Bond energy :** It is the amount of energy required to break one mole of bonds present between the atoms in the gaseous molecules.

$$\Delta_r H = \Sigma B.E._{(reactants)} - \Sigma B.E._{(products)}$$

✓ **SELF** CHECK

3. Using the data provided, calculate the multiple bond energy (kJ mol^{-1}) of a C≡C bond in C_2H_2. That energy is (take the bond energy of a C—H bond as 350 kJ mol^{-1}).

$2C_{(s)} + H_{2(g)} \longrightarrow C_2H_{2(g)}$; $\Delta H = 225$ kJ mol^{-1}
$2C_{(s)} \longrightarrow 2C_{(g)}$; $\Delta H = 1410$ kJ mol^{-1}
$H_{2(g)} \longrightarrow 2H_{(g)}$; $\Delta H = 330$ kJ mol^{-1}

(a) 1165   (b) 837
(c) 865   (d) 815   (IIT-JEE 2012)

🗨 **KEY** POINT

• The heat of neutralisation is taken for 1 gram equivalent of the acid and base. This is because neutralisation involves combination of 1 mol of H$^+$ ions with 1 mol of OH$^-$ ions to form one mol of H$_2$O.

• One gram equivalent of any acid on complete dissociation gives 1 mol of H$^+$ ions but 1 mol of an acid on dissociation may not give 1 mol of H$^+$ ions.

❑ **Kirchhoff's Equation :** Variation of heat of reaction with temperature

○ at constant pressure,

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = C_{p(products)} - C_{p(reactants)}$$

○ at constant volume,

$$\frac{\Delta U_2 - \Delta U_1}{T_2 - T_1} = C_{v(\text{products})} - C_{v(\text{reactants})}$$

❑ **Clausius–Clapeyron Equation**

$$\log \frac{P_2}{P_1} = \frac{\Delta H_v}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)$$

here, ΔH_v = molar heat of vaporisation

Second Law of Thermodynamics

❑ **Spontaneous process :** A process which under some given conditions may take place by itself or by initiation independent of the rate.

❑ **Non-spontaneous process :** A process which does not have any natural tendency to occur.

❑ **Entropy :** It is the measure of degree of disorder or randomness of the system. $S_{\text{gas}} > S_{\text{liquid}} > S_{\text{solid}}$

○ Change in entropy,

$$\Delta S = \Sigma S_{(\text{products})} - \Sigma S_{(\text{reactants})}$$

$$\Delta S = \frac{q_{rev}}{T}$$

○ **Entropy changes during phase transformations :** It is the change in entropy when one mole of a substance changes into its another form at a particular temperature.

$$\Delta S_{\text{total}} = \Delta S_{\text{system}} + \Delta S_{\text{surroundings}}$$

$$\Delta_{\text{fus}}S = \frac{\Delta_{\text{fus}}H}{T_m}, \ \Delta_{\text{vap}}S = \frac{\Delta_{\text{vap}}H}{T_b}, \ \Delta_{\text{sub}}S = \frac{\Delta_{\text{sub}}H}{T}$$

○ **Entropy changes for various types of processes :**

Process	ΔS
Isothermal reversible expansion of an ideal gas	$nR\ln\left(\dfrac{V_2}{V_1}\right)$
Adiabatic reversible expansion	0 as $q = 0$ (isoentropic)
Adiabatic free expansion	$\neq 0$
Isobaric process	$C_p \ln\dfrac{T_2}{T_1}$
Isochoric process	$C_v \ln\dfrac{T_2}{T_1}$

❑ Second law of thermodynamics states that the entropy of the universe is continuously increasing

or heat cannot flow on its own from colder to hotter region.

○ For a reversible process, $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} = 0$

○ For an irreversible process, $\Delta S_{\text{sys}} + \Delta S_{\text{surr}} > 0$

✓ SELF CHECK

4. For the process :

$$H_2O_{(l)} \rightarrow H_2O_{(g)}$$
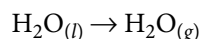
at $T = 100°C$ and 1 atmosphere pressure, the correct choice is

(a) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} > 0$

(b) $\Delta S_{\text{system}} > 0$ and $\Delta S_{\text{surroundings}} < 0$

(c) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} > 0$

(d) $\Delta S_{\text{system}} < 0$ and $\Delta S_{\text{surroundings}} < 0$

(JEE Advanced 2014)

🖐 KEY POINT

- For molecules having nearly same molecular mass and nearly same heat capacity, a *more symmetrical molecule has lower entropy than less symmetrical.*

- Those solids in which structure is composed of *single simple unit have lesser entropy than the solids having complex structural unit.*

- During stretching of a rubber band, *entropy decreases* due to uncoiling of macromolecules to arrange in more ordered manner and during boiling of egg, *entropy increases* due to denaturation of proteins from helical form into random coiled structure.

- The entropies of liquids or solids are *not much affected* by change in pressure because volume of condensed material is not much changed with pressure and spatial distribution remains almost same.

❑ **Gibbs free energy :** It is the maximum amount of energy available to system to convert into useful work during the process.

○ $G = H - TS$

○ $\Delta G = \Delta H - T\Delta S$ (Gibbs–Helmholtz equation)

○ $\Delta G° = -nFE°$

○ $\Delta G° = \Sigma G^°_{f(\text{products})} - \Sigma G^°_{f(\text{reactants})}$

○ $\Delta G° = -2.303 \ RT \log K_{eq}$

❑ **Gibbs free energy and spontaneity :**

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$	Reaction characteristic	Example
–	+	Always –ve	Spontaneous at all temperatures	$2O_{3(g)} \longrightarrow 3O_{2(g)}$
+	–	Always +ve	Non-spontaneous at all temperatures	$3O_{2(g)} \longrightarrow 2O_{3(g)}$
–	–	–ve at low temperature and +ve at high temperature	Spontaneous at low temperature Non-spontaneous at high temperature	$CaO_{(s)} + CO_{2(g)} \longrightarrow CaCO_{3(s)}$
+	+	+ve at low temperature and –ve at high temperature	Non-spontaneous at low temperature Spontaneous at high temperature	$CaCO_{3(s)} \longrightarrow CaO_{(s)} + CO_{2(g)}$

Third Law of Thermodynamics

❑ At absolute zero temperature, the entropy of a perfectly crystalline substance is taken as zero.

❑ For solid at temperature, T K

$$\Delta S = S_{T\,K} - S_{0\,K} = \int_0^T \frac{C_p\,dT}{T} = \int_0^T C_p\,d\ln T$$

From third law of thermodynamics, $S_{0\,K} = 0$

$S_T = C_p \ln T = 2.303\, C_p \log T$

For liquids and gases, the absolute entropy at a given temperature T is given by the expression,

$$S = \int_0^{T_f} \frac{C_{p(s)}\,dT}{T} + \frac{\Delta H_f}{T_f} + \int_{T_f}^{T_b} \frac{C_{p(l)}\,dT}{T} + \frac{\Delta H_{vap}}{T_b}$$
$$+ \int_{T_b}^{T} \frac{C_{p(g)}\,dT}{T}$$

SOLUTIONS

- Introduction
- Different Methods for Expressing Concentration of Solution
- Vapour Pressure of Solutions and Raoult's Law
- Ideal and Non-ideal Solutions
- Colligative Properties
- Abnormal Molecular Mass and van't Hoff Factor

TIPS TO REMEMBER

❑ **Solution :** A perfectly homogeneous mixture (having number of phases equal to one) of two or more components is called solution.

❑ **Solute :** The component which is present in lesser amount or whose physical state is changed during the formation of solution is called solute.

❑ **Solvent :** The component which is present in larger amount and determines the physical state of the solution is called solvent.

Types of Solutions

- On the basis of number of components
- On the basis of physical state of solute and solvent

Binary (Having two components)
Ternary (Having three components)
Quaternary (Having four components)

Types of binary solutions = $3^2 = 9$
Types of ternary solutions = $3^3 = 27$
Types of quaternary solutions = $3^4 = 81$
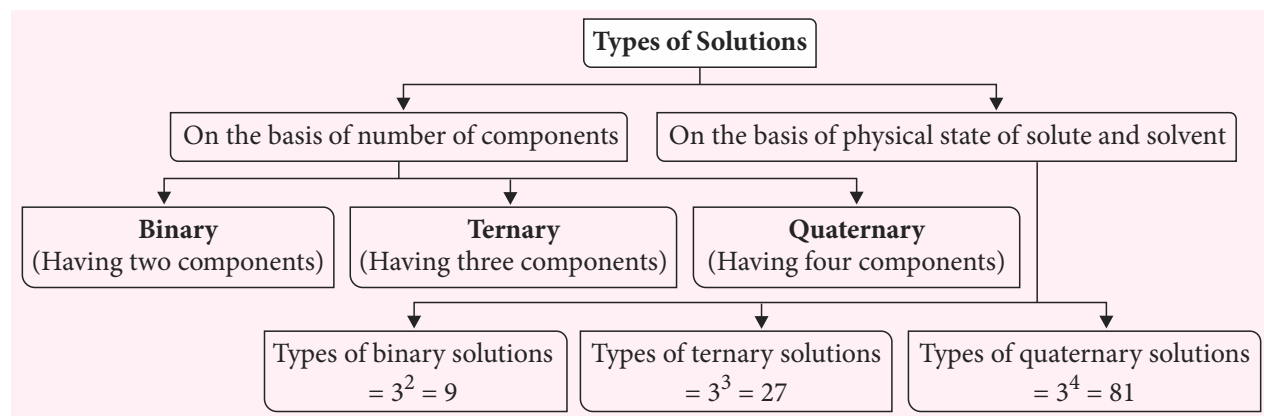
Different Types of Binary Solutions

S.No.	Solute	Solvent	Example
1.	Solid	Solid	Alloy
2.	Solid	Liquid	Sugar solution in water
3.	Solid	Gas	Iodine vapours in air
4.	Liquid	Solid	Hydrated salt
5.	Liquid	Liquid	Ethanol in water
6.	Liquid	Gas	Water vapours in air
7.	Gas	Solid	Dissolved gases in minerals
8.	Gas	Liquid	Aerated drinks
9.	Gas	Gas	Air

□ A solution in which more of the solute can be dissolved at a given temperature is called *unsaturated solution* and a solution in which no more solute can be dissolved is called *saturated solution* while the solution in which amount of solute is more than it can dissolve at a particular temperature is called *supersaturated solution*.

Different Methods for Expressing Concentration of Solution

S. No.	Method of expressing	Formula
1.	Mass percentage, $\left(\dfrac{w}{W}\right)\%$	$\dfrac{w_2}{(w_1+w_2)}\times 100$
2.	Volume percentage, $\left(\dfrac{v}{V}\right)\%$	$\dfrac{V_2}{(V_1+V_2)}\times 100$
3.	Mass by volume percentage, $\left(\dfrac{w}{V}\right)\%$	$\dfrac{w_2}{V_{\text{solution(in mL)}}}\times 100$
4.	Mass fraction, $\left(\dfrac{w}{W_{\text{total}}}\right)$	$x_1=\dfrac{w_1}{w_1+w_2}$ or $x_2=\dfrac{w_2}{w_1+w_2}$
5.	Strength (g L^{-1})	$\dfrac{w_{2\text{(in g)}}}{V_{\text{solution (in mL)}}}\times 1000$
6.	Parts per million (ppm)	$\dfrac{w_2}{(w_1+w_2)}\times 10^6$
7.	Molarity, (M) (mol L^{-1})	$\dfrac{w_2\times 1000}{M_2\times V_{\text{solution(in mL)}}}$
8.	Normality, (N) (g-eq L^{-1})	$\dfrac{w_2\times 1000}{(\text{Eq. wt.})_{\text{solute}}\times V_{\text{solution(in mL)}}}$
9.	Molality, (m) (mol kg^{-1})	$\dfrac{w_2\times 1000}{M_2\times w_{1\text{(in g)}}}$
10.	Mole fraction, (x)	$x_1=\dfrac{n_1}{n_1+n_2}$ or $x_2=\dfrac{n_2}{n_1+n_2}$, $(x_1+x_2=1)$ In case of gases only $y_1=\dfrac{p_1}{p_1+p_2}$ or $y_2=\dfrac{p_2}{p_1+p_2}$, $(y_1+y_2=1)$
11.	Formality, (F)	$\dfrac{\text{No. of gram formula mass of solute}}{\text{Volume of solution in litre}}$
12.	Demal, (D)	$\dfrac{w_2\times 1000}{M_2\times V_{\text{solution(in mL)}}}$ (at 0°C)

□ Mathematical relationships between commonly used concentration methods :

S. No.	Concentration terms	Relationship/Formula
1.	Molality (m) and molarity (M)	$m=\left(\dfrac{M}{1000d_{\text{(in g mL}^{-1})}-M\cdot M_{2\text{(in g mol}^{-1})}}\right)\times 1000$
2.	Molality (m) and mole fraction (x_2)	$x_2=\dfrac{m\cdot M_{1\text{(in g mol}^{-1})}}{1000+m\cdot M_{1\text{(in g mol}^{-1})}}$
3.	Molarity (M) and mole fraction (x_2)	$x_2=\dfrac{M\cdot M_{1\text{(in g mol}^{-1})}}{M\left(M_{1\text{(in g mol}^{-1})}-M_{2\text{(in g mol}^{-1})}\right)+1000d_{\text{(in g mL}^{-1})}}$
4.	Normality (N) and molarity (M)	$N=n\times M$
5.	Volume and normality	$N_1V_1=N_2V_2$ (For dilution or reaction between two reactants)
6.	Volume and molarity	$M_1V_1=M_2V_2$ (For dilution)

✓ **SELF** CHECK

5. The density of a solution prepared by dissolving 120 g of urea (mol. mass = 60 u) in 1000 g of water is 1.15 g/mL. The molarity of this solution is
   (a) 1.78 M   (b) 1.02 M
   (c) 2.05 M   (d) 0.50 M   (AIEEE 2012)

KEY POINT

- When V_a mL of acid of normality N_a is mixed with V_b mL of base of normality N_b, then,
  if $V_aN_a = V_bN_b$, solution is neutral.
  if $V_aN_a > V_bN_b$; solution is acidic.
  if $V_aN_a < V_bN_b$; solution is basic.

- Normality of acidic mixture = $\dfrac{V_aN_a - V_bN_b}{(V_a + V_b)}$

- Normality of basic mixture = $\dfrac{V_bN_b - V_aN_a}{(V_a + V_b)}$

- $\dfrac{M_1V_1}{n_1} = \dfrac{M_2V_2}{n_2}$ (For reaction between two reactants)
  where, n_1 and n_2 are their stoichiometric coefficients in the balanced equation

- On mixing two non-reacting solutions,
  $N_1V_1 + N_2V_2 = N_3V_3$
  $M_1V_1 + M_2V_2 = M_3(V_1 + V_2)$

Vapour Pressure of Solutions and Raoult's Law

❑ Pressure exerted by the vapours over the solution when it is in equilibrium state at a given temperature is called *vapour pressure of the solution*.

❑ **Factors affecting vapour pressure :**
   ○ Vapour pressure is related to the temperature of the liquid by Clausius–Clapeyron equation :

   $$\log \frac{P_2}{P_1} = \frac{\Delta_{vap}H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

   where P_1 and P_2 are the vapour pressures at temperatures T_1 and T_2 respectively.
   ○ Liquids having weak cohesive forces are more volatile and have higher vapour pressure at a given temperature.
   ○ Higher the boiling point of a liquid, lesser is its vapour pressure at a given temperature.

○ Vapour pressure of the solution at a given temperature is generally lower than the vapour pressure of the pure solvent at the same temperature.
   — In the solution, the surface has both solute and solvent molecules, thereby the fraction of the surface covered by the solvent molecules gets reduced. Consequently, the number of solvent molecules escaping from the surface is correspondingly reduced, thus, the vapour pressure is also reduced.

○ If the solute is volatile, the vapour pressure of solution depends upon the escaping tendency of the solute molecules from the surface of the solution.

○ If the solute is non-volatile, then the vapour pressure of solution decreases because of the decrease in escaping tendency of solvent molecules from the surface.

❑ **Raoult's law for liquid-liquid solutions :** It states that for a solution of volatile liquids, the partial vapour pressure of each component of the solution is directly proportional to its mole fraction in the solution.
   For component 1, $p_1 = p_1^\circ x_1$
   For component 2, $p_2 = p_2^\circ x_2$
   $$P_{\text{total}} = p_1 + p_2 = x_1p_1^\circ + x_2p_2^\circ$$
   $$= p_1^\circ + (p_2^\circ - p_1^\circ)x_2$$
   where p_1° and p_2° are the vapour pressures of pure components 1 and 2 respectively.
   Mole fraction of components 1 and 2 in the vapour phase when both the components are volatile,

   $$x_1 = \frac{p_1}{P_{\text{total}}} \text{ and } x_2 = \frac{p_2}{P_{\text{total}}}$$

❑ **Raoult's law for solid-liquid solutions :** It states that relative lowering in vapour pressure of a solution containing a non-volatile solute is equal to the mole fraction of the solute.
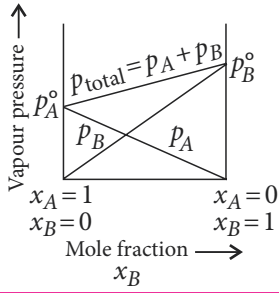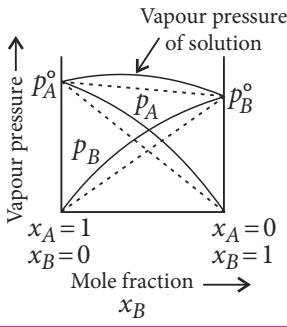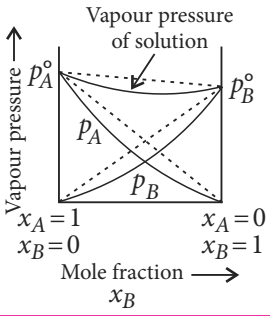
   $$\frac{p^\circ - p_s}{p^\circ} = x_2$$

   where, p° = vapour pressure of pure solvent
   p_s = vapour pressure of solution
   x_2 = mole fraction of solute

Ideal and Non-ideal Solutions

Ideal solutions	Non-ideal solutions	
	Positive deviation from Raoult's law	Negative deviation from Raoult's law
$A - B$ interactions $\approx A - A$ and $B - B$ interactions	$A - B$ interactions $<< A - A$ and $B - B$ interactions	$A - B$ interactions $>> A - A$ and $B - B$ interactions
$\Delta H_{mix} = 0$, $\Delta V_{mix} = 0$	$\Delta H_{mix} > 0$, $\Delta V_{mix} > 0$	$\Delta H_{mix} < 0$, $\Delta V_{mix} < 0$
e.g., dilute solution, benzene + toluene, *n*-hexane + *n*-heptane	*e.g.*, acetone + ethanol, acetone + CS_2, water + methanol	*e.g.*, acetone + aniline, acetone + chloroform, $CH_3OH + CH_3COOH$
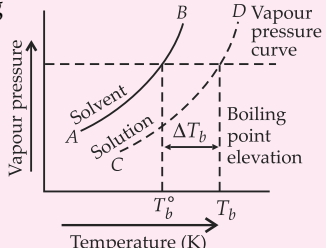
- ❑ **Azeotropes :** The mixtures of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as vapour phase are called *constant boiling mixtures* or *azeotropic mixtures*.

  - ○ *Minimum boiling azeotropes* are formed by those liquid pairs which show positive deviations from ideal behaviour *e.g.*, ethanol-water mixture.

  - ○ *Maximum boiling azeotropes* are formed by those liquid pairs which show negative deviations from ideal behaviour *e.g.*, nitric acid-water mixture.

Colligative Properties

- ❑ Properties which depend only on the number of solute particles dissolved in a definite amount of the solvent and not on the nature of the solute are called *colligative properties*.

Colligative properties	Expression
Relative lowering of vapour pressure : When a non-volatile solute is dissolved in a solvent, vapour pressure of the solution is lower than that of the pure solvent which is known as *lowering of vapour pressure*. Relative lowering of vapour pressure is equal to the mole fraction of the solute in the solution.	$\dfrac{p_1^{\circ} - p_1}{p_1^{\circ}} = x_2 = \dfrac{n_2}{n_1 + n_2}$ $= \dfrac{n_2}{n_1} = \dfrac{w_2 \times M_1}{M_2 \times w_1}$ ($\because$ for dilute solutions, $n_2 << n_1$)
Elevation in boiling point : The boiling point of a solution containing a non-volatile solute is always higher than the boiling point of the pure solvent. This increase in boiling point is termed as elevation in boiling point.	$\Delta T_b = T_b - T_b^{\circ}$ $\Delta T_b \propto m$ or $\Delta T_b = K_b\, m$ $= K_b \left(\dfrac{w_2 \times 1000}{M_2 \times w_{1(\text{in g})}} \right)$ or $M_2 = \dfrac{K_b \times w_2 \times 1000}{\Delta T_b \times w_{1(\text{in g})}}$ K_b is called boiling point elevation constant or molal elevation constant or Ebullioscopic constant, having unit K kg mol^{-1}.

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Depression in freezing point :

The freezing point of a solution containing a non-volatile solute is always less than the freezing point of the pure solvent. This decrease in freezing point is termed as depression in freezing point.

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$\Delta T_f = T_f^\circ - T_f$

$\Delta T_f \propto m$ or $\Delta T_f = K_f m$

$$= K_f \left(\frac{w_2 \times 1000}{M_2 \times w_{1\,(\text{in g})}} \right)$$

or $M_2 = \dfrac{K_f \times w_2 \times 1000}{\Delta T_f \times w_{1(\text{in g})}}$

K_f is known as freezing point depression constant or molal depression constant or Cryoscopic constant, having unit K kg mol^{-1}.

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Osmosis and osmotic pressure : When a solution is separated from the pure solvent with the help of a semipermeable membrane, the solvent molecules from the pure solvent move towards the solution. The movement of solvent molecules from less concentrated solution to more concentrated solution through semipermeable membrane is termed as osmosis. The hydrostatic pressure which develops on account of osmosis is called osmotic pressure or the excess pressure that must be applied on the solution to prevent osmosis is called osmotic pressure.

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$\pi = CRT = \left(\dfrac{n_2}{V} \right) RT$,

$\pi V = \dfrac{w_2 RT}{M_2}$

or $M_2 = \dfrac{w_2 RT}{\pi V}$

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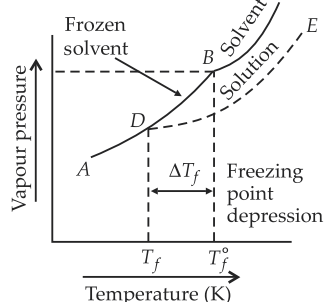
Abnormal Molecular Mass

❑ When the molecular mass of a substance determined by any of the colligative properties comes out to be different than the expected value, the substance is said to show abnormal molecular mass.

❑ Abnormal molecular masses are observed when the solution is non-ideal (not dilute) or the solute undergoes association or dissociation.

van't Hoff Factor

❑ It is defined as the ratio of the experimental value of the colligative property to the calculated value of the colligative property.

$i = \dfrac{\text{Observed value of the colligative property}}{\text{Calculated value of the colligative property}}$

$i = \dfrac{\text{Calculated molecular mass}}{\text{Observed molecular mass}}$

$i = \dfrac{\text{Total number of moles of particles after association / dissociation}}{\text{Total number of moles of particles before association / dissociation}}$

○ If $i > 1$, solute undergoes dissociation in the solution and if $i < 1$, solute undergoes association in the solution.

$\alpha_{\text{dissociation}} = \dfrac{i - 1}{n - 1}$

$\alpha_{\text{association}} = \dfrac{1 - i}{1 - \dfrac{1}{n}}$

○ For substances undergoing association or dissociation in the solution, the various expressions for the colligative properties are modified as follows :

$\dfrac{p_1^\circ - p_1}{p_1^\circ} = i x_2$; $\Delta T_b = i K_b m$; $\Delta T_f = i K_f m$; $\pi = iCRT$

✓ **SELF** CHECK

6. The vapour pressure of acetone at 20°C is 185 torr. When 1.2 g of a non-volatile substance was dissolved in 100 g of acetone at 20°C, its vapour pressure was 183 torr. The molar mass (g mol^{-1}) of the substance is
(a) 128   (b) 488
(c) 32   (d) 64   (JEE Main 2015)

7. Consider separate solutions of 0.500 M $C_2H_5OH_{(aq)}$, 0.100 M $Mg_3(PO_4)_{2(aq)}$, 0.250 M $KBr_{(aq)}$ and 0.125 M $Na_3PO_{4(aq)}$ at 25°C. Which statement is true about these solutions, assuming all salts to be strong electrolytes?
(a) 0.500 M $C_2H_5OH_{(aq)}$ has the highest osmotic pressure.
(b) They all have the same osmotic pressure.
(c) 0.100 M $Mg_3(PO_4)_{2(aq)}$ has the highest osmotic pressure.
(d) 0.125 M $Na_3PO_{4(aq)}$ has the highest osmotic pressure.   (JEE Main 2014)

8. For a dilute solution containing 2.5 g of a non-volatile non-electrolyte solution in 100 g of water, the elevation in boiling point at 1 atm pressure is 2°C. Assuming concentration of solute is much lower than the concentration of solvent, the vapour pressure (mm of Hg) of the solution is (take $K_b = 0.76$ K kg mol^{-1})
   (a) 724   (b) 740
   (c) 736   (d) 718   (IIT-JEE 2012)

9. The freezing point (in °C) of a solution containing 0.1 g of $K_3[Fe(CN)_6]$ (mol. wt. = 329) in 100 g of water ($K_f = 1.86$ K kg mol^{-1}) is
   (a) -2.3×10^{-2} (b) -5.7×10^{-2}
   (c) -5.7×10^{-3} (d) -1.2×10^{-2}
                                 (IIT-JEE 2011)

🛈 KEY POINT

- Different solutions having same vapour pressure are called *isopiestic solutions*.
- Different solutions having same osmotic pressure at same temperature are called *isotonic solutions*.
- When osmotic pressures of two solutions are compared at same temperature, the solution whose osmotic pressure is less, is called *hypotonic solution* while that with higher osmotic pressure is called *hypertonic solution*.
- If pressure higher than the osmotic pressure is applied on the solution, the solvent molecules will flow in reverse direction. This process is called *reverse osmosis* and is used in desalination of water.
- Association generally occurs in the non-aqueous solution because in the aqueous solution, the high dielectric constant of water helps in the dissociation of the associated molecules.

EQUILIBRIUM

- Introduction
- Equilibria Involving Physical Processes
- Equilibria Involving Chemical Processes
- Ionic Equilibrium

TIPS TO REMEMBER

- **Equilibrium :** It is the state attained by a system in which the system has no tendency for a change without external stimulation and hence, no net change occurs.

Equilibria Involving Physical Processes

- **Physical equilibrium :** Equilibrium attained between different physical forms of a chemical entity.
  - **Types of equilibrium :**
    — Solid-Liquid equilibrium :
    $$\text{Ice} \rightleftharpoons \text{Water}$$
    — Liquid-Gas equilibrium :
    $$H_2O_{(l)} \rightleftharpoons H_2O_{(g)}$$
    — Solid-Gas equilibrium :
    $$I_{2(s)} \rightleftharpoons I_{2(g)}$$
    — Solid-Solution equilibrium :
    $$\text{Sugar}_{(s)} \rightleftharpoons \text{Sugar}_{(solution)}$$
    — Gas-Solution equilibrium :
    $$O_{2(g)} \rightleftharpoons O_{2(aq)}$$
  - **Henry's law** states that "the partial pressure of the gas in vapour phase (p) is proportional to the mole fraction of the gas (x) in the solution". $p = K_H x$ where, K_H is the Henry's law constant and is different for different gases at a particular temperature.
    — Higher the value of K_H at a given pressure, lower is the solubility of the gas in the liquid.
- **General characteristics :**
  - Equilibrium can be attained only in closed system. It cannot be attained in open system.
  - At equilibrium, all the measurable properties of system become constant and rates of two opposing processes become equal.
  - The ratio of concentrations of reactants and products becomes constant (equilibrium constant) and the value of equilibrium constant indicates the extent to which reaction has proceeded. Higher the value of equilibrium constant, higher is the concentration of product in equilibrium mixture.
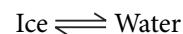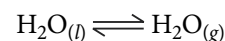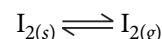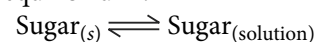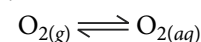
Equilibria Involving Chemical Processes

- **Chemical equilibrium :** Equilibrium attained between opposing chemical reactions.
  $$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$
  $$2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$$
  $$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$$
- **Dynamic nature of equilibrium :** In dynamic equilibrium, changes occur but in opposite directions and at constant rate *i.e.*, forward and backward reactions take place even after the equilibrium is attained but at equal speeds.
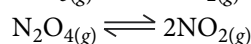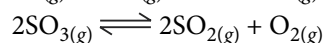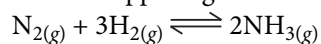
❑ **Law of chemical equilibrium**

  ○ For the reversible reaction
  $aA_{(aq)} + bB_{(aq)} \rightleftharpoons xX_{(aq)} + yY_{(aq)}$,

  At equilibrium, $\dfrac{[X]^x[Y]^y}{[A]^a[B]^b} = K_c$, K_c is called

  equilibrium constant which is constant for a reaction at constant temperature.

  ○ For the reversible reaction
  $aA_{(g)} + bB_{(g)} \rightleftharpoons xX_{(g)} + yY_{(g)}$

  $K_p = \dfrac{(p_X)^x(p_Y)^y}{(p_A)^a(p_B)^b}$

  ○ $K_p = K_c(RT)^{\Delta n_g}$ where, $\Delta n_g = n_{p(g)} - n_{r(g)}$

✓ **SELF CHECK**

10. For the reaction, $SO_{2(g)} + \dfrac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$,

  if $K_p = K_c(RT)^x$ where the symbols have usual meaning then the value of x is (assuming ideality)
  (a) 1 (b) – 1
  (c) $-\dfrac{1}{2}$ (d) $\dfrac{1}{2}$ (JEE Main 2014)

🔑 **KEY POINT**

• At 12.18 K temperature, $K_p = K_c$ for all reactions independent of the value of Δn.
• When $RT > 1$, $K_p > K_c$ if Δn is +ve
  $K_p = K_c$ if $\Delta n = 0$
  $K_p < K_c$ if Δn is –ve
• When $RT < 1$; $K_p < K_c$ if Δn is + ve
  $K_p = K_c$ if $\Delta n = 0$
  $K_p > K_c$ if Δn is –ve

❑ **General characteristics of equilibrium constant :**

  ○ Equilibrium constant has a definite value for every chemical reaction at a particular temperature and is independent of the initial concentration of reacting species.

  ○ It is independent of the presence of catalyst.

  ○ It is dependent on stoichiometry of reactants and products at equilibrium.
    — If reaction is reversed, equilibrium constant is inversed i.e., $K' = 1/K$.
    — If equation for a reaction is divided by a factor of 'n', the new equilibrium constant becomes n^{th} root of the previous equilibrium constant.
      i.e., $K' = \sqrt[n]{K}$

  — If equation for a reaction is multiplied by a factor 'n' then the new equilibrium constant (K') becomes equal to K^n. i.e., $K' = K^n$
  — If equation is written in a number of steps, then its equilibrium constant will be multiple of equilibrium constants of each step.
    i.e., $K = K_1 \times K_2 \times K_3 \times \ldots K_n$

✓ **SELF CHECK**

11. The equilibrium constant (K_c) for the reaction $N_{2(g)} + O_{2(g)} \rightarrow 2NO_{(g)}$ at temperature T is 4×10^{-4}. The value of K_c for the reaction,

  $NO_{(g)} \rightarrow \dfrac{1}{2}N_{2(g)} + \dfrac{1}{2}O_{2(g)}$ at the same temperature is
  (a) 2.5×10^2 (b) 4×10^{-4}
  (c) 50.0 (d) 0.02 (AIEEE 2012)

❑ **Units of equilibrium constant :** Equilibrium constant is expressed as dimensionless quantity by specifying the standard states of reactants and products.

❑ **Effect of temperature on equilibrium constant :**

  ○ For endothermic reactions, the equilibrium constant increases (k_f increases more than k_b) with rise in temperature and decreases with decrease in temperature.

  ○ For exothermic reactions, equilibrium constant decreases (k_b increases more than k_f) with rise in temperature and increases with fall in temperature.

  ○ van't Hoff equation
  $\log \dfrac{K_2}{K_1} = \dfrac{\Delta H°}{2.303R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

❑ The expression $\dfrac{[X]^x[Y]^y}{[A]^a[B]^b}$ is called reaction quotient, Q_c at any stage other than the equilibrium.

$Q_c < K_c$	$Q_c = K_c$	$Q_c > K_c$
Reaction will shift forward forming more products	Reaction in equilibrium	Reaction will shift backward forming more reactants

❑ **Equilibrium constant and free energy change :**
  $\Delta G = \Delta G° + RT \ln Q_c$
  At equilibrium, $\Delta G = 0$, $Q_c = K_c$
  $\Delta G° = -2.303RT \log K_c$ (van't Hoff isotherm)

When $K_c = 1$, $\Delta G° = 0$ (Reaction is in equilibrium.)
When $K_c > 1$, $\Delta G° = -ve$
(Forward reaction is favoured.)
When $K_c < 1$, $\Delta G° = +ve$
(Backward reaction is favoured.)

✓ SELF CHECK

12. The following reaction is performed at 298 K.
$$2NO_{(g)} + O_{2(g)} \rightleftharpoons 2NO_{2(g)}$$
The standard free energy of formation of $NO_{(g)}$ is 86.6 kJ/mol at 298 K. What is the standard free energy of formation of $NO_{2(g)}$ at 298 K?
$$(K_p = 1.6 \times 10^{12})$$
(a) $8660 - \dfrac{\ln(1.6 \times 10^{12})}{R(298)}$
(b) $0.5[2 \times 86600 - R(298)\ln(1.6 \times 10^{12})]$
(c) $R(298)\ln(1.6 \times 10^{12}) - 86600$
(d) $86600 + R(298)\ln(1.6 \times 10^{12})$

(JEE Main 2015)

13. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \dfrac{1}{2}$, $[B] = 2$ and $[C] = \dfrac{1}{2}$. The reaction proceeds in the $[R = 8.314\ J\ K^{-1}\ mol^{-1}, e = 2.718]$
(a) forward direction because $Q < K_c$
(b) reverse direction because $Q < K_c$
(c) forward direction because $Q > K_c$
(d) reverse direction because $Q > K_c$.

(JEE Main 2015)

❑ **Le Chatelier's principle :** If a system in equilibrium is subjected to a change of concentration, temperature or pressure, the equilibrium shifts in a direction so as to undo the effect of the change imposed.

❑ **Effect on chemical equilibria :**

	Change imposed at equilibrium	Equilibrium shift
1.	Increase in the concentration of one or more reactants	in forward direction
2.	Increase in the concentration of one or more products	in backward direction
3.	Increase in temperature	towards endothermic reaction
4.	Decrease in temperature	towards exothermic reaction
5.	Increase in pressure	favours lesser number of gaseous moles
6.	Decrease in pressure	favours larger number of gaseous moles
7.	Addition of catalyst	has no effect
8.	Addition of inert gas (a) at constant volume (b) at constant pressure	has no effect favours larger number of gaseous moles

❑ **Effect on physical equilibria :**
○ Water $\rightleftharpoons$ Vapours; An increase in pressure will favour the backward reaction because $V_{vapour} > V_{water}$ i.e., boiling point of water increases with increase in pressure.
○ Ice $\rightleftharpoons$ Water; An increase in pressure will favour the forward reaction because $V_{ice} > V_{water}$ i.e., melting point of ice decreases with increase in pressure.
○ Solid $\rightleftharpoons$ Liquid; An increase in pressure will favour the backward reaction because $V_{liquid} > V_{solid}$ i.e., melting point of solid increases with increase in pressure.
○ Gas + Solvent $\rightleftharpoons$ Solution; An increase in pressure will favour the forward reaction because $V_{reactants} > V_{products}$ i.e., solubility of gas increases with increase in pressure.

✓ SELF CHECK

14. The % yield of ammonia as a function of time in the reaction
$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}, \Delta H < 0$$
at (P, T_1) is given below.
If this reaction is conducted at (P, T_2), with $T_2 > T_1$, the % yield of ammonia as a function of time is represented by
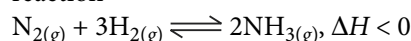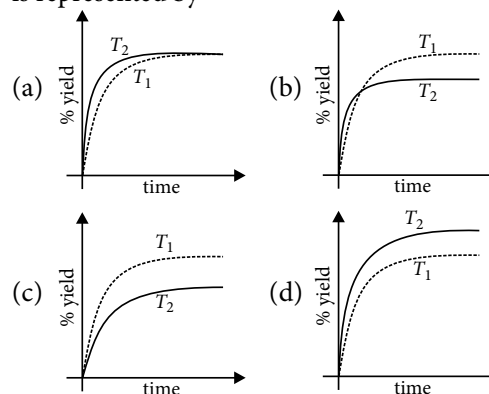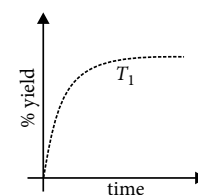
(JEE Advanced 2015)

Ionic Equilibrium

❑ A substance whose aqueous solution or melt conducts electricity is called *electrolyte* while a substance whose aqueous solution or melt does not conduct electricity is called *non-electrolyte*.

❑ **Types of electrolytes :**

Strong electrolytes
They have high degree of dissociation and are almost completely ionised in aqueous solution. Their aqueous solution is highly conducting and contains solute almost as ions. *e.g.*, H_2SO_4, HNO_3, NaOH, KOH etc.

Weak electrolytes
They dissociate to small extent and their aqueous solution is weakly conducting. *e.g.*, H_2CO_3, HCN, H_3BO_3 etc.

Based on the extent of degree of dissociation

Electrolytes

Based on the nature of electrolyte

True electrolytes
They are made-up of ions and conduct electricity in liquid or fused state. *e.g.*, NaCl, KCl

Potential electrolytes
They do not conduct electricity in pure liquid or molten state but give conducting aqueous solutions. *e.g.*, HCl in H_2O.

🔑 KEY POINT

- Classification of substances into strong and weak electrolytes depends on the nature of solvent *e.g.*, NaCl is a strong electrolyte in H_2O but a weak electrolyte in organic solvents like alcohols or benzene.

❑ **Dissociation :** An ionic compound when dissolved in water, the ions which are already present in the solid compound separate out.

❑ **Ionisation :** A neutral molecule like HCl (*i.e.*, a polar covalent compound) which does not contain ions but when dissolved in water splits to produce ions in the solution.

❑ **Degree of dissociation :** The fraction of the total number of molecules of an electrolyte which dissociates into ions is called the degree of dissociation.

  ○ For strong electrolytes, $\alpha = 1$.
  ○ For weak electrolytes, $\alpha < 1$.

❑ **Ostwald's dilution law :** Consider a binary electrolyte AB which dissociates into A^+ and B^- ions and the equilibrium state is represented by the equation
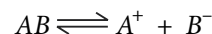
$$AB \rightleftharpoons A^+ + B^-$$

Initially	C	0	0
At equilibrium	$C(1-\alpha)$	$C\alpha$	$C\alpha$

So, dissociation constant may be given as

$$K = \frac{[A^+][B^-]}{[AB]} = \frac{C\alpha \times C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-\alpha)} \qquad \ldots \text{(i)}$$

For very weak electrolytes,

$$\alpha <<< 1, (1-\alpha) \approx 1$$

$$\therefore \quad K = C\alpha^2$$

$$\alpha = \sqrt{\frac{K}{C}} \qquad \ldots \text{(ii)}$$

Concentration of any ion $= C\alpha = \sqrt{CK}$

From equation (ii), it is clear that degree of ionisation increases on dilution.

Thus, degree of dissociation of a weak electrolyte is proportional to the square root of dilution.

❑ **Various concepts of acids and bases :**

Concepts	Definitions	
	Acid	**Base**
Arrhenius concept	Substance which produces H^+ ions in aq. solution *e.g.*, HCl, H_2SO_4	Substance which produces OH^- ions in aq. solution *e.g.*, NaOH, KOH, NH_4OH
Bronsted–Lowry concept	Protogenic substances or proton donors *e.g.*, CH_3COOH, HCl	Protophilic or proton acceptors. *e.g.*, NH_3
Lewis concept	Electrophiles or electron pair acceptors *e.g.*, BF_3, $AlCl_3$	Nucleophiles or electron pair donors *e.g.*, $\ddot{N}H_3$, $H_2\ddot{O}$:, F^-

□ **Conjugate acid-base pair :** A pair of acid and base, which differs by a proton is known as conjugate acid-base pair.

$$\overset{-H^+}{\underset{+H^+}{\text{Acid + Base} \rightleftharpoons \text{Conjugate + Conjugate}}}$$
$$\text{Base} \qquad \text{Acid}$$
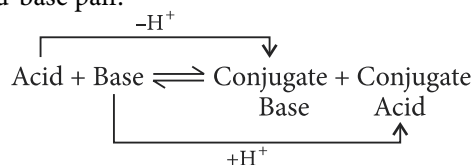
> ### ① KEY POINT
>
> - Solvents which influence the acid-base characteristics of solute by accepting or donating protons are called *amphiprotic solvents e.g.*, water, ammonia etc.
> - Solvents which do not influence the acid-base characteristics of solute (neither accept nor donate protons) are called *aprotic solvents e.g.*, benzene, carbon disulphide etc.
> - Strong acids of different strengths, when dissolved in water dissociate almost completely. These acids behave as equally strong in water. Thus, in aqueous solution, all acids stronger than H_3O^+ appear equally strong. Similarly, strong bases of different strengths behave as equally strong in water. This is called *levelling effect* of water.
> - All Arrhenius acids are also Bronsted acids but all Arrhenius bases are not Bronsted bases. Similarly, all Bronsted bases are also Lewis bases but all Bronsted acids are not Lewis acids.

□ **Ionisation of acids and bases**

$$\underset{\text{Acid}}{HA} \rightleftharpoons H^+ + A^-, \quad K_a = \frac{[H^+][A^-]}{[HA]}$$
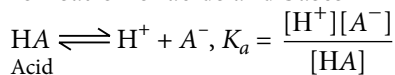
Degree of ionisation, $\alpha = \sqrt{\dfrac{K_a}{C}}$

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^+ + OH^-, \quad K_b = \frac{[B^+][OH^-]}{[BOH]}$$
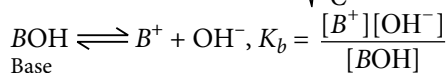
Degree of ionisation, $\alpha = \sqrt{\dfrac{K_b}{C}}$

Greater the degree of ionisation or greater the dissociation constant (K_a or K_b), stronger is the acid or base.

Multistage Ionisation of Acids and Bases

□ Acids which dissociate to give more than one proton in its aqueous solution are called polybasic acids *e.g.*, H_2SO_4, H_2CO_3, H_3PO_4 etc.

□ Their successive ionisation constants are called K_{a_1}, K_{a_2}, K_{a_3} etc.

For a tribasic acid H_3A, the ionisation can be represented as :

$$H_3A \xrightleftharpoons{K_{a_1}} H^+ + H_2A^-, \quad H_2A^- \xrightleftharpoons{K_{a_2}} H^+ + HA^{2-}$$
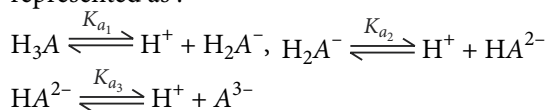
$$HA^{2-} \xrightleftharpoons{K_{a_3}} H^+ + A^{3-}$$

$$K_{a_1} = \frac{[H^+][H_2A^-]}{[H_3A]}, \quad K_{a_2} = \frac{[H^+][HA^{2-}]}{[H_2A^-]},$$

$$K_{a_3} = \frac{[H^+][A^{3-}]}{[HA^{2-}]}$$

□ $K_{a_1} > K_{a_2} > K_{a_3}$; because it is more difficult to remove a proton from a negative ion.

□ Similarly, for polyacidic bases, $K_{b_1} > K_{b_2} > K_{b_3}$ and so on.

□ **Acidic salts** are formed by the incomplete neutralisation of polybasic acids and still contain some acidic hydrogen *e.g.* $NaHCO_3$, $NaHSO_4$.

□ **Basic salts** are formed by incomplete neutralisation of polyacidic bases and still contain one or more hydroxyl groups *e.g.*, $Zn(OH)Cl$, $Mg(OH)Cl$ etc.

Ionisation of Water

□ Water undergoes self-ionisation (or autoprotolysis) to small extent as given below :
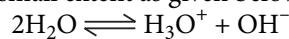
$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

Applying, the law of equilibrium

$$K_{H_2O} = \frac{[H_3O^+][OH^-]}{[H_2O]^2}$$

As the concentration of water remains practically constant therefore,

$$K_{H_2O} \times [H_2O]^2 = K_w = [H_3O^+][OH^-]$$

The constant K_w is called ionic product of water. Its value at 298 K is 1.008×10^{-14} mol^2 L^{-2}. In pure water, $[H_3O^+]$ and $[OH^-]$ are equal. Hence,

$$[H_3O^+] = \sqrt{1.008 \times 10^{-14}} = 1 \times 10^{-7} \text{ mol L}^{-1}$$

and $[OH^-] = [H_3O^+] = 1 \times 10^{-7}$ mol L^{-1}

□ **Effect of temperature on K_w :** With increase in temperature dissociation of water increases therefore, value of K_w increases with increase in temperature.

pH Scale

□ pH of a solution may be defined as negative logarithm of hydronium ion concentration expressed in moles per litre of the solution.

$$pH = -\log[H_3O^+] = \log\frac{1}{[H_3O^+]}$$

□ pOH of a solution is defined as the negative logarithm of hydroxyl ion concentration expressed in moles per litre of the solution.

$$pOH = -\log[OH^-] = \log\frac{1}{[OH^-]}$$

□ At 25°C, pH scale extends from 0 to 14 because at this temperature value of K_w is 10^{-14}.

□ The extension of pH scale can be shown as

$$\overset{\longleftarrow \quad pH \quad \longrightarrow}{0 \longleftarrow \underset{\text{Acidic} \quad \text{Neutral} \quad \text{Alkaline}}{7} \longrightarrow 14}$$

CONCEPT MAP
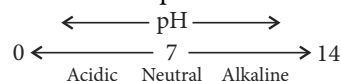
STATES OF MATTER

States of matter are distinguished by the strength of the bonds holding the molecules of the matter together. Gases, liquids and solids are all made up of microscopic particles, but the behaviour of these particles differs in the three phases.

SOLID STATE

Classification

- **Amorphous solids :** Constituent particles are not arranged in regular pattern.
  – short range order and isotropic in nature.
  – supercooled liquids or pseudo solids.
- **Crystalline solids :** Constituent particles are arranged in definite geometric pattern.
  – long range order and anisotropic in nature.
  – true solids.
  - Crystalline solids can be *molecular solids*, *ionic solids*, *metallic solids* or *covalent solids* depending upon the nature of intermolecular forces.

Crystal Lattice and Unit Cell

- **Crystal lattice :** The regular arrangement of constituent particles in a three dimensional space.
- **Unit cell :** The smallest repeating unit of space lattice.
- **Types of unit cells :**
  – **Simple cubic :** Particles at the corners only, $r = \dfrac{d}{2} = \dfrac{a}{2}$, $Z = 1$, efficiency = 52%, C.No. = 6.
  – **Body centred :** Particles at the corners as well as body centre, $Z = 2$, $r = \dfrac{d}{2} = \dfrac{\sqrt{3}a}{4}$, efficiency = 68%, C.No. = 8
  – **Face centred :** Particles at the corners as well as face centres, $Z = 4$, $r = \dfrac{d}{2} = \dfrac{a}{2\sqrt{2}}$, efficiency = 74%, C.No. = 12
  - If N is no. of spheres in *ccp* then tetrahedral voids = $2N$, having radius = 0.225 R and octahedral voids = N, having radius = 0.414 R.

Imperfections in Solids

- **Defects in stoichiometric crystals :**
  – **Schottky defect :** Arises when equal number of cations and anions are missing from the lattice sites and results in *decrease in density* of the crystal.
  – **Frenkel defect :** Arises due to dislocation of smaller ion from its normal site to interstitial site and *does not affect the density*.
- **Defects in non-stoichiometric crystals :**
  – **Metal excess defect :**
  ➡ Arises when a negative ion is missing from its lattice site, leaving a hole which is occupied by an electron (*F-centre*).
  ➡ When an extra cation is at interstitial site and electrical neutrality is maintained by electron present in another interstitial site.
  – **Metal deficiency defect :**
  ➡ Arises when metal shows variable valency and is characterised by missing of a cation from its lattice site and the presence of a cation having higher charge in the adjacent site.
  ➡ When extra anion is at interstitial site and electrical neutrality is maintained by extra charge on adjacent metal ion.

Magnetic Properties

- **Diamagnetic substances :** Weakly repelled by external magnetic field. *e.g.*, N_2, NaCl, Zn, TiO_2, etc.
- **Paramagnetic substances :** Weakly attracted by external magnetic field. *e.g.*, O_2, Cu^{2+}, Fe^{3+}, Cr^{3+}, etc.
- **Ferromagnetic substances :** Show permanent magnetism even in the absence of external magnetic field. *e.g.*, Ni, Fe, Co, etc.
- **Antiferromagnetic substances :** Have zero net dipole moment due to presence of equal number of domains in the opposite directions. *e.g.*, MnO.
- **Ferrimagnetic substances :** Possess very small net magnetic moment due to unequal number of domains in the opposite directions. *e.g.*, Fe_3O_4.

Electrical Properties

- **Conductors :** Conductivity range, 10^4 to 10^7 ohm^{-1} m^{-1}
- **Insulators :** Conductivity range, 10^{-20} to 10^{-10} ohm^{-1} m^{-1}
- **Semiconductors :** Conductivity range, 10^{-6} to 10^4 ohm^{-1} m^{-1}
  – **n-type semiconductors :** Group 14 elements doped with group 15 elements, free electrons increase conductivity.
  – **p-type semiconductors :** Group 14 elements doped with group 13 elements, holes increase conductivity.

GASEOUS STATE

- A substance exists in *gaseous state* if the thermal energy of molecules predominates over the intermolecular forces.
- **Gas laws :**
  – **Boyle's law :** $P \propto \dfrac{1}{V}$ (at constant T and n)
  – **Charles' law :** $V \propto T$ (at constant P and n)
  – **Gay Lussac's law :** $P \propto T$ (at constant V and n)
  – **Avogadro's law :** $V \propto n$ (at constant P and T)
  – **Dalton's law of partial pressures :** $P_{total} = p_1 + p_2 + ... + p_n$ (at constant V and T)
  $P_{dry\,gas} = P_{moist\,gas} -$ aq. tension
  – **Graham's law of diffusion :** $\dfrac{r_1}{r_2} = \sqrt{\dfrac{d_2}{d_1}} = \sqrt{\dfrac{M_2}{M_1}}$
- **Ideal gases :** Follow gas laws in all conditions of temperature and pressure.
  – Follow ideal gas equation; $PV = nRT$
- **Real gases :** Follow gas laws only at high temperature and low pressure.
  – Follow van der Waals equation;
  $$\left(P + \dfrac{an^2}{V^2}\right)(V - nb) = nRT$$
- **Critical constants and van der Waals constants :**
  $$V_c = 3b, \quad P_c = \dfrac{a}{27b^2},$$
  $$T_c = \dfrac{8a}{27Rb}$$

LIQUID STATE

- A substance exists in *liquid state* if the intermolecular forces lie between gaseous and solid states.
- **Properties of liquids :**
  – **Vapour pressure :** Pressure exerted by vapours in equilibrium with the liquid at a particular temperature.
  – **Boiling point :** Temperature at which the vapour pressure of a liquid becomes equal to the atmospheric pressure.
  – **Surface tension :** Tangential force acting along the surface of a liquid at right angle to a line of one unit length drawn on the surface of the liquid.
  – **Viscosity :** Measure of resistance to flow.
  - **Eotvos equation :** Relates surface tension (γ), temperature (T) and critical temperature (T_c) of liquid to its density (d) and molar mass (M),
  $$\gamma = k(T_c - T)\left(\dfrac{d}{M}\right)^{2/3}$$

❑ This extension may be broader or narrower depending upon other factors.

- ⭘ pH of boiling water is 6.5625 though it is neutral.
- ⭘ At 273 K, pH of neutral solution is 7.5 and pH scale is 0 to 15.
- ⭘ At 333 K, pH of neutral solution is 6.5 and pH range is 0 to 13.

🔑 KEY POINT

- A decrease in pH by one unit indicates increase in hydronium ion conentration by 10 times. Thus, if pH decreases by 3, $[H_3O^+]$ increases by 1000 times.
- While calculating the pH of very dilute solutions of acids and bases (such as 10^{-8} M HCl or 10^{-8} M KOH) the hydronium ions formed by dissociation of water have also to be taken into consideration.

❑ **pK_a and pK_b :** If K_a and K_b are the dissociation constants of weak acid and weak base respectively then, $pK_a = - \log K_a$ and $pK_b = - \log K_b$

Consider a weak acid, HA

$$HA \rightleftharpoons H^+ + A^-, \quad K_a = \frac{[H^+][A^-]}{[HA]}$$

$$A^- + H_2O \rightleftharpoons HA + OH^-,$$
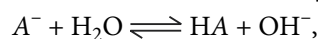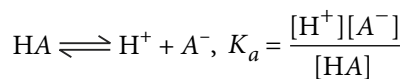
$$K_b = \frac{[OH^-][HA]}{[A^-]}$$

Multiplying K_a and K_b, $K_a \times K_b = [H^+][OH^-]$

But $[H^+][OH^-] = K_w$, $\therefore K_a \times K_b = K_w$

Taking log on both sides, $\log K_a + \log K_b = \log K_w$

or $- \log K_a - \log K_b = - \log K_w$, $pK_a + pK_b = pK_w$

❑ **Salt hydrolysis**

Salts of strong acids and strong bases *do not undergo hydrolysis* and the resulting solution is *neutral*.

Salt	Hydrolysis	Resulting solution	Hydrolysis constant (K_h)	Degree of hydrolysis (h)	pH
Weak acid and Strong base	Anionic	Alkaline pH > 7	$K_h = \dfrac{K_w}{K_a}$	$h = \sqrt{\dfrac{K_h}{C}}$	$pH = \dfrac{1}{2}[pK_w + pK_a + \log C]$
Strong acid and Weak base	Cationic	Acidic pH < 7	$K_h = \dfrac{K_w}{K_b}$	$h = \sqrt{\dfrac{K_h}{C}}$	$pH = \dfrac{1}{2}[pK_w - pK_b - \log C]$
Weak acid and Weak base	Anionic and cationic both	Neutral, pH = 7 (If $K_a = K_b$)	$K_h = \dfrac{K_w}{K_a K_b}$	$h = \sqrt{K_h}$	$pH = \dfrac{1}{2}[pK_w + pK_a - pK_b]$

❑ **Calculation of pH**

	Types of solution	Formula
1.	Dilute aqueous solution of a strong acid or a strong base	$pH = -\log\{[H^+]_{acid} + [H^+]_{H_2O}\}$ $pOH = -\log\{[OH^-]_{base} + [OH^-]_{H_2O}\}$
2.	Highly concentrated solution of a strong acid or a strong base (concentration > 1 M)	pH of acidic solution is taken as 0. pH of basic solution is taken as 14.
3.	Solution of a weak acid or a weak base	$pH = -\log(C\alpha)$ or $= -\log(\sqrt{K_a C})$ $pOH = -\log(C\alpha)$ or $= -\log(\sqrt{K_b C})$
4.	Mixture of two or more strong monoprotic acids or strong bases	$pH = -\log\left(\dfrac{\Sigma NV}{\Sigma V}\right)$, $pOH = -\log\left(\dfrac{\Sigma NV}{\Sigma V}\right)$
5.	Mixture of an acid and a base	$pH = -\log\left(\dfrac{(N_1V_1)_{acid} - (N_2V_2)_{base}}{V_1 + V_2}\right)$ (if acid is in excess) $pOH = -\log\left(\dfrac{(N_2V_2)_{base} - (N_1V_1)_{acid}}{V_1 + V_2}\right)$ (if base is in excess)
6.	Amphiprotic system	$pH = \dfrac{pK_{a_1} + pK_{a_2}}{2}$

Solubility Product

- ❑ It is defined as the product of the molar concentrations of ions of an electrolyte in a saturated solution, each concentration raised to the power equal to the number of ions produced on dissociation of one molecule of the electrolyte.

$$A_xB_y \rightleftharpoons xA^{y+} + yB^{x-}$$
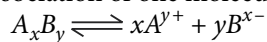
Applying the law of mass action,

$$K_{eq} = \frac{[A^{y+}]^x[B^{x-}]^y}{[A_xB_y]}$$

As conc. of $[A_xB_y]$ undissociated is almost constant.
$$K_{eq}[A_xB_y] = [A^{y+}]^x[B^{x-}]^y$$
$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

- ❑ **Relation between solubility and solubility product**
  - ○ If solubility of a sparingly soluble salt, A_xB_y is s mol/litre, then

  $$\underset{s\ moles}{A_xB_y} \rightleftharpoons \underset{xs\ moles}{xA^{y+}} + \underset{ys\ moles}{yB^{x-}}$$
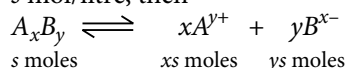
  Thus, $[A^{y+}] = xs$ and $[B^{x-}] = ys$

  $$\therefore \quad K_{sp} = [A^{y+}]^x[B^{x-}]^y$$
  $$= (xs)^x\,(ys)^y \text{ or } x^x.y^y.s^{(x+y)}$$

Type of salt	Example	Relation between s and K_{sp}
Binary electrolyte 1 : 2 (*AB*)	AgCl, BaSO$_4$, etc.	$s = \sqrt{K_{sp}}$ or $K_{sp} = s^2$
Ternary electrolyte 1 : 2 (*AB$_2$*)	PbCl$_2$, Ca(OH)$_2$, etc.	$s = \sqrt[3]{K_{sp}/4}$ or $K_{sp} = 4s^3$
Ternary electrolyte 2 : 1 (*A$_2$B*)	Ag$_2$CrO$_4$, Ag$_2$CO$_3$, etc.	$s = \sqrt[3]{K_{sp}/4}$ or $K_{sp} = 4s^3$
Quaternary electrolyte 1 : 3 (*AB$_3$*)	Fe(OH)$_3$, Al(OH)$_3$, etc.	$s = \sqrt[4]{K_{sp}/27}$ or $K_{sp} = 27s^4$
3 : 2 (*A$_3$B$_2$*)	Ca$_3$(PO$_4$)$_2$, Ba$_3$(PO$_4$)$_2$ etc.	$s = \sqrt[5]{K_{sp}/108}$ or $K_{sp} = 108s^5$

- ❑ **Criteria of precipitation of an electrolyte**
  - ○ $K_{ip} > K_{sp}$, Solution is supersaturated and precipitation occurs.
  - ○ $K_{ip} < K_{sp}$, Solution is unsaturated and precipitation does not occur.
  - ○ $K_{ip} = K_{sp}$, Solution is saturated.
    where, K_{ip} = ionic product of ions in solution.

- ❑ The suppression of degree of dissociation of a weak electrolyte on addition of a strong electrolyte having one ion common to it, is called *common ion effect*.
  - ○ This phenomenon is explained on the basis of Le Chatelier's principle and is used in qualitative analysis.

Buffer Solution

- ❑ It is defined as a solution which resists the change in its pH value when small amount of an acid or a base is added to it or when the solution is diluted.
- ❑ Buffer solution has a definite pH value at specific temperature.
- ❑ **Types of buffer solutions**
  - ○ *Simple buffer solution* : Salt of weak acid and weak base. *i.e.*, CH$_3$COONH$_4$
  - ○ *Acidic buffer solution* :
    - — A mixture of weak acid and its salt with a strong base.
      i.e., CH$_3$COOH + CH$_3$COONa
    - — has pH < 7.
    - — $\mathrm{pH} = \mathrm{p}K_a + \log\dfrac{[\text{Salt}]}{[\text{Acid}]}$
  - ○ *Basic buffer solution* :
    - — A mixture of weak base and its salt with a strong acid.
      i.e., NH$_4$OH + NH$_4$Cl
    - — has pH > 7.
    - — $\mathrm{pOH} = \mathrm{p}K_b + \log\dfrac{[\text{Salt}]}{[\text{Base}]}$
- ❑ **Buffer capacity :** It is the number of moles of an acid or a base added to change pH of one litre of a buffer solution by one unit.
  Hence, buffer capacity

  $$= \frac{\begin{array}{c}\text{Number of moles of acid or}\\ \text{base added per litre of buffer}\end{array}}{\text{Change in pH}} = \frac{dn}{d(\text{pH})}$$

ANSWER KEYS (SELF CHECK)

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

Exam Café

QUESTIONS FOR PRACTICE

1. For which of the following processes, $q = \Delta U$?
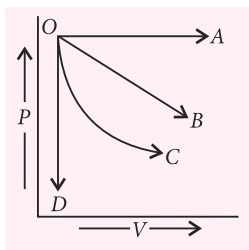
(a) $O \to A$ (b) $O \to D$
(c) $O \to B$ (d) $O \to C$

2. Two solutions of same solute-solvent system exert osmotic pressures of 6 atm and 2 atm at 300 K respectively. If these are separated by a semipermeable membrane, what would be the observation?
   (a) Solvent will move from solution having 6 atm pressure to solution having 2 atm pressure.
   (b) Solute will move from solution having 6 atm pressure to solution having 2 atm pressure.
   (c) Solvent will move from solution having 2 atm pressure to solution having 6 atm pressure.
   (d) No movement of solute or solvent takes place.

3. For the reaction $X_{(g)} + Y_{(g)} \rightleftharpoons 3Z_{(g)}$ at 25°C, a 3 litre vessel contains 1, 2 and 4 moles of X, Y and Z respectively. Identify the correct statement.
   (a) The reaction will occur in forward direction if K_c for the reaction is 10.
   (b) The reaction will occur in backward direction if K_c for the reaction is 15.
   (c) The reaction will be at equilibrium if K_c for the reaction is 10.66.
   (d) All of these.

4. In a closed insulated container, a liquid is stirred with a paddle to increase its temperature. In this process, which of the following is true?
   (a) $\Delta U = w \neq 0$, $q = 0$ (b) $\Delta U \neq 0$, $q = 0$, $w = 0$
   (c) $\Delta U = w = q = 0$ (d) $\Delta U = 0$, $q \neq 0$, $w = 0$

5. 1.4 g of acetone dissolved in 100 g of benzene gave a solution which freezes at 277.12 K. Pure benzene freezes at 278.4 K. 2.8 g of a solid A dissolved in 100 g of benzene gave a solution which freezes at 277.76 K. Calculate the molecular weight of A.
   (a) 180   (b) 96
   (c) 352   (d) 232

6. What is the % dissociation of H_2S, if 1 mole of H_2S is introduced in one litre vessel at 1000 K?
   K_c for the reaction :
   $$2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)} \text{ is } 1 \times 10^{-6}.$$
   (a) 1.67%   (b) 1.3%
   (c) 1.58%   (d) 0.01%

7. For the process, $CO_{2(s)} \longrightarrow CO_{2(g)}$
   (a) both ΔH and ΔS are +ve
   (b) ΔH is –ve and ΔS is +ve
   (c) ΔH is +ve and ΔS is –ve
   (d) both ΔH and ΔS are –ve.

8. For an ideal solution containing two components A and B, the Gibbs free energy of mixing is minimum when the mole fraction of A and B are
   (a) $x_A = x_B = \dfrac{1}{2}$ (b) $x_A = x_B = 1$
   (c) $x_A = x_B = \dfrac{3}{4}$ (d) $x_A = \dfrac{1}{2}$; $x_B = \dfrac{2}{3}$

9. How much 0.3 M NH_4OH should be added to 30 mL of 0.2 M solution of NH_4Cl to obtain a buffer solution of pH 10. [Given, pK_b for $NH_4OH = 4.75$]
   (a) 130.7 mL   (b) 225 mL
   (c) 112.5 mL   (d) 109.5 mL

10. The $\Delta_f H$ for SO_3 will be
    $$PbO + S + \frac{3}{2}O_2 \to PbSO_4 + 165.5 \text{ kcal} \quad ...(i)$$
    $$PbO + H_2SO_4 \cdot 5H_2O \to PbSO_4 + 6H_2O + 23.3 \text{ kcal} \quad ...(ii)$$
    $$SO_3 + 6H_2O \to H_2SO_4 \cdot 5H_2O + 41.0 \text{ kcal} \quad ...(iii)$$
    (a) 101.2 kcal   (b) –101.2 kcal
    (c) +146.8 kcal   (d) –146.8 kcal

11. x g of solute is separately dissolved in y g of two different liquids A and B. The relative lowering of vapour pressure of solution in A is twice that of solution in B. If the number of moles of solute is negligible in comparison to the number of moles of solvent, then which of the following expressions for molecular masses A and B is correct?

(a) $xM_A = yM_B$ (b) $yM_A = xM_B$
(c) $M_A = 2M_B$ (d) $2M_A = M_B$

12. Equilibrium constant K_p for
$$2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$$
is 0.0118 atm at 1065°C and heat of dissociation is 42.4 kcal. Find equilibrium constant at 1132°C.
(a) 0.076 atm (b) 0.052 atm
(c) 0.0118 atm (d) 0.025 atm
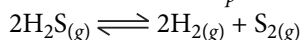
13. Temperature and heat are
(a) extensive properties
(b) intensive properties
(c) intensive and extensive properties respectively
(d) extensive and intensive properties respectively.

14. On the basis of information given below mark the correct option.
(I) In bromoethane and chloroethane mixture, intermolecular interactions of A—A and B—B type are nearly same as A—B type interactions.
(II) In ethanol and acetone mixture, A—A or B—B type intermolecular interactions are stronger than A—B type interactions.
(III) In chloroform and acetone mixture, A—A or B—B type intermolecular interactions are weaker than A—B type interactions.
(a) Solution (II) and (III) will follow Raoult's law.
(b) Solution (I) will follow Raoult's law.
(c) Solution (II) will show negative deviation from Raoult's law.
(d) Solution (III) will show positive deviation from Raoult's law.

15. In a saturated solution of the sparingly soluble strong electrolyte $AgIO_3$ (molecular mass = 283) the equilibrium which sets in is
$$AgIO_{3(s)} \rightleftharpoons Ag^+_{(aq)} + IO^-_{3(aq)}.$$
If the solubility product constant K_{sp} of $AgIO_3$ at a given temperature is 1.0×10^{-8}, what is the mass of $AgIO_3$ contained in 100 mL of its saturated solution?
(a) 1.0×10^{-4} g (b) 28.3×10^{-2} g
(c) 2.83×10^{-3} g (d) 1.0×10^{-7} g
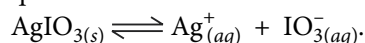
16. 16 g of oxygen gas expands at STP to occupy double of its original volume. The work done during the process is
(a) 260 kcal (b) 180 kcal
(c) 130 kcal (d) 0.2 kcal

17. NaCl is added to 1 litre water to such an extent that $\Delta T_f / K_f$ becomes $\dfrac{1}{500}$, the wt. of NaCl added is
(a) 5.85 g (b) 0.585 g
(c) 0.0585 g (d) none of these.

18. If first dissociation of $X(OH)_3$ is 100%, second dissociation is 50% and third dissociation is negligible then, the pH of 4×10^{-3} M $X(OH)_3$ is
(a) 7.5 (b) 9.54
(c) 11.78 (d) 13.25

19. An ideal gas is taken in a reversible cyclic process as follows :
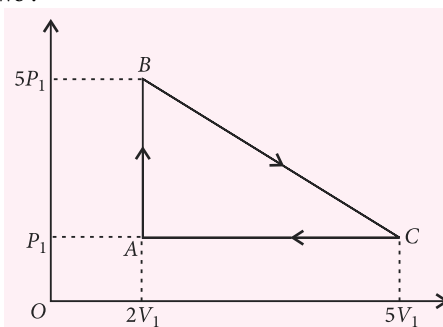
The work done in the cyclic process is
(a) $12\,V_1P_1$ (b) $5\,V_1P_1$
(c) $6\,V_1P_1$ (d) $4\,V_1P_1$

20. The vapour pressure of a solution containing 2 g of an electrolyte BA (which dissociates in one B^+ and one A^- ion in water), in 100 g water, is 751 mm at 100°C. Calculate degree of ionisation of BA if its mol. wt. is 56.
(a) 86.42% (b) 52.43%
(c) 26.62% (d) 35.48%

21. For the equilibrium of the reaction,
$$HgO_{(s)} \rightleftharpoons Hg_{(g)} + \frac{1}{2}O_{2(g)},$$
K_p at total pressure P is
(a) $\dfrac{2}{3^{3/2}}P^{3/2}$ (b) $\dfrac{2}{3^{1/2}}P^{1/2}$
(c) $\dfrac{1}{3^{2/3}}P^{3/2}$ (d) $\dfrac{2}{3^{2/3}}P$
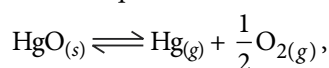
22. The entropy change accompanying the heating of one mole of helium gas, assuming ideal behaviour from a temperature of 300 K to a temperature of 1000 K, at constant pressure is
(a) 25.03 J K^{-1} mol^{-1} (b) 20 J K^{-1} mol^{-1}
(c) 2.503 J K^{-1} mol^{-1} (d) 0.2503 J K^{-1} mol^{-1}

23. A mixture of ethyl alcohol and propyl alcohol has a vapour pressure of 290 mm at 300 K. The vapour

pressure of propyl alcohol is 200 mm. If the mole fraction of ethyl alcohol is 0.6, its vapour pressure (in mm) at the same temperature will be
(a) 360
(b) 350
(c) 300
(d) 700

24. An aqueous solution contains 10% ammonia by mass and has a density 0.99 g cm^{-3}. If K_a for NH$_4^+$ is 5.0×10^{-10} M, the value of hydrogen ion concentration will be
(a) 9.28×10^{-13} M
(b) 9.28×10^{-11} M
(c) 9.28×10^{-10} M
(d) 9.28×10^{-6} M

25. Quick lime CaO is produced by heating limestone CaCO$_3$ to drive off CO$_2$ gas. The temperature at which the reaction becomes spontaneous is
($\Delta H° = 178.3$ kJ mol^{-1}, $\Delta S° = 0.166$ kJ K^{-1} mol^{-1})
(a) $< 100°C$
(b) $< 800°C$
(c) $< 900°C$
(d) < 500 K

26. K_H values for Ar$_{(g)}$, CO$_{2(g)}$, HCHO$_{(g)}$ and CH$_{4(g)}$ are 40.39, 1.67, 1.83×10^{-5} and 0.413 respectively. Arrange these gases in the order of their increasing solubility.
(a) HCHO < CH$_4$ < CO$_2$ < Ar
(b) HCHO < CO$_2$ < CH$_4$ < Ar
(c) Ar < CO$_2$ < CH$_4$ < HCHO
(d) Ar < CH$_4$ < CO$_2$ < HCHO

27. The equilibrium constant K_p for the reaction,
$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$
is 4.0 at 1660°C. Initially 0.80 mole H$_2$ and 0.80 mole CO$_2$ are injected into a 5.0 litre flask. What is the equilibrium concentration of CO$_{2(g)}$?
(a) 0.533 M
(b) 0.0534 M
(c) 5.35 M
(d) None of these
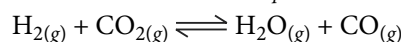
28. 0.8 g of carbon was converted into carbon dioxide producing 'x' cal of heat. When 0.8 g of carbon was converted in carbon monoxide 'y' cal of heat was produced. If $x > y$ then, what will be the heat produced when 1.86 g of carbon monoxide is converted to carbon dioxide?
(a) $x - y$
(b) $15y - 15x$
(c) $20x - 20y$
(d) $y - x$

29. The value of K_f for water is 1.86, calculated from glucose solution. The value of K_f for water calculated for NaCl solution will be
(a) $= 1.86$
(b) < 1.86
(c) > 1.86
(d) Zero

30. The standard internal energy change during the course of reaction at equilibrium at 300 K :
$2A_{(g)} + B_{(g)} \rightleftharpoons A_2B_{(g)}$ is (Given, $K_p = 10^{-10}$ atm^{-2} and $\Delta S = 5$ J K^{-1})
(a) -63.93 kJ
(b) $+63.93$ kJ
(c) $+58.94$ kJ
(d) -58.94 kJ
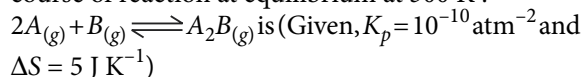
SOLUTIONS

1. (b): The process $O \to D$, occurs at constant volume, thus, $\Delta V = 0$
∴ $w = P\Delta V = 0$, then
$\Delta U = q + w$
$\Delta U = q + 0 = q$

2. (c): Osmosis will occur, *i.e*, solvent will move from dilute solution (low osmotic pressure) to concentrated solution (higher osmotic pressure).

3. (c): $X_{(g)} + Y_{(g)} \rightleftharpoons 3Z_{(g)}$
$[X] = 1/3, [Y] = 2/3, [Z] = 4/3$

$$\Rightarrow \quad Q = \frac{\left(\dfrac{4}{3}\right)^3}{\left(\dfrac{1}{3}\right)\left(\dfrac{2}{3}\right)} = 10.66$$

(a) Since, $K_c = 10$ *i.e.* $Q > K_c$, thus reaction will occur in backward direction.
(b) Since, $K_c = 15$ *i.e.* $K_c > Q$, thus the reaction will occur in forward direction.
(c) Since, $Q = K_c$, reaction is at equilibrium.

4. (a): As the system is closed and insulated, no heat enters or leaves the system, *i.e.*, $q = 0$.
$\Delta U = q + w = 0 + w = w$
And $\Delta U \neq 0$ as ΔT is not zero. Thus, $\Delta U = w \neq 0$.

5. (d): For acetone + benzene mixture :
$$\Delta T_f = \frac{K_f \times 1000 \times w_2}{M_2 \times w_{1(\text{in g})}}$$

$$(278.4 - 277.12) = \frac{K_f \times 1000 \times 1.4}{58 \times 100}$$

$$1.28 = \frac{K_f \times 1000 \times 1.4}{58 \times 100}$$

$$K_f = \frac{1.28 \times 58 \times 100}{1000 \times 1.4} = 5.303 \qquad \qquad ...(1)$$

For solute A + benzene mixture :
$$(278.4 - 277.76) = \frac{K_f \times 1000 \times 2.8}{M_2 \times 100}$$

$$0.64 = \frac{K_f \times 1000 \times 2.8}{M_2 \times 100}$$

$$K_f = \frac{0.64 \times M_2 \times 100}{1000 \times 2.8} \qquad \qquad ...(2)$$

From eqns. (1) and (2),

$$5.303 = \frac{0.64 \times M_2 \times 100}{1000 \times 2.8} \Rightarrow M_2 = 232$$

6. (b):

$$2H_2S_{(g)} \rightleftharpoons 2H_{2(g)} + S_{2(g)}$$
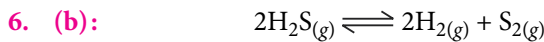
Initial moles :   1   0   0

Moles at equilibrium : $(1 - \alpha)$ α $\alpha/2$

At equilibrium,

$$[H_{2(g)}] = \frac{\alpha}{1}; [S_{2(g)}] = \frac{\alpha/2}{1}$$

$$[H_2S_{(g)}] = \frac{1-\alpha}{1}$$

$$K_c = \frac{[H_2]^2[S_2]}{[H_2S]^2} = \frac{\alpha^2(\alpha/2)}{(1-\alpha)^2} \qquad (\because \alpha <<< 1)$$

$$K_c = \frac{\alpha^3}{2} \Rightarrow 1 \times 10^{-6} = \frac{\alpha^3}{2}$$

$$\alpha^3 = 2 \times 10^{-6}$$

$$\alpha = (2 \times 10^{-6})^{1/3}$$

$$= 1.2599 \times 10^{-2} \simeq 1.3 \times 10^{-2}$$

% dissociation = $1.3 \times 10^{-2} \times 100 = 1.3\%$

7. (a): Sublimation requires energy, *i.e.*, ΔH = +ve, also, ΔS = + ve as randomness increases due to the formation of gaseous CO_2.

8. (a): $x_A + x_B = 1$,

$$\Delta_{mix}G = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\frac{\Delta_{mix}G}{RT} = x_A \ln x_A + x_B \ln x_B$$

For $\Delta_{mix}G$ to be minimum at a given T and P

$$\left(\frac{\partial(\Delta_{mix}G)}{\partial x_A}\right)_{T,P} = 0$$

Thus, $\frac{\partial}{\partial x_A}[x_A \ln x_A + (1-x_A)\ln(1-x_A)] = 0$

or $x_A\left(\frac{1}{x_A}\right) + \ln x_A + (1-x_A)\left(\frac{1}{1-x_A}\right) \times (-1)$

$$+ \ln(1-x_A)(-1) = 0$$

or $1 + \ln x_A - 1 - \ln(1-x_A) = 0$

$$\ln\left(\frac{x_A}{1-x_A}\right) = 0; \frac{x_A}{1-x_A} = 1 \text{ or } x_A = \frac{1}{2}; x_B = \frac{1}{2}$$

9. (c): We know, pH + pOH = 14

$\therefore$ pOH of the buffer = 14 – 10 = 4

For basic buffers, $pOH = pK_b + \log\frac{[Salt]}{[Base]}$

$$4 = 4.75 + \log\frac{[Salt]}{[Base]}$$

or $\log\frac{[Salt]}{[Base]} = -0.75$ or $\frac{[Salt]}{[Base]} = 0.1778$

or $\dfrac{\dfrac{0.2}{1000} \times 30}{\dfrac{0.3}{1000} \times V} = 0.1778$ $\therefore V = 112.5$ mL

10. (a): Subtracting equations (ii) and (iii) from (i), we get

$$S + \frac{3}{2}O_2 \rightarrow SO_3; \Delta_f H = 165.5 - 23.3 - 41 = +101.2 \text{ kcal}$$
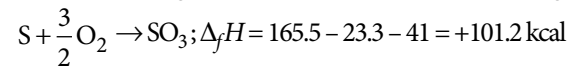
11. (c): Relative lowering of vapour pressure is equal to the mole fraction of the solute.

$\therefore$ Mole fraction of A = 2 × Mole fraction of B

$x_A = 2x_B$

$\Rightarrow \dfrac{n_{solute}}{n_A} = 2\dfrac{n_{solute}}{n_B} \Rightarrow n_B = 2n_A$

$\Rightarrow \dfrac{y}{M_B} = 2 \cdot \dfrac{y}{M_A} \Rightarrow M_A = 2M_B$

12. (d): $2.303 \log_{10}\dfrac{K_{p_2}}{K_{p_1}} = \dfrac{\Delta H}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$

$$2.303 \log_{10}\frac{K_{p_2}}{K_{p_1}} = \frac{42.4 \times 10^3}{2}\left[\frac{1405 - 1338}{1405 \times 1338}\right]$$

$\therefore \dfrac{K_{p_2}}{K_{p_1}} = 2.128$

$K_{p_2} = 2.128 \times 0.0118 = 0.025$ atm

13. (c): Temperature is a measure of intensity of energy, whereas heat is a measure of quantity of energy.

14. (b): When A—A and B—B interactions are nearly same as A—B type interactions, ideal solution is obtained which follows Raoult's law in all conditions of temperature and pressure. Thus, (I) follows Raoult's law.

When A—A or B—B interactions are stronger than A—B interactions, a solution shows positive deviation from Raoult's law. Thus, (II) exhibits positive deviation from Raoult's law.

When A—A or B—B interactions are weaker than A—B interactions solution shows negative deviation from Raoult's law. Thus, (III) exhibits negative deviation from Raoult's law.

15. (c): $AgIO_3 \rightleftharpoons \underset{s}{Ag^+} + \underset{s}{IO_3^-}$ [s = Solubility]

$K_{sp} = s^2$

or, $s^2 = 1.0 \times 10^{-8}$

or, $s = 1.0 \times 10^{-4}$ mol/L

$= 1.0 \times 10^{-4} \times 283$ g/L

$= \dfrac{1.0 \times 10^{-4} \times 283}{1000}$ g/mL

$= \dfrac{1.0 \times 10^{-4} \times 283 \times 100}{1000}$ g/100mL

$= 28.3 \times 10^{-4}$ g/100 mL

$= 2.83 \times 10^{-3}$ g/100 mL

16. (d): At STP, 16 g of O_2 or $\dfrac{1}{2}$ mole of O_2 will occupy 11.2 litre.

Thus, if volume is doubled, it means
$(V_2 - V_1) = 22.4 - 11.2 = 11.2$ litre
Now, $w = P \times (V_2 - V_1) = 1 \times 11.2$ litre atm
$= 11.2 \times 101.3$ J $= 1134.56 \times 0.24$ cal
$= 272$ cal $= 0.2$ kcal

17. (c): For NaCl, $i = 2$

$\therefore \quad \Delta T_f = iK_f m \Rightarrow \dfrac{\Delta T_f}{K_f} = 2 \times m$

$\dfrac{1}{500} = 2 \times m$ or $m = \dfrac{1}{1000}$

i.e., $\dfrac{1}{1000}$ moles of NaCl in 1 kg of water

or $\dfrac{1}{1000}$ moles of NaCl in 1 litre of water

$= \dfrac{1}{1000} \times 58.5$ g NaCl

$= 0.0585$ g NaCl in 1 litre of water

18. (c): First dissociation,
$X(OH)_3 \longrightarrow X(OH)_2^+ + OH^-$
Second dissociation,
$X(OH)_2^+ \longrightarrow X(OH)^{2+} + OH^-$
Total $[OH^-] = 4 \times 10^{-3} + 2 \times 10^{-3} = 6 \times 10^{-3}$
$pOH = 3 - \log 6 = 3 - 0.78 = 2.22$
$pH = 14 - 2.22 = 11.78$
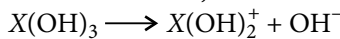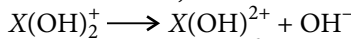
19. (c): Work done in the cyclic process =
Area bounded ($ABCA$)

$= \dfrac{1}{2} \times AC \times AB = \dfrac{1}{2} \times 3V_1 \times 4P_1 = 6\,V_1 P_1$

20. (a): $\dfrac{p^\circ - p_s}{p_s} = \dfrac{w_2 \times M_1}{M_2 \times w_1}$

$\dfrac{760 - 751}{751} = \dfrac{2 \times 18}{M_2 \times 100}$

$\therefore \quad M_{2(exp)} = 30.04$

For $\qquad BA \rightleftharpoons B^+ + A^-$
Before dissociation $\quad 1 \qquad\quad 0 \qquad 0$
After dissociation $\quad (1 - \alpha) \quad\;\; \alpha \qquad \alpha$

Now, $\dfrac{M_{2(normal)}}{M_{2(exp)}} = 1 + \alpha$

$\Rightarrow \quad \dfrac{56}{30.04} = 1 + \alpha$

$\Rightarrow \quad \alpha = 0.8642$ or 86.42%

21. (a): $\qquad\qquad HgO_{(s)} \rightleftharpoons Hg_{(g)} + \dfrac{1}{2}O_{2(g)}$

Initial moles : $\qquad\qquad 1 \qquad\quad 0 \qquad 0$

Moles at equilibrium : $\;\; 1 - x \qquad x \qquad \dfrac{x}{2}$

$K_p = p_{Hg} \cdot (p_{O_2})^{1/2}$

Total gaseous moles at equilibrium $= \dfrac{3x}{2}$

$p_{Hg} = \dfrac{x}{3x/2} P = p_{Hg} = \dfrac{2}{3} P$

$p_{O_2} = \dfrac{x/2}{3x/2} P = \dfrac{1}{3} P$

$K_p = \dfrac{2}{3} P \left(\dfrac{1}{3} P \right)^{1/2} = \dfrac{2}{3^{3/2}} P^{3/2}$

22. (a): $\Delta S = 2.303 C_p \log \dfrac{T_2}{T_1} = 2.303 \times \dfrac{5}{2} R \times \log \dfrac{T_2}{T_1}$

$\left[C_p \text{ for monoatomic gas} = \dfrac{5}{2} R \right]$

$= 2.303 \times \dfrac{5}{2} \times 8.314 \times \log \dfrac{1000}{300}$

$= 2.303 \times \dfrac{5}{2} \times 8.314 (\log 10 - \log 3)$

$= 2.303 \times \dfrac{5}{2} \times 8.314 \times [1 - 0.4771]$

$= 2.303 \times \dfrac{5}{2} \times 8.314 \times 0.523$

$= 25.03$ J K^{-1} mol^{-1}

23. (b): According to Raoult's law,
$P = p_A + p_B = p_A^\circ x_A + p_B^\circ x_B$
or $\;\; 290 = p_A^\circ \times (0.6) + 200 \times (1 - 0.6)$
or $\;\; 290 = 0.6 \times p_A^\circ + 0.4 \times 200$
or $\;\; p_A^\circ = 350$ mm

24. (a): Mass of 1 L solution $= 1000 \times 0.99$ g $= 990$ g
NH_3 present in 990 g solution $= 10\%$ of $990 = 99$ g

$= \dfrac{99}{17} = 5.8$ mol
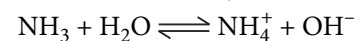
$\qquad\qquad NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
At $t = 0$: $\qquad\;\; 5.8 \qquad\qquad\quad 0 \qquad 0$
At equilibrium : $(5.8 - x) \qquad\qquad x \qquad x$

$\therefore \quad K_b = \dfrac{[NH_4^+][OH^-]}{[NH_3]} = \dfrac{x \cdot x}{(5.8 - x)} \approx \dfrac{x^2}{5.8} \qquad ...(i)$

Again, $K_b = \dfrac{K_w}{K_a} = \dfrac{10^{-14}}{5.0 \times 10^{-10}} = 2 \times 10^{-5} \qquad ...(ii)$

From eqn. (i) and (ii), we get

$\dfrac{x^2}{5.8} = 2 \times 10^{-5}$

$x^2 = 5.8 \times 2 \times 10^{-5}$

i.e., $[OH^-] = x = 1.077 \times 10^{-2}$ M
$\therefore \quad [H^+][OH^-] = 10^{-14}$

$\therefore \quad [H^+] = \dfrac{10^{-14}}{1.077 \times 10^{-2}} = 9.28 \times 10^{-13}$ M
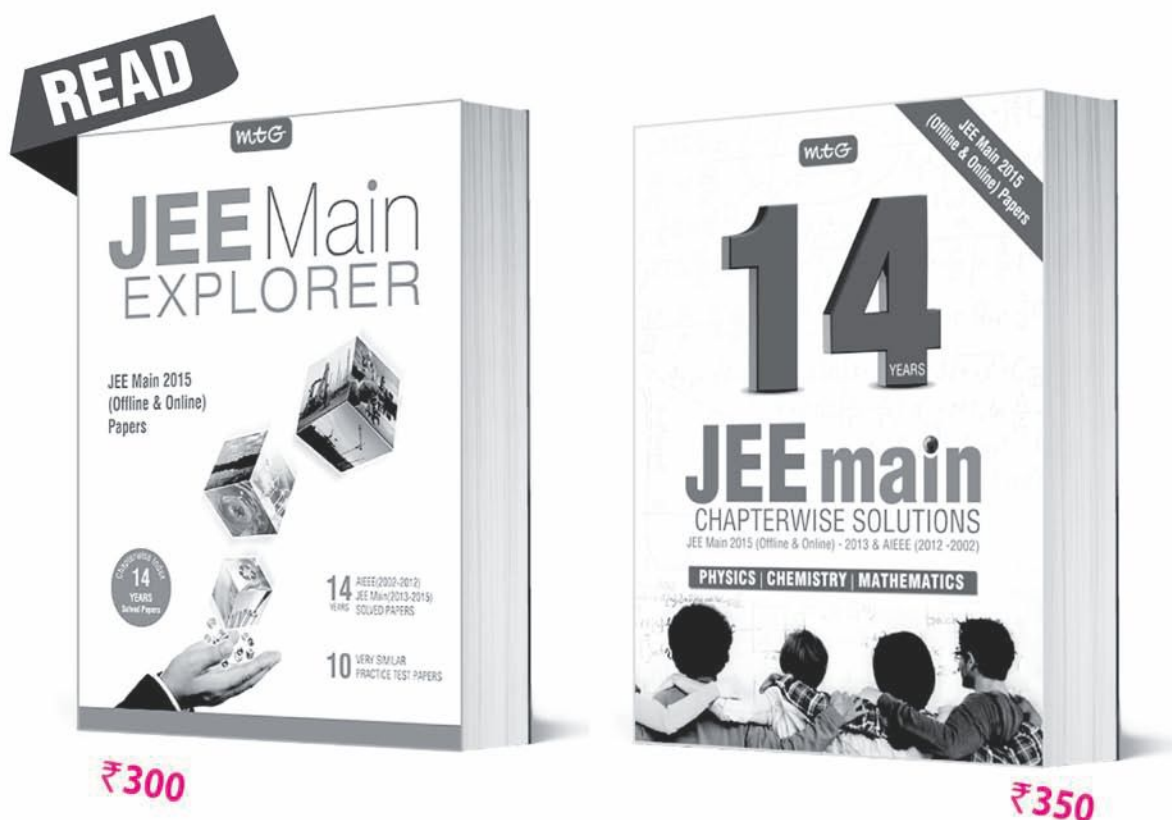
25. (c) : The spontaneity of the reaction at a given temperature can be found by determining whether $\Delta G°$ is positive or negative.

At 25°C we have $\Delta G° = \Delta H° - T\Delta S°$

$= 178.3 \text{ kJ mol}^{-1} - 298 \text{ K} \times 0.166 \text{ kJ K}^{-1} \text{ mol}^{-1}$

$= +128.8 \text{ kJ mol}^{-1}$

Since $\Delta G°$ is positive at this temperature, the reaction is non spontaneous.

The changeover point between spontaneous and non spontaneous can be found by setting $\Delta G° = 0$

$$T = \frac{\Delta H°}{\Delta S°} = \frac{178.3 \text{ kJ mol}^{-1}}{0.166 \text{ kJ K}^{-1}\text{mol}^{-1}} = 1074.09 \text{ K}$$
$$= 801.09°C$$

So, the reaction becomes spontaneous above 801.09°C.

26. (c) : Higher the value of K_H, lower is the solubility of gas in the liquid.

Thus, the order of increasing solubility is

$$\text{Ar} < \text{CO}_2 < \text{CH}_4 < \text{HCHO}$$
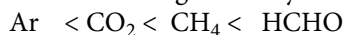
K_H values : 40.39   1.67   0.413 1.83×10^{-5}

27. (b) :

$$H_{2(g)} + CO_{2(g)} \rightleftharpoons H_2O_{(g)} + CO_{(g)}$$

Moles at equi : $0.8 - x$ $0.8 - x$ x x

Conc. at equi : $\left(\dfrac{0.8-x}{5}\right)$ $\left(\dfrac{0.8-x}{5}\right)$ $\left(\dfrac{x}{5}\right)$ $\left(\dfrac{x}{5}\right)$

$K_p = K_c (RT)^{\Delta n_g}$

$\Delta n_g = 0, \therefore K_p = K_c$

$$\therefore \quad K_c = \frac{\left(\dfrac{x}{5}\right)^2}{\left(\dfrac{0.8-x}{5}\right)^2} = 4$$

$$\Rightarrow \quad 2 = \frac{x}{0.8 - x} \quad \Rightarrow \quad x = 0.533$$

$$[CO_2] = \frac{0.8 - 0.533}{5} = 0.0534 \text{ M}$$

28. (d) : $C_{(s)} + O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H_1$

$C_{(s)} + \dfrac{1}{2} O_{2(g)} \longrightarrow CO_{(g)}; \Delta H_2$
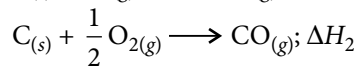
$\Delta H_1 = \dfrac{-x}{0.8} \times 12 = -15x$

$\Delta H_2 = \dfrac{-y}{0.8} \times 12 = -15y$

The required equation is :

$$CO_{(g)} + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)}; \Delta H_3$$
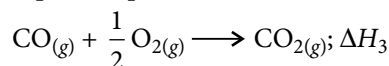
$\Delta H_3 = \Delta H_1 - \Delta H_2$
$= -15x - (-15y) = 15y - 15x$

For 1.86 g,

$$\Delta H_3 = (15y - 15x) \times \frac{1.86}{28} \approx (y - x)$$

29. (a) : K_f is characteristic constant for a given solvent.

30. (b) : $\Delta G° = -2.303 \, RT \log K_p$
$= -2.303 \times 8.314 \times 10^{-3} \times 300 \log 10^{-10}$
$= +57.44 \text{ kJ}$

Now, $\Delta G° = \Delta H° - T\Delta S°$
$+57.44 = \Delta H° - 300 \times 5 \times 10^{-3}$
$\Delta H° = +58.94 \text{ kJ}$

Also, $\Delta H° = \Delta U° + \Delta nRT$
$58.94 = \Delta U° + (-2) \times 8.314 \times 10^{-3} \times 300$

$\therefore \quad \Delta U° = 63.93 \text{ kJ}$

◆◆

AMU ENGG.
SOLVED PAPER 2015

1. What is the minimum volume of water required to dissolve 1 g of calcium sulphate at 298 K?
K_{sp} for $CaSO_4$ is 9.0×10^{-6}.
(Molar mass of $CaSO_4$ = 136 g mol^{-1})
(a) 2.45 L (b) 4.08 L (c) 4.90 L (d) 3.00 L

2. What will be the value of $[OH^-]^2$ in the 0.1 M solution of ammonium hydroxide having $K_b = 1.8 \times 10^{-5}$?
(a) 1.8×10^{-7}　　　(b) 1.8×10^{-6}
(c) 1.8×10^{-4}　　　(d) 1.8×10^{-3}

3. One mole of $N_2O_{4(g)}$ at 300 K is kept in a closed vessel at 1 atm pressure. It is heated to 600 K when 20% by mass of $N_2O_{4(g)}$ decomposes to $NO_{2(g)}$. The resultant pressure is
(a) 1.2 atm　　　　　(b) 2.4 atm
(c) 2.0 atm　　　　　(d) 1.0 atm

4. A boy after swimming comes out from a pool covered with a film of water weighing 80 g. How much heat must be supplied to evaporate this water?
(ΔH_v^o = 40.79 kJ mol^{-1})
(a) 1.61×10^2 kJ　　(b) 1.71×10^2 kJ
(c) 1.81×10^2 kJ　　(d) 1.91×10^2 kJ

5. Which of the following is planar?
(a) XeO_4 (b) XeO_3 (c) XeO_2F_2 (d) XeF_4

6. Schrödinger wave equation for a particle in a one-dimension box is
(a) $\dfrac{\delta^2 \psi}{\delta x^2} + \dfrac{2m}{h}(E - \infty)\psi = 0$

(b) $\dfrac{\delta^2 \psi}{\delta x^2} + \dfrac{8\pi^2 m}{h^2}(E - V) = 0$

(c) $\dfrac{\delta^2 \psi}{\delta x^2} + \dfrac{2m}{h}(E - V)\psi = 0$

(d) $\dfrac{\delta^2 \psi}{\delta x^2} + \dfrac{8\pi^2 m}{h^2}(E - \infty) = 0$

7. The number of Cl^- ions in 100 mL of 0.001 M HCl solution is
(a) 6.022×10^{23}　　　(b) 6.022×10^{20}
(c) 6.022×10^{19}　　　(d) 6.022×10^{24}

8. The energy associated with first orbital of hydrogen atom is
(a) -8.72×10^{-18} J　　(b) -8.80×10^{-18} J
(c) -87.0×10^{-18} J　　(d) -8.82×10^{-19} J

9. The energy of one mole of photons of radiation whose frequency is 5×10^{14} Hz is
(a) 192.51 kJ mol^{-1}　　(b) 199.51 kJ mol^{-1}
(c) 195.45 kJ mol^{-1}　　(d) 170 kJ mol^{-1}

10. The number of unshared valence electron pairs in XeF_2 is
(a) 2　　　　　　　(b) 4
(c) 3　　　　　　　(d) 1

11. Mustard gas is
(a) $COCl_2$　　　　　(b) CCl_3NO_2
(c) $CHCl_2NO_2$　　　(d) $ClCH_2CH_2SCH_2CH_2Cl$

12. Amorphous solids are characterised by property as
(a) isotropic
(b) anisotropic
(c) sharp melting point
(d) true solids.

13. The species having no S—S bond is
(a) $S_2O_4^{2-}$　　　　　(b) $S_2O_3^{2-}$
(c) $S_2O_7^{2-}$　　　　　(d) $S_2O_5^{2-}$

14. Television picture tubes are
(a) cathode-ray tubes (b) α-particle tubes
(c) γ-ray tubes　　　(d) X-ray tubes.

15. Density of 3 M NaCl solution is 1.25 g/cc. The molality of the solution is
(a) 2.79 molal　　　(b) 0.279 molal
(c) 1.279 molal　　　(d) 3.85 molal

16. Molecular structures of XeO_3 and $XeOF_4$ respectively are
    (a) trigonal planar and octahedral
    (b) pyramidal and square pyramidal
    (c) pyramidal and trigonal bipyramidal
    (d) both have imperfect tetrahedral shape.

17. Which of the following defects are present in AgBr and ZnS crystal systems?
    (a) Frenkel and Schottky
    (b) Schottky and Frenkel
    (c) Frenkel and Frenkel
    (d) Schottky and Schottky

18. The hybridisation of atomic orbitals of nitrogen in NO_2^+, NO_3^- and NH_4^+ are
    (a) sp, sp^2, sp^3 (b) sp^2, sp^3, sp
    (c) sp^2, sp, sp^3 (d) sp^2d, sp^3, sp

19. The correct order of increasing polarising power of the cations in the following $AlCl_3$, $MgCl_2$, $NaCl$ is
    (a) $AlCl_3 < MgCl_2 < NaCl$
    (b) $MgCl_2 < NaCl < AlCl_3$
    (c) $NaCl < MgCl_2 < AlCl_3$
    (d) $NaCl < AlCl_3 < MgCl_2$

20. Which of the following oxides of nitrogen is not an air pollutant?
    (a) NO_2 (b) N_2O
    (c) N_2O_5 (d) NO

21. The chemical reaction

    is known as
    (a) Gatterman reaction
    (b) Tischenko reaction
    (c) Gatterman–Koch reaction
    (d) Frankland reaction.

22. Which one of the following is an aromatic compound?

23. The number of possible alcohol isomers for $C_4H_{10}O$ is
    (a) 4   (b) 3   (c) 2   (d) 5

24. Intra-molecular hydrogen bonding is found in
    (a) *o*-nitrophenol   (b) *m*-nitrophenol
    (c) *p*-nitrophenol   (d) phenol.

25. The heat produced on combustion of methane is approximately
    (a) 890 kJ per g   (b) 74.2 kJ per g
    (c) 55.6 kJ per g   (d) 49.5 kJ per g

26. Maximum number of σ-bonds that may be present in an isomer of C_4H_8 are
    (a) 10   (b) 11
    (c) 12   (d) 13

27. Tick the statement which is not true.
    (a) Boiling point of ethanol is greater than ethoxyethane due to H-bonding.
    (b) Ethoxyethane is soluble in water due to H-bonding.
    (c) Ethanol is soluble in water due to H-bonding.
    (d) Ethoxyethane has nearly same boiling point as that of propane.

28. Which one of the following statements is not true about vitamins?
    (a) They were known as vitamine in their early discovery.
    (b) Vitamin C and D are water soluble.
    (c) Deficiency of vitamin B_6 is responsible for convulsions.
    (d) Thiamine is one from the class vitamin B.

29. Tick the statement which is not true about carboxylic acids.
    (a) Higher carboxylic acids are odourless.
    (b) Benzoic acid is insoluble in water.
    (c) Acetic acid exists as dimer in vapour phase.
    (d) Carboxylic acids show higher boiling points than alcohols of comparable molecular masses.

30. Which one of the following alcohols is known as wood's spirit?
    (a) Methanal   (b) Ethanol
    (c) Propanol   (d) Butanol

31. Which one of the following is an essential amino acid?
    (a) Valine   (b) Serine
    (c) Cystein   (d) Proline

32. Polymer with low degree of polymerisation is known as
    (a) higher polymer   (b) oligomer
    (c) macromolecule   (d) copolymer.

33. The reaction

$$R-NH_2 + CHCl_3 + 3KOH \xrightarrow{heat} R-NC + 3KCl + 3H_2O$$
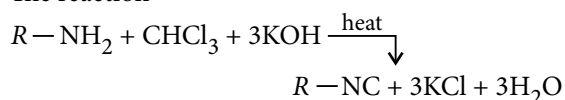
is known as
(a) Gabriel phthalimide synthesis
(b) Hoffmann reaction
(c) Carbylamine reaction
(d) Leibermann nitroso reaction.

34. Schiff's base is formed by the reaction of aldehyde with
(a) amine   (b) alcohol
(c) phenol   (d) carboxylic acid.

35. The chemical reaction,
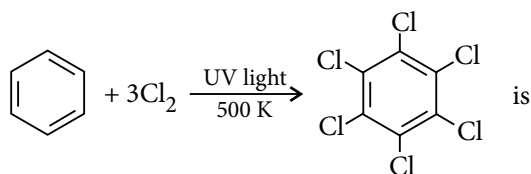
is
(a) a substitution reaction
(b) an addition reaction
(c) an elimination reaction
(d) rearrangement reaction.

36. $:CCl_2$ is
(a) an electrophile   (b) a free radical
(c) a nucleophile   (d) none of these.

37. DIBAL-H is
(a) $AlH(i\text{-}Bu)_2$ (b) $Al(OC_2H_5)_3$
(c) $Al[(CH_3)_2CHO]_3$ (d) $AlCl_3$
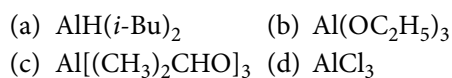
38. Which of the following is not correct?
(a) Chemical adsorption is reversible in nature.
(b) Physical adsorption is reversible in nature.
(c) ΔH is small in physical adsorption.
(d) ΔH is large in chemical adsorption.

39. What is the mole fraction of the solute in 2.5 molal aqueous solution?
(a) 0.043   (b) 0.053
(c) 0.063   (d) 0.073

40. A solution containing 2.44 g of a solute dissolved in 75 g of water boiled at 100.413°C. What will be the molar mass of the solute?
(K_b for water = 0.52 K kg mol^{-1})
(a) 40.96 g mol^{-1} (b) 20.48 g mol^{-1}
(c) 81.92 g mol^{-1} (d) None of these
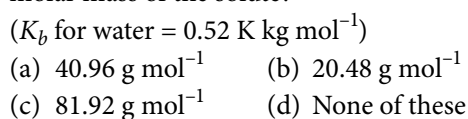
41. In the lead-acid battery during charging, the cathode reaction is
(a) formation of PbO_2
(b) formation of $PbSO_4$
(c) reduction of Pb^{2+} to Pb
(d) decomposition of Pb at the anode.
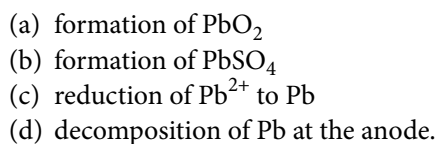
42. Which concentration plot is linear for a first order reaction?
(a) $[A]$ versus time
(b) $\ln[A]$ versus time
(c) $\log[A]$ versus 1/time
(d) square root of $[A]$ versus time
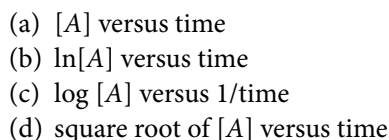
43. For the reaction $H_2F_{2(g)} \rightarrow H_{2(g)} + F_{2(g)}$; $\Delta E = -14.2$ kcal/mole at 25°C. The change in enthalpy of the reaction is
(a) –1.36 kJ/mole   (b) –13.6 kJ/mole
(c) 1.36 kJ/mole   (d) 13.6 kJ/mole
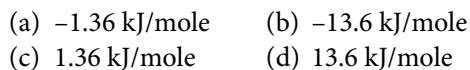
44. In the reversible reaction, $2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$, the rate of disappearance of NO_2 is equal to
(a) $\dfrac{2k_1}{k_2}[NO_2]^2$
(b) $2k_1[NO_2] - 2k_2[N_2O_4]$
(c) $2k_1[NO_2]^2 - 2k_2[N_2O_4]$
(d) $(2k_1 - k_2)[NO_2]$
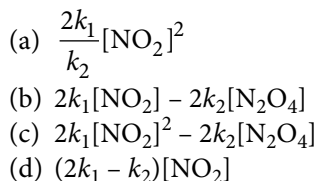
45. A metal oxide has the empirical formula $M_{0.96}O_{1.00}$. What will be the percentage of M^{2+} ions in the crystal?
(a) 90.67   (b) 91.67
(c) 8.33   (d) 9.33

46. 2 g of benzoic acid (C_6H_5COOH) is dissolved in 25 g of benzene. The observed molar mass of benzoic acid is found to be 241.98. What is the percentage association of acid if it forms dimer in solution?
(a) 85.2%   (b) 89.2%
(c) 95.2%   (d) 99.2%

47. 0.6 mL of acetic acid is dissolved in 1 litre of water. The value of van't Hoff factor is 1.04. What will be the degree of dissociation of the acetic acid?
(a) 0.01   (b) 0.02
(c) 0.03   (d) 0.04

48. What pressure of H_2 would be required to make emf of the hydrogen electrode zero in pure water at 25°C?
(a) 10^{-7} atm   (b) 10^{-14} atm
(c) 1 atm   (d) 0.5 atm

49. The root mean square velocity of an ideal gas at constant pressure varies with density (d) as

(a) d^2 (b) d

(c) $\sqrt{d}$ (d) $\dfrac{1}{\sqrt{d}}$

50. How many grams of potassium dichromate are required to oxidise 20.0 g of Fe^{2+} in $FeSO_4$ to Fe^{3+} if the reaction is carried out in an acidic medium? Molar masses of $K_2Cr_2O_7$ and $FeSO_4$ are 294 and 152 respectively.

(a) 6.45 g   (b) 7.45 g

(c) 8.45 g   (d) 9.45 g

SOLUTIONS

1. (a): $CaSO_{4(s)} + aq. \rightleftharpoons Ca^{2+}_{(aq)} + SO^{2-}_{4(aq)}$

$K_{sp} = [Ca^{2+}][SO_4^{2-}]$

Let the solubility of $CaSO_4$ be s.

Then, $K_{sp} = (s)(s) = s^2$

$9.0 \times 10^{-6} = s^2$

$s = 3 \times 10^{-3}$ mol L^{-1}

Now, number of moles in 1 g of $CaSO_4$

$$= \frac{\text{Weight}}{\text{Molar mass}}$$

$$= \frac{1 \text{ g}}{136 \text{ g mol}^{-1}} = \frac{1}{136} \text{ mol}$$

3×10^{-3} mol of $CaSO_4$ requires 1 L of water to dissolve.

$\therefore \dfrac{1}{136}$ mol of $CaSO_4$ will require

$$= \frac{1}{3 \times 10^{-3}} \times \frac{1}{136} = 2.45 \text{ L of water to dissolve.}$$

2. (b): $NH_4OH \rightleftharpoons NH_4^+ + OH^-$

Initial conc.   0.1   0   0

At equilibrium $0.1(1-\alpha)$ $0.1\,\alpha$ $0.1\,\alpha$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_4OH]}$$

$$1.8 \times 10^{-5} = \frac{(0.1\,\alpha)(0.1\,\alpha)}{0.1(1-\alpha)}$$

$\Rightarrow 1.8 \times 10^{-5} = (0.1)\alpha^2$ $[\because \alpha <<< 1]$ ... (1)

Now, $[OH^-]^2 = (0.1)^2(\alpha^2) = (0.1)[(0.1)\alpha^2]$ ... (2)

From equations (1) and (2)

$[OH^-]^2 = 0.1 \times 1.8 \times 10^{-5} = 1.8 \times 10^{-6}$

3. (b): Initially, $P_1 = 1$ atm, $T_1 = 300$ K, $n_1 = 1$ mol

Finally, $P_2 = ?$, $T_2 = 600$ K

When 20% of N_2O_4 decomposes to NO_2 then

       $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$
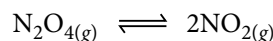
Initial conc.   1 mol   0 mol

Final conc. $1(1-0.2)$ $2(0.2)$

           = 0.8 mol   = 0.4 mol

Total no. of moles after decomposition

           $= 0.8 + 0.4 = 1.2$ mol $= n_2$

Now, using ideal gas equation, we get

$$\frac{P_1 V}{P_2 V} = \frac{n_1 R T_1}{n_2 R T_2} \quad \text{or} \quad \frac{1}{P_2} = \frac{1 \times 300}{1.2 \times 600}$$

$\Rightarrow P_2 = 2.4$ atm

4. (c): Given : Standard heat of vaporisation,

$\Delta H_v^\circ = 40.79$ kJ mol^{-1}

Mass of water = 80 g

No. of moles of water $= \dfrac{80 \text{ g}}{18 \text{ g mol}^{-1}} = 4.44$ mol

Now, heat required to vaporise one mole of water = 40.79 kJ

$\therefore$ Heat required to vaporise 4.44 moles of water

           $= 4.44 \times 40.79 = 1.81 \times 10^2$ kJ

5. (d):

Compound	Geometry	Structure
XeO_4	Tetrahedral	
XeO_3	Trigonal pyramidal	
XeO_2F_2	Trigonal bipyramidal	
XeF_4	Square planar	

6. (None): Shrödinger wave equation for a particle in a one-dimension box :

$$\frac{\delta^2 \psi}{\delta x^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

7. (c): 1 L or 1000 mL of 0.001 M HCl solution contains 0.001 mole of Cl^- ions

$\therefore$ 100 mL of 0.001 M HCl solution will contain

$$= \frac{0.001}{10} \text{ mol of Cl}^- = 10^{-4} \text{ mol of Cl}^- \text{ ions}$$

1 mol of Cl^- ions $\equiv 6.023 \times 10^{23}$ Cl^- ions

[∵ Avogadro's law]

$\therefore$ 10^{-4} mol of $Cl^- \equiv 6.022 \times 10^{23} \times 10^{-4}$ Cl^- ions

$= 6.022 \times 10^{19}$ Cl^- ions

8. **(None)** : Energy associated with n^{th} orbital of hydrogen atom, $E_n = \dfrac{-21.78}{n^2} \times 10^{-19}$ J

For first orbital, $n = 1$

$E_1 = -21.78 \times 10^{-19}$ J

Note : If we take fifth in place of first, then for fifth orbital, $n = 5$

$E_5 = \dfrac{-21.78 \times 10^{-19}}{5^2} = -8.71 \times 10^{-20}$ J

9. **(b)** : Energy of a photon, $E = h\upsilon$

where, $h = 6.626 \times 10^{-34}$ J s

$\upsilon = 5 \times 10^{14}$ s^{-1} (or Hz)

$E = 6.626 \times 10^{-34}$ J s $\times 5 \times 10^{14}$ $s^{-1} = 3.313 \times 10^{-19}$ J

$\therefore$ Energy of 1 mole of photons

$= 3.313 \times 10^{-19}$ J $\times 6.022 \times 10^{23}$ mol^{-1}

$= 199.51$ kJ mol^{-1}

10. **(c)** : The structure of XeF_2 is
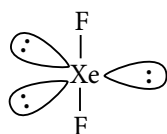
So, there are 3 unshared valence electron pairs.

11. **(d)** : IUPAC name of mustard gas is bis(2-chloroethyl)sulphide.

12. **(a)** : Amorphous solids are isotropic in nature *i.e.*, physical properties like electrical conductivity, refractive index, thermal expansion etc. are identical in all directions. On the other hand, crystalline solids are anisotropic, have sharp melting point and are called true solids.

13. **(c)** :
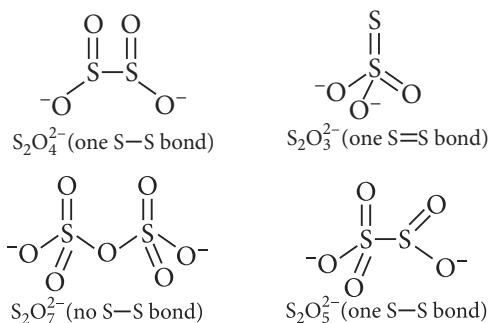
14. **(a)** : Cathode-ray tubes are the vacuum tubes in which electron beams are generated from cathode which is deflected towards fluorescent screen that displays images in the form of light.

15. **(a)** : Mass of 3 M NaCl solution

= density × volume

= 1.25 g/cc × 1000 cc = 1250 g

Molar mass of NaCl = 58.5 g/mol

$\Rightarrow$ Mass of 3 moles of NaCl = 3 × 58.5 = 175.5 g

So, mass of solvent in 3 M NaCl solution

= 1250 – 175.5 = 1074.5 g

Molality of solution = $\dfrac{\text{No. of moles of NaCl}}{\text{Mass of solvent in kg}}$

$= \dfrac{3}{1074.5} \times 1000 = 2.79$ molal

16. **(b)**:

Compound	Structure	Shape
XeO_3		Pyramidal
$XeOF_4$		Square pyramidal

17. **(b and c)** : In case of AgBr and ZnS, the cations Ag^+ and Zn^{2+} are small in size thus, some of these ions in the lattice shifts to the interstitial sites that arises Frenkel defect in these crystals.

AgBr shows both Shottky and Frenkel defects.

18. **(a)** : To predict hybridisation of a species calculate the number of hybrid orbitals, X.

$$X = \frac{1}{2}\left[\begin{pmatrix}\text{No. of valence} \\ \text{electrons of the} \\ \text{central atom}\end{pmatrix} + \begin{pmatrix}\text{No. of monovalent} \\ \text{atoms/groups} \\ \text{surrounding} \\ \text{central atom}\end{pmatrix} - \begin{pmatrix}\text{Charge on the} \\ \text{cation}\end{pmatrix} + \begin{pmatrix}\text{Charge on the} \\ \text{anion}\end{pmatrix}\right]$$

Value of X	2	3	4	5	6	7
Hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

$NO_2^+ \Rightarrow X = \dfrac{1}{2}[5 + 0 - 1 + 0] = 2$

so, hybridisation of NO_2^+ is sp.

$NO_3^- \Rightarrow X = \dfrac{1}{2}[5 + 0 - 0 + 1] = 3$

so, hybridisation of NO_3^- is sp^2.

$NH_4^+ \Rightarrow X = \dfrac{1}{2}[5 + 4 - 1 + 0] = 4$

so, hybridisation of NH_4^+ is sp^3.

19. (c) : Polarising power of cations increases with the increasing charge.

$$\underset{(+1)}{NaCl} < \underset{(+2)}{MgCl_2} < \underset{(+3)}{AlCl_3}$$
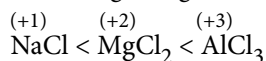
20. (c)

21. (c) : Friedel–Crafts acylation of benzene and its substitutes to form aromatic aldehydes using carbon monoxide, hydrochloric acid and catalyst is known as Gatterman–Koch reaction.

22. (b): For a compound to be aromatic, it must be planar and it must have $(4n + 2)\pi$ electrons (where, $n = 1, 2, 3, ...$) which are in conjugation.

and have 4 π electrons.

has 6 π electrons in conjugation and planar structure.

has 6 π electrons and is non planar.
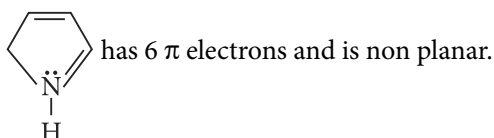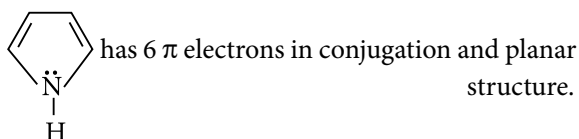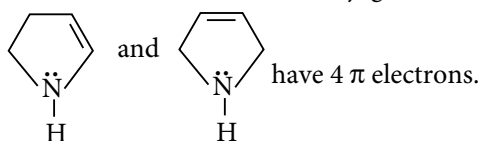
23. (d) : Possible isomers are

$CH_3CH_2CH_2CH_2OH$
Butan-1-ol

$CH_3CH_2CH(OH)CH_3$
Butan-2-ol

$CH_3CH(CH_3)CH_2OH$
2-Methylpropan-1-ol

$CH_3C(OH)(CH_3)CH_3$
2-Methylpropan-2-ol
(optically active *d* and *l* form)

So, total number of possible isomers is 5.

24. (a) : In *o*-nitrophenol, hydrogen of alcoholic group and oxygen of nitro group are in correct position to form intra-molecular hydrogen bonding and form a six-membered ring.
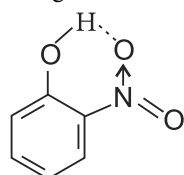
o-Nitrophenol

While in *m*-nitrophenol, *p*-nitrophenol and phenol, inter-molecular hydrogen bonding is present.

25. (c) : $CH_4 + 2O_2 \longrightarrow CO_2 + 2H_2O$

$\Delta_c H° = -890$ kJ mol^{-1} (Must be given in question)

Molar mass of $CH_4 = 16$ g mol^{-1}

So, heat produced per gram on combustion of methane $= \dfrac{-890 \text{ kJ mol}^{-1}}{16 \text{ g mol}^{-1}} = -55.6$ kJ per g

Here, negative sign implies that heat is evolved.

26. (c) : In all acyclic isomers of C_4H_8, number of σ-bonds = 11

In cyclic isomer of C_4H_8,
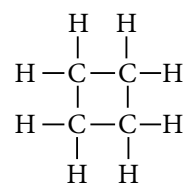
number of σ-bonds = 12 which is maximum.

27. (d): Ethers have much lower boiling points than alcohols as there is no association between the molecules as in alcohols due to hydrogen bonding. Both ethanol and ethoxyethane are soluble in water due to H-bonding.

Ethoxyethane has higher boiling point than that of propane.

28. (b): Vitamin C is water soluble while vitamin D is fat soluble.

Earlier, vitamins were known as vitamine derived from vital + amine.

Deficiency of vitamin B_6 causes convulsions. Thiamine is vitamin B_1.

29. (b): Higher carboxylic acids have low volatility hence, they are odourless. Carboxylic acids have electron withdrawing carbonyl group attached to —OH group which makes it more polar. Hence, carboxylic acids shows stronger H-bonding. Due to strong H-bonding, acetic acid exists as dimer even in vapour phase.

Benzoic acid forms strong H-bonds with water molecules hence, it is soluble in water.

30. (None): Methanol is known as wood's spirit as the earliest method for its preparation was by destructive distillation of wood.

31. (a) : Essential amino acids are those which are not synthesised by human body. Valine is one of the ten essential amino acids.

32. (b): Oligomers are the polymers with very few monomer units.

33. (c)

34. (a): Schiff's base is formed by the reaction of carbonyl compound (aldehyde) with aliphatic or aromatic amine. Most stable Schiff's bases are derived from aromatic aldehydes and aromatic 1° amines.

$$C_6H_5CHO + H_2NC_6H_5 \xrightarrow{H^+, \Delta}$$
$$C_6H_5CH{=}NC_6H_5 + H_2O$$
$$\text{(Schiff's base)}$$
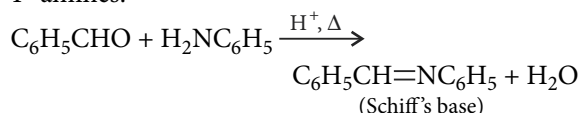
35. (a):
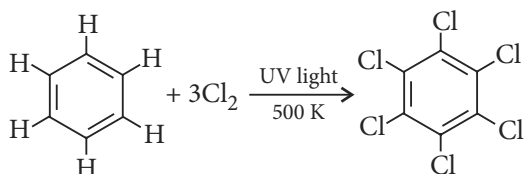
Here, hydrogen atoms are substituted by chlorine atoms so, the reaction is a substitution reaction.

36. (a): In :CCl$_2$, the carbon atom has only six electrons in its outermost shell and requires two more electrons to complete its octet. Hence, it is an electrophile.

37. (a): DIBAL-H is the abbreviation for diisobutylaluminium hydride, $AlH(i\text{-Bu})_2$.

38. (a): Chemical adsorption is irreversible in nature as it involves the formation of a compound and the effort to free the adsorbate will release the compound only.

39. (a): 2.5 moles of solute are present in 1000 g of water as solvent.
Number of moles of water in 1000 g
$$= \frac{1000\,\text{g}}{18\,\text{g mol}^{-1}} = 55.56\,\text{mol}$$
Mole fraction of solute,
$$x_{\text{solute}} = \frac{\text{Moles of solute}}{\text{Moles of solute + Moles of solvent}}$$
$$= \frac{2.5}{2.5 + 55.56} = 0.043$$

40. (a): $\Delta T_b = 373.413\,\text{K} - 373\,\text{K} = 0.413\,\text{K}$
$$(\because \text{b.pt. of pure water is 373 K})$$
$K_b = 0.52\,\text{K kg mol}^{-1}$
Molality of the solution,
$$m = \frac{w_2}{M_2} \times \frac{1}{w_1\,(\text{in kg})}$$

$$m = \frac{2.44}{M_2} \times \frac{1000}{75}$$
$$\Delta T_b = K_b m$$
$$\Rightarrow \quad 0.413 = 0.52 \times \frac{2.44}{M_2} \times \frac{1000}{75}$$
$$M_2 = 40.96\,\text{g mol}^{-1}$$

41. (c): During charging of lead acid battery Pb^{2+} ions of $PbSO_4$ are reduced to Pb on cathode while at anode, oxidation occurs with the formation of PbO_2.
At cathode : $PbSO_{4(s)} + 2e^- \longrightarrow Pb_{(s)} + SO^{2-}_{4(aq)}$
At anode : $PbSO_{4(s)} + 2H_2O \longrightarrow PbO_{2(s)} + SO^{2-}_{4(aq)}$
$$+ 4H^+_{(aq)} + 2e^-$$
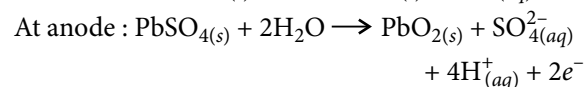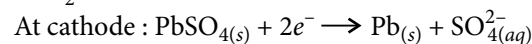
42. (b): Expression that relates concentration of reactant and time for first order reaction is
$$\log[A] = \frac{-kt}{2.303} + \log[A]_0$$
So, the plot of $\log[A]$ vs t will be linear with slope
$$= -\frac{k}{2.303} \text{ and intercept} = \log[A]_0$$

43. (None): $\Delta H = \Delta E + \Delta n_g RT$
$$\Delta H = -14.2 \times 10^3 + (2 \times 298) \qquad [\because \Delta n_g = 1]$$
$$= -13604\,\text{cal/mol} = -13604 \times 4.184\,\text{J/mol}$$
$$[\because 1\,\text{cal} = 4.184\,\text{J}]$$
$$= -56919.136\,\text{J/mol} = -56.919\,\text{kJ/mol}$$

44. (c): $2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$

Rate of reaction $= -\dfrac{1}{2}\dfrac{d[NO_2]}{dt} = k_1[NO_2]^2 - k_2[N_2O_4]$

$\therefore$ Rate of disappearance of NO_2
$$= -\frac{d[NO_2]}{dt} = 2k_1[NO_2]^2 - 2k_2[N_2O_4]$$

45. (b): Let the amount of M^{2+} ions in $M_{0.96}O_{1.00}$ be x. Then, amount of M^{3+} ions in the oxide $= 0.96 - x$.
As the oxide is neutral,
$$(+2)x + (+3)(0.96 - x) + (-2)(1.00) = 0$$
$$2x + 2.88 - 3x - 2.00 = 0$$
$$x = 0.88$$
So, the amount of M^{2+} ions is 0.88.
Percentage of M^{2+} ions $= \dfrac{0.88}{0.96} \times 100 = 91.67\%$

46. (d): Normal molecular mass of C_6H_5COOH
$[12(6) + 1(5) + 12(1) + 16(2) + 1(1)]$
$$= 122\,\text{g mol}^{-1}$$

Observed molecular mass of C_6H_5COOH

$$= 241.98 \text{ g mol}^{-1}$$

So, van't Hoff factor,

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}$$

$$i = \frac{122}{241.98} = 0.504 \qquad \ldots (1)$$

Now, $\alpha_{\text{association}} = (1-i)\dfrac{n}{n-1}$

$\Rightarrow \quad \alpha = (1 - 0.504)\,\dfrac{2}{2-1}$ [$n = 2$ as it forms a dimer]

$$= 0.992 = 99.2\%$$

47. (d): The value of van't Hoff factor, $i = 1.04$

Now, $\alpha_{\text{dissociation}} = \dfrac{i-1}{n-1}$

$\alpha = \dfrac{1.04-1}{2-1}$ [$n = 2$, as acetic acid dissociates into two ions.]

$$= 0.04$$

48. (c)

49. (d): Root mean square velocity, $u_{\text{rms}} = \sqrt{\dfrac{3RT}{M}}$

For an ideal gas, $PV = nRT \;\Rightarrow\; \dfrac{PV}{n} = RT$

$$\Rightarrow \quad u_{\text{rms}} = \sqrt{\frac{3PV}{nM}} = \sqrt{\frac{3P}{n}\left(\frac{1}{d}\right)} \qquad \left(\because d = \frac{M}{V}\right)$$

So, at constant pressure, $u_{\text{rms}} \propto \sqrt{\dfrac{1}{d}}$

50. (a): Number of moles of $FeSO_4 = \dfrac{20 \text{ g}}{152 \text{ g mol}^{-1}}$

$$= 0.132 \text{ mol}$$

Ionic equation for oxidation of Fe^{2+} ions to Fe^{3+} ions from $K_2Cr_2O_7$ in acidic medium is

$$Cr_2O_7^{2-} + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O$$
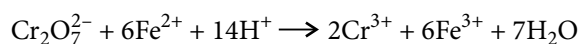
6 moles of $Fe^{2+} \equiv 1$ mol of $K_2Cr_2O_7$

$\therefore \quad 0.132$ moles of $Fe^{2+} \equiv \dfrac{1}{6} \times 0.132 = 0.022$ mol of $K_2Cr_2O_7$

$\Rightarrow \quad$ Mass of $K_2Cr_2O_7$ in 0.022 mol

$$= 0.022 \text{ mol} \times 294 \text{ g mol}^{-1}$$

$$= 6.468 \text{ g}$$

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EXAMINER'S MIND CLASS XII

NCERT

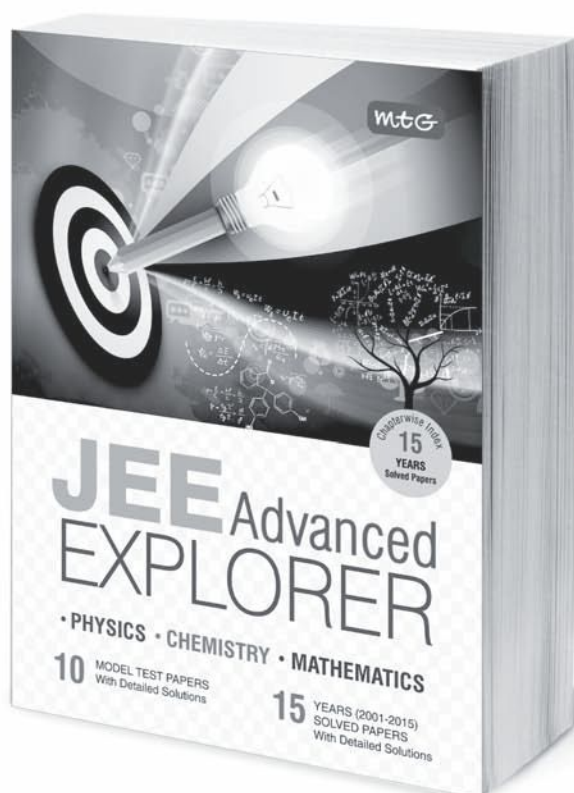## ELECTROCHEMISTRY | CHEMICAL KINETICS

SECTION - I

Only One Option Correct Type

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

1. Which of the following is correct for the solution of C_2H_5COOH upon dilution regarding current carrying species?
   (a) The number in $1\,cm^3$ as well as in total volume increases.
   (b) The number in $1\,cm^3$ decreases whereas that in the total volume remains constant.
   (c) The number in $1\,cm^3$ decreases but that in the total volume increases.
   (d) The number in $1\,cm^3$ as well as in total volume decreases.

2. In the reaction; $A + 2B \rightarrow 3C + D$, which of the following expressions does not describe changes in the concentration of various species as a function of time?
   (a) $\dfrac{d[C]}{dt} = \dfrac{-3d[A]}{dt}$ (b) $\dfrac{3d[D]}{dt} = \dfrac{d[C]}{dt}$
   (c) $\dfrac{3d[B]}{dt} = \dfrac{-2d[C]}{dt}$ (d) $\dfrac{2d[B]}{dt} = \dfrac{d[A]}{dt}$

3. A 1.0 M solution with respect to each of metal halides AX_3, BX_2, CX_3 and DX_2 is electrolysed using platinum electrodes. If $E^\circ_{A^{3+}/A} = 1.50$ V, $E^\circ_{B^{2+}/B} = 0.34$ V, $E^\circ_{C^{3+}/C} = -0.74$ V, $E^\circ_{D^{2+}/D} = -2.37$ V, the correct sequence in which the various metals are deposited at the cathode, is
   (a) A, B, C, D (b) D, C, B, A
   (c) A, B, C (d) C, B, A

4. For the reaction, $A + B \rightarrow C + D$, the variation of the concentration of the products with time is given by the curve

   (a) X (b) Y
   (c) Z (d) W
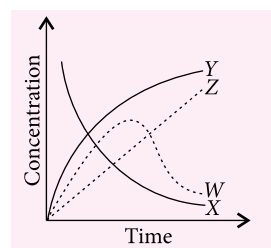
5. The equilibrium constant for the disproportionation reaction : $2Cu^+_{(aq)} \rightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$ at 25°C is
   (Given : $E^\circ_{Cu^+/Cu} = 0.52$ V; $E^\circ_{Cu^{2+}/Cu^+} = 0.16$ V)
   (a) 1.2×10^{-6} (b) 6×10^4
   (c) 6×10^6 (d) 1.2×10^6

6. How much faster would a reaction proceed at 25°C than at 0°C if the activation energy is 65 kJ?
   (a) 2 times   (b) 16 times
   (c) 11 times   (d) 6 times

7. The number of coulombs required to reduce 12.3 g of nitrobenzene to aniline, is
   (a) 96500 C   (b) 5790 C
   (c) 95700 C   (d) 57900 C

8. A substance undergoes first order decomposition. The decomposition follows two parallel first order reactions as :

   If $k_1 = 1.26 \times 10^{-4}\,s^{-1}$, $k_2 = 3.8 \times 10^{-5}\,s^{-1}$, then the percentage distributions of B and C are respectively
   (a) 80%, 20%   (b) 76.83%, 23.17%
   (c) 90%, 10%   (d) 63.94%, 36.06%

9. Specific conductance of 0.1 M HA is 3.75×10^{-4} ohm^{-1} cm^{-1}. If Λ^∞ (HA) = 250 ohm^{-1} cm^2 mol^{-1}, the dissociation constant K_a of HA is
   (a) 1.0×10^{-5} (b) 2.25×10^{-4}
   (c) 2.25×10^{-5} (d) 2.25×10^{-3}

10. For the reaction :
    $[Cu(NH_3)_4]^{2+} + H_2O \rightleftharpoons [Cu(NH_3)_3(H_2O)]^{2+} + NH_3$
    the net rate of reaction at any time is given by:
    Net rate $= 2.0 \times 10^{-4} \left[\left[Cu(NH_3)_4 \right]^{2+} \right] -$
    $3.0 \times 10^5 \left[\left[Cu(NH_3)_3(H_2O) \right]^{2+} \right].[NH_3]$

    The correct statement is
    (a) rate constant for forward reaction = 2×10^{-4}
    (b) rate constant for backward reaction = 3×10^5
    (c) equilibrium constant for the reaction = 6.6×10^{-10}
    (d) all of these.

11. If a salt bridge is removed from the two half-cells, the voltage
    (a) drops to zero   (b) does not change
    (c) increases gradually   (d) increases rapidly.

12. Combustion of carbon is exothermic, but coal stored in coal depots does not burn automatically because of
    (a) high threshold energy barrier
    (b) kinetic stability of coal
    (c) higher energy of activation needed for burning
    (d) all of these.

13. Which of the following statements is not correct during the working of the cell :
    $Cu_{(s)}|Cu^{2+}_{(aq)}(M_1)||Cu^{2+}_{(aq)}(M_2)|Cu_{(s)}$
    $M_1 < M_2$, M's being the molarities of $Cu^{2+}_{(aq)}$?
    (a) E_{cell} decreases and falls ultimately to zero.
    (b) M_1 increases and M_2 decreases due to direct transfer of Cu^{2+} ions.
    (c) M_1 increases due to oxidation of $Cu_{(s)}$ and M_2 decreases due to reduction of Cu^{2+} ions.
    (d) E°_{cell} = 0.0 V

14. In an exothermic reaction $A \rightarrow B$, the activation energy of reverse reaction is twice that of forward reaction. If enthalpy of the reaction is – 80 kJ mol^{-1}, the activation energy of the reverse reaction is
    (a) 80.0 kJ mol^{-1} (b) 60.0 kJ mol^{-1}
    (c) 40.0 kJ mol^{-1} (d) 160.0 kJ mol^{-1}

15. On the basis of electrochemical theory of aqueous corrosion, the reaction occurring at the cathode is
    (a) $O_{2(g)} + 4H^+_{(aq)} + 4e^- \longrightarrow 2H_2O_{(l)}$

    (b) $2H_2O_{(l)} + 2e^- \longrightarrow H_{2(g)} + 2OH^-_{(aq)}$
    (c) $Fe^{2+}_{(aq)} + 2e^- \longrightarrow Fe_{(s)}$
    (d) $Fe^{3+}_{(aq)} + e^- \longrightarrow Fe^{2+}_{(aq)}$

16. For the second order reaction, $A + B \rightarrow$ Products, the rate constant k is given by : $k = \dfrac{2.303}{(a-b)t} \log \dfrac{b(a-x)}{a(b-x)}$, a and b are the initial concentrations of A and B and x is the change in concentration after time t.
    If $b >> a$, the reaction reduces to
    (a) first order w.r.t. A (b) zero order w.r.t. A
    (c) first order w.r.t. B (d) overall zero order.

17. Cu^+ ion is not stable in aqueous solution because of disproportionation reaction. E° value for disproportionation of Cu^+ is
    (Given : $E^\circ_{Cu^{2+}/Cu^+} = 0.15$ V, $E^\circ_{Cu^{2+}/Cu} = 0.34$ V)
    (a) + 0.38 V   (b) – 0.38 V
    (c) + 0.49 V   (d) – 0.49 V

18. Activation energy and pre-exponential factor of a chemical reaction are 2×10^2 kJ mol^{-1} and 3.0×10^{15} s^{-1} respectively. If the rate constant of the reaction at 298 K is 5.0×10^{-1}, its value when $T \rightarrow \infty$ is
    (a) 2.0×10^5 s^{-1} (b) 1.5×10^{11} s^{-1}
    (c) 3.0×10^{15} s^{-1} (d) 2.0×10^2 s^{-1}

19. Which of the following cells has constant EMF during its working?
    (a) $Hg_{(l)}, Hg_2Cl_{2(s)} || KCl_{(aq)} || AgNO_{3(aq)} | Ag_{(s)}$
    (b) $Pt(H_2) | HCl_{(aq)} | (Cl_2) Pt$
    (c) $Zn_{(s)} | Zn^{2+}_{(aq)} || Cu^{2+}_{(aq)} | Cu_{(s)}$
    (d) $Fe_{(s)} | FeO_{(s)} || KOH_{(aq)} || NiO_{(s)}, Ni_2O_{3(s)} | Ni$

20. The following data were obtained for a given reaction at 300 K :

Reaction	Energy of activation (kJ mol^{-1})
(i) Uncatalysed	76
(ii) Catalysed	57

    The factor by which rate of catalysed reaction is increased, is
    (a) 21   (b) 2132
    (c) 2032   (d) 1200

SECTION - II

One or More Options Correct Type

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

21. The oxidation potential of hydrogen half-cell will be negative if
    (a) $p_{(H_2)} = 1$ atm and $[H^+] = 1$ M
    (b) $p_{(H_2)} = 1$ atm and $[H^+] = 2$ M
    (c) $p_{(H_2)} = 0.2$ atm and $[H^+] = 1$ M
    (d) $p_{(H_2)} = 0.2$ atm and $[H^+] = 0.2$ M

22. Which of the following is/are pseudo first order reactions?
    (a) The basic hydrolysis of ethyl acetate.
    (b) The inversion of sucrose in the presence of an acid.
    (c) The acidic hydrolysis of ethyl acetate.
    (d) The decomposition of ammonium nitrite in aqueous solution.

23. Given : $Br_2 + 2e^- \rightarrow 2Br^-$; $E° = + 1.09$ V
    $I_2 + 2e^- \rightarrow 2I^-$; $E° = 0.54$ V
    $Fe^{2+} + 2e^- \rightarrow Fe$; $E° = - 0.44$ V
    Which of the following reactions will not be spontaneous?
    (a) $Fe + Br_2 \rightarrow FeBr_2$
    (b) $Fe + I_2 \rightarrow FeI_2$
    (c) $I_2 + 2Br^- \rightarrow 2I^- + Br_2$
    (d) $Br_2 + 2I^- \rightarrow 2Br^- + I_2$

24. When the temperature of a reaction is changed from T_1 to T_2, half-life is found to decrease. Thus
    (a) $T_2 > T_1$
    (b) the reaction is exothermic
    (c) the reaction is endothermic
    (d) the reaction can be exothermic or endothermic.

25. Which of the following statements is/are correct?
    (a) The conductance of one cm^3 (or 1 $unit^3$) of a solution is called specific conductance.
    (b) Specific conductance increases while molar conductivity decreases on progressive dilution.
    (c) The limiting equivalent conductivity of weak electrolyte cannot be determine exactly by extrapolation of the plot of Λ_{eq} against $\sqrt{c}$.
    (d) The conductance of metal is due to the movement of free electrons.

SECTION - III

Paragraph Type

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

Paragraph for Questions 26 to 28

Collision theory is based on kinetic theory of gases. According to this theory, the reactant molecules are assumed to be hard spheres and reaction is postulated to occur when molecules collide with each other. The number of collisions per second per unit volume of the reaction mixture is known as collision frequency (Z). Another factor which affects the rate of chemical reactions is activation energy.

26. Which of the following statement(s) about the Arrhenius equation is incorrect?
    (a) If $E_a = 0$, then $k = A$
    (b) When the activation energy of the reaction is high, the rate becomes independent of temperature.
    (c) Two reactions having same value of E_a do not necessarily have same rate.
    (d) A reaction with higher value of E_a will have smaller value of rate constant.

27. In most cases, for a rise of 10 K temperature the rate constant is doubled. This is due to the reason that
    (a) collision frequency increases by a factor of 2 to 3
    (b) fraction of molecules possessing threshold energy increases by a factor of 2 to 3
    (c) activation energy is lowered by a factor of 2 to 3
    (d) none of these.

28. The increase in reaction rate as a result of temperature rise from 10° to 100° is .... times.
    (a) 112   (b) 512   (c) 400   (d) 614

Paragraph for Questions 29 to 31

Michael Faraday was the first scientist who described the quantitative aspects of electrolysis. Products of electrolysis depend on the nature of material being electrolysed and the type of electrodes being used. The products of electrolysis may be different for reactive and inert electrodes. The products of electrolysis depend on the different oxidising and reducing species present in the electrolytic cell and their standard electrode potentials. Moreover, some of the electrochemical processes although feasible, are so slow kinetically that at lower voltages these do not seem to take place and extra potential (called overpotential) has to be applied, which makes such process more difficult to occur.

29. The products of electrolysis of an aqueous solution of Na_2SO_4 using inert electrodes will be
    (a) sodium at cathode and SO_2 at anode
    (b) hydrogen at cathode and SO_2 at anode
    (c) sodium at cathode and oxygen at anode
    (d) hydrogen at cathode and oxygen at anode.

30. If the potential drop across the cell is 3 volts and quantity of electricity required is 115800 coulomb, the energy consumed will be
(a) 115800 J　　　(b) 38600 J
(c) 347400 J　　　(d) 231600 J

31. On the electrolysis of acidified water, if volume of hydrogen liberated is 5.6 cm^3, then the volume of oxygen liberated is equal to
(a) 2.8 cm^3　　　(b) 5.6 cm^3
(c) 8.4 cm^3　　　(d) 11.2 cm^3

SECTION - IV

Matching List Type

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

32. Match the plots given in List I with their slopes given in List II and select the correct answer using the code given below the lists :

List I		List II
P.	C vs t (abscissa) for zero order reaction	1. Unity
Q.	log C vs t (abscissa) for first order reaction	2. Zero
R.	$\left(-\dfrac{dC}{dt}\right)$ vs C for zero order reaction	3. $-k$
S.	$\ln\left(-\dfrac{dC}{dt}\right)$ vs $\ln C$ for first order reaction	4. $-\dfrac{k}{2.303}$

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

33. Match the List I with List II and select the correct answer using the code given below the lists :
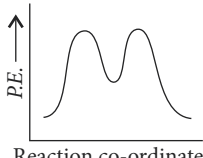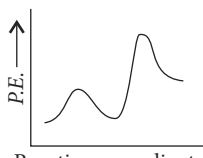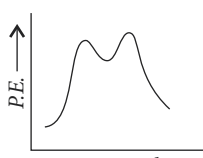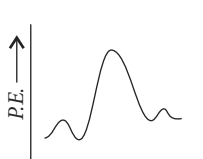
List I		List II
P.	Λ_m of KCl increases on dilution	1. is a linear graph
Q.	Λ_m of CH_3COOH increases on dilution	2. is a non-linear graph
R.	Λ_m of KCl versus (molarity)$^{1/2}$	3. due to increased degree of ionisation
S.	Λ_m of CH_3COOH versus (molarity)$^{1/2}$	4. due to weakening of interionic attractions

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

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

List I	List II
P. Reaction co-ordinate	1. The intermediates are the final products.
Q. Reaction co-ordinate	2. The reactants quickly form intermediates that slowly form products.
R. Reaction co-ordinate	3. The presence of intermediate is difficult to determine kinetically although the two steps reaction is not ultra fast.
S. Reaction co-ordinate	4. The intermediate accumulates in measurable quantities and the reaction is easily resolved in two steps.

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

SECTION - V

Assertion-Reason Type

In the following questions, a statement of assertion is followed by a statement of reason. Mark the correct choice as :
(a) If both assertion and reason are true and reason is the correct explanation of assertion.
(b) If both assertion and reason are true but reason is not the correct explanation of assertion.
(c) If assertion is true but reason is false.
(d) If both assertion and reason are false.

35. **Assertion :** Order of reaction can never be fractional for an elementary reaction.

Reason : Elementary reaction takes place by one step mechanism.

36. **Assertion :** The correct order of equivalent conductance at infinite dilution is
KCl > NaCl > LiCl
Reason : KCl is stronger electrolyte than NaCl which is stronger than LiCl.

37. **Assertion :** If the activation energy of a reaction is zero, temperature will have no effect on the rate constant.
Reason : Lower the activation energy, faster is the reaction.

38. **Assertion :** Increase in the concentration decreases the value of conductance.
Reason : Increase in the concentration increases interionic forces of attraction.

39. **Assertion :** For each 10° rise in temperature, the specific rate constant is nearly doubled.
Reason : For each 10° rise in temperature, the number of effective collisions becomes double.

40. **Assertion :** In Daniell cell if concentrations of Cu^{2+} and Zn^{2+} ions are doubled, the EMF of the cell does not change.
Reason : If the concentration of ions in contact with the metal is doubled, the electrode potential will be doubled.

SECTION - VI

Integer Value Correct Type

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

41. If the time required to complete a definite fraction of a reaction varies inversely to the concentration of reactant, then the order of reaction is

42. A current of 2.0 A passed for 5 hr. through a molten metal salt deposits 22.2 g of metal (at. mass = 177). The valency of the metal in the metal salt is

43. An alloy of Pb-Ag weighing 1.08 g was dissolved in dilute HNO_3 and the volume made to 100 mL. A silver electrode was dipped in the solution and EMF of the cell set up was 0.62 V.
$Pt_{(s)}, H_{2(g)}(1\ atm)|H^+_{(aq)}(1\ M)||Ag^+_{(aq.)}|Ag_{(s)}$
The percentage of Ag in the alloy is
$[E^\circ_{cell} = 0.80\ V, 2.303\ RT/F = 0.06\ at\ 25°C]$

44. ΔG for the reaction, $\dfrac{4}{3}Al + O_2 \longrightarrow \dfrac{2}{3}Al_2O_3$
is – 772 kJ mol^{-1}.
The minimum EMF in volts required to carry out an electrolysis of Al_2O_3 is

45. The equivalent conductance of 1.0 M CH_3COOH is 12 $\Omega^{-1}\ cm^2\ eq^{-1}$ and that at infinite dilution is 240 $\Omega^{-1}\ cm^2\ eq^{-1}$. The % ionisation of CH_3COOH is

46. The half-cell potentials of a half-cell $A^{(x+n)+}, A^{x+}|Pt$ were found to be as follows

% of reduced form	24.4	48.8
Half-cell potential (V)	0.115	0.101

The value of n is

47. Following are the two first order reactions with their half-lives given at 25°C :
$A \xrightarrow{t_{1/2}\ =\ 30\ min.} Products$
$B \xrightarrow{t_{1/2}\ =\ 40\ min.} Products$
The temperature coefficients of their reaction rates are 3 and 2, respectively, between 25°C and 35°C. If the above two reactions are carried out taking 0.4 M of each reactant but at different temperature 25°C for the first order reaction and 35°C for the second order reaction, then the ratio of the concentrations of A and B after an hour is
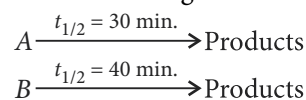
48. Consider $H_{2(g)}, Pt|H^+_{(aq.)}$; $E = 0.1$ V; the pH of the solution is

49. For a second order reaction, $t_{75\%} = xt_{50\%}$. The value of x is

50. The current (in ampere) passed for 0.25 s for deposition of a certain weight of metal, which is equal to its electrochemical equivalent is

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SOLUTIONS

1. **(c) :** On dilution, degree of ionisation of a weak electrolyte increases but not in proportion to volume. Hence, total number of ions in solution increases but that per unit volume decreases.

2. **(d) :** For the given reaction,
$A + 2B \longrightarrow 3C + D$
$-\dfrac{d[A]}{dt} = -\dfrac{1}{2}\dfrac{d[B]}{dt} = \dfrac{1}{3}\dfrac{d[C]}{dt} = \dfrac{d[D]}{dt}$

3. **(c) :** The cations will be liberated in the sequence of decreasing reduction potentials. Cations having $E°$ value < -0.83 V (reduction potential of water) will not be liberated from aqueous solutions.

4. **(b) :** The curve Y shows a gradual increase in the concentration of products with time.

5. **(d) :** $2Cu^+_{(aq)} \longrightarrow Cu_{(s)} + Cu^{2+}_{(aq)}$

$$E_{cell} = E°_{cell} - \frac{0.0591}{1} \log \frac{[Cu^{2+}_{(aq)}]}{[Cu^+_{(aq)}]^2}$$

where $\dfrac{[Cu^{2+}_{(aq)}]}{[Cu^+_{(aq)}]^2} = K_{eq}$, $E_{cell} = 0$

Hence, $\log K_{eq} = \dfrac{E°_{cell}}{0.0591} = \dfrac{0.52 - 0.16}{0.0591} = 6.09$

$$K_{eq} = 1.2 \times 10^6$$

6. **(c) :** $2.303 \log \dfrac{k_2}{k_1} = \dfrac{E_a}{R}\left[\dfrac{T_2 - T_1}{T_1 T_2}\right]$;

$$\therefore \quad 2.303 \log \frac{k_2}{k_1} = \frac{65 \times 10^3}{8.314}\left[\frac{298 - 273}{298 \times 273}\right]$$

$$\therefore \quad \frac{k_2}{k_1} = 11.04 \simeq 11$$

7. **(d) :** $C_6H_5NO_2 + 6H^+ + 6e^- \longrightarrow C_6H_5NH_2 + 2H_2O$

1 mol *i.e.*, 123 g of nitrobenzene requires 6 moles of electrons $= 6 \times 96500$ C charge

$\therefore$ 12.3 g of nitrobenzene will require charge

$$= \frac{6 \times 96500 \times 12.3}{123}$$

$$= 6 \times 9650 = 57900 \text{ C}$$

8. **(b) :** For parallel path reaction,
$k_{average} = k_1 + k_2 = 1.26 \times 10^{-4} + 3.8 \times 10^{-5}$
$\qquad\qquad = 1.64 \times 10^{-4}$ s^{-1}

Fractional yield of $B = \dfrac{k_1}{k_{average}} = \dfrac{1.26 \times 10^{-4}}{1.64 \times 10^{-4}} = 0.7683$

Percentage distribution of $B = 76.83\%$

Fractional yield of $C = \dfrac{k_2}{k_{average}} = \dfrac{3.8 \times 10^{-5}}{1.64 \times 10^{-4}} = 0.2317$

Percentage distribution of $C = 23.17\%$

9. **(c) :** $\Lambda_m = \dfrac{1000 \times \kappa}{c}$

$$\Lambda_m = \frac{1000 \times \kappa}{0.1} = \frac{1000 \times 3.75 \times 10^{-4}}{0.1} = 3.75;$$

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{3.75}{250} = 1.5 \times 10^{-2};$$

$$K_a = \frac{c\alpha^2}{1 - \alpha}, \text{ neglecting `}\alpha\text{' in comparison to 1}$$
$$K_a = c\alpha^2 = 0.1 \times (1.5 \times 10^{-2})^2 = 2.25 \times 10^{-5}$$

10. **(d) :** Net rate of reaction = Rate of forward reaction – Rate of backward reaction or,
Net rate of reaction $= k_f$ [reactants] $- k_b$ [products]
Thus,
Rate constant for forward reaction, $k_f = 2.0 \times 10^{-4}$
Rate constant for backward reaction, $k_b = 3 \times 10^5$
Equilibrium constant, K_c in given as :

$$K_c = \frac{k_f}{k_b} = \frac{2.0 \times 10^{-4}}{3 \times 10^5} = 6.6 \times 10^{-10}$$

11. **(a) :** When the salt bridge is removed then movement of electrons or ions between two half-cells stops hence, potential drops to zero.

12. **(d) :** The higher threshold energy barrier prevents coal to burn spontaneously and provides kinetic stability to fuel.

13. **(b) :** At cathode : $Cu^{2+}_{(aq)} (M_2) + 2e^- \longrightarrow Cu_{(s)}$
At anode : $\dfrac{Cu_{(s)} \longrightarrow Cu^{2+}_{(aq)} (M_1) + 2e^-}{Cu^{2+}_{(aq)} (M_2) \longrightarrow Cu^{2+}_{(aq)} (M_1)}$
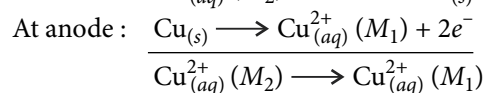
Here, both the half reactions have same $E°$ value with opposite sign. So, $E°_{cell} = 0$.

Then, $E_{cell} = -\dfrac{0.0591}{2} \log \dfrac{M_1}{M_2} = \dfrac{0.0591}{2} \log \dfrac{M_2}{M_1}$

As reaction proceeds M_1 increases and M_2 decreases consequently, E_{cell} decreases. Ultimately, $M_2 = M_1$ and then $E_{cell} = 0$

14. **(d) :** E_a is activation energy for forward reaction, E'_a is activation energy for reverse reaction.
Then, $E_a - E'_a = \Delta H$
or, $E_a - 2E_a = -80$, $E_a = 80$ kJ mol^{-1}, $E'_a = 2 \times 80$ kJ mol^{-1}
$\qquad\qquad\qquad\qquad\qquad\qquad = 160$ kJ mol^{-1}

15. **(a) :** At cathode :

$$2H^+_{(aq)} + 2e^- \longrightarrow 2H$$
$$2H + \frac{1}{2}O_{2(g)} \longrightarrow H_2O_{(l)}$$
$$\overline{2H^+_{(aq)} + \frac{1}{2}O_{2(g)} + 2e^- \longrightarrow H_2O(l)}$$
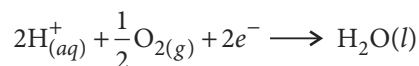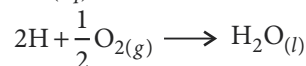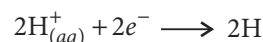
16. **(a) :** $[B]$ $(= b)$, being present in large excess, does not change practically. The rate becomes independent of $[B]$, *i.e.*, order $= 0$ w.r.t. B.

17. **(a) :** The reaction, $Cu^{2+} + Cu \longrightarrow 2Cu^+$ can be obtained by using the following reactions :

$Cu^{2+} + e^- \longrightarrow Cu^+, \ E^\circ_{Cu^{2+}/Cu^+} = 0.15 \, V$ ... (i)

$Cu^{2+} + 2e^- \longrightarrow Cu, \ E^\circ_{Cu^{2+}/Cu} = 0.34 \, V$ ... (ii)
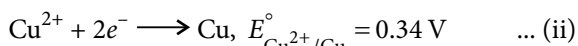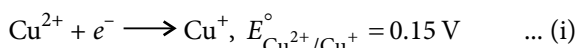
Multiplying eq. (i) by 2, we get

$2Cu^{2+} + 2e^- \longrightarrow 2Cu^+,$

$\Delta G^\circ_1 = -nFE^\circ = -2 \times F \times 0.15$ ... (iii)

$Cu^{2+} + 2e^- \longrightarrow Cu$

$\Delta G^\circ_2 = -nFE^\circ = -2 \times F \times 0.34$ ... (iv)
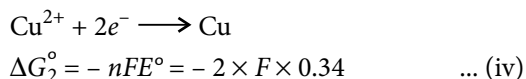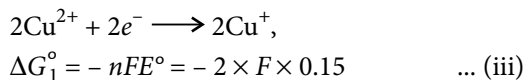
Subtract eq. (iv) from Eq. (iii)

$Cu^{2+} + Cu \longrightarrow 2Cu^+$

$\Delta G^\circ_3 = -nFE^\circ = -1 \times F \times E^\circ$
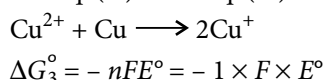
Also, $\Delta G^\circ_3 = \Delta G^\circ_1 - \Delta G^\circ_2$

$\therefore \ -1FE^\circ = (-2F \times 0.15) - (-2F \times 0.34)$

$E^\circ = -0.38 \, V$

This is the value for the reaction,

$Cu^{2+} + Cu \longrightarrow 2Cu^+$
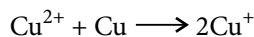
But the given reaction is just reverse of it.

$\therefore \ E^\circ_{cell}$ for given reaction $= +0.38 \, V$

18. (c) : $k = Ae^{-E_a/RT}$; when $T \to \infty$

$k = Ae^{-E_a/R \times \infty} = Ae^{-E_a \times 0} = Ae^0 = A = 3.0 \times 10^{15} \, s^{-1}$

19. (d) : If the species involved in cell reaction either oxidise or reduce, are in aqueous state or in gaseous state then the EMF of the cell depends on the concentration or pressure of these species which keeps on changing during working of cell. The cell in option (d) has all these species in solid state whose concentration does not change during the working of cell hence, it gives a constant EMF.

20. (c) : Using Arrhenius equation,

$k = A.e^{-\dfrac{E_a}{RT}}$ we get,

$\log k = \log A - \dfrac{E_a}{2.303RT}$

$\therefore \ \ \log k_1 = \log A - \dfrac{E_{a(1)}}{2.303RT}$ ...(i)

and $\log k_2 = \log A - \dfrac{E_{a(2)}}{2.303RT}$ ...(ii)

or $\log \dfrac{k_2}{k_1} = \dfrac{1}{2.303RT}[E_{a(1)} - E_{a(2)}]$

[From (i) and (ii)]

$= \dfrac{1}{2.303 \times 8.314 \times 300}(76000 - 57000)$

or $\log \dfrac{k_2}{k_1} = \dfrac{19000}{2.303 \times 8.314 \times 300} = 3.308$

or $\dfrac{k_2}{k_1} = 2032.35$

21. (b, c) : $H_2 \longrightarrow 2H^+ + 2e^-$

$E_{ox} = E^\circ_{ox} - \dfrac{0.0591}{n} \log \dfrac{[H^+]^2}{p_{H_2}}$

$n = 2, E^\circ_{ox} = 0$

$E_{ox} = -\dfrac{0.0591}{2} \log \dfrac{[H^+]^2}{p_{H_2}}$

(a) $p_{(H_2)} = 1 \, atm, [H^+] = 1 \, M$

$E_{ox} = -\dfrac{0.0591}{2} \log \dfrac{(1)^2}{1} = 0$

(b) $p_{(H_2)} = 1 \, atm, [H^+] = 2 \, M$

$E_{ox} = -\dfrac{0.0591}{2} \log \dfrac{(2)^2}{1} = -\dfrac{0.0591}{2} \times 2 \log 2$

$= -0.0178 \, V$

(c) $p_{(H_2)} = 0.2 \, atm, [H^+] = 1 \, M$

$E_{ox} = -\dfrac{0.0591}{2} \log \dfrac{(1)^2}{0.2} = -\dfrac{0.0591}{2} \log 5$

$= -0.0207 \, V$

(d) $p_{(H_2)} = 0.2 \, atm, [H^+] = 0.2 \, M$

$E_{ox} = -\dfrac{0.0591}{2} \log \dfrac{(0.2)^2}{0.2} = -\dfrac{0.0591}{2} \log 0.2$

$= -\dfrac{0.0591}{2} \times (-0.6989)$

$= +0.0207 \, V$

22. (b, c) : Inversion of sucrose and acid hydrolysis of ethyl acetate are pseudo-unimolecular reactions.

23. (c) : As per reaction in (c), reduction of iodine and oxidation of bromide ion takes place. Hence,

$E^\circ_{cell} = E^\circ_{I_2/I^-} - E^\circ_{Br_2/Br^-} = 0.54 - 1.09 = -0.55 \, V$

Thus, according to $\Delta G^\circ = -nFE^\circ_{cell,} \Delta G^\circ$ is positive. Hence, the reaction is not spontaneous.

24. (a, d) : Half-life of a reaction will decrease only when rate constant increases. Rate constants of all reactions (endothermic or exothermic) increase on increasing temperature (except the reaction $2NO + O_2 \to 2NO_2$).

25. (a, c, d) : Specific conductance is the conductance of 1 unit^3 volume of solution.

A weak electrolyte, dissociates more on dilution thus, molar conductivity increases. Number of ions per cubic unit volume of solution decreases due

to increase in volume hence, specific conductance decreases. The plot of Λ_{eq} against $\sqrt{c}$ increases steeply at low concentration (on dilution) for weak electrolyte thus, on extrapolation result obtained for conductivity is wrong. Conduction in metals is due to mobile electrons.

26. (b)

27. (b) : For a 10 K rise in temperature, collision frequency increases merely by 1 to 2% but the number of effective collisions increases by 100 to 200%.

28. (b) : Increase in steps of $10°$ has been made 9 times. Hence, rate of reaction should increase 2^9 times. *i.e.*, 512 times.

29. (d) : At cathode, H^+ is more easily reduced than Na^+ to give H_2 because $E^\circ_{red}(H^+) > E^\circ_{red}(Na^+)$.
At anode, OH^- is more easily oxidized than SO_4^{2-} to give O_2 because $E^\circ_{red}(OH^-) < E^\circ_{red}(SO_4^{2-})$.

30. (c) : Energy consumed = EMF × Qty. of electricity
$$= 3 \times 115800 \text{ J} = 347400 \text{ J}$$

31. (a) : $H_2O \longrightarrow H_2 + \dfrac{1}{2}O_2$,
i.e., Volume of O_2 liberated is half that of H_2.

32. (b) : (P) For a zero order reaction, $C = C_0 - kt$

(Q) For a first order reaction, $\log C = \log C_0 - \dfrac{k}{2.303} \times t$

(R) For a zero order reaction, $-\dfrac{dC}{dt} = k$ (constant)

Hence, slope of $-\dfrac{dC}{dt}$ *vs* $C = 0$

(S) For a first order reaction, $-\dfrac{dC}{dt} = kC$,
$$\ln\left(-\dfrac{dC}{dt}\right) = \ln k + \ln C.$$

Hence, plot of $\ln\left(-\dfrac{dC}{dt}\right)$ against $\ln C$ will have slope equal to unity.

33. (a) : KCl is a strong electrolyte thus, on dilution its Λ_m increases due to weakening of interionic attractions and its plot of Λ_m *vs* $\sqrt{\text{conc.}}$ is linear.
CH_3COOH is a weak electrolyte, its degree of ionisation increases on dilution thus, Λ_m increases. Its plot of Λ_m *vs* $\sqrt{\text{conc.}}$ is slowly increases on decreasing concentration (in highly conc. solution) but increases rapidly with decreasing conc. in very dilute solution.

34. (b)   **35. (a)**

36. (b) : On moving from Li^+ to K^+, degree of solvation decreases due to increase in size, therefore, mobility of ions increases.

37. (b) : According to Arrhenius equation, $k = Ae^{-E_a/RT}$ when $E_a = 0$, $k = A$.

38. (a)

39. (a) : For every $10°$ rise in temperature, the specific rate constant, k nearly doubles. (Although it is not correct for all reactions. For some reactions, k even gets tripled). The rate of collision among the molecules doubles for $10°$ rise in temperature.

40. (c) : Effect of concentration on electrode potential is found by Nernst equation. On doubling the concentrations, the EMF will remain unchanged because $\dfrac{[Zn^{2+}]}{[Cu^{2+}]}$ will remain same.

41. (2) : For a second order reaction
$$\dfrac{1}{[A]_t} = kt + \dfrac{1}{[A]_0}$$
$$kt = \dfrac{1}{[A]_t} - \dfrac{1}{[A]_0}$$

42. (3) : $W = \dfrac{E \cdot i \cdot t}{96500}$
or $E = \dfrac{W \times 96500}{i \cdot t} = \dfrac{22.2 \times 96500}{2 \times 5 \times 60 \times 60} = 59.5$
$\therefore$ Valency $= \dfrac{\text{Atomic mass}}{\text{Equivalent mass}} = \dfrac{177}{59.5} = 2.974 \simeq 3$

43. (1) : $H_{2(g)} + 2Ag^+_{(aq)} \longrightarrow 2H^+_{(aq)} + 2Ag_{(s)}$
$$E_{cell} = E^\circ_{cell} - \dfrac{2.303RT}{nF} \log \dfrac{[H^+]^2}{p_{(H_2)}[Ag^+]^2}$$
$0.62 = 0.80 + 0.06 \log [Ag^+]$
or $\log[Ag^+] = \dfrac{-0.18}{0.06} = -3$
or $[Ag^+] = 1.0 \times 10^{-3}$ M
$= 1.0 \times 10^{-3} \times 108 = 0.108$ g L^{-1}
$\therefore$ Amount of Ag in 100 mL solution = 0.0108 g
$\therefore$ %Ag $= \dfrac{0.0108}{1.08} \times 100 = 1$

44. (2) : $Al \longrightarrow Al^{3+} + 3e^-$
$\dfrac{4}{3}$ mol of Al $= \dfrac{4}{3} \times 3$ mol of electrons
$= 4$ mol of electrons
Then, $n = 4$
$\Delta G = -nFE$
-772×1000 J $mol^{-1} = -4 \times 96500 \times E$
$\therefore$ $E = \dfrac{772 \times 1000}{4 \times 96500} = 2.0$ V.

45. (5) : $\alpha = \dfrac{\Lambda_m^c}{\Lambda_m^\infty} = \dfrac{12}{240} = 0.05$

$\therefore$ % ionisation = 5

46. (2) : Considering the reduction reaction
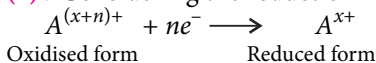
$$\underset{\text{Oxidised form}}{A^{(x+n)+}} + ne^- \longrightarrow \underset{\text{Reduced form}}{A^{x+}}$$

If $[A^{x+}] = 24.4$; $[A^{(x+n)+}] = 75.6$, $E_{red} = 0.115$ V

Now, from Nernst equation;

$$E_{red} = E_{red}^\circ + \frac{0.059}{n}\log\frac{[A^{(x+n)+}]}{[A^{x+}]}$$

$$0.115 = E_{red}^\circ + \frac{0.059}{n}\log\frac{75.6}{24.4} \qquad \text{... (i)}$$

If $[A^{x+}] = 48.8$; $[A^{(x+n)+}] = 51.2$, $E = 0.101\ V$

$$\therefore \quad 0.101 = E_{red}^\circ + \frac{0.059}{n}\log\frac{51.2}{48.8} \qquad \text{... (ii)}$$

By equation (ii) – (i),

$$\therefore \quad -0.014 = \frac{0.059}{n}\left[\log\frac{51.2}{48.8} - \log\frac{75.6}{24.4}\right]$$

$$-0.014 = \frac{0.059}{n}[\log 1.049 - \log 3.098]$$

$$-0.014 = \frac{0.059}{n}[0.0207 - 0.491]$$

$$-0.014 = \frac{0.059}{n}[-0.4703]$$

$$\therefore \quad n = \frac{0.059}{0.014}[0.4703]$$

$$n = 1.98 \approx 2$$

47. (2) : $0.4\text{ M of } A \xrightarrow{30\text{ min.}} 0.2\text{ M} \xrightarrow{30\text{ min.}} 0.1\text{ M (for } A)$

Temperature coefficient $= 2 = \dfrac{k(\text{at }35°C)}{k(\text{at }25°C)}$

$\Rightarrow 2k\ (\text{at }25°C) = k\ (\text{at }35°C)$

Now, for second order reaction rate cosntant (k) is inversely proportional to half-life ($t_{1/2}$).

As, k at 35°C gets doubled so, $t_{1/2}$ will be halved.

$0.4\text{ M of } B \xrightarrow{20\text{ min.}} 0.2\text{ M} \xrightarrow{20\text{ min.}} 0.1\text{ M} \xrightarrow{20\text{ min.}}$
$\qquad\qquad\qquad\qquad\qquad\qquad\qquad 0.05\text{ M (for } B)$

$$\therefore \quad \frac{[A]}{[B]} = \frac{0.1}{0.05} = 2$$

48. (2) : $H_2 + 2e^- \longrightarrow 2H_{(aq)}^+$

$$E = E° - \frac{0.0591}{2}\log[H^+]^2$$

$$0.1 = 0 - \frac{0.0591}{2} \times 2\log[H^+]$$

$$-\log[H^+] = \frac{0.1}{0.0591} = 1.69 \approx 2$$

$$\therefore \quad pH = -\log[H^+] = 2$$

49. (3) : For a second order reaction,

$$t = \frac{1}{k}\left[\frac{1}{[A]} - \frac{1}{[A]_0}\right]$$

For $t_{1/2}$ or $t_{50\%}$;

$$t_{1/2} = \frac{1}{k}\left[\frac{1}{\dfrac{[A]_0}{2}} - \frac{1}{[A]_0}\right] = \frac{1}{k}\left[\frac{2}{[A]_0} - \frac{1}{[A]_0}\right]$$

$$= \frac{1}{k} \times \frac{1}{[A]_0}$$

For $t_{75\%}$ or $t_{3/4}$;

$$t_{75\%} = \frac{1}{k}\left[\frac{1}{\dfrac{[A]_0}{4}} - \frac{1}{[A]_0}\right] = \frac{1}{k}\left[\frac{4}{[A]_0} - \frac{1}{[A]_0}\right]$$

$$= \frac{1}{k} \times \frac{3}{[A]_0}$$

$$t_{75\%} = xt_{50\%} \quad \Rightarrow \quad \frac{t_{75\%}}{t_{50\%}} = \frac{\dfrac{1}{k} \times \dfrac{3}{[A]_0}}{\dfrac{1}{k} \times \dfrac{1}{[A]_0}} = x$$

$$\therefore \quad x = 3$$

50. (4) : Electrochemical equivalent is the weight deposited by 1 C.

$\therefore \quad Q = i\cdot t$

$1 = i \times 0.25 \quad \therefore \quad i = 4$ A

$\diamond\diamond$

SOLUTIONS TO JULY 2015 CROSSWORD
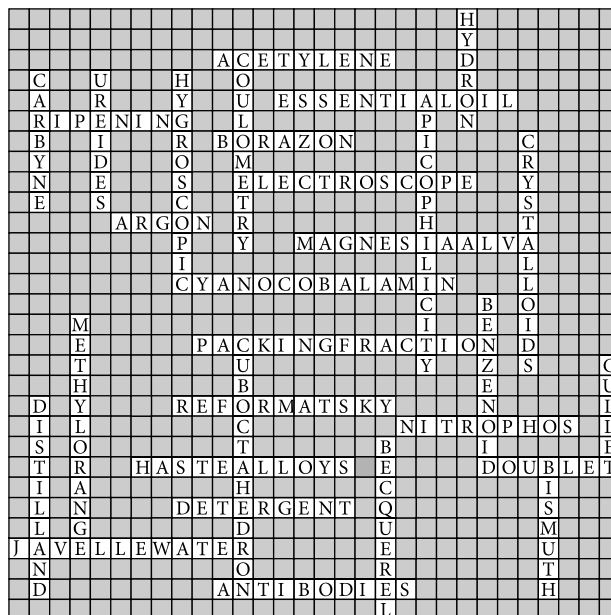
Winners of July 2015 Crossword

- **Roohi Srivastava (Uttar Pradesh)**
- **Kiran Joshi (Delhi)**
- **Praveen Semwal (Haryana)**

CONCEPT BOOSTER

Dear students!! Hope you all are fine. An important chapter of Class-XII is Electrochemistry. Very acute and minute details are there in this chapter. I am presenting the different cells and problem solving strategy in this issue. Hope you will like it as always. Take care.

Arunava Sarkar

ELECTROCHEMISTRY

Different Types of Half-cells

○ **Gas-ion half-cell :**

Ion in the aqueous medium is converted into gas form or *vice versa* depending on the fact whether it is working as a cathode or an anode.

e.g., $H^+_{(aq)} \mid H_{2(g)}$ (1 atm), Pt

$$H^+_{(aq)} + e^- \longrightarrow \frac{1}{2}H_{2(g)} \text{ (1 atm)}$$
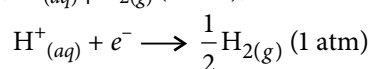
$$\therefore \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{1}\log\frac{\left(p_{H_{2(g)}}\right)^{1/2}}{[H^+]}$$

$$E_{\text{cell}} = 0 - 0.0591\log\frac{1}{[H^+]}$$

$$E_{\text{cell}} = -0.0591\{-\log[H^+]\} = -0.0591\text{pH}$$

○ **Calomel electrode :**
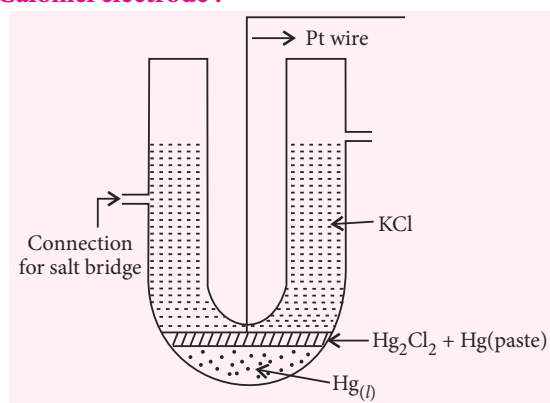
At anode : $2Hg_{(l)} + 2Cl^-_{(aq)} \rightleftharpoons Hg_2Cl_{2(s)} + 2e^-$

$$\therefore \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{1}{[Cl^-]^2}$$

At cathode : $Hg_2Cl_{2(s)} + 2e^- \rightleftharpoons 2Hg_{(l)} + 2Cl^-_{(aq)}$

$$\therefore \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log[Cl^-]^2$$

Generally, in standard calomel electrode, 3.5 N KCl solution is used, $E_{\text{SCE}} = 0.24$ V.

Sometimes, as per the requirement, concentration of KCl is changed. Hence, E_{SCE} changes too.

Cell representation of calomel electrode :

Anode : $Pt_{(s)} \mid Hg_{(l)} \mid Hg_2Cl_{2(s)} \mid Cl^-_{(aq)}$

Cathode : $Cl^-_{(aq)} \mid Hg_2Cl_{2(s)} \mid Hg_{(l)} \mid Pt_{(s)}$

○ **Mercury-mercurous sulphate electrode (Hg – Hg$_2$SO$_4$) half-cell :**

Here, Hg is covered with Hg_2SO_4 and in turn Hg_2SO_4 is in contact with H_2SO_4 or K_2SO_4 or Na_2SO_4. Use of Na_2SO_4 is rare. Constant supply of SO_4^{2-} is possible from H_2SO_4, K_2SO_4 or Na_2SO_4. Representation of the cell is as below :

$$Hg_{(l)}, Hg_2SO_{4(s)} \mid SO_{4(aq)}^{2-}$$

At cathode : $Hg_2SO_{4(s)} + 2e^- \longrightarrow 2Hg_{(l)} + SO_{4(aq)}^{2-}$

$$\therefore \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log[SO_4^{2-}]$$

At anode : $2Hg_{(l)} + SO_{4(aq)}^{2-} \longrightarrow Hg_2SO_{4(s)} + 2e^-$

$$\therefore \quad E_{\text{cell}} = E^\circ_{\text{cell}} - \frac{0.0591}{2}\log\frac{1}{[SO_4^{2-}]}$$

○ **Mercury-mercuric sulphate electrode (Hg – HgSO$_4$) half-cell :**

Similar to the mercury-mercurous sulphate electrode, here also Hg is covered with $HgSO_4$ which is in contact with K_2SO_4 or H_2SO_4.

---

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

Representation of the cell is as below :

$$Hg_{(l)}, HgSO_{4(s)} \mid SO_{4(aq)}^{2-}$$

At anode : $Hg_{(l)} + SO_{4(aq)}^{2-} \longrightarrow HgSO_{4(s)} + 2e^-$

$$\therefore \quad E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log \frac{1}{[SO_4^{2-}]}$$

At cathode : $HgSO_{4(s)} + 2e^- \longrightarrow Hg_{(l)} + SO_{4(aq)}^{2-}$
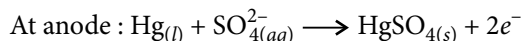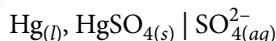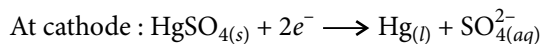
$$\therefore \quad E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2} \log[SO_4^{2-}]$$

○ **Amalgam electrode** :

Most popular are sodium amalgam, cadmium amalgam, etc. The main principle of this electrode is when an active metal (like Na) is dissolved in mercury then the metal can be in reversible reaction with its ion. General representation is

$$Na \text{ (in Hg, } C_1) \mid Na^+ (C_2)$$
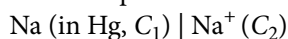
(Concentrations are measured in molarity)

At cathode : $Na^+ (C_2) + e^- \longrightarrow Na \text{ (in Hg, } C_1)$
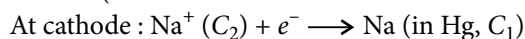
$$\therefore \quad E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{1} \log \frac{1}{[Na^+]}$$

At anode : $Na \text{ (in Hg, } C_1) \longrightarrow Na^+ (C_2) + e^-$
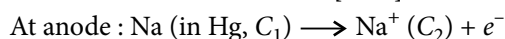
$$\therefore \quad E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{1} \log[Na^+]$$

○ **Quinhydrone electrode :**

It is a redox electrode. Quinhydrone refers to an equimolar mixture of benzoquinone and hydroquinone.

Benzoquinone is [structure] and hydroquinone is
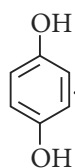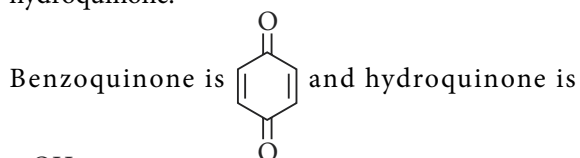
[structure]. They are interconvertible and thus can serve the purpose of electrode reactions.

At cathode : [structure] $+ 2H^+ + 2e^- \longrightarrow$ [structure]
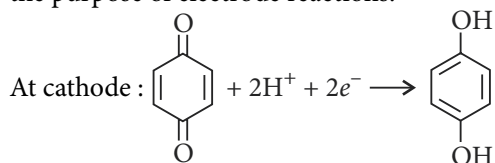
Therefore, $E_{cell} = E_{cell}^{\circ} - \dfrac{0.0591}{2} \log \dfrac{1}{[H^+]^2}$

$$\Rightarrow \quad E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2}(-2)\log[H^+]$$

$$\Rightarrow \quad E_{cell} = E_{cell}^{\circ} - 0.0591\{-\log[H^+]\}$$

$$\Rightarrow \quad E_{cell} = E_{cell}^{\circ} - 0.0591 \text{ pH}$$

At anode : [structure] $\longrightarrow$ [structure] $+ 2H^+ + 2e^-$
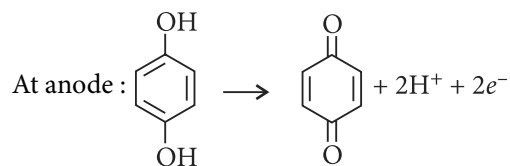
$$\therefore \quad E_{cell} = E_{cell}^{\circ} - \frac{0.0591}{2}\log[H^+]^2$$

$$\Rightarrow \quad E_{cell} = E_{cell}^{\circ} + 0.0591 \text{pH}$$

Problem-1 : In a certain reaction, a metal is changing its oxidation state as below :

MO_4^{3-} to MO_2^- and $E_{MO_4^{3-}/MO_2^-}^{\circ} = -0.62$ V
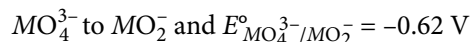
The reduction of MO_4^{3-} to MO_2^- is carried out by adding KI solution. Find $E_{MO_4^{3-}/MO_2^-}$ if 20 mL of 0.1 N KI solution is added to 25 mL of 0.1 N MO_4^{3-} solution.

[Given : pH of the solution = 3]

Soln.: The equation form of reduction half-cell is as below :

$$MO_4^{3-} + 4H^+ + 2e^- \longrightarrow MO_2^- + 2H_2O$$
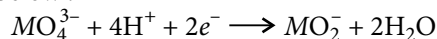
$$\therefore \quad E_{MO_4^{3-}/MO_2^-} = E_{MO_4^{3-}/MO_2^-}^{\circ}$$
$$- \frac{0.0591}{2}\log\frac{[MO_2^-]}{[MO_4^{3-}][H^+]^4} \quad ...(i)$$

Now, meq. of $MO_4^{3-} = 25 \times 0.1 = 2.5$ meq.

meq. of KI $= 20 \times 0.1 = 2.0$ meq.

$\therefore$ meq. of MO_4^{3-} left $= (2.5 - 2) = 0.5$ meq.

[$\because$ 2.0 meq. of KI will completely react with 2.0 meq. of MO_4^{3-}]

and meq. of MO_2^- produced = 2.0 meq.

Now, total volume = (20 + 25) mL = 45 mL

Hence, $[MO_4^{3-}] = \dfrac{0.5}{45} = \dfrac{1}{90}$ and $[MO_2^-] = \dfrac{2}{45}$

As pH = 3 $\Rightarrow -\log[H^+] = 3 \Rightarrow [H^+] = 10^{-3}$ M

From equation (i)

$$E_{MO_4^{3-}/MO_2^-} = -0.62 - \frac{0.06}{2}\log\frac{\frac{2}{45}}{\frac{1}{90}\times 10^{-12}}$$

[Taking 0.0591 ≈ 0.06]

$$= -0.62 - \frac{0.06}{2}\log\frac{2}{45}\times\frac{90}{10^{-12}}$$

$$= -0.62 - \frac{0.06}{2}\left[\log 4 + \log 10^{12}\right]$$

$$= -0.62 - 0.03\,[0.602 + 12]$$

$$= -0.62 - 0.37806 = -0.99806 \text{ V}$$

Problem-2 : Find the standard electrode potential for MnO_4^-/MnO_2.

[Given : $E_{MnO_4^-/Mn^{2+}}^{\circ} = +1.511$ V and $E_{MnO_2/Mn^{2+}}^{\circ} = +1.23$ V]

Soln.: E_{cell} is not additive but energy is additive. So, the following method will be adopted.

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \; ; \Delta G_1^\circ \;\; ...(1)$$

$$MnO_2 + 4H^+ + 2e^- \longrightarrow Mn^{2+} + 2H_2O \; ; \Delta G_2^\circ \;\; ...(2)$$

Reverse the reaction (2) and add it to reaction (1),

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

$$Mn^{2+} + 2H_2O \longrightarrow MnO_2 + 4H^+ + 2e^-$$

$$\overline{MnO_4^- + 4H^+ + 3e^- \longrightarrow MnO_2 + 2H_2O \; ; \Delta G_3^\circ}$$
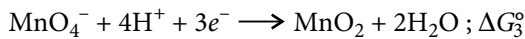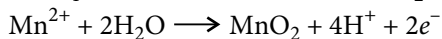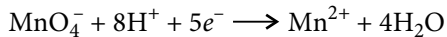
$$\therefore \quad \Delta G_3^\circ = \Delta G_1^\circ - \Delta G_2^\circ$$

$$\Rightarrow \quad -n_3 F E_3^\circ = -n_1 F E_1^\circ - (-n_2 F E_2^\circ)$$

$$\Rightarrow \quad -3 E_3^\circ = -5 E_1^\circ + 2 E_2^\circ$$

$$\Rightarrow \quad E_3^\circ = \frac{5 E_1^\circ - 2 E_2^\circ}{3} = \frac{(5 \times 1.511) - (2 \times 1.23)}{3}$$

$$= \frac{7.555 - 2.46}{3} = 1.698 \text{ V}$$

Problem 3 : Standard reduction potential for Cu^{2+}/Cu is +0.34 V. Calculate the reduction potential at pH = 14 for the above couple.

[Given : K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19}]

Soln.: As the solution has pH = 14, therefore,

$$[H^+] = 10^{-14} \text{ M}$$

As, $K_w = 10^{-14}$, hence, $[OH^-] = 10^0 = 1$ M

In the solution, $Cu(OH)_2 \longrightarrow Cu^{2+} + 2OH^-$

$$\therefore \quad K_{sp} = [Cu^{2+}][OH^-]^2$$

$$\Rightarrow \quad 1 \times 10^{-19} = [Cu^{2+}] \cdot 1^2 \Rightarrow [Cu^{2+}] = 10^{-19} \text{ M}$$

Now, for the Cu^{2+}/Cu couple,

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
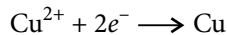
$$\therefore \quad E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]}$$

$$= 0.34 - \frac{0.0591}{2} \log \frac{1}{10^{-19}}$$

$$= 0.34 - \frac{0.0591}{2} \times \log 10^{19}$$

$$= 0.34 - \frac{0.0591}{2} \times 19 \log 10$$

$$= 0.34 - \frac{0.0591}{2} \times 19 = -0.22145 \text{ V}$$

Concentration Cells

The name is as such because cell reactions are carried out as per the concentrations of different materials used. Two types of concentration cells are found.

Type-1 : Electrolytic concentration cells

For every case, similar electrodes are dipped into the same electrolyte of different concentrations separated into two compartments.

The electrical energy is generated through the passage of ions which in turn occurs due to the difference in concentration *i.e.*, the tendency of electrolyte to flow from high to low concentration.

Representation of the cell is as below :

$$M_{(s)} \mid M^{n+}(C_1) \mid\mid M^{n+}(C_2) \mid M_{(s)}$$

$$\underbrace{\phantom{M_{(s)} \mid M^{n+}(C_1)}}_{\text{Anode}} \quad \underbrace{\phantom{M^{n+}(C_2) \mid M_{(s)}}}_{\text{Cathode}}$$

$\therefore$ At anode : $\qquad M_{(s)} \longrightarrow M^{n+}(C_1) + ne^-$

At cathode : $\qquad M^{n+}(C_2) + ne^- \longrightarrow M_{(s)}$

Overall cell reaction : $\quad \overline{M^{n+}(C_2) \longrightarrow M^{n+}(C_1)}$

$$[\text{Cathode} \rightarrow \text{Anode}]$$
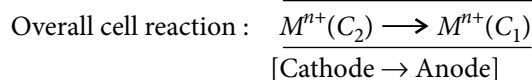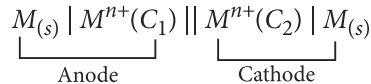
For concentration cell, $E^\circ_{cell} = 0$

$$\therefore \quad E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[M^{n+}]_{RHS}}{[M^{n+}]_{LHS}}$$

$$= 0 - \frac{0.0591}{n} \log \frac{C_1}{C_2}$$

Forward reaction will be spontaneous if $C_2 > C_1$ *i.e.*, $\Delta G < 0$; hence, exergonic.

If $C_1 > C_2$, cell reaction is non-spontaneous *i.e.*, $\Delta G > 0$; hence, endergonic.

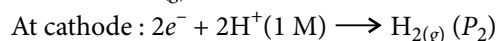**Some common examples :**

(i) $Zn_{(s)} \mid Zn^{2+}(C_1) \mid\mid Zn^{2+}(C_2) \mid Zn_{(s)}$

(ii) Gas electrode :

Pt, $H_{2(g)}$ (1 atm) $\mid H^+(C_1) \mid\mid H^+(C_2) \mid H_{2(g)}$ (1 atm), Pt
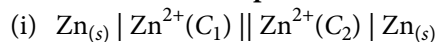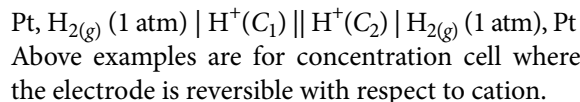
Above examples are for concentration cell where the electrode is reversible with respect to cation. The following example is for concentration cell where the electrode is reversible with respect to anion.

Pt, $Cl_{2(g)}$ (1 atm)$\mid Cl^-(C_1) \mid\mid Cl^-(C_2) \mid Cl_{2(g)}$ (1 atm), Pt
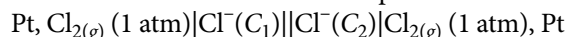
Type-2 : Electrode concentration cells

As from the name it can be understood that the different concentrations of electrodes are taken. Gas electrodes of different concentrations are immersed in the same electrolytic solution.
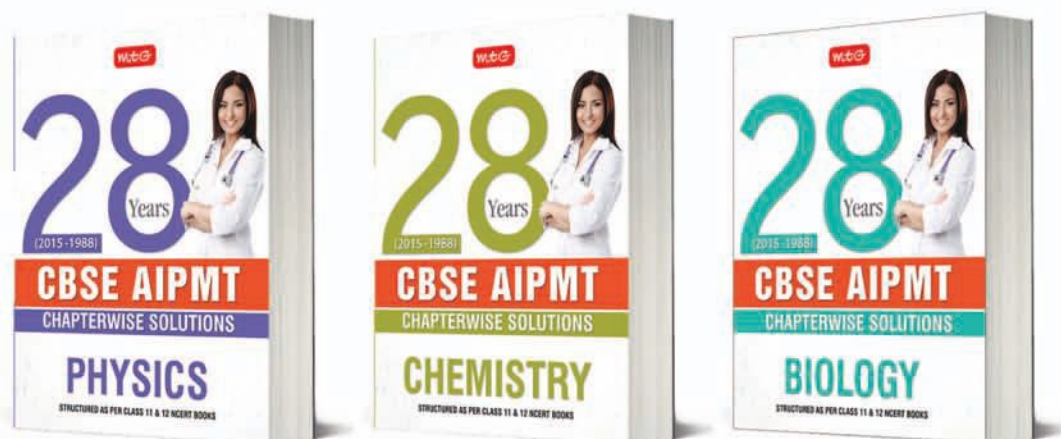
e.g., Pt, $H_{2(g)}$ (P_1) $\mid H^+$ (1 M) $\mid H_{2(g)}$ (P_2), Pt

$\therefore$ At anode : $H_{2(g)}(P_1) \longrightarrow 2H^+$(1 M) + $2e^-$

At cathode : $2e^- + 2H^+$(1 M) $\longrightarrow H_{2(g)}$ (P_2)

$$\overline{\text{Overall cell reaction : } H_{2(g)} (P_1) \longrightarrow H_{2(g)} (P_2)}$$
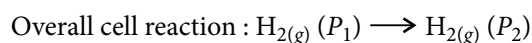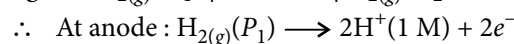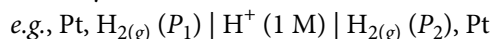
Here, $E_{cell} = E^\circ_{cell} - \frac{0.0591}{2} \log \frac{P_2}{P_1}$

$$\Rightarrow \quad E_{cell} = 0 + \frac{0.0591}{2} \log \frac{P_1}{P_2} = \frac{0.0591}{2} \log \frac{P_1}{P_2}$$

For spontaneous forward reaction, $P_1 > P_2$
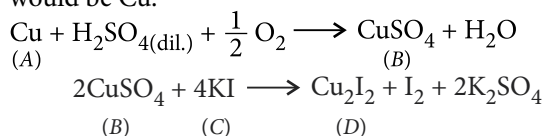
◈ ◈

CHEMISTRY MUSING

SOLUTION SET 24

1. **(c) :** Melting points of ionic compounds NaF, NaCl and NaBr are 993 °C, 801 °C and 747 °C respectively. Hence, compound X would be NaCl.

   None of the oxides of period 3, has any free or mobile electrons. This means that none of them will conduct electricity when they are solid. But, electrolysis is possible if they are molten. Hence, compound Y would be MgO.

   Both $C_{(graphite)}$ and $C_{(diamond)}$ boil and melt at 4827 °C and 3550 °C respectively. But, $C_{(diamond)}$ is an excellent insulator, with little or no tendency to carry an electric current whereas, $C_{(graphite)}$ is a good conductor of electricity in solid. Hence, Z would be $C_{(graphite)}$.

2. **(c) :** Magnetic moment, $\mu = \sqrt{n(n+2)}$ B.M.

   When $n = 1$, $\mu = 1.73$ B.M. ~ 1.8 B.M. (Given)

   $Cu(29) : 1s^2, 2s^2 2p^6, 3s^2 3p^6 3d^{10}, 4s^1$

   Cu has one unpaired electron. Hence, the metal 'A' would be Cu.

   $\underset{(A)}{Cu} + H_2SO_{4(dil.)} + \frac{1}{2} O_2 \longrightarrow \underset{(B)}{CuSO_4} + H_2O$

   $2\underset{(B)}{CuSO_4} + 4\underset{(C)}{KI} \longrightarrow Cu_2I_2 + \underset{(D)}{I_2} + 2K_2SO_4$

3. **(b) :** The dissolution of NaH in water occurs to eliminate H_2 as follows,

   $NaH_{(aq)} + H_2O_{(l)} \longrightarrow NaOH_{(aq)} + H_{2(g)}$

   or, $H^-_{(aq)} + H_2O_{(l)} \longrightarrow OH^-_{(aq)} + H_{2(g)}$
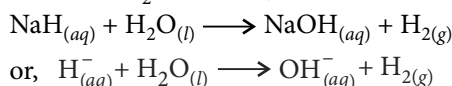
   Since H^- is a strong base it will abstract H^+ from H_2O.

4. **(b) :**

5. **(b) :**
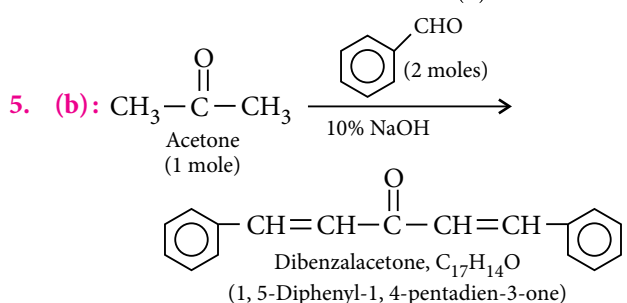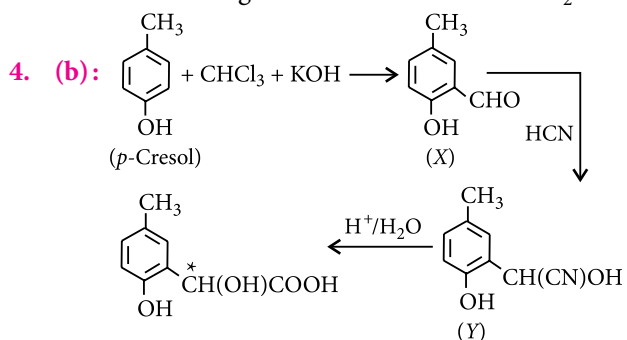
6. **(c) :** The correct order for S_N1, S_N2, E1 and E2 reactions of alkyl halides is :

   $\xleftarrow{\text{Increasing order of } S_N1 \text{ or E1 or E2}}$

   $3° C^+, 2° C^+, 1° C^+, -CH_3^+$

   $\xrightarrow{\text{Increasing order of } S_N2}$
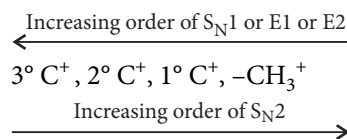
   More is the stability of intermediate carbonium ion, more is the chance of S_N1 mechanism. The intermediates obtained will be (i) $Ph\overset{+}{C}H_2$, (ii) $Ph\overset{+}{C}HMe$, (iii) $Ph\overset{+}{C}Me_2$, (iv) $Ph\overset{+}{C}MePh$. The stability order is (iv) > (iii) > (ii) > (i).

7. **(a) :** (b) Collision number is directly proportional to mean speed as $Z = \frac{1}{\sqrt{2}} \pi\sigma^2 C_{av} n^2$

   where, σ = molecular diameter; n = no. of molecules per cc of the gas; C_{av} = average velocity

   $C_{av} \propto \sqrt{T}$

   (c) : E_a is almost constant for a wide range of temperature.

   (d) : On adding a catalyst, the activation energy of the reaction is not lowered because the reaction proceeds *via* the formation of new activated complex which requires less energy for its formation.

8. **(a) :** $f = exp\left[\dfrac{-75000}{8.314 \times 298}\right] = e^{-30.3} = 7 \times 10^{-14}$

9. **(3) :** $Cr_2O_7^{2-} + 14H^+ + 3Sn^{2+} \longrightarrow 2Cr^{3+} + 3Sn^{4+} + 7H_2O$

   One mole of $Cr_2O_7^{2-}$ ion oxidises 3 moles of Sn^{2+} to Sn^{4+} ion.

10. **(4) :** At a given temperature,

    Relative humidity

    $= \dfrac{\text{Partial pressure of } H_2O \text{ in air}}{\text{Vapour pressure of } H_2O} \times 100$

    $\therefore$ Partial pressure of H_2O in air $= \dfrac{45}{100} \times 17.5$

    $= 7.88$ torr $= 0.0104$ atm [$\because$ 1 atm = 760 torr]

    $PV = nRT$

    $\therefore n = \dfrac{PV}{RT} = \dfrac{0.0104 \text{ atm} \times 1 \text{ L}}{0.0821 \text{ L atm K}^{-1} \text{ mol}^{-1} \times 293 \text{ K}}$

    $= 4.3 \times 10^{-4}$ mol

    ◆◆

ADVANCED CHEMISTRY BLOC

(CONTRACTION AND EXPANSION OF ORBITALS)

Mukul C. Ray, Odisha

Conditions under which *d*-orbitals Participate in Hybridization

Orbitals having slight difference in energy participate in hybridization. What happens if they are widely different in energy? Take the example of $3s$, $3p$ and $3d$-orbitals of phosphorus atom (in excited state its valence shell has the configuration $3s^1\ 3p^3\ 3d^1$) participating in hybridization. Promoting the electron from $3s$-orbital to $3d$-orbital raises the energy of the system. Also the hybrid orbitals are equivalent in shape and energy. With the participation of high energy $3d$-orbital, the energy of hybrid orbital has now increased. So an electron, which was earlier in a $3s$-orbital, will have now higher energy when in hybrid orbital *i.e.*, the energy of the electron has increased. But such an energy increase trying to destabilize the system is overpowered when the hybrid orbitals make more bonds and also stronger bonds than pure orbitals. Hence, the system manages to achieve low energy and high stability. This is absolutely true but only under special circumstances. Under ordinary situation this is never possible because, the increase in energy while promoting an electron (called promotion energy) if high, the hybrid orbital energy will also be high and the system cannot afford such high energy investments as the upcoming bond makings may not compensate the high energy requirement. This explains why PF_5 is formed but not PH_5. So the d-orbital energy must drop for making suitable conditions to facilitate hybridization between s, p and d-orbitals.

The Theory of *d*-orbital Contraction

O The d-orbitals of an atom in a molecule are different in energy and size from those in an isolated atom. When the strong electronegative atoms like fluorine progress towards the central atom, even under no bond formation condition the interaction may be considered as purely electrostatic. Due to this field, a positive charge develops on the central atom. All orbitals contract if the central atom carries a positive charge, $3d$-orbitals the most. The contraction is larger with larger d-orbitals like $4d$ and $5d$. Orbital contraction stabilizes central atom. These contracted orbitals are now closer to the nucleus. Electrons in such orbitals feel more attracted, more stabilized hence, less energetic. **This contraction is an adaptation of the central atom to the field of the substituents.** Contracted low energy d-orbitals participate in hybridization.

O The contraction of orbitals is determined by the number and kind of the substituents exerting field. The contracting power or field strength varies as :

Fluorine > Chlorine >> Hydrogen

The atoms exerting the contracting field may be bound with other atoms, which do not contribute. For example, compounds like PF_4H, PF_3H_2 are known.

O The contraction depends on the particular d-orbitals since on geometric grounds, the interaction with different substituents should be of different strength. In making an octahedral molecule, the electronegative atoms are approaching the central atom along the co-ordinates. The d-orbitals, which have their lobes along the co-ordinates, interact strongly as compared to non-axial d-orbitals. So, they are more strongly contracted as they feel the field more. Thus, in sp^3d^2 or d^2sp^3 hybridization the participating orbitals are s, p_x, p_y, p_z, $d_{x^2-y^2}$, d_{z^2}. With similar arguments the following conclusions can be drawn :

Hybridization	Participating orbitals	Examples
sp^3d^2 or d^2sp^3	s, p_x, p_y, p_z, $d_{x^2-y^2}$, d_{z^2}	SF_6
sp^3d or dsp^3	s, p_x, p_y, p_z, d_{z^2}	PF_5
sd^3	s, d_{xy}, d_{yz}, d_{zx}	Permanganate ion

○ The energy to promote two electrons to the 3*d*-orbitals remains enormous, even if the *d*-orbital fields are strongly modified by substituent fields. Only substituents, which make strong bonds with the central atom, can compensate the promotion energy.

Fluorine can bring about the promotion of two or more electrons to a *d*-level, with heavier central atom and low promotion energies. Oxygen is also suitable as in SF_6, ClF_5, IF_5, XeF_6 and $Te(OH)_6$.

○ These contractions do not apply if the *d*-orbitals are employed to form co-ordinate bonds involving no valence electron promotion as in $[AsCl_4]^-$.

pi-Bonds with *d*-orbital Participation

These *d*-orbitals are well suited to form *pi*-bonds. Hence, *d*-orbital contraction is not required for *p*-*d* –*pi* bonds, as it is necessary for sigma bonding. The atoms of the second full row (Si, P, S and Cl) thus employ *d*-orbitals even for small number of substituents as in SO_2 or NSF or for weak substituent fields as in P_4S_{10} or $PSCl_3$.

Relativistic Contraction

The effects discussed above are observed when the central atom is amidst the field of the substituents. There is another kind of fundamental contraction observed in heavier elements.

For an element with $Z = 80$ (Hg), the electrons in the 6*s*-orbital has velocity value that is very close to 0.6 times that of the velocity of light. Applying the relativistic correction :

$$m = \frac{m_0}{\sqrt{1 - \dfrac{v^2}{c^2}}}$$

The relativistic mass of an electron now becomes 1.2 times the rest mass of electron. With increase in mass, the centrifugal force on the electron increases and the electron tries to escape from the nucleus. To keep the atom in the stable form, the nucleus exercises heavy force on the outer orbital and the concerned orbital shrinks. This relativistic effect becomes prominent in the sixth period, particularly on the 6*s*-electron. The contraction of 6*s*-orbital (the outermost orbital) explains the decrease in size of the atom. This effect is in addition to the lanthanide contraction. In Pauling scale, electronegativity of Hg is 1.9 against that of Cd as 1.6. This increase in electronegativity is a consequence of relativistic contraction. Only lanthanide contraction cannot explain such higher value of electronegativity.

Relativistic Expansion

The contracted 6*s*-orbital creates another difference. The 6*s*-electrons are now closer to the nucleus and shield the nuclear charge more effectively. As a result 5*d*-orbitals experience less nuclear charge and get expanded. This explains why Pt(IV) oxidation state is stable but not Pd(IV). In Pt, the 6*s*- orbital is contracted and 5*d*-orbital is expanded. These two orbitals are now closer in energy. They together can participate in bonding. While due to large energy separation between 5*s* and 4*d*- orbitals, Pd cannot afford to loose 4*d*-electrons under the same conditions as 5*s*-electrons.

In a similar line of arguments it can be explained that actinides exhibit variety of oxidation states including +6 while lanthanides only exhibit +3 and rarely +4 oxidation states.

◈ ◈

Y❓U ASK
WE ANSWER

**Do you have a question that you just can't get answered?**

Use the vast expertise of our mtg team to get to the bottom of the question. From the serious to the silly, the controversial to the trivial, the team will tackle the questions, easy and tough.

The best questions and their solutions will be printed in this column each month.

Q1. Di-*sec*-butylacetylene (3,6-dimethyl-4-octyne) fails to isomerise to another alkyne when treated with $NaNH_2/NH_3$. Explain.

Lijo Abraham (Kerala)

Ans. In this case the isomerisation is blocked by the alkyl groups. An allene can be formed, but the reaction can go no further as there is no allenic hydrogen that can be removed by base to produce a new resonance stabilised anion.
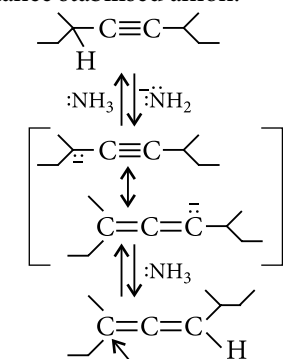
There is no hydrogen on this carbon to remove and carry the isomerisation further.

Q2. $[Fe(H_2O)_6]^{3+}$ and $[Cr(H_2O)_6]^{3+}$ are equally stable thermodynamically but the former is labile whereas the latter is inert.

Sunaina Rajput (Ghaziabad)

Ans. Metal ions having one or more electrons in their e_g orbitals or less than 3 electrons in t_{2g} orbitals will form labile complexes whereas ions having no electron in their e_g orbitals or 3 electrons in their t_{2g} orbitals will form inert complexes. Fe^{3+} (d^5) in the complex has 2 electrons in its e_g orbitals; hence this complex is labile. But Cr^{3+} in complex (d^3) has no electron in its e_g orbitals; hence this complex is inert.

Q3. To prevent the growth of bacteria and other microorganisms various chemicals are added to water in a swimming pool. Doesn't it harm the swimmer? If yes, then how is it made suitable for swimming?

Sumit Arora (Delhi)

Ans. Water in the swimming pool is a highly dilute solution of chemicals that prevent the growth of bacteria and help stabilise the pool lining. These substances can affect the pH of the pool water, making it unpleasant for swimmers. Therefore, the pH has to be monitored and controlled.

Adding non-toxic $NaHCO_3$ (pH ~ 7.0) as buffer is an effective way to keep the pool's pH at an acceptable value, preferably between 7.0 and 7.6. The bicarbonate ion is an example of a single ion that is able to neutralise excess H^+ or OH^- ions. The reactions are

$$HCO_{3(aq)}^- + H_{(aq)}^+ \longrightarrow H_2CO_{3(aq)}$$
$$HCO_{3(aq)}^- + OH_{(aq)}^- \longrightarrow H_2O_{(l)} + CO_{3(aq)}^{2-}$$
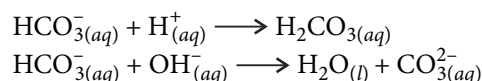
Maintaining the level of bicarbonate ions between 80 and 120 ppm produces the optimal results. Concentrations above this makes the pool water cloudy and also chlorine loses its effectiveness. On the other hand when the bicarbonate ion concentration is too low, wide swings in pH can occur, plaster walls can get etched, metals can corrode, the pool's walls and floor can get stained, the water can turn green and can cause burning sensation in eyes.

Q4. When a liquid is heated bumping takes place which can be avoided by adding few porcelain bits to the liquid. Why?

Kalpana Singh (Mumbai)

Ans. Almost all liquids tend to superheat *i.e.* rise to a temperature above boiling point. This is a metastable condition and is interrupted periodically by a sudden violent surge of vapours from the liquid. This is called bumping. When some small pieces of porcelain are added, the small pores on porcelain surface provide sites for the formation of bubble nuclei and thereby results in smooth boiling.

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CROSS WORD

CROSSWORD

Readers can send their responses at editor@mtg.in or post us with complete address by 25th of every month to win exciting prizes. Winners' name with their valuable feedback will be published in next issue.

ACROSS

4. The process of commercial preparation of chlorobenzene. (7)

5. Most unsymmetrical crystal system. (9)

7. A complex in which an electron is trapped in the hole present in the cryptand. (9)

8. Meson theory for the stability of nucleus was put forward by _____. (6)

10. The protein - cofactor complex. (10)

11. A blood red complex of Fe^{2+} ion with 1, 10-phenanthroline, used as a redox indicator. (7)

14. Chemical name of artificial camphor. (16)

15. Substance added to cement to slow down its rate of setting. (6)

18. A mixture of two or more substances with melting point lower than that of any other mixture of the same substances. (8)

19. A synthetic steroid that blocks the effects of progesterone. (12)

23. A material that spreads along a surface, changing the properties of the surface. (10)

24. The mutual conversion of a particle and antiparticle into electromagnetic radiation. (12)

25. Monocyclic compounds having general formula $(-CH=CH-)_n$. (9)

26. Yellow form of PbO. (8)

28. Fluorochlorobromocarbons used as fire fighting in tanks and armoured personal carriers. (6)

29. Stereochemical form of polypropylene having methyl groups alternating regularly on the opposite sides of the zig-zag backbone. (12)

30. When the strength of a base is determined with the help of a standard solution of an acid, it is known as _____. (11)

DOWN

1. Trivial name of methyl alcohol. (8)

2. The process of heating steel at about 973 K in an atmosphere of ammonia. (9)

3. A number of cells connected in series. (7)

5. A mixture of TiO_2 and $BaSO_4$. (7)

6. An important ore of gold. (10)

9. Thermodynamically stable form of selenium. (13)
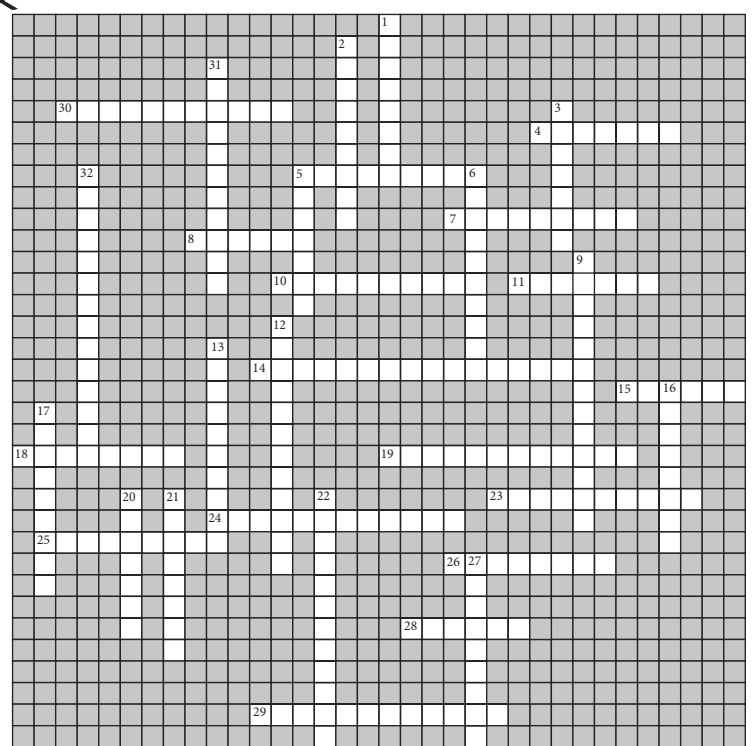
12. The technique used for drying substances which are sensitive to heat. (12)

13. Product obtained by the reaction of ethylene with sulphur monochloride. (10)

16. Most ductile metal. (8)

17. Ionic salt of glutamic acid used as flavour enhancer in many foods. (9)

20. A substance that has different composition than another, but has the same crystalline structure. (7)

21. Elements belonging to the same group. (8)

22. Brown's catalyst. (12)

27. The process of separation of two gases on the basis of their different rates of diffusion due to difference in their densities. (9)

31. Double sulphates of divalent ions and trivalent ions with 24 water molecules of crystallisation. (11)

32. The reaction which gives a mixture of ortho and para-hydroxybenzyl alcohol when phenol is treated with 40% HCHO in presence of dilute acid or alkali. (14)