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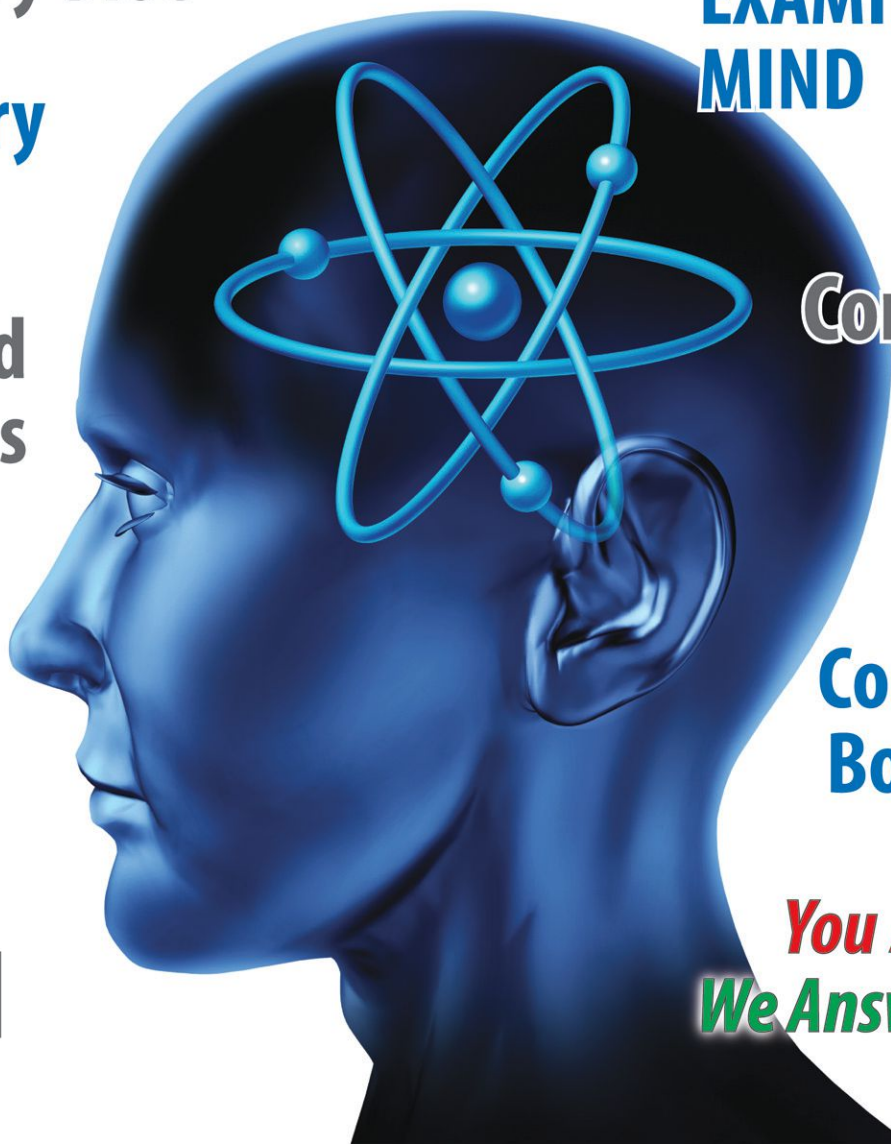
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**EXAMINER'S  
MIND** Class XI  
Class XII

Concept  
Map

Concept  
Booster

**You Ask ?**  
**We Answer ✓**



# CHEMISTRY today

Vol. XXIV No. 9 September 2015

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# edit Q rial

## Philosophy and its Various Names

The supreme power is called by various names in various countries and by different philosophers. The function is the same. Natural philosophers do the same. Whether one studied English, Physics or Chemistry, the post-graduate degree was M.A. That is Master of Arts. Till Cambridge changed the post-graduate degree for science to M.Sc., our universities kept M.A. For clarity, in the printed degree, it was added in ink. For example, M.A. was given as M.A. (Chemistry), M.A. (Physics) etc. The names may be different, but the functions are the same, particularly in research.

To understand the chemical structure of DNA and RNA, the scientists had to use every trick in Mathematics, competing with a chemist, Linus Pauling who never left any topic untouched. One can learn various symmetries for the sake of understanding the beauty of Mathematics. One can use it for printing materials for dresses or it can be used for the purpose of decoration as in "rangoli", playing with various colours. When Mathematics was introduced for art students or even science students of other subjects, there was a revolt against imposition of Mathematics. It was actually a gift of Mathematics for non-mathematics students and not imposition.

Shastras—application of *vedas* to technology and Vignān—superior knowledge are from the same source. Because of the limitation of knowledge of the common man and inability to concentrate on many subjects simultaneously, specialists rose to treat only nose or knees but not the whole body. We want students to understand the philosophy of integrated learning with each subject helping man to understand the other subject better.

The need of the hour is integration and not division in science or philosophy.

Anil Ahlawat  
Editor

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

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

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

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

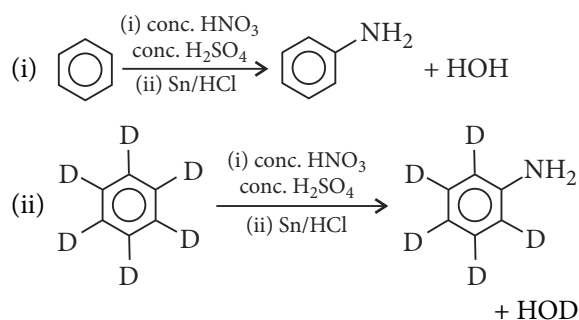
## PROBLEM Set 26

### JEE MAIN/PMTs

1. A hydrogen electrode placed in a buffer solution of  $\text{CH}_3\text{COONa}$  and acetic acid in the ratios  $x : y$  and  $y : x$  has electrode potential values  $E_1$  volt and  $E_2$  volt respectively at  $25^\circ\text{C}$ . The  $\text{p}K_a$  values of acetic acid is ( $E_1$  and  $E_2$  are oxidation potential values):

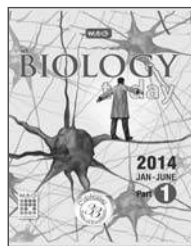
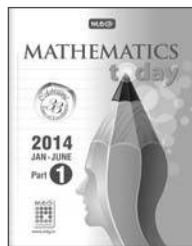
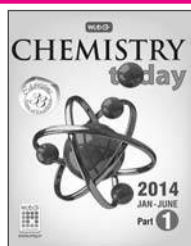
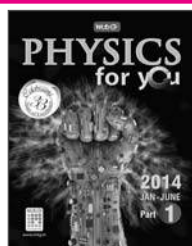
- (a)  $\frac{E_1 + E_2}{0.118}$                       (b)  $\frac{E_2 - E_1}{0.118}$   
 (c)  $-\frac{E_1 + E_2}{0.118}$                       (d)  $\frac{E_1 - E_2}{0.118}$

2. Which of the two reactions proceeds faster?



- (a) (i)                                      (b) (ii)  
 (c) (i) = (ii)                              (d) Cannot be predicted

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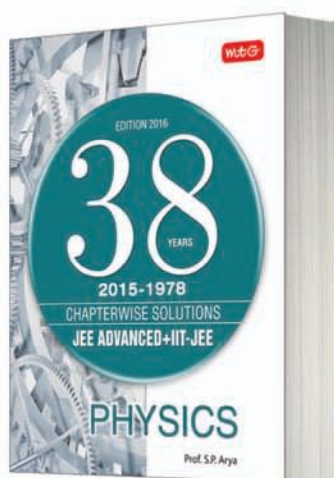
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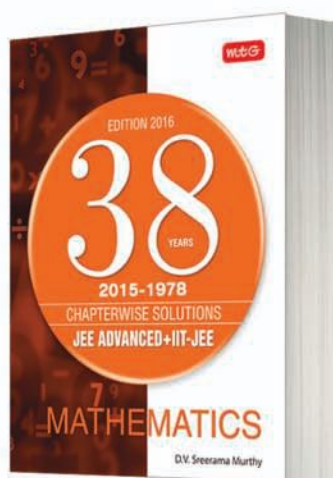
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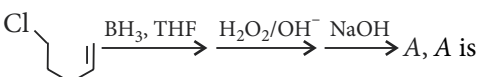
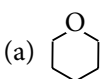
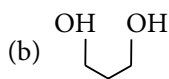
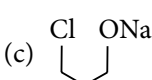
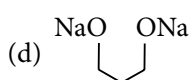
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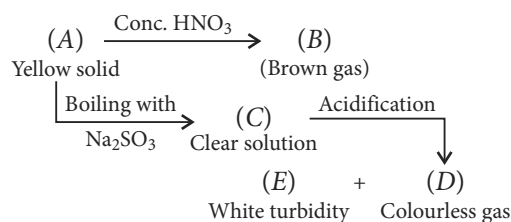
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3. H—O—H bond angle in the water molecule is  $105^\circ$ , the H—O bond distance being  $0.94 \text{ \AA}$ . Dipole moment for the molecule is 1.85 D. Charge on the oxygen atom is:
- (a)  $2.01 \times 10^{-10}$  esu    (b)  $3.23 \times 10^{-10}$  esu  
(c)  $5 \times 10^{-9}$  esu        (d)  $4 \times 10^{-10}$  esu
4. Dehydrogenation of 1-bromo-1,2-diphenylpropane proceeds through E2 mechanism to form 1,2-diphenylpropene; what do you expect about this reaction?
- (a) It is a stereoselective reaction.  
(b) It is a stereospecific reaction.  
(c) Both (a) and (b).  
(d) None of the two.
5. When an electron of H-atom jumps from a higher to lower energy state, then
- (a) its potential energy increases  
(b) its kinetic energy increases  
(c) its angular momentum remains unchanged  
(d) wavelength of de Broglie wave associated with the electron increases.

### JEE ADVANCED

6.  A, A is
- (a)                       (b) 
- (c)                       (d) 

### COMPREHENSION



7. Brown gas (B) is :
- (a)  $\text{H}_2\text{S}$                                       (b)  $\text{NH}_3$   
(c)  $\text{NO}_2$                                       (d) None of these
8. Colourless gas (D) and turbidity (E) respectively are :
- (a) S,  $\text{SO}_2$                                       (b)  $\text{SO}_2$ , S  
(c)  $\text{SO}_2$ ,  $\text{BaSO}_4$                               (d) None of these

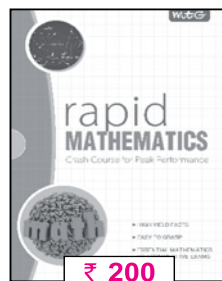
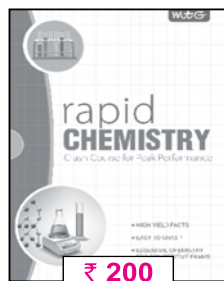
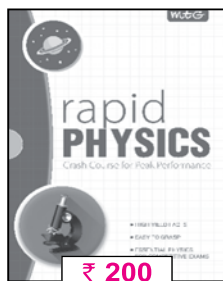
### INTEGER VALUE

9. Temperature of 1 mole of a gas is increased by  $1^\circ$  at constant pressure. Work done in  $\text{cal mol}^{-1} \text{K}^{-1}$  is :
10. A very small amount of radioactive isotope of  $^{213}\text{Pb}$  was mixed with a non-radioactive lead salt containing 0.01 g of Pb (atomic mass 207). The whole lead was brought into solution and lead chromate was precipitated by addition of a soluble chromate. Evaporation of  $10 \text{ cm}^3$  of the supernatant liquid gave a residue having a radioactivity  $1/24000$  of that of the original quantity of  $^{213}\text{Pb}$ . If the solubility of lead chromate is  $x \times 10^{-y} \text{ mol dm}^{-3}$ , then value of x is :

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# EXAMINER'S MIND

## CLASS XI



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

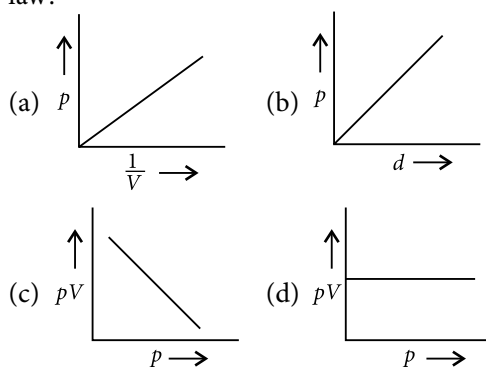
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#### SECTION - I

##### 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.

- Which pair of molecules has the strongest dipole-dipole interactions?  
(a)  $\text{NH}_3$  and  $\text{CH}_4$  (b)  $\text{NH}_3$  and  $\text{NH}_3$   
(c)  $\text{CH}_4$  and  $\text{CH}_4$  (d)  $\text{CO}_2$  and  $\text{CO}_2$
- 1 mole of  $\text{Al}_4\text{C}_3(\text{s})$  reacts with  $\text{H}_2\text{O}$  in a closed vessel at  $27^\circ\text{C}$  against atmospheric pressure. Work done is  
(a)  $-1800$  cal (b)  $-600$  cal  
(c)  $+1800$  cal (d) zero
- Which is not a correct representation of Boyle's law?



- When 1 mole of  $\text{CO}_2(\text{g})$  occupying volume 10 L at  $27^\circ\text{C}$  is expanded under adiabatic condition, temperature falls to 150 K. Hence, final volume is  
(a) 20 L (b) 5 L  
(c) 80 L (d) 40 L
- A jar contains a gas and a few drops of water at  $T$  K. The pressure in the jar is 830 mm of Hg. The temperature of the jar is reduced by 1%. The vapour pressure of water at two temperatures

are 30 and 25 mm of Hg. The new pressure in the jar is

- (a) 717 mm Hg (b) 1000 mm Hg  
(c) 817 mm Hg (d) 60 mm Hg
- When  $\text{CaCO}_3$  is heated to a high temperature, it undergoes decomposition into  $\text{CaO}$  and  $\text{CO}_2$  whereas it is quite stable at room temperature. The most likely explanation of it, is  
(a) the enthalpy of reaction ( $\Delta H$ ) overweighs the term  $T\Delta S$  at high temperature  
(b) the term  $T\Delta S$  overweighs the enthalpy of reaction at high temperature  
(c) at high temperature, both enthalpy of reaction and entropy change become negative  
(d) none of these.
  - A vacuum tube having a volume of  $1 \text{ dm}^3$  was evacuated at a constant temperature of  $-23^\circ\text{C}$ . The pressure dropped down to  $7.6 \times 10^{-5}$  torr. What is the number of molecules of air still present in the tube?  
(a)  $2.9 \times 10^{15}$  (b)  $1.56 \times 10^{16}$   
(c)  $1.56 \times 10^{19}$  (d)  $2.9 \times 10^{20}$
  - $\Delta H = \Delta E$  is for the case  
(a)  $\text{C}_2\text{H}_4(\text{g}) + \text{H}_2(\text{g}) \longrightarrow \text{C}_2\text{H}_6(\text{g})$   
(b)  $\text{C}(\text{s}) + \text{CO}_2(\text{g}) \longrightarrow 2\text{CO}(\text{g})$   
(c)  $\text{NH}_4\text{HS}(\text{s}) \longrightarrow \text{NH}_3(\text{g}) + \text{H}_2\text{S}(\text{g})$   
(d)  $\text{CH}_4(\text{g}) + 2\text{O}_2(\text{g}) \longrightarrow \text{CO}_2(\text{g}) + 2\text{H}_2\text{O}(\text{g})$
  - Select the correct statement:  
(a) A mixture of ideal gases is cooled up to liquid the temperature (4.22 K) to form ideal solution  
(b) Ideal gas can be liquefied on applying pressure and lowering temperature.  
(c) Kinetic energy of a gas is zero at  $0^\circ\text{C}$ .  
(d) Ideal gas on subjecting to Joule-Thomson effect does not show cooling on account of absence of molecular forces of attraction.

10. The standard heats of formation of  $\text{CH}_4(\text{g})$ ,  $\text{CO}_2(\text{g})$  and  $\text{H}_2\text{O}(\text{g})$  are  $-76.2$ ,  $-394.8$  and  $-241.6$   $\text{kJ mol}^{-1}$  respectively. Calculate the amount of heat evolved by burning  $1 \text{ m}^3$  methane measured under normal conditions.

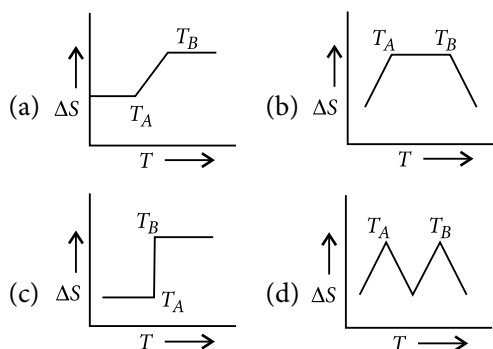
- (a) 162897.3 kJ            (b)  $-64078.2$  kJ  
(c)  $-35794.6$  kJ        (d) 35182 kJ

11. The kinetic molecular theory attributes an average translational kinetic energy of  $\frac{3RT}{2N}$  to each particle.

What *rms* speed would a mist particle of mass  $10^{-12}$  g have at room temperature ( $27^\circ\text{C}$ ) according to kinetic theory of gases?

- (a)  $0.41 \text{ cm s}^{-1}$             (b)  $0.35 \text{ cm s}^{-1}$   
(c)  $0.21 \text{ cm s}^{-1}$             (d)  $0.11 \text{ cm s}^{-1}$

12. If for a given substance,  $T_B$  is the m.p.t. and  $T_A$  is the freezing point, then correct variation of entropy by graph between entropy change ( $\Delta S$ ) and temperature is



13. Consider the following statements.

If the van der Waals' parameters of two gases are given as

	$a(\text{atm L}^2 \text{ mol}^{-2})$	$b(\text{L mol}^{-1})$
Gas X:	6.5	0.056
Gas Y:	8.0	0.011

then A :  $V_c(X) < V_c(Y)$

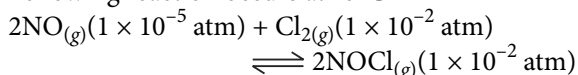
B :  $p_c(X) < p_c(Y)$

C :  $T_c(X) < T_c(Y)$

Select the correct alternate.

- (a) A alone                    (b) A and B  
(c) A, B and C            (d) B and C

14. Following reaction occurs at  $25^\circ\text{C}$



$\Delta G^\circ$  is

- (a)  $-45.65$  kJ            (b)  $-28.53$  kJ  
(c)  $-22.82$  kJ            (d)  $-57.06$  kJ

15. The *rms* velocity of hydrogen is  $\sqrt{7}$  times the *rms* velocity of nitrogen. If  $T$  is the temperature of the gas then

- (a)  $T(\text{H}_2) = T(\text{N}_2)$         (b)  $T(\text{H}_2) > T(\text{N}_2)$   
(c)  $T(\text{H}_2) < T(\text{N}_2)$         (d)  $T(\text{H}_2) = \sqrt{7}T(\text{N}_2)$

16. For the non-zero value of force of attraction between gas molecules and zero volume of gas molecules, gas equation will be

(a)  $PV = nRT - \frac{n^2 a}{V}$         (b)  $PV = nRT + nbP$

(c)  $PV = nRT$             (d)  $P = \frac{nRT}{V-b}$

17. The reciprocal of viscosity can be termed as

- (a) surface tension        (b) fluidity  
(c) density                (d) elasticity

18. Anhydrous  $\text{AlCl}_3$  is covalent. From the data given below, predict whether it would remain covalent or become ionic in aqueous solution (ionisation energy of Al =  $5137 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{Hydration}}$  for  $\text{Al}^{3+} = -4665 \text{ kJ mol}^{-1}$ ,  $\Delta H_{\text{Hydration}}$  for  $\text{Cl}^- = -381 \text{ kJ mol}^{-1}$ )

- (a) Ionic                    (b) Covalent  
(c) Both                    (d) None of these

19. Which one is incorrect statement of the second law of thermodynamics ?

- (a) It is impossible for a cyclic process to transfer heat from a system at a lower temperature to one at a higher temperature without converting some work to heat.  
(b) It is impossible to convert heat completely into equivalent amount of work without producing changes elsewhere.  
(c) Every perfect machine working reversibly between the same temperatures of source and sink has the same efficiency whatever be the nature of the substance used.  
(d) Heat engines can be made 100% efficient.

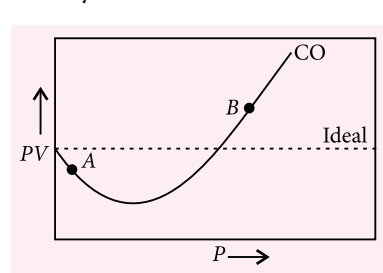
20. For CO, isotherm is of the type as shown. Near the point A, compressibility factor Z is

(a)  $\left(1 + \frac{b}{V}\right)$

(b)  $\left(1 - \frac{b}{V}\right)$

(c)  $\left(1 + \frac{a}{RTV}\right)$

(d)  $\left(1 - \frac{a}{RTV}\right)$



## 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. Which is correct statement?  
 (a) The entropy of the universe increases and tends towards the maximum value.  
 (b) All natural processes are generally irreversible.  
 (c) For reversible isolated processes, change of entropy is zero.  
 (d) For irreversible isolated processes, entropy change  $> 0$ .
22. Ratio of the rate of diffusion of He and H<sub>2</sub> at 0°C is same to the case:  
 (a) when temperature is changed to 100°C  
 (b) when O<sub>2</sub> and CH<sub>4</sub> are taken instead of He and H<sub>2</sub>  
 (c) when volume of the flask is doubled  
 (d) when CH<sub>4</sub> and O<sub>2</sub> are taken instead of He and H<sub>2</sub>.
23. In a closed insulated container a liquid is stirred with a paddle to increase the temperature which of the following is true?  
 (a)  $\Delta E = W \neq 0, q = 0$  (b)  $\Delta E = W = q \neq 0$   
 (c)  $\Delta E = 0, W = q \neq 0$  (d)  $W = 0, \Delta E = q \neq 0$
24. Which of the following is the correct statement(s)?  
 (a) Absolute zero (0 K) is the temperature reached when all possible thermal energy has been removed from a substance.  
 (b) A substance cannot be cooled any further after all thermal energy has been removed.  
 (c) Volume occupied by 1 mol of a real gas at STP is 22.4 L.  
 (d) At absolute zero, vibrational energy is zero.
25. If  $x$  and  $y$  are arbitrary extensive variable, then  
 (a)  $(x + y)$  is an extensive variable  
 (b)  $x/y$  is intensive variable  
 (c)  $dx/dy$  is intensive variable  
 (d) Both (b) and (c)

## 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

Having taken into account the corrections for pressure and volume, we can write the equation as

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

The above equation is known as van der Waals equation. In this equation  $n$  is number of moles of the gas. Constants  $a$  and  $b$  are called van der Waals constants and their value depends on the characteristic of gas. The deviation from ideal behaviour can be measured in terms of compressibility factor  $Z$ , which is the ratio of product  $PV$  and  $nRT$ . Mathematically,

$$Z = \frac{PV}{nRT}$$

26. Gas equation  $PV = nRT$  is obeyed by  
 (a) only isothermal process  
 (b) only adiabatic process  
 (c) both (a) and (b)  
 (d) none of these.
27. The compressibility of a gas is less than unity at STP. Therefore  
 (a)  $V_m > 22.4$  L (b)  $V_m < 22.4$  L  
 (c)  $V_m = 22.4$  L (d)  $V_m = 44.8$  L
28. An ideal gas will have maximum density when  
 (a)  $P = 0.5$  atm,  $T = 600$  K  
 (b)  $P = 2$  atm,  $T = 150$  K  
 (c)  $P = 1$  atm,  $T = 300$  K  
 (d)  $P = 1.0$  atm,  $T = 500$  K

## Paragraph for Questions 29 to 31

Gibbs energy or Gibbs function,  $G$  is given as

$$G = H - TS$$

Gibbs function,  $G$  is an extensive property and a state function.

The change in Gibbs energy for the system,  $\Delta G_{\text{sys}}$  can be written as

$$\Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}} - S_{\text{sys}}\Delta T$$

At constant temperature,  $\Delta T = 0$

$$\therefore \Delta G_{\text{sys}} = \Delta H_{\text{sys}} - T\Delta S_{\text{sys}}$$

$\Delta G$  gives a criteria for spontaneity at constant pressure and temperature.

- (i) If  $\Delta G$  is negative ( $< 0$ ), the process is spontaneous.  
 (ii) If  $\Delta G$  is positive ( $> 0$ ), the process is non spontaneous.  
 Gibbs energy for a reaction in which all reactants and products are in standard state,  $\Delta_r G^\circ$  is related to the equilibrium constant of the reaction as follows:  
 or  $\Delta_r G^\circ = -RT \ln K$



29. In which of the following processes, the process is always feasible?  
 (a)  $\Delta H > 0, \Delta S > 0$  (b)  $\Delta H < 0, \Delta S > 0$   
 (c)  $\Delta H > 0, \Delta S < 0$  (d)  $\Delta H < 0, \Delta S < 0$
30. For the reaction,  $\text{H}_2\text{O}_{(s)} \rightleftharpoons \text{H}_2\text{O}_{(l)}$  at  $0^\circ\text{C}$  and normal pressure  
 (a)  $\Delta H < T\Delta S$  (b)  $\Delta H = \Delta G$   
 (c)  $\Delta H = T\Delta S$  (d)  $\Delta H > T\Delta S$
31. If  $\Delta G^\circ$  for a reaction is  $46.06 \text{ kcal mol}^{-1}$  at  $27^\circ\text{C}$ ,  $K_p$  for the reaction is  
 (a)  $10^{-8}$  (b)  $10^{-22.22}$   
 (c)  $10^{-33.55}$  (d) none of these

## SECTION - IV

## Matching List Type

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

32. Match the elements in List I with their properties in List II and select the correct answer using the code given below the lists :

List I		List II	
(Molecules)		(Intermolecular forces)	
P. $\text{H}_2\text{S}$ molecules		1. London dispersion forces	
Q. $\text{Cl}_2$ and $\text{CCl}_4$ molecules		2. Dipole-induced dipole forces	
R. Ethyl amine molecules		3. Dipole-dipole interactions	
S. He atoms and HCl molecules		4. Hydrogen bonding	
<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(a) 3	4	2	1
(b) 2	1	3	4
(c) 3	1	4	2
(d) 1	2	4	3

33. Standard heats of formation ( $\Delta H_f^\circ$ ) are given below.

Compound	$\Delta H_f^\circ (\text{kcal mol}^{-1})$
$\text{CO}_{(g)}$	- 26.4
$\text{CO}_{2(g)}$	- 94.1
$\text{Fe}_2\text{O}_{3(s)}$	- 197.0
$\text{Fe}_3\text{O}_{4(s)}$	- 267.0
$\text{FeO}_{(s)}$	- 63.7
$\text{H}_2\text{O}_{(g)}$	- 58.0

Match the reactions in List I with their  $\Delta H_f^\circ$  in List II and select the correct answer using the code given in the lists :

List I		List II	
P. $3\text{Fe}_2\text{O}_{3(s)} + \text{CO}_{(g)} \longrightarrow$		1. + 8.2	
	$2\text{Fe}_3\text{O}_{4(s)} + \text{CO}_{2(g)}$		
Q. $\text{Fe}_3\text{O}_{4(s)} + \text{CO}_{(s)} \longrightarrow$		2. - 4.0	
	$3\text{FeO}_{(s)} + \text{CO}_{2(g)}$		
R. $\text{FeO}_{(s)} + \text{CO}_{(g)} \longrightarrow$		3. - 35.0	
	$\text{Fe}_{(s)} + \text{CO}_{2(g)}$		
S. $3\text{Fe}_{(s)} + 4\text{H}_2\text{O}_{(g)} \longrightarrow$		4. - 10.7	
	$\text{Fe}_3\text{O}_{4(s)} + 4\text{H}_2(g)$		
<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(a) 4	2	3	1
(b) 1	3	2	4
(c) 4	1	2	3
(d) 3	4	2	1

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. Efficiency of tooth-paste and mouthwash		1. is the molar volume of the liquid at a temperature when its surface tension is in unity.	
Q. If $n_1$ and $n_2$ are number of drops of equal volume of two liquids of density $D_1$ and $D_2$ then		2. the downward force due to the weight of water column equals the upward force exerted by surface tension.	
R. Parachore of a liquid		3. lower surface tension	
S. The water rises upward when a capillary tube is inserted in water		4. $\frac{\text{surface tension-1}}{\text{surface tension-2}} = \frac{n_2 D_1}{n_1 D_2}$	
<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>
(a) 4	2	3	1
(b) 1	3	2	4
(c) 2	1	4	3
(d) 3	4	1	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.

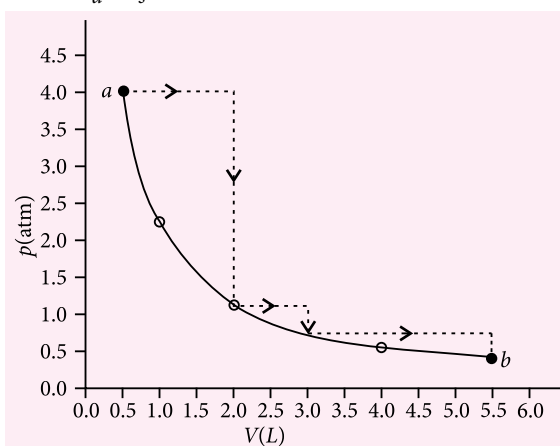
- 35. Assertion :** Hot air balloon rises up by displacing the denser air of the atmosphere.  
**Reason :** The given mass of a gas occupies larger volume at high temperature.
- 36. Assertion :** Molar entropy of vaporisation of water is different from ethanol.  
**Reason :** Water is more polar than ethanol.
- 37. Assertion :** At constant temperature, if pressure on the gas is doubled, density is also doubled.  
**Reason :** At constant temperature, molecular mass of a gas is directly proportional to the density and inversely proportional to pressure.
- 38. Assertion :** Decrease in free energy during the process under particular conditions provides a measure of its spontaneity.  
**Reason :** A spontaneous process must have positive sign of  $\Delta S_{\text{total}}$ .
- 39. Assertion :** A lighter gas diffuses more rapidly than a heavier gas.  
**Reason :** At a given temperature, the rate of diffusion of a gas is inversely proportional to the density.
- 40. Assertion :** Heat energy is completely transferred into work during the isothermal expansion of an ideal gas.  
**Reason :** During an isothermal process, the change in internal energy of a gas due to decrease in pressure is nullified by the change due to increase in volume.
- 45.** A compound exists in the gaseous phase both as monomer (A) and dimer ( $A_2$ ). The molecular weight of A is 48. In an experiment 96 g of the compound was confined in a vessel of volume 33.6 L and heated to  $273^\circ\text{C}$ . If the compound exists as dimer to the extent of 50% by weight under these conditions. The pressure is
- 46.** Heat of neutralisation of HA (weak acid) by strong base is  $-9.7$  kcal per equivalent. The dissociation energy of HA (in kcal) is
- 47.** If pressure of a gas is quadrupled and the temperature in degrees kelvin is doubled, the density of the gas will become  $P$  times. The  $P$  is
- 48.** Given that,  $S^\circ_{\text{H}_2} = 131 \text{ J K}^{-1} \text{ mol}^{-1}$ ,  $S^\circ_{\text{Cl}_2} = 223 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $S^\circ_{\text{HCl}} = 183 \text{ J K}^{-1} \text{ mol}^{-1}$ . The standard entropy change in the formation of 1 mole of  $\text{HCl}_{(g)}$  from  $\text{H}_{2(g)}$  and  $\text{Cl}_{2(g)}$  will be
- 49.** The time taken for a certain volume of gas to diffuse through a small hole was 2 min. Under similar conditions an equal volume of oxygen took 5.65 min to pass. The molecular mass of the gas is
- 50.** One mole of an ideal gas is taken from  $a$  to  $b$  along two paths denoted by the solid and the dotted lines as shown in the following graph. If the work done along the solid line path is  $W_s$  and that along the dotted line is  $W_d$ , then the integer closest to the ratio  $W_d/W_s$  is

## 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.** At 400 K, the root mean square speed of a gas X (molecular weight = 40) is equal to the most probable speed of gas Y at 60 K. The molecular weight of Y is
- 42.** Heat of combustion of  $C_{(\text{Diamond})} = -7.583$  kcal/g  
Heat of combustion of  $C_{(\text{Graphite})} = -7.833$  kcal/g  
12 g diamond is converted to graphite. The  $\Delta H^\circ$  is
- 43.** 2 moles of a perfect gas at  $27^\circ\text{C}$  is compressed reversibly and isothermally from a pressure of  $1.01 \times 10^5 \text{ Nm}^{-2}$  to  $5.05 \times 10^6 \text{ Nm}^{-2}$ . The free energy change is  $x \times 10^4$  joule where  $x$  is
- 44.**  $\Delta C_p$  of the following is  $-x(R)$ .  
 $\text{N}_{2(g)} + 3\text{H}_{2(g)} \longrightarrow 2\text{NH}_{3(g)}$   
The value of  $x$  is



## SOLUTIONS

1. (b)
2. (d):  $w = -p\Delta V$   
Since, vessel is closed hence, volume = constant  
 $\therefore \Delta V = 0$   
 $\therefore w = -p\Delta V = 0$

3. (c)

4. (c): For adiabatic expansion

$$\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$$

$\gamma = 1.33$  For  $\text{CO}_2$  (Triatomic gas)

$$\left(\frac{150}{300}\right) = \left(\frac{10}{V_2}\right)^{0.33} \Rightarrow \left(\frac{1}{2}\right) = \left(\frac{10}{V_2}\right)^{1/3}$$

$$\frac{10}{V_2} = \frac{1}{8} \Rightarrow V_2 = 80 \text{ L}$$

5. (c): The pressure of gas at  $T \text{ K} = 830 - 30$   
= 800 mm HgAfter the temperature of the jar is reduced by 1%, the temperature,  $T'$  becomes,

$$T' = T - \frac{1}{100}T = \frac{99}{100}T$$

Let the new pressure be  $P'$ .

Thus,

$$\frac{800}{T} = \frac{P'}{T'} \quad (\text{Charles' law})$$

$$\frac{800}{T} = \frac{P'}{\frac{99}{100}T}$$

$$P' = \frac{800}{T} \times \frac{99T}{100} = 792 \text{ mm Hg}$$

Thus, total pressure in the jar at  $T' = 792 + 25$   
= 817 mm Hg6. (b):  $\text{CaCO}_{3(s)} \rightarrow \text{CaO}_{(s)} + \text{CO}_{2(g)}$ 

$\Delta H$  for the process is positive and so also  $\Delta S$ . At low temperature  $\Delta H > T\Delta S$ , so  $\Delta G = \Delta H - T\Delta S$  will be positive signaling non-spontaneity of the process. At high temperature,  $\Delta H < T\Delta S$  and  $\Delta G$  will be negative signaling the spontaneity of the process.

7. (a):  $PV = nRT$ 

$$\Rightarrow \frac{7.6 \times 10^{-5}}{760} \times 1 = n \times 0.082 \times 250$$

$$n = \frac{10^{-7}}{20.5}$$

$$\Rightarrow \text{No. of molecules} = \frac{10^{-7}}{20.5} \times 6 \times 10^{23} = 2.9 \times 10^{15}$$

8. (d):  $\Delta H = \Delta E + \Delta n_g RT$ 

$\Delta n_g =$  moles of gaseous products – moles of gaseous reactants

$$\Delta H = \Delta E \text{ if } \Delta n_g = 0$$

(a)  $\Delta n_g = 1 - 2 = -1$ , (b)  $\Delta n_g = 2 - 1 = 1$ , (c)  $\Delta n_g = 2$ (d)  $\Delta n_g = 2 - 2 = 0$  so,  $\Delta H = \Delta E$ 

9. (d): Ideal gas does not show cooling or heating.

10. (c):  $\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$ 

$$\Delta H = \sum \Delta H_f^\circ(\text{Products}) - \sum \Delta H_f^\circ(\text{Reactants})$$

$$= [\Delta H_f(\text{CO}_2) + 2\Delta H_f(\text{H}_2\text{O})] - [\Delta H_f(\text{CH}_4) + 2\Delta H_f(\text{O}_2)]$$

$$= [-394.8 + 2 \times -241.6] - [-76.2 + 2 \times 0]$$

$$= -878 + 76.2 = -801.8 \text{ kJ mol}^{-1}$$

Heat evolved by burning 22.4 L (1 mol) methane  
=  $-801.8 \text{ kJ mol}^{-1}$ So, heat evolved by burning 1000 L ( $1\text{m}^3$ ) methane  
=  $\frac{-801.8}{22.4} \times 1000 = -35794.6 \text{ kJ}$ 11. (b): K.E. per molecule =  $\frac{3RT}{2N}$ 

$$\Rightarrow \frac{1}{2}mu^2 = \frac{3RT}{2N} \text{ or } u = \sqrt{\frac{3RT}{m \times N}}$$

$$= \sqrt{\frac{3 \times 8.314 \times 10^7 \times 300}{6.023 \times 10^{23} \times 10^{-12}}} = 0.35 \text{ cm s}^{-1}$$

12. (c): For dissolution of gases in water  $\Delta S = -ve$  (Non favourable factor). Since this process is spontaneous i.e.,  $\Delta G = -ve$  so  $\Delta U$  has to be  $-ve$  (favourable factor) and process is exothermic.

13. (d)

14. (a):  $2\text{NO}_{(g)} + \text{Cl}_{2(g)} \rightleftharpoons 2\text{NOCl}_{(g)}$ 

$$K_p = \frac{p_{\text{NOCl}}^2}{p_{\text{NO}}^2 \times p_{\text{Cl}_2}} = \frac{(1 \times 10^{-2})^2}{(1 \times 10^{-5})^2 \times (1 \times 10^{-2})} = 1 \times 10^8$$

 $K_p$  is thermodynamic equilibrium constant (relative to 1 atm) and is considered as unitless quantity.

$$\Delta G^\circ = -2.303 RT \log K_p$$

$$= -2.303 \times 8.314 \times 10^{-3} \times 298 \log 10^8 \text{ kJ}$$

$$= -45.65 \text{ kJ}$$

15. (c):  $rms(\text{H}_2) = \sqrt{\frac{3RT(\text{H}_2)}{2}}$ ;  $rms(\text{N}_2) = \sqrt{\frac{3RT(\text{N}_2)}{28}}$ 

$$rms(\text{H}_2) = \sqrt{7}rms(\text{N}_2); \sqrt{\frac{3RT(\text{H}_2)}{2}} = \sqrt{7} \cdot \sqrt{\frac{3RT(\text{N}_2)}{28}}$$

$$\therefore \frac{T(\text{H}_2)}{2} = \frac{T(\text{N}_2)}{4}$$

$$T(\text{H}_2) = \frac{T(\text{N}_2)}{2}$$

16. (a): For  $n$  mole of a real gas

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

when  $\frac{n^2 a}{V^2} \neq 0$  and  $nb = 0$

$$\left(P + \frac{n^2 a}{V^2}\right)V = nRT$$

$$PV + \frac{n^2 a}{V} = nRT \Rightarrow PV = \left(nRT - \frac{n^2 a}{V}\right)$$

17. (b): If viscosity refers to resistance, then its inverse is ease of flow *i.e.*, fluidity.

18. (a): If  $\text{AlCl}_3$  is present in ionic state in aqueous solution ( $\text{Al}^{3+}$  and three  $\text{Cl}^-$  ions), then standard heat of hydration of  $\text{Al}^{3+}$  and three  $\text{Cl}^-$  ions

$$= -4665 + (3 \times -381) = -5808 \text{ kJ mol}^{-1}$$

This hydration energy is greater than ionisation energy of Al, hence  $\text{AlCl}_3$  would be ionic in aqueous solution.

19. (d): A heat engine cannot have 100% efficiency.

20. (d): At point A near low pressure region, volume is very high thus

$$(V - b) \approx V$$

$$\therefore \left(P + \frac{a}{V^2}\right)V = RT \quad (\text{For 1 mole})$$

$$PV + \frac{a}{V} = RT \Rightarrow \frac{PV}{RT} + \frac{a}{RTV} = \frac{RT}{RT}$$

$$Z + \frac{a}{RTV} = 1 \Rightarrow Z = 1 - \frac{a}{RTV}$$

21. (a, b, d)                      22. (a, b, c)

23. (a): The mathematical form of first law of thermodynamics  $q = \Delta E + W$

Since the system is closed and insulated,  $q = 0$

And as liquid is stirred with a paddle hence work is done on system.  $\therefore W \neq 0$ .

Temperature and hence internal energy of the system increases.  $\therefore \Delta E \neq 0$ .

24. (a, b)                      25. (a, b, c, d)

26. (c): Gas equation  $PV = nRT$  is obeyed by any ideal gas irrespective of the fact that the process is isothermal or adiabatic.

27. (b):  $Z = \frac{PV}{nRT}$  *i.e.*,  $\frac{PV}{nRT} < 1$  or  $PV < nRT$

$$(P = 1 \text{ atm at STP})$$

$$V < 1 \times 0.0821 \times 273 \text{ or } V < 22.4 \text{ L}$$

28. (b):  $d = \frac{PM}{RT}$

Higher the pressure and lower the temperature, greater is the density, *i.e.*, it depends upon  $P/T$ .

29. (b): A process is always feasible if it is accompanied with decrease in free energy, *i.e.*,  $\Delta G$  is -ve but,

$\Delta G = \Delta H - T\Delta S$ . Therefore, if  $\Delta H$  is -ve and  $\Delta S$  is +ve, then  $\Delta G$  is always -ve.

30. (c): The reaction is in a state of equilibrium, therefore,  $\Delta G = 0$  and hence,  $\Delta H = T\Delta S$ .

31. (c): Here,  $\Delta G = -2.303RT \log K_p$

$$46.06 \times 1000 \times 4.184 = -2.303 \times 8.314 \times 300 \log K_p$$

$$\therefore K_p = 10^{-33.55}$$

32. (c)                      33. (c)

34. (d): (P  $\rightarrow$  3): Efficiency of a tooth paste and mouth wash is based on the phenomenon of surface tension as on lowering the surface tension the tooth paste or mouth wash spreads evenly over the surface when they come in contact hence it increases the efficiency of its antiseptic property.

$$(\text{Q} \rightarrow 4): \text{Mass of drop-1} = M_1 = \frac{VD_1}{n_1}$$

$$\text{Mass of drop-2} = M_2 = \frac{VD_2}{n_2}$$

$$\frac{\text{Surface tension-1}}{\text{Surface tension-2}} = \frac{M_1}{M_2} = \frac{D_1}{n_1} \times \frac{n_2}{D_2}$$

(R  $\rightarrow$  1): The parachore of liquid is the molar volume of liquid at a temperature when its surface tension is unity.

(S  $\rightarrow$  2): Rise or fall of liquid in a capillary tube is due to the phenomenon of surface tension. The water rises upwards when a capillary tube is inserted in water till the downward force due to weight of water column equals the upward force exerted by surface tension.

35. (a)                      36. (b)

37. (d): Molecular mass has a fixed value for a particular gas and does not depend upon density. From

$$M = \frac{dRT}{P}, \text{ if } P \text{ is doubled, } d \text{ is halved at constant temperature to keep } M \text{ constant.}$$

38. (b)

39. (c): At a given temperature, the rate of diffusion of a gas is inversely proportional to the square roots of its density.

40. (a)

41. (4): Given  $T_1 = 400 \text{ K}$ ,  $T_2 = 60 \text{ K}$

Molecular weight of X,  $M_1 = 40$

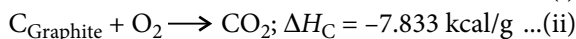
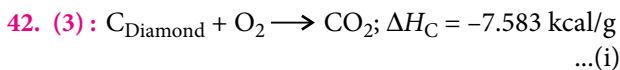
Molecular weight of Y,  $M_2 = ?$

$$u_{rms(X)} = \sqrt{\frac{3RT_1}{M_1}}, \quad u_{mp(Y)} = \sqrt{\frac{2RT_2}{M_2}}$$

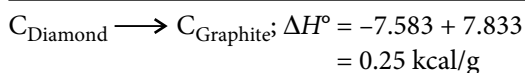
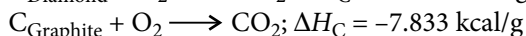
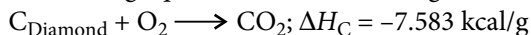
Given,  $u_{\text{rms}(X)} = u_{\text{mp}(Y)}$

$$\therefore \sqrt{\frac{3R \times 400}{40}} = \sqrt{\frac{2R \times 60}{M_2}}$$

$$30 = \frac{120}{M_2} \Rightarrow M_2 = 4$$



Subtracting equation (ii) from (i), we get



For 12 g diamond,  $\Delta H^\circ = 12 \times 0.25 = 3 \text{ kcal}$

43. (2): For reversible process

$$W_{\text{rev}} = -2.303 nRT \log_{10} \frac{P_1}{P_2}$$

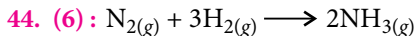
$$= -2.303 \times 2 \times 8.314 \times 300 \log_{10} \frac{1.01 \times 10^5}{5.05 \times 10^6}$$

$$= + 1.9518 \times 10^4 \text{ joule}$$

Since,  $W_{\text{rev}}$  is a measure of free energy change

$$\therefore -\Delta G = -W_{\text{rev}} = -W_{\text{max}}$$

$$\text{or } \Delta G = 1.9518 \times 10^4 \text{ joule} \approx 2 \times 10^4 \text{ joule}$$



$$\Delta C_p = -xR$$

For diatomic gas,  $C_p = \frac{7R}{2}$

For tetraatomic gas,  $C_p = 4R$

$$C_{p(\text{reactants})} = \frac{7}{2}R + 3 \times \frac{7}{2}R = \frac{28R}{2} = 14R$$

$$C_{p(\text{product})} = 2 \times 4R = 8R$$

$$\Delta C_p = C_{p(\text{Products})} - C_{p(\text{reactants})}$$

$$= 8R - 14R = -6R$$

$$\therefore -xR = -6R \quad (\because \Delta C_p = -xR)$$

$$x = 6$$

45. (2): Since A and A<sub>2</sub> are two states in gaseous phase having their weight ratio 50%, i.e. 1 : 1

$$\therefore \text{Mole of A} = \frac{96}{2} \times \frac{1}{48} = 1 \quad \left( n = \frac{w}{m} \right)$$

$$\text{Mole of A}_2 = \frac{96}{2} \times \frac{1}{96} = \frac{1}{2}$$

$$\therefore \text{Total mole of A and A}_2 \text{ are} = 1 + \frac{1}{2} = \frac{3}{2}$$

Thus,  $PV = nRT$

$$P \times 33.6 = \frac{3}{2} \times 0.0821 \times 546 \Rightarrow P = 2 \text{ atm}$$

46. (4): Heat evolved when one mole of strong base is neutralised by one mole of strong acid is  $-57.1 \text{ kJ mol}^{-1}$  or  $13.65 \text{ kcal mol}^{-1}$ .

$$\text{Thus, dissociation energy of HA} = 13.65 - 9.7$$

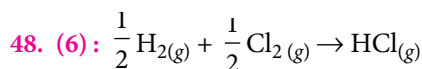
$$= 3.95 \approx 4$$

47. (2):  $d = \frac{PM}{RT}$

$$\therefore \frac{d_1}{d_2} = \frac{P_1}{P_2} \times \frac{T_2}{T_1} = \frac{P_1}{P_2} \times \frac{T_2}{T_1} = \frac{P_1}{4P_1} = \frac{2T_1}{T_1}$$

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

$$\therefore d_2 = 2d_1$$



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

$$= S_{\text{HCl}}^\circ - \left( \frac{1}{2} S_{\text{H}_2}^\circ + \frac{1}{2} S_{\text{Cl}_2}^\circ \right) = 183 - \frac{1}{2}(131 + 223)$$

$$= 6 \text{ J K}^{-1} \text{ mol}^{-1}$$

49. (4): According to Graham's law of diffusion,

$$\frac{V_1}{t_1} \cdot \frac{t_2}{V_2} = \sqrt{\frac{M_2}{M_1}}; V_1 = V_2$$

$$\therefore \left( \frac{t_2}{t_1} \right)^2 = \frac{M_2}{M_1} \Rightarrow \frac{5.65 \times 5.65}{2 \times 2} = \frac{32}{M_1} \Rightarrow M_1 = 4.0$$

50. (2): Solid line path work done ( $w_s$ ) is isothermal because  $PV$  is constant (Boyle's law) and dashed line (horizontal) path work done  $w_d$  is isobaric. Work done in vertical line is zero as  $\Delta V = 0$ .

Total work done on solid line path ( $w_s$ )

$$= 2.303 nRT \log \frac{V_2}{V_1}$$

$$= 2.303 PV \log \frac{V_2}{V_1}$$

$$= 2.303 \times 4 \times 0.5 \log \frac{5.5}{0.5}$$

$$= 4.8 \text{ L atm.}$$

Total work done on dash line path ( $w_d$ ) =  $P\Delta V$

$$= 4 \times (2 - 0.5) + 1(3 - 2) + 0.5(5.5 - 3)$$

$$= 6 + 1 + 1.25$$

$$= 8.25$$

$$\text{So, } \frac{w_d}{w_s} = \frac{8.25}{4.8} \approx 2.$$



# ACE

## YOUR WAY **CBSE XI**


**Series 1**

CHAPTERWISE UNIT TEST : SOME BASIC CONCEPTS OF CHEMISTRY |  
STRUCTURE OF ATOM | CLASSIFICATION OF ELEMENTS AND PERIODICITY IN PROPERTIES |  
CHEMICAL BONDING AND MOLECULAR STRUCTURE

**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 17 are also short answer questions and carry 3 marks each.
- (v) Q. no. 18 is a value based question and carries 4 marks.
- (vi) Q. no. 19 and 20 are long answer questions and carry 5 marks each.
- (vii) Use log tables if necessary, use of calculators is not allowed.

1. At what temperature will both the Celsius and Fahrenheit scales read the same value?
2. Using VSEPR theory, draw the shape of  $\text{BrF}_5$ .
3. An electron is in one of the  $3d$ -orbitals. Give the possible values of  $n$ ,  $l$  and  $m_l$  for this electron.
4. With which quantum number does every period in the periodic table begin?
5. Wavelengths of different radiations are given below.  
 $\lambda(A) = 300 \text{ nm}$ ,  $\lambda(B) = 300 \mu\text{m}$ ,  $\lambda(C) = 3 \text{ nm}$ ,  
 $\lambda(D) = 30 \text{ \AA}$   
Arrange these radiations in the increasing order of energies.
6. In three moles of ethane ( $\text{C}_2\text{H}_6$ ), calculate the following :
  - (i) Number of moles of carbon atoms.
  - (ii) Number of moles of hydrogen atoms.
  - (iii) Number of molecules of ethane.

**OR**

From each set, choose the atom which has the
- higher ionisation enthalpy. Explain your answer in brief.
  - (i) F, O, N and
  - (ii) Mg, P, Ar
7. The average molar mass of a mixture of methane ( $\text{CH}_4$ ) and ethene ( $\text{C}_2\text{H}_4$ ) present in the ratio of  $a : b$  is found to be  $20.0 \text{ g mol}^{-1}$ . If the ratio is reversed, what would be the molar mass of the mixture?
8. Helium has an electronic configuration of  $1s^2$  but it is placed in  $p$ -block in group 18. Explain.
9. The energy of  $\sigma 2p_z$  molecular orbital is greater than  $\pi 2p_x$  and  $\pi 2p_y$  molecular orbitals in nitrogen molecule. Write the complete sequence of energy levels in the increasing order of energy in the molecule. Compare the bond order and the magnetic behaviour of the following species :  
 $\text{N}_2, \text{N}_2^+, \text{N}_2^-, \text{N}_2^{2+}$
10. The first ionisation enthalpy of carbon atom is greater than that of boron whereas the reverse is true for the second ionisation enthalpy. Explain.

11. You are given the electronic configurations of five neutral atoms— A, B, C, D and E.

A :  $1s^2 2s^2 2p^6 3s^2$ , B :  $1s^2, 2s^2, 2p^6 3s^1$ , C :  $1s^2 2s^2 2p^1$ ,  
D :  $1s^2 2s^2 2p^5$ , E :  $1s^2 2s^2 2p^6$ .

Write the empirical formula for the substance containing (i) A and D (ii) B and D (iii) only D (iv) only E?

12. Explain the following on the basis of valence bond theory.

- (i)  $\text{BF}_3$  is planar but  $\text{NH}_3$  is not.  
(ii)  $\text{CCl}_4$  and  $\text{SiCl}_4$  are tetrahedral.  
(iii) The HSH bond angle in  $\text{H}_2\text{S}$  is closer to  $90^\circ$  than HOH bond angle in  $\text{H}_2\text{O}$ .

13. (i) How would you define a polar covalent bond? Give an example.

(ii) Write formal charges of the atoms in the carbonate ion,  $\text{CO}_3^{2-}$ .

14. Find the number of atoms of each type present in 3.42 g of cane sugar ( $\text{C}_{12}\text{H}_{22}\text{O}_{11}$ ).

15. Arrange the following elements (electronic configuration given) in order of increasing electron gain enthalpy:

- (a)  $1s^2 2s^2 2p^5$   
(b)  $1s^2 2s^2 2p^4$   
(c)  $1s^2 2s^2 2p^3$   
(d)  $1s^2 2s^2 2p^6 3s^2 3p^4$

16. If 4 g of NaOH dissolves in 36 g of  $\text{H}_2\text{O}$ , calculate the mole fraction of each component in the solution. Also, determine the molarity of solution (specific gravity of solution is  $1 \text{ g mL}^{-1}$ ).

OR

Iron forms two chlorides, 1.27 g of first chloride gave 2.87 g of AgCl while 16.25 g of second chloride gave 43.05 g of AgCl. Prove that the law of multiple proportions is true.

17. What transition in the hydrogen spectrum would have the same wavelength as the Balmer transition ( $n = 4$  to  $n = 2$ ) of  $\text{He}^+$  spectrum?

18. Shikha and Monika are sisters. They have opposite behaviour. Shikha has many friends while Monika has no friends. Most of the times, she stays alone and not interested in talking to others the way noble gases do not combine with other elements.

- (i) What values are displayed by Shikha?  
(ii) Why are noble gases least reactive?

(iii) Where are noble gases placed in the periodic table?

(iv) The size of the atoms of inert gases are larger than those of preceding halogens. Explain.

19.  $8.058 \times 10^{-2} \text{ kg}$  of washing soda ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ) is dissolved in water to obtain 1 L of a solution of density  $1077.2 \text{ kg/m}^3$ . Calculate

- (i) molarity (ii) molality and  
(iii) mole fraction of  $\text{Na}_2\text{CO}_3$  in the solution.

OR

Three moles of  $\text{N}_2$  combine with five moles of  $\text{H}_2$  to form  $\text{NH}_3$  by Haber's process.

- (i) What is the limiting reactant?  
(ii) Calculate the grams of the reactant left in the container.  
(iii) How many moles of  $\text{NH}_3$  are produced?  
(iv) How many litres of  $\text{NH}_3$  are produced at STP?

20. How are bonding and antibonding molecular orbitals formed from a given pair of atomic orbitals. Compare molecular orbitals with each other in terms of

- (i) energy  
(ii) presence of nodes  
(iii) internuclear electron density

OR

Account for the following :

- (i)  $\text{He}_2$  does not exist in nature.  
(ii)  $\text{F}_2$  is diamagnetic substance.  
(iii) The dissociation energy of  $\text{H}_2^+$  is almost the same as that of  $\text{He}_2^+$ .

## SOLUTIONS

1. Suppose both read the same value as  $x$ .

Then as  $^\circ\text{C} = \frac{5}{9} (^\circ\text{F} - 32)$

$$\therefore x = \frac{5}{9} (x - 32)$$

$$\text{or } 9x = 5x - 160$$

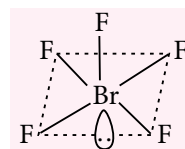
$$\text{or } 4x = -160$$

$$\text{or } x = -40^\circ$$

2. In  $\text{BrF}_5$ , the number of electrons in the valence shell of the central atom Br is given as

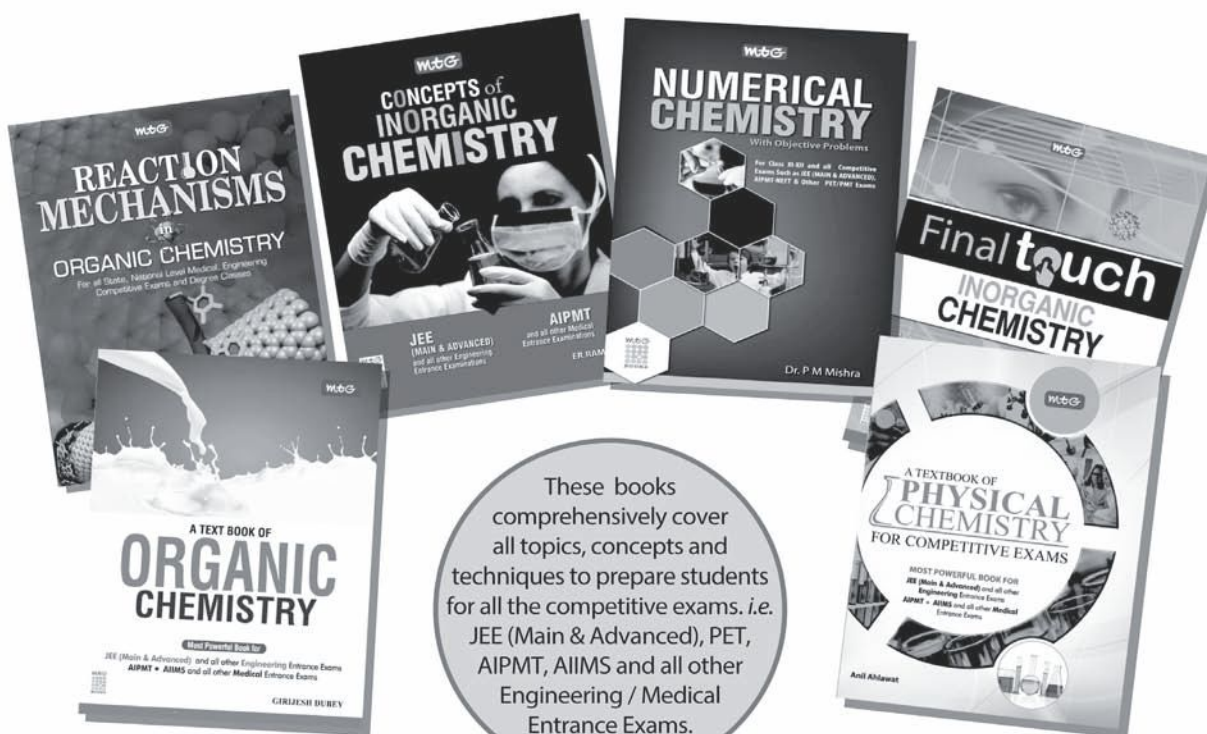
$$7 + 5 = 12 = 6 \text{ pairs}$$

Out of these, 5 pairs are bond pairs and 1 pair is lone pair. Hence, hybridisation is  $sp^3d^2$  and shape of the molecule is square pyramidal.



mtg

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3. For  $3d$ -orbital,  $n = 3$   
For a given value of  $n$ , azimuthal quantum number  $l$  can have 0 to  $(n - 1)$  values, therefore,  $l$  can be 0, 1 and 2.

But when the electron is in  $d$ -orbital,  $l = 2$

When  $l = 2$ , the permitted values of  $m_l$  are +2, +1, 0, -1, -2

4. Every period in the periodic table starts with principal quantum number.
5. (A)  $\lambda = 300 \text{ nm} = 300 \times 10^{-9} \text{ m} = 3 \times 10^{-7} \text{ m}$   
(B)  $\lambda = 300 \mu\text{m} = 300 \times 10^{-6} \text{ m} = 3 \times 10^{-4} \text{ m}$   
(C)  $\lambda = 3 \text{ nm} = 3 \times 10^{-9} \text{ m}$   
(D)  $\lambda = 30 \text{ \AA} = 30 \times 10^{-10} \text{ m} = 3 \times 10^{-9} \text{ m}$

$$\therefore \text{Energy, } E = \frac{hc}{\lambda}$$

$$\text{or } E \propto \frac{1}{\lambda}$$

$\therefore$  Increasing order of energies is  $B < A < C = D$

6. (i) 1 mole of  $\text{C}_2\text{H}_6$  contains 2 moles of carbon atoms.  
Number of moles of carbon atoms in 3 moles of  $\text{C}_2\text{H}_6 = 3 \times 2 = 6$
- (ii) 1 mole of  $\text{C}_2\text{H}_6$  contains 6 moles of hydrogen atoms.  
Number of moles of hydrogen atoms in 3 moles of  $\text{C}_2\text{H}_6 = 3 \times 6 = 18$
- (iii) 1 mole of  $\text{C}_2\text{H}_6 = 6.022 \times 10^{23}$  molecules  
Number of molecules in 3 moles of  $\text{C}_2\text{H}_6 = 3 \times 6.022 \times 10^{23} = 1.807 \times 10^{24}$  molecules

OR

- (i) F, O and N belong to second period and their arrangement from left to right is O, N and F. In general, ionisation enthalpy increases from left to right in a period. Therefore, F having the smallest size and the highest nuclear charge among these, has the highest ionisation enthalpy. But nitrogen due to stable half-filled  $p$ -orbital has higher ionisation enthalpy than oxygen atom.
- (ii) Mg, P and Ar are members of the third period. Ar, being a noble gas, has the highest ionisation enthalpy because it has very stable closed shell, octet configuration.
7. Molar mass of  $\text{CH}_4 = 16 \text{ g mol}^{-1}$   
Molar mass of  $\text{C}_2\text{H}_4 = 28 \text{ g mol}^{-1}$   
When they are present in the ratio of  $a : b$ , their average molar mass

$$= \frac{a \times 16 + b \times 28}{a + b} = 20 \text{ g mol}^{-1} \quad (\text{Given})$$

$$\text{i.e., } 16a + 28b = 20(a + b)$$

$$\text{or } 4a + 7b = 5(a + b)$$

$$\text{or } a = 2b$$

$$\text{or } \frac{a}{b} = \frac{2}{1} = 2:1$$

If the ratio is reversed, then

$$a : b = 1 : 2$$

$$\therefore \text{Average molar mass} = \frac{1 \times 16 + 2 \times 28}{1 + 2} = 24 \text{ g mol}^{-1}$$

8. The electronic configuration of helium is  $1s^2$ , so it should be kept in  $s$ -block as the last electron enters in  $s$  orbital. But it is placed in  $p$ -block with elements of group 18, due to the presence of completely filled valence or outermost shell ( $1s^2$ ) and hence, similarity in properties with other noble gases.

9. Sequence of energy levels

$$\sigma 1s < \sigma^* 1s < \sigma 2s < \sigma^* 2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z$$

For  $\text{N}_2$  molecule, the M.O. configuration is :

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2$$

$$\text{B.O.} = \frac{1}{2} (10 - 4) = 3, \text{ diamagnetic}$$

$$\text{N}_2^+ : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^1$$

$$\text{B.O.} = \frac{1}{2} (9 - 4) = 2.5, \text{ paramagnetic}$$

$$\text{N}_2^- : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2 \sigma 2p_z^2 \pi^* 2p_x^1$$

$$\text{B.O.} = \frac{1}{2} (10 - 5) = 2.5, \text{ paramagnetic}$$

$$\text{N}_2^{2+} : \sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \pi 2p_x^2 = \pi 2p_y^2$$

$$\text{B.O.} = \frac{1}{2} (8 - 4) = 2, \text{ diamagnetic}$$

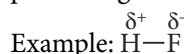
$$\text{Bond order : } \text{N}_2 > \text{N}_2^- = \text{N}_2^+ > \text{N}_2^{2+}$$

10. Electronic configuration of C-atom is  $1s^2 2s^2 2p^2$  and electronic configuration of B-atom is  $1s^2 2s^2 2p^1$ . The first electron to be removed in both cases is from a  $2p$ -orbital but nuclear charge of C is more than that of B. Therefore, the  $\Delta_i H_1$  of C is greater than that of B. After the removal of first electron, the second electron in C-atom is removed from a  $2p$ -orbital whereas in B-atom it is removed from a  $2s$ -orbital. Since a  $s$ -orbital is more penetrating and more strongly attracted by the nucleus than a  $p$ -orbital, therefore,  $\Delta_i H_2$  of B is higher than that of C.

11. (i) Empirical formula of the compound formed by  $A$  and  $D$  is  $AD_2$  as  $A$  has two valence electrons and  $D$  has seven. Atom  $A$  transfers its two electrons to two  $D$  atoms to complete their octets.
- (ii) Empirical formula of the compound formed by  $B$  and  $D$  is  $BD$  as  $B$  transfers its one electron to  $D$ .
- (iii) Empirical formula of the compound formed by  $D$  only is  $D_2$  as both the atoms of  $D$  share one electron each to form a covalent bond.
- (iv) Since it is a noble gas, no compound is formed.
12. (i) In  $BF_3$ , B-atom undergoes  $sp^2$  hybridisation. Hence,  $BF_3$  is triangular planar. In  $NH_3$ , N-atom undergoes  $sp^3$  hybridisation. Hence,  $NH_3$  has pyramidal shape with one lone pair on N-atom.
- (ii) Both C in  $CCl_4$  and Si in  $SiCl_4$  undergo  $sp^3$  hybridisation hence, they are tetrahedral.
- (iii) This is because of lower electronegativity of S as compared to O. In  $H_2O$ , the bond pair of electrons are more towards oxygen atom and hence causes more repulsion which results in higher HOH bond angle than HSH.
13. (i) A polar covalent bond is a covalent bond between two atoms of different electronegativity in which the electron pair is not equally shared. This gives rise to ionic character and the separation of charges.



The more electronegative atom acquires a partial negative charge.



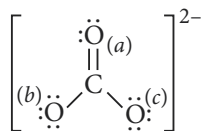
- (ii) Formal charge on O atom (a)

$$= 6 - 4 - \frac{1}{2} \times 4 = 0$$

Formal charge on O atom (b) and (c) each is

$$= 6 - 6 - \frac{1}{2} \times 2 = -1$$

Formal charge on C atom is  $4 - 0 - \frac{1}{2} \times 8 = 0$



14. As molecular mass of cane sugar =  $12 \times 12 + 22 \times 1 + 11 \times 16 = 342 \text{ g mol}^{-1}$

$$\therefore \text{Number of moles of cane sugar} = \frac{3.42}{342} = 10^{-2}$$

1 mole of  $C_{12}H_{22}O_{11}$  has 12 mole atoms of carbon,

22 mole atoms of hydrogen and 11 mole atoms of oxygen.

Hence, mole atoms of carbon in  $10^{-2}$  mole (3.42 g) sugar =  $12 \times 10^{-2}$

Therefore, number of atoms of carbon (C)

$$= 12 \times 10^{-2} \times 6.022 \times 10^{23} \\ = 7.226 \times 10^{22}$$

Mole atoms of hydrogen =  $22 \times 10^{-2}$

Number of atoms of hydrogen (H)

$$= 22 \times 10^{-2} \times 6.022 \times 10^{23} \\ = 1.325 \times 10^{23}$$

Mole atoms of oxygen =  $11 \times 10^{-2}$

Number of atoms of oxygen (O) =  $11 \times 10^{-2} \times 6.022 \times 10^{23} \\ = 6.624 \times 10^{22}$

15. These elements are  $F(1s^2 2s^2 2p^5)$ ,  $O(1s^2 2s^2 2p^4)$ ,  $N(1s^2 2s^2 2p^3)$  and  $S(1s^2 2s^2 2p^6 3s^2 3p^4)$ . Out of these elements, only N has +ve electron gain enthalpy because of its stable exactly half-filled  $p$ -subshell electronic configuration. Other elements have -ve electron gain enthalpies. As F attains very stable noble gas configuration after gain of one electron, it has the most -ve electron gain enthalpy. Out of O and S, O has less negative electron gain enthalpy than S because electron adds to a small compact  $2p$ -subshell experiencing greater electron-electron repulsion. Thus, the overall order of increasing electron gain enthalpy is
- (a) < (d) < (b) < (c)

16. Mole fraction of  $H_2O$

$$= \frac{\text{No. of moles of } H_2O}{\text{Total no. of moles } (H_2O + NaOH)}$$

$$\text{No. of moles of } H_2O = \frac{36}{18} = 2 \text{ moles}$$

$$\text{No. of moles of } NaOH = \frac{4}{40} = 0.1 \text{ mol}$$

$$\text{Total number of moles} = 2 + 0.1 = 2.1$$

$$\text{Mole fraction of } H_2O = \frac{2}{2.1} = 0.95$$

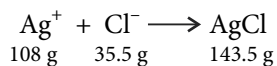
$$\text{Mole fraction of } NaOH = \frac{0.1}{2.1} = 0.047$$

$$\text{Mass of solution} = \text{Mass of } H_2O + \text{Mass of } NaOH \\ = 36 + 4 = 40 \text{ g}$$

$$\text{Volume of solution} = \frac{\text{Mass of solution}}{\text{Specific gravity of solution}} \\ = \frac{40}{1} = 40 \text{ mL}$$

$$\begin{aligned}\text{Molarity} &= \frac{\text{No. of moles of solute}}{\text{Volume of solution in L}} \\ &= \frac{0.1 \text{ mol}}{0.04 \text{ L}} = 2.5 \text{ M}\end{aligned}$$

OR



143.5 g AgCl contain 35.5 g Cl

$$\therefore 2.87 \text{ g AgCl will contain } 35.5 \times \frac{2.87}{143.5} = 0.71 \text{ g Cl}$$

$$\begin{aligned}\text{Similarly, 43.05 g of AgCl will contain } & 35.5 \times \frac{43.05}{143.5} \\ & = 10.65 \text{ g Cl}\end{aligned}$$

Now, in the first chloride,

Mass of iron chloride = 1.27 g

Mass of Cl = 0.71 g

Mass of Fe = 1.27 - 0.71 = 0.56 g

In the second chloride,

Mass of chloride = 10.65 g

Mass of Fe = 16.25 - 10.65 = 5.60 g

 $\therefore$  5.6 g Fe combines with 10.65 g Cl

0.56 g Fe combines with 1.065 g Cl

 $\therefore$  For a fixed mass of Fe (0.56 g), the Cl in two chlorides bears a ratio of 0.71 : 1.065 or 2 : 3.

Hence, the law of multiple proportion is proved.

$$17. \frac{1}{\lambda} = \bar{\nu} = 1.097 \times 10^7 Z^2 \left[ \frac{1}{n_L} - \frac{1}{n_H} \right] \text{m}^{-1}$$

where,  $n_L$  = number of the lower energy level,  
 $n_H$  = number of the higher energy level,  $Z$  = atomic number,  $\lambda$  = wavelength,  $\bar{\nu}$  = wavenumber

For  $\text{He}^+$ ,

$$\begin{aligned}\frac{1}{\lambda} &= 1.097 \times 10^7 \times (2)^2 \left[ \frac{1}{(2)^2} - \frac{1}{(4)^2} \right] \text{m}^{-1} \\ &= 1.097 \times 10^7 \times 4 \left( \frac{3}{16} \right) = 1.097 \times 10^7 \times \frac{3}{4}\end{aligned}$$

$$\text{For H atom, } \frac{1}{\lambda} = 1.097 \times 10^7 \times (1)^2 \times \frac{3}{4}$$

$$= 1.097 \times 10^7 \left[ \frac{1}{n_L^2} - \frac{1}{n_H^2} \right]$$

$$\frac{1}{n_L^2} - \frac{1}{n_H^2} = \frac{3}{4}. \text{ This gives } n_L = 1, n_H = 2$$

The transition  $n_L = 1$  to  $n_H = 2$  in H-atom would have the same wavelength as Balmer transition  $n = 4$  to  $n = 2$  of  $\text{He}^+$ .

18. (i) Shikha is very social and extrovert.

(ii) All the orbitals in the valence shell of noble gases are completely filled by electrons ( $ns^2 np^6$ ) and it is very difficult to alter this stable arrangement by the addition or removal of electrons. Hence, they do not react with other elements.

(iii) Noble gases are placed at the extreme right of the periodic table in accordance with their electronic configuration as each period starts with the filling of  $s$ -subshell and is completed with the filling of  $p$ -subshell of the same principal shell.

(iv) Noble gases do not form chemical compounds therefore, their radii are usually expressed as van der Waals radii which are always larger than the covalent radii.

19. Molar mass of washing soda is

$$\begin{aligned}2 \times 23 + 12 + 3 \times 16 + 10 \times 18 \\ = 286 \text{ g mol}^{-1} = 286 \times 10^{-3} \text{ kg mol}^{-1}\end{aligned}$$

$$n_{\text{solute}} = \frac{8.058 \times 10^{-2} \text{ kg}}{286 \times 10^{-3} \text{ kg mol}^{-1}} = 0.282 \text{ mol}$$

$$(i) \text{ Molarity} = \frac{n_{\text{solute}}}{V} = \frac{0.282}{1} = 0.282 \text{ M}$$

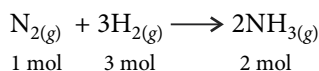
$$\begin{aligned}(ii) \text{ Mass of 1 L solution } (10^{-3} \text{ m}^3) &= d \times V \\ &= 1077.2 \text{ kg m}^{-3} \times 10^{-3} \text{ m}^3 \\ &= 1.0772 \text{ kg}\end{aligned}$$

$$\begin{aligned}\therefore \text{ Mass of solvent} &= (1.0772 - 0.08058) \text{ kg} \\ &= 0.996 \text{ kg}\end{aligned}$$

$$\begin{aligned}\text{Molality} &= \frac{\text{Moles of solute}}{\text{Mass of solvent in kg}} \\ &= \frac{0.282}{0.996} = 0.283\end{aligned}$$

$$\begin{aligned}(iii) x_{\text{solute}} &= \frac{n_{\text{solute}}}{n_{\text{solute}} + n_{\text{solvent}}} = \frac{0.282}{0.282 + \frac{996}{18}} \\ x_{\text{solute}} &= 0.0051\end{aligned}$$

OR



So, 3 moles of  $\text{N}_2$  will combine with 9 moles of  $\text{H}_2$  but, there are only 5 moles of  $\text{H}_2$ . Hence,

(i)  $\text{H}_2$  is the limiting reactant.

(ii)  $\text{N}_2$  is left in the container as it is present in excess.

3 moles of  $\text{H}_2$  will combine with 1 mole of  $\text{N}_2$

∴ 1 mole of H<sub>2</sub> will combine with 1/3 mole of N<sub>2</sub> and 5 moles of H<sub>2</sub> will combine with

$$\frac{1}{3} \times 5 = 1.66 \text{ moles of N}_2$$

So moles of N<sub>2</sub> left unreacted = 3 - 1.66  
= 1.34 mol N<sub>2</sub>

1 mol of N<sub>2</sub> = 28 g N<sub>2</sub>

∴ Mass of 1.34 mol N<sub>2</sub> = 28 × 1.34 = 37.52 g N<sub>2</sub>

(iii) Number of moles of product formed depends on the limiting reactant.

3 moles of H<sub>2</sub> ≡ 2 moles of NH<sub>3</sub>

∴ 5 moles of H<sub>2</sub> =  $\frac{2}{3} \times 5 = 3.33$  moles of NH<sub>3</sub>.

So, 3.33 moles of NH<sub>3</sub> are produced.

(iv) 1 mole of any gas at STP occupies 22.4 L of volume.

∴ 3.33 moles of NH<sub>3</sub> at STP will occupy 22.4 × 3.33 = 74.6 L of volume.

20. Bonding molecular orbital is formed by adding two atomic orbitals of same sign (same symmetry).

$$\Psi_{\text{BMO}} = \Psi_A + \Psi_B$$

Antibonding molecular orbital is formed by subtraction of two atomic orbitals.

$$\Psi_{\text{ABMO}} = \Psi_A - \Psi_B$$

But the number of molecular orbitals formed is equal to the number of combining atomic orbitals.

Comparison of molecular orbitals in terms of

(i) *Energy*: A bonding molecular orbital is always of lower energy than either of the atomic orbitals that have combined to form it.

An antibonding molecular orbital is always of higher energy than either of the atomic orbitals that have combined to form it.

(ii) *Presence of nodes*: For π molecular orbitals, the electron density is zero along the internuclear axis. Both π bonding and π antibonding molecular orbitals contain nodal planes.

There is no such nodal plane in σ molecular orbitals.

(iii) *Internuclear electron density*: In bonding molecular orbital, most of the electron density is located between the nuclei of bonded atoms while in an antibonding molecular orbital, most of the electron density is located away from the space between the nuclei.

OR

(i) In He<sub>2</sub>, total 4 electrons are present. Its molecular orbital configuration is σ1s<sup>2</sup>σ\*1s<sup>2</sup>. As N<sub>b</sub> = N<sub>a</sub>, the bond order is zero. Hence, He<sub>2</sub> does not exist.

(ii) Fluorine atom contains 9 electrons. So, fluorine molecule contains 18 electrons. The electronic configuration of F<sub>2</sub> molecule is

$$\sigma 1s^2 \sigma^* 1s^2 \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2 \pi^* 2p_x^2 = \pi^* 2p_y^2$$

As all molecular orbitals are fully filled, there is no unpaired electron present. Therefore, F<sub>2</sub> molecule is diamagnetic.

(iii) The bond dissociation energy is directly related to the bond order.

The bond order of H<sub>2</sub><sup>+</sup> is  $\frac{1}{2}$  and the bond order of He<sub>2</sub><sup>+</sup> (σ1s<sup>2</sup>σ\*1s<sup>1</sup>) is also  $\frac{1}{2}$ .

As bond order is same, the bond dissociation energy of H<sub>2</sub><sup>+</sup> is almost same as that of He<sub>2</sub><sup>+</sup>.



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# CONCEPT BOOSTER

Dear students!! Flavour of electrochemistry is back with electrified applications of concepts. While you go through the article, do take care of understanding the logic behind it. Keep solving the problems as much as possible. Take care!!

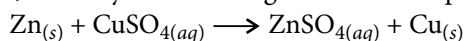
\*Arunava Sarkar

## ELECTROCHEMICAL CELL

Electrochemical cells are those cells where chemical energy (arises due to the chemical reactions) gets converted into electrical energy. These cells are also often called as chemical cells or galvanic cells or voltaic cells. Scientists Luigi Galvani and Alessandro Volta worked on the production of electrical energy from chemical energy and hence the names are given.

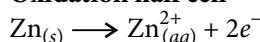
The fundamental observation is, if a zinc rod is dipped in  $\text{CuSO}_4$  solution for 1 hour then copper gets coated on the zinc rod. But if a copper rod is dipped into  $\text{ZnSO}_4$  solution, no coating of zinc is found on copper rod. So, the tendency of zinc to get oxidised is higher as compared to copper.

Now, basically the following reaction takes place here :

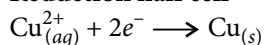


If this is a complete cell reaction, then it is divided into two half cell reactions :

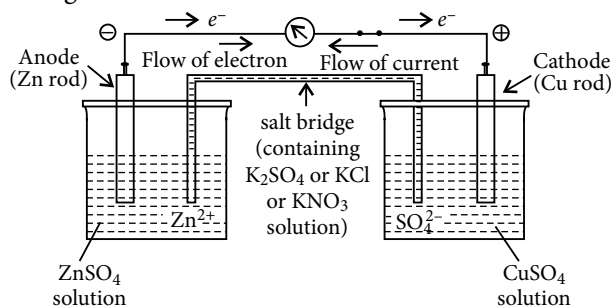
(1) **Oxidation half cell**



(2) **Reduction half cell**



Now in order to construct the galvanic cell, following arrangement is made :



Zn rod is dipped into  $\text{ZnSO}_4$  in one beaker and Cu rod into  $\text{CuSO}_4$  in another beaker. Remember that reaction takes place at the interface of metal and its salt solution. In the beaker having zinc rod both the oxidised ( $\text{Zn}^{2+}$ ) and reduced forms (Zn) are present and the same thing is in the beaker having copper rod. They can be represented as  $\text{Zn}^{2+}/\text{Zn}$  or  $\text{Cu}^{2+}/\text{Cu}$  and are commonly known as redox couple. Two half cells are internally connected by a salt bridge.

A salt bridge is a U-tube which contains inert electrolyte like KCl,  $\text{KNO}_3$ ,  $\text{K}_2\text{SO}_4$ ,  $\text{NH}_4\text{NO}_3$  etc. Inert electrolyte is boiled first with agar-agar and gelatine (sometimes in laboratory barley is used) and on cooling, it becomes gelly type.

Now, salt bridge is an essential tool in these cells. This can be explained as follows :

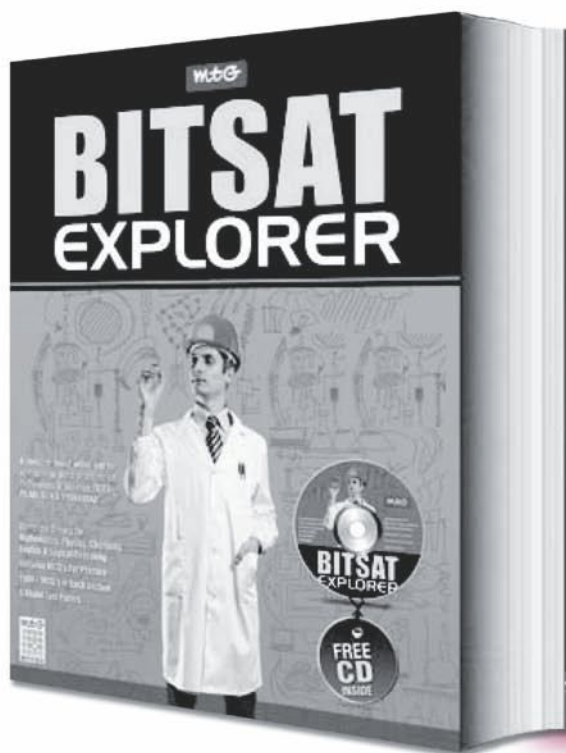
- Salt bridge makes an internal connection between the two half cells. Externally two half cells are connected by a wire and internally they are connected by salt bridge. Internal connection is maintained by the flow of ions from one beaker to the another. The main advantage for this flow of ions is that the solutions need not be mixed.
- Electrical neutrality is maintained due to the presence of salt bridge.

The electrode where the oxidation takes place is known as anode and the electrode where reduction is taking place is known as cathode. Here, Zn rod is working as anode (more tendency to release electrons) and Cu rod is working as cathode (more tendency to accept electrons).

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



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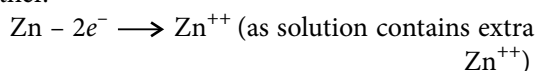


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Now, Zn rod is rich in electrons (as it releases electrons) and internally it is the negative pole. Cu rod is deficient of electrons and is internally known to be the positive pole. Now, definitely electrons flow from Zn to copper and in the copper beaker some of the  $\text{Cu}^{2+}$  ions gets reduced and get deposited on the cathode. This is why cathode gains weight. In the zinc beaker,  $\text{Zn}^{2+}$  ions are in excess (due to rapid oxidation) and in copper beaker  $\text{SO}_4^{2-}$  ions are in excess. So the solution in zinc beaker gets slightly positive charge and the solution in the copper beaker gets slightly negative charge. This phenomenon stops the following two reactions further.



and  $\text{Cu}^{++} + 2e^- \longrightarrow \text{Cu}$  (as electrons stop flowing from zinc electrode)

As a result, current flow stops. To tackle this situation salt bridge is used. Salt bridge allows the movement of ions from one solution to the other without mixing of the two solutions.

Thus, electrical neutrality is maintained.

- The materials used in salt bridge have unique feature. They are inert of course *i.e.* they do not react with the electrolytic solutions and of course with the electrode materials. Moreover, they obstruct the formation of liquid junction potential (LJP) when two electrolytic solutions are in direct contact, ions flow in them with different speeds. Different speeds arise due to different transport number. Hence, such material is selected where transport number of cation is almost equal to transport number of anion. *e.g.* KCl.

Finally, Zn rod and Cu rod are connected externally by a wire. Circuit gets completed. Conventionally, flow of current in the external circuit is taken from cathode to anode, *i.e.* opposite to the flow of electrons.

The EMF of the cell

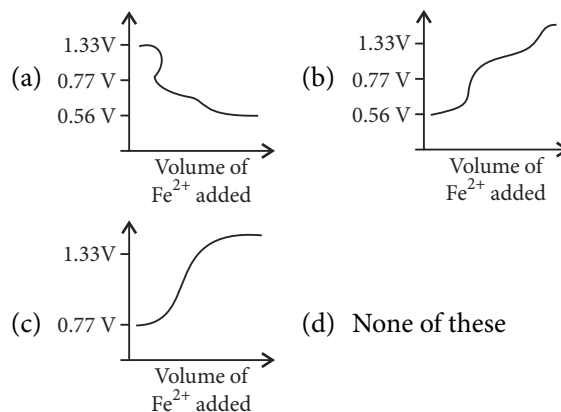
$$\begin{aligned} &= \text{oxidation potential of anode (standard)} \\ &\quad + \text{reduction potential of cathode (standard)} \\ &= E^\circ_{\text{Zn}/\text{Zn}^{2+}} + E^\circ_{\text{Cu}^{2+}/\text{Cu}} \end{aligned}$$

### PROBLEMS FOR PRACTICE

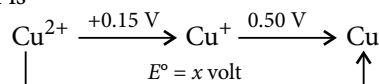
- Suppose, you are given a solution of potassium dichromate (VI) in a container and a solution of iron (II) sulphate in a burette. Concentration of iron (II) sulphate solution is known however that of potassium dichromate (VI) solution is unknown. You have to carry out a redox titration so that you

can determine the concentration of dichromate (VI) ions. What will be the graph of change of EMF during the course of the titration?

Given,  $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$ ;  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$



- The conductivity of a solution of AgCl at 298 K is found to be  $1.382 \times 10^{-6} \Omega^{-1} \text{ cm}^{-1}$ . The ionic conductance of  $\text{Ag}^+$  and  $\text{Cl}^-$  at infinite dilution are  $61.9 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  and  $76.3 \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ , respectively. The solubility of AgCl is  
(a)  $1.4 \times 10^{-5} \text{ mol L}^{-1}$  (b)  $1 \times 10^{-2} \text{ mol L}^{-1}$   
(c)  $1 \times 10^{-5} \text{ mol L}^{-1}$  (d)  $1.9 \times 10^{-5} \text{ mol L}^{-1}$
- The reduction potential diagram for Cu in acid solution is



Which of the following is correct?

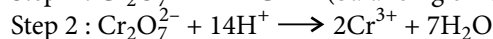
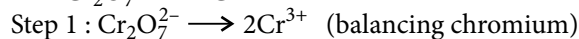
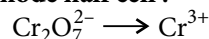
- $x = 0.65 \text{ V}$ ; disproportionation takes place.
- $x = 0.35 \text{ V}$ ; disproportionation takes place.
- $x = 0.325 \text{ V}$ ; disproportionation doesn't take place.
- None of these

### SOLUTIONS

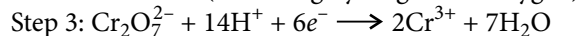
- (d): Anode half cell :



Cathode half cell :



(balancing hydrogen and oxygen)

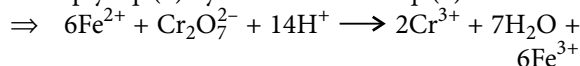


(balancing charge)

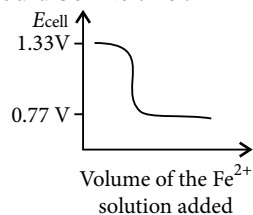
...(2)

**Complete cell reactions :**

Multiply eq. (1) by 6 and add it to eq. (2)



Now, at first in the container there were  $\text{Cr}_2\text{O}_7^{2-}$  ions. When a small drop of  $\text{Fe}^{2+}$  is added, there will be  $\text{Cr}^{3+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cr}_2\text{O}_7^{2-}$  ions in the container. Hence, emf will be close to 1.33 V as  $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$ . So the graph should start from a point at near 1.33 V. With the passage of time, on addition of more and more  $\text{Fe}^{2+}$ , there will be  $\text{Fe}^{3+}$ ,  $\text{Fe}^{2+}$  and  $\text{Cr}^{3+}$  ions in the container. Now, emf will be near 0.77 V as  $E^\circ_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$ . So the final graph should be like this :



This graph matches with none of the given graphs.

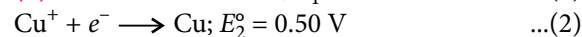
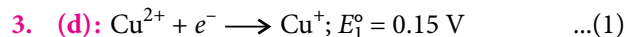
2. (c) :  $\text{AgCl}$  is a sparingly soluble salt. So, it dissolves very little into solution. Practically, it gives zero concentration or infinite dilution. So, we have

$$\kappa_{m(\text{Saturated})} = \frac{\infty}{\Lambda_m} = \kappa \times \frac{1000}{\text{Solubility}(s)}$$

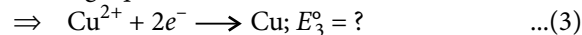
$$\Rightarrow s = \frac{\kappa \times 1000}{\frac{\infty}{\Lambda_m}}$$

$$\text{Hence, } s = \frac{1.382 \times 10^{-6} \times 10^3}{(61.9 + 76.3)}$$

$$= \frac{1.382 \times 10^{-3}}{138.2} = 10^{-5} \text{ mol L}^{-1}$$



Adding eq. (1) and (2)



EMFs are not additive but energies are additive. So calculate Gibbs' energy for each reaction.

For reaction (1),  $\Delta G_1^\circ = -n_1 F E_1^\circ$

(using the formula  $\Delta G^\circ = -n F E^\circ$ )

$\Rightarrow \Delta G_1^\circ = -1 \times F \times 0.15 = -0.15 F$

For reaction (2),  $\Delta G_2^\circ = -n_2 F E_2^\circ$

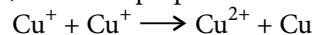
$\Rightarrow \Delta G_2^\circ = -1 \times F \times 0.50 = -0.5 F$

For reaction (3),  $\Delta G_3^\circ = -2 \times F \times E_3^\circ$

Therefore,  $-2 F E_3^\circ = -0.15 F - 0.5 F$

$\Rightarrow E_3^\circ = \frac{0.65}{2} = 0.325 \text{ V}$

Now, for the disproportionation reaction,



$E_{\text{cell}}^\circ = (0.5 - 0.15) \text{ V} = 0.35 \text{ V}$

Hence, disproportionation takes place. ◆◆

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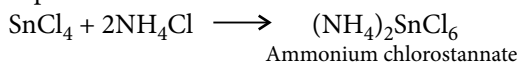
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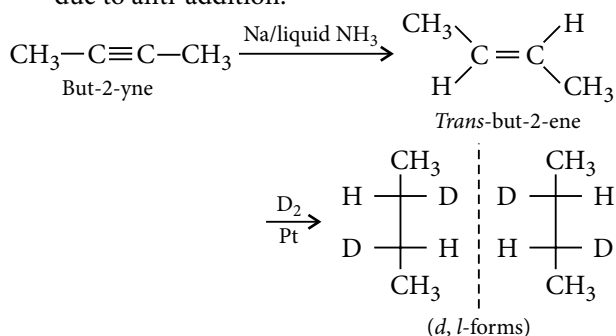
# CHEMISTRY MUSING

## SOLUTION SET 25

1. (b): Ammonolysis of  $\text{SnCl}_4$  is affected by  $\text{NH}_4\text{Cl}$  vapours as follows:



2. (c): *Trans*-but-2-ene reacts with  $\text{D}_2$  (Deuterium or Heavy hydrogen) and Pt to give a racemic mixture due to anti-addition.



- (a) is ruled out because Na/liquid  $\text{NH}_3$  leads to anti-addition and forms *trans*-but-2-ene.  
 (b) is ruled out because *trans*-but-2-ene will react with  $\text{D}_2/\text{Pt}$  to give a racemic mixture and not a meso compound.  
 (d) is not possible because *cis*-but-2-ene cannot be formed by Birch reduction.

3. (a): The given data are  $p^\circ_{\text{water}} = 17.0$  torr;  
 $p_{\text{total}}$  of the 4 mole % solution =  $p_{\text{NH}_3} + p_{\text{water}} = 50.0$  torr

$$x_{\text{NH}_3} = 0.04 \text{ and } x_{\text{water}} = 0.96$$

Now, according to Raoult's law;

$$p_{\text{water}} = x_{\text{water}} p^\circ_{\text{water}} = 0.96 \times 17.0 \text{ torr} = 16.32 \text{ torr}$$

$$p_{\text{NH}_3} = p_{\text{total}} - p_{\text{water}} = 50 - 16.32 = 33.68 \text{ torr}$$

Now, Henry's law constant for ammonia is

$$K_{\text{H}(\text{NH}_3)} = \frac{p_{\text{NH}_3}}{x_{\text{NH}_3}} = \frac{33.68 \text{ torr}}{0.04} = 842 \text{ torr}$$

Hence, for 5 mole % solution, we have

$$p_{\text{NH}_3} = K_{\text{H}(\text{NH}_3)} x_{\text{NH}_3} = (842 \text{ torr})(0.05) = 42.1 \text{ torr}$$

$$p_{\text{water}} = p^\circ_{\text{water}} x_{\text{water}} = (17 \text{ torr})(0.96) = 16.32 \text{ torr}$$

$$\text{Thus, } p_{\text{total}} \text{ of 5 mole \% solution} = p_{\text{NH}_3} + p_{\text{water}} = 42.1 + 16.32 = 58.42 \text{ torr}$$

4. (a): Hybridisation of Fe in the complex is  $sp^3d^2$ . The complex has 3 unpaired electrons and have  $\mu = 3.87$  B.M.

5. (d): It involves gain and loss of electron pair (Lewis concept).

6. (a): For  $n = 2$  and  $n = 3$ ,

$$\text{Energy difference} = 10 + 17 - 4.25 - 5.95 = 16.8 \text{ eV}$$

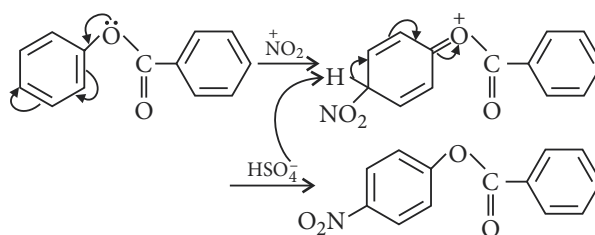
$$16.8 = 13.6 \left( \frac{1}{2^2} - \frac{1}{3^2} \right) Z^2 \Rightarrow Z = 2.98 \approx 3$$

$$\text{Energy difference } (n_2 = n \text{ and } n_1 = 2) = 10 + 17 = 27 \text{ eV}$$

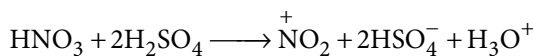
$$27 = 13.6 \left( \frac{1}{2^2} - \frac{1}{n^2} \right) \times 3^2$$

$$3.0 = 13.6 \left( \frac{1}{4} - \frac{1}{n^2} \right), n \approx 6$$

7. (b):



8. (c): When solute is non-ionising then,  
 $\Delta T_f = K_f m$                        $K_f = X^\circ \text{ kg mol}^{-1}$   
 $\text{HNO}_3$ , ionises as follows:



Hence,  $i = 4$

$$\text{Now, } \Delta T_f = iK_f m$$

$$\Rightarrow \Delta T_f = 4 \times X \times 1 = 4X^\circ$$

9. (2):  $\text{Be}_2\text{SiO}_4$ ,  $\text{ZrSiO}_4$  and  $\text{Mg}_2\text{SiO}_4$  are orthosilicates.

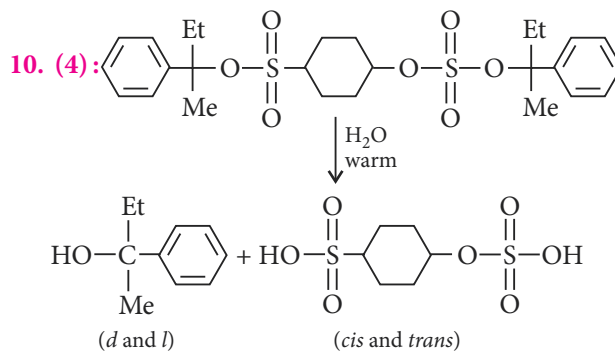
$\text{Zn}_4\text{Si}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$  and  $\text{Sc}_2(\text{Si}_2\text{O}_7)$  are pyrosilicates.

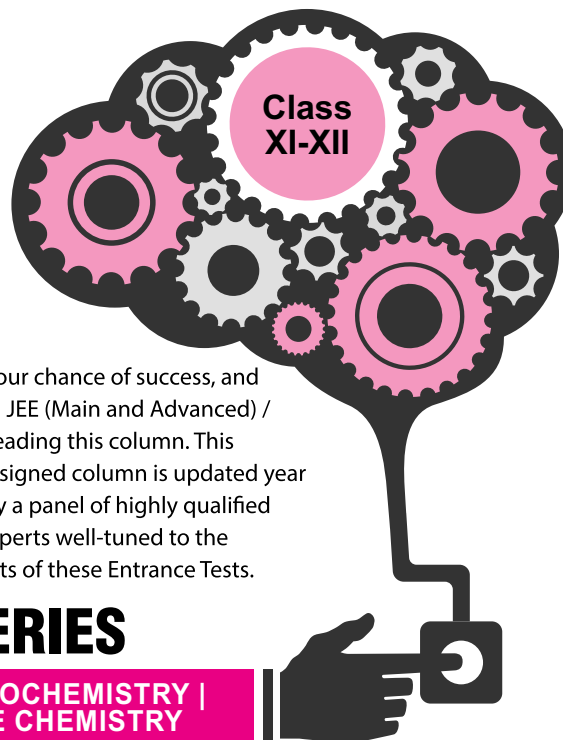
$\text{MgSiO}_3$  and  $\text{Ca}_2\text{Mg}_5(\text{Si}_4\text{O}_{11})_2$  are chain silicates.

Beryl and wollastonite are cyclic silicates.

Mica is a sheet silicate.

Quartz is a 3-D silicate.





# JEE

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## ACCELERATED LEARNING SERIES

### Unit 3 REDOX REACTIONS AND ELECTROCHEMISTRY | CHEMICAL KINETICS | SURFACE CHEMISTRY

#### REDOX REACTIONS AND ELECTROCHEMISTRY

- Redox Reactions
- Oxidation Number
- Balancing of Redox Reactions
- Electrolytic and Metallic Conduction
- Kohlrausch's Law and its Applications
- Different Types of Cells
- Electrode Potential and EMF
- Nernst Equation and its Applications
- Relation between Cell Potential and Gibbs Energy Change
- Laws of Electrolysis
- Dry Cell, Lead Accumulator and Fuel Cells

#### TIPS TO REMEMBER

- **Oxidation** is a process which involves
  - Addition of oxygen or an electronegative element.
  - Removal of hydrogen or an electropositive element.
  - Loss of electrons or increase in oxidation number.
- **Reduction** is a process which involves
  - Addition of hydrogen or an electropositive element.
  - Removal of oxygen or an electronegative element.
  - Gain of electrons or decrease in oxidation number.
- **Redox reactions** are the reactions which involve oxidation and reduction simultaneously.

- In *intermolecular redox reaction* one molecule of reactant is oxidised whereas molecule of other reactant is reduced.
- In *intramolecular redox reaction* one atom of a molecule is oxidised and other atom of the same molecule is reduced.
- A substance which undergoes reduction acts as an *oxidising agent* and the substance which undergoes oxidation acts as a *reducing agent*.
- **Oxidation number** : It is the residual charge which an atom appears to have when all the atoms surrounding it are removed.
  - The method of representing the oxidation state of a metal by Roman numerals like I, II, etc. within the parenthesis after the symbol of the metal is called *stock notation*.

#### Rules for assigning oxidation number :

Species	Oxidation number	Examples
Elements	Zero (0)	N <sub>2</sub> , Cl <sub>2</sub> , O <sub>2</sub> , P <sub>4</sub> , S <sub>8</sub>
Monatomic ions	Same as charge	Na <sup>+</sup> (+1), Mg <sup>2+</sup> (+2), Cl <sup>-</sup> (-1)
Hydrogen :		
- with non-metals	+1	H <sub>2</sub> O, H <sub>2</sub> S, HCl
- with metals	-1	LiH, CaH <sub>2</sub> , KH
Oxygen :		
- in peroxides	-2 (mostly)	H <sub>2</sub> O, CaO, NaOH
- in superoxides	-1	H <sub>2</sub> O <sub>2</sub> , BaO <sub>2</sub>
- in fluorides	-1/2	KO <sub>2</sub> , CsO <sub>2</sub>
	+1, +2	O <sub>2</sub> F <sub>2</sub> , OF <sub>2</sub> (respectively)

Alkali metals	+1	Li, Na, K, etc.
Alkaline earth metals	+2	Be, Mg, Ca, etc.
Fluorine (most electronegative)	-1 (always)	HF, OF <sub>2</sub> , LiF
Sulphides	-2	H <sub>2</sub> S, ZnS
<i>p</i> -, <i>d</i> - and <i>f</i> -block elements	Variable	<i>d</i> -block : Fe(+2, +3), Cu(+1, +2), Mn(+7, +6, +5, +4, +3, +2) etc. <i>p</i> -block : As (+3, +5), Sb (+3, +5), Sn (+2, +4), etc. <i>f</i> -block : Ce (+3, +4), Eu (+2, +3)

#### □ Balancing of Redox Reactions :

##### ○ Oxidation number method :

- Identify atoms which undergo change in oxidation number in the reaction.
- Calculate the increase or decrease in the oxidation number per atom and multiply it by number of atoms undergoing that change, if increase or decrease is not equal then multiply by suitable number to make them equal.
- Add H<sup>+</sup> (if medium is acidic) or OH<sup>-</sup> (if medium is basic) on the appropriate side so that the total ionic charges of reactants and products are equal.
- Make the number of hydrogen atoms in the expression on the two sides equal by adding H<sub>2</sub>O to the reactants or products and finally check the number of oxygen atoms.

##### ○ Half reaction method :

- Separate the equation into half-reactions.
- Balance the atoms other than O and H in each half-reaction individually.
- For reactions occurring in acidic medium, add H<sub>2</sub>O to balance O atoms and H<sup>+</sup> to balance H atoms and for basic medium, H atoms are balanced by adding H<sub>2</sub>O molecule to the side deficient in H atoms and equal number of OH<sup>-</sup> ions are added to opposite side and then duplicacy is removed if any.

- Add electrons to one side of the half-reaction to balance the charges and make the number of electrons equal in two half-reactions by multiplying one or both half-reactions by appropriate number.
- Add two half-reactions to achieve the overall reaction and cancel the electrons on both sides.

#### 🔑 KEY POINT

- Any oxy anion in an acidic medium acts as a stronger oxidising agent as compared to alkaline or neutral medium.
- Fluorine is the strongest oxidising agent and lithium is the strongest reducing agent.
- If a compound contains two or more atoms of the same element, they may have same or different oxidation states depending upon the chemical bonding.
- Fractional oxidation states actually represent the average oxidation states of several atoms of the same element in a structure.

#### ✓ SELF CHECK

1. Hydrogen peroxide in its reaction with KIO<sub>4</sub> and NH<sub>2</sub>OH respectively, is acting as a
  - (a) reducing agent, oxidising agent
  - (b) reducing agent, reducing agent
  - (c) oxidising agent, oxidising agent
  - (d) oxidising agent, reducing agent.

(JEE Advanced 2014)
2. In which of the following reactions, H<sub>2</sub>O<sub>2</sub> acts as a reducing agent?
  - (1) H<sub>2</sub>O<sub>2</sub> + 2H<sup>+</sup> + 2e<sup>-</sup> → 2H<sub>2</sub>O
  - (2) H<sub>2</sub>O<sub>2</sub> - 2e<sup>-</sup> → O<sub>2</sub> + 2H<sup>+</sup>
  - (3) H<sub>2</sub>O<sub>2</sub> + 2e<sup>-</sup> → 2OH<sup>-</sup>
  - (4) H<sub>2</sub>O<sub>2</sub> + 2OH<sup>-</sup> - 2e<sup>-</sup> → O<sub>2</sub> + 2H<sub>2</sub>O
  - (a) (2), (4)
  - (b) (1), (2)
  - (c) (3), (4)
  - (d) (1), (3)

(JEE Main 2014)
3. Which ordering of compounds is according to the decreasing order of the oxidation state of nitrogen?
  - (a) HNO<sub>3</sub>, NO, NH<sub>4</sub>Cl, N<sub>2</sub>
  - (b) HNO<sub>3</sub>, NO, N<sub>2</sub>, NH<sub>4</sub>Cl
  - (c) HNO<sub>3</sub>, NH<sub>4</sub>Cl, NO, N<sub>2</sub>
  - (d) NO, HNO<sub>3</sub>, NH<sub>4</sub>Cl, N<sub>2</sub>

(IIT-JEE 2012)

## Electrolytic and Metallic Conduction

### Types of conductors :

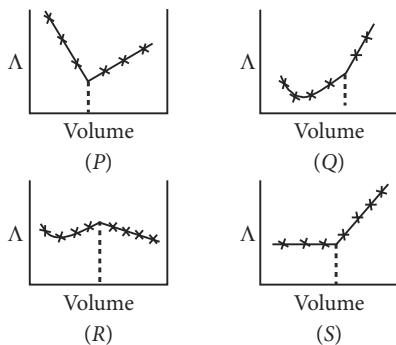
Electronic conductors	Electrolytic conductors
Flow of electricity is due to flow of electrons.	Flow of electricity is due to flow of ions.
Flow of electricity takes place without decomposition of the substance.	Flow of electricity is accompanied by decomposition of the substance.
Conduction decreases with increase in temperature because kernels start vibrating which interfere in the flow of electrons.	Conduction increases with increase in temperature because dissociation increases.

### Conductance in Electrolytic Solutions :

Property	Formula	Units	Effect of dilution
Conductance (G)	$\frac{1}{R}$	$\text{Ohm}^{-1} (\Omega^{-1})/\text{Siemens (S)}$	Increases as larger number of ions are produced.
Specific conductance ( $\kappa$ ) or conductivity	$\frac{1}{\rho}$ or $G \frac{l}{a}$	$\text{Ohm}^{-1} \text{cm}^{-1}/\text{S m}^{-1}$	Decreases as number of ions per $\text{cm}^3$ decreases.
Equivalent conductivity ( $\Lambda_{eq}$ )	$\kappa \times V$ or $\kappa \times \frac{1000}{N}$	$\Omega^{-1} \text{cm}^2 \text{eq}^{-1}/\text{S m}^2 \text{eq}^{-1}$	Increases with dilution due to large increase in V.
Molar conductivity ( $\Lambda_m$ )	$\kappa \times V$ or $\kappa \times \frac{1000}{M}$	$\Omega^{-1} \text{cm}^2 \text{mol}^{-1}/\text{S m}^2 \text{mol}^{-1}$	Increases with dilution due to large increase in V.

### SELF CHECK

4. Resistance of 0.2 M solution of an electrolyte is 50  $\Omega$ . The specific conductance of the solution is 1.4  $\text{S m}^{-1}$ . The resistance of 0.5 M solution of the same electrolyte is 280  $\Omega$ . The molar conductivity of 0.5 M solution of the electrolyte in  $\text{S m}^2 \text{mol}^{-1}$  is  
 (a)  $5 \times 10^2$  (b)  $5 \times 10^{-4}$   
 (c)  $5 \times 10^{-3}$  (d)  $5 \times 10^3$   
 (JEE Main 2014)
5.  $\text{AgNO}_3(\text{aq})$  was added to an aqueous KCl solution gradually and the conductivity of the solution was measured. The plot of conductance ( $\Lambda$ ) versus the volume of  $\text{AgNO}_3$  is

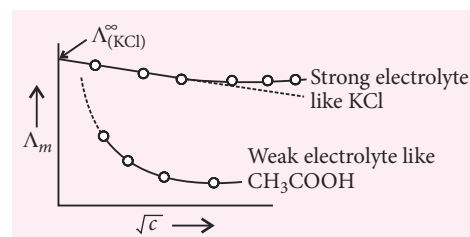


- (a) P (b) Q  
 (c) R (d) S (IIT-JEE 2011)

### Variation of Molar Conductivity with Concentration

- For a strong electrolyte it is shown by Debye-Huckel Onsager equation as follows :

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{c}$$



Here,  $\Lambda_m^\infty$  = Molar conductivity at infinite dilution  
 (Limiting molar conductivity)

$\Lambda_m$  = Molar conductivity at V-dilution

$b$  = Constant which depends upon nature of solvent and temperature

$c$  = Concentration

### Kohlrausch's Law

- It states that equivalent conductivity of any electrolyte at infinite dilution is the sum of the limiting ionic conductivities of the cations and anions or molar conductivity of an electrolyte at infinite dilution is the sum of the limiting ionic

conductivities of the cations and the anions each multiplied by the number of ions present in one formula unit of the electrolyte.

$$\Lambda_{eq}^{\circ} = \lambda_c^{\circ} + \lambda_a^{\circ} \text{ or } \Lambda_m^{\circ} \text{ for } A_xB_y = x\lambda_A^{\circ} + y\lambda_B^{\circ}$$

□ **Applications of Kohlrausch's law :**

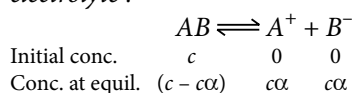
- *Calculation of molar conductivity of weak electrolytes :*

$$\begin{aligned} \Lambda_m^{\circ} \text{CH}_3\text{COOH} &= \lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{H}^+}^{\circ} \\ &= (\lambda_{\text{H}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}) + (\lambda_{\text{CH}_3\text{COO}^-}^{\circ} + \lambda_{\text{Na}^+}^{\circ}) - \\ &\quad (\lambda_{\text{Na}^+}^{\circ} + \lambda_{\text{Cl}^-}^{\circ}) \\ &= \Lambda_m^{\circ} \text{HCl} + \Lambda_m^{\circ} \text{CH}_3\text{COONa} - \Lambda_m^{\circ} \text{NaCl} \end{aligned}$$

- *Calculation of degree of dissociation :*

$$\begin{aligned} \text{Degree of dissociation } (\alpha) &= \frac{\Lambda_m^c}{\Lambda_m^{\circ}} \\ &= \frac{\text{Molar conductivity at concentration } c}{\text{Molar conductivity at infinite dilution}} \end{aligned}$$

- *Calculation of dissociation constant ( $K_c$ ) of weak electrolyte :*



$$K_c = \frac{c\alpha \times c\alpha}{(c - c\alpha)} = \frac{c\alpha^2}{(1 - \alpha)}$$

- *Determination of ionic product of water :*

$$\Lambda_{\text{H}_2\text{O}}^{\circ} = \lambda_{\text{H}^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ}$$

$$\Lambda_{\text{H}_2\text{O}}^{\circ} = \kappa \times \frac{1000}{\text{Molarity}}$$

$$\text{Molarity} = [\text{H}^+] = [\text{OH}^-] = \frac{\kappa \times 1000}{\Lambda_{\text{H}_2\text{O}}^{\circ}}$$

$$= \frac{\kappa \times 1000}{\lambda_{\text{H}^+}^{\circ} + \lambda_{\text{OH}^-}^{\circ}} = 1.01 \times 10^{-7} \text{ g ions L}^{-1}$$

$$\left[ \begin{array}{l} \because \lambda_{\text{H}^+}^{\circ} = 349.8 \text{ S cm}^2 \text{ mol}^{-1}, \\ \lambda_{\text{OH}^-}^{\circ} = 198.5 \text{ S cm}^2 \text{ mol}^{-1} \\ \kappa = 5.54 \times 10^{-8} \text{ S cm}^{-1} \end{array} \right]$$

$$\text{Ionic product of water } (K_w) = [\text{H}^+][\text{OH}^-] = 1.02 \times 10^{-14}$$

- *Determination of solubility of a sparingly soluble salt :*

$$\Lambda_m^{\circ} = \frac{\kappa \times 1000}{\text{Molarity}} = \frac{\kappa \times 1000}{\text{Solubility}}$$

$$\text{Solubility} = \frac{\kappa \times 1000}{\lambda_+^{\circ} + \lambda_-^{\circ}}$$

- *Determination of transport number :*

$$t_{\pm}^{\circ} = \frac{\lambda_{\pm}^{\circ}}{\Lambda_m^{\circ}} = \frac{\lambda_{\pm}^{\circ}}{\lambda_+^{\circ} + \lambda_-^{\circ}}$$

$$t_+^{\circ} = \text{Transport number of cation}$$

$$t_-^{\circ} = \text{Transport number of anion}$$

📌 **KEYPOINT**

- In solutions, the smaller ion has lower ionic conductivity due to extensive solvation.
- The unusual higher values of molar conductivity of  $\text{H}^+$  and  $\text{OH}^-$  ions than those of other ions is due to proton jump from one water molecule to other which are present in solution (Grotthuss conductance).

📌 **SELF CHECK**

6. The equivalent conductance of NaCl at concentration  $C$  and at infinite dilution are  $\lambda_C$  and  $\lambda_{\infty}$ , respectively. The correct relationship between  $\lambda_C$  and  $\lambda_{\infty}$  is given as (where, the constant  $B$  is positive)

(a)  $\lambda_C = \lambda_{\infty} + (B)\sqrt{C}$       (b)  $\lambda_C$  and  $\lambda_{\infty} + (B)C$

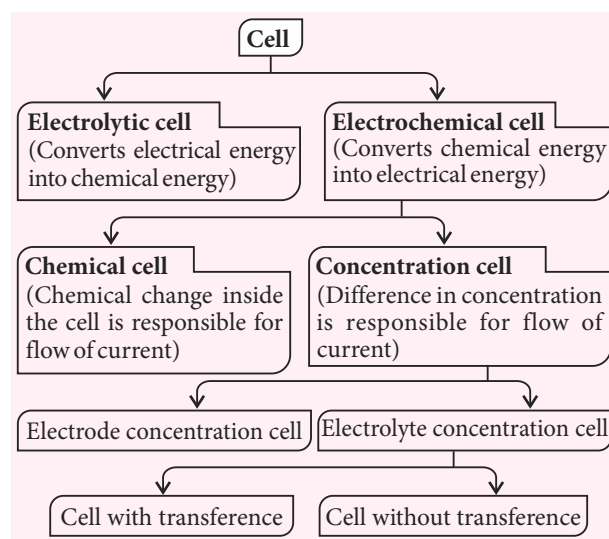
(c)  $\lambda_C$  and  $\lambda_{\infty} - (B)C$       (d)  $\lambda_C = \lambda_{\infty} - (B)\sqrt{C}$

(JEE Main 2014)

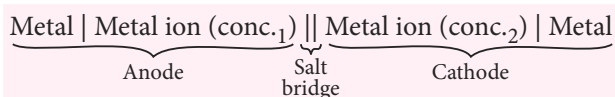
**Different Types of Cells**

- The device where electrochemical processes take place is known as *cell*.

- **Classification of cells :**



□ **Representation of an electrochemical cell :**



**Electrode**

□ A device in which a metallic (or electronic) conductor is in contact with electrolytic conductor is called an *electrode*.

- An electrode behaves as *anode* if oxidation takes place on it.
- An electrode behaves as *cathode* if reduction takes place on it.
- An electrode which does not take part in the chemical reaction and helps only in the exchange of electrons is called *inert electrode*.

□ **Electrode signs :**

	Electrolytic cell		Electrochemical cell	
	Anode	Cathode	Anode	Cathode
<b>Sign</b>	+	-	-	+
<b>Reaction</b>	Oxidation	Reduction	Oxidation	Reduction

□ **Different types of electrodes :**

- *Metal-metal ion electrode* : It includes a metal strip dipped in the solution of its own cations. Some examples are  
 $\text{Zn}/\text{Zn}^{2+}$ ;  $\text{Cu}/\text{Cu}^{2+}$ ;  $\text{Ag}/\text{Ag}^+$ , etc.
- *Amalgam electrode* : It is similar to metal-metal ion type electrode, but here, metal is replaced by its amalgam with Hg. This is done to improve the activity of metal.  $\text{Zn} - \text{Hg}/\text{Zn}^{2+}$  is a common example.
- *Gas electrode* : It involves the inert metal foil like Pt immersed in the solution capable of furnishing ions of gas. Pt,  $\text{H}_2/\text{H}^+$  and Pt,  $\text{Cl}_2/\text{Cl}^-$  are common examples of gas electrodes.
- *Metal-metal insoluble salt-salt anion* : This type of electrode includes metal in contact with its sparingly soluble salt and aqueous solution of some salt containing same anion.  
*e.g.*,  $\text{Hg} - \text{Hg}_2\text{Cl}_{2(s)} - \text{KCl}_{(aq)}$  Calomel electrode,  $\text{Pb} - \text{PbSO}_{4(s)} - \text{K}_2\text{SO}_{4(aq)}$  and  $\text{Ag} - \text{AgCl}_{(s)} - \text{KCl}_{(aq)}$
- *Redox electrode* : This electrode includes a platinum wire dipped in a solution of mixture of the two salts of the same metal but with different oxidation states. The common example is Pt,  $\text{Fe}^{2+}/\text{Fe}^{3+}$ .

□ **Electrode potential** : Tendency of an electrode to lose or gain electrons when it is in contact with the solution of its own ions.

- The tendency to lose electrons is called *oxidation potential*.
- The tendency to gain electrons is called *reduction potential*.
- If standard conditions are used ( $T = 298 \text{ K}$ , concentration = 1 M and  $P = 1 \text{ atm}$ ), the electrode potential is called *standard electrode potential*.
- The standard electrode potential values are determined with respect to standard hydrogen electrode (SHE) whose standard electrode potential is taken to be zero by convention.

□ **EMF** : The electrode potential difference between the two half-cells is known as electromotive force (EMF) of the cell or cell potential or cell voltage.

○ It can be calculated from the values of electrode potentials of the two half-cells constituting the cell by using following methods :

- $E_{\text{cell}}^{\circ} = E_{\text{ox}}^{\circ}(\text{anode}) + E_{\text{red}}^{\circ}(\text{cathode})$
- When only reduction potential is taken into account,  
 $E_{\text{cell}}^{\circ} = E_{\text{red}}^{\circ}(\text{cathode}) - E_{\text{red}}^{\circ}(\text{anode})$   
 $= E_{\text{right}}^{\circ} - E_{\text{left}}^{\circ}$
- When only oxidation potential is taken into account,  
 $E_{\text{cell}}^{\circ} = E_{\text{ox}}^{\circ}(\text{anode}) - E_{\text{ox}}^{\circ}(\text{cathode})$

**Nernst Equation**

□ For a reduction reaction,  
 $M_{(aq)}^{n+} + ne^- \rightarrow M_{(s)}$ ;

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[M_{(s)}]}{[M_{(aq)}^{n+}]}$$

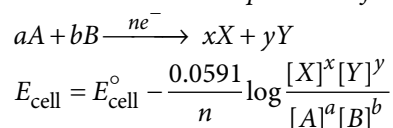
For pure solid or liquid or gas at 1 atm pressure, the molar concentration is taken as unity;  $[M] = 1$

$$E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M_{(aq)}^{n+}]}$$

$$E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M_{(aq)}^{n+}]}$$

□ **Applications of Nernst equation :**

○ *To calculate electrode potential of a cell :*



- To calculate equilibrium constant :  
At equilibrium,  $E_{\text{cell}} = 0$

$$E_{\text{cell}}^{\circ} = \frac{0.0591}{n} \log K_c \quad \text{at } 298 \text{ K}$$

### Relation between Cell Potential and Gibbs Energy Change

$$\Delta G^{\circ} = -nFE_{\text{cell}}^{\circ}$$

$$\Delta G^{\circ} = -2.303 RT \log K_c$$

### Relation between standard potentials of half cells containing a metal in different oxidation states :

- If two half-reactions having potentials  $E_1^{\circ}$  and  $E_2^{\circ}$  are combined to give a third half reaction having a potential  $E_3^{\circ}$  then

$$\begin{aligned} \Delta G_3^{\circ} &= \Delta G_1^{\circ} + \Delta G_2^{\circ} \\ -n_3 \times F \times E_3^{\circ} &= -n_1 \times F \times E_1^{\circ} - n_2 \times F \times E_2^{\circ} \\ n_3 \times E_3^{\circ} &= n_1 \times E_1^{\circ} + n_2 \times E_2^{\circ} \\ E_3^{\circ} &= \frac{n_1 E_1^{\circ} + n_2 E_2^{\circ}}{n_3} \end{aligned}$$

If equal number of electrons are involved, then  
 $E_3^{\circ} = E_1^{\circ} + E_2^{\circ}$

### KEY POINT

- Salt bridge provides cations and anions of almost same ionic conductance and remove the *liquid junction potential* which arises because of the difference in the rates of diffusion of cations and anions from more concentrated solution to less concentrated solution.

### SELF CHECK

7. Consider the following cell reaction,  
 $2\text{Fe}_{(s)} + \text{O}_{2(g)} + 4\text{H}^+_{(aq)} \longrightarrow 2\text{Fe}^{2+}_{(aq)} + 2\text{H}_2\text{O}_{(l)}$   
 $E^{\circ} = 1.67 \text{ V}$   
At  $[\text{Fe}^{2+}] = 10^{-3} \text{ M}$ ,  $p(\text{O}_2) = 0.1 \text{ atm}$  and  $\text{pH} = 3$ , the cell potential at  $25^{\circ}\text{C}$  is  
(a) 1.47 V                      (b) 1.77 V  
(c) 1.87 V                      (d) 1.57 V (IIT-JEE 2011)

### Products of electrolysis :

Electrolyte	Products		Reactions involved	
	At cathode	At anode	At cathode	At anode
Molten NaCl	Na metal	Cl <sub>2</sub> gas	$\text{Na}^+_{(l)} + e^- \longrightarrow \text{Na}_{(l)}$	$\text{Cl}^-_{(l)} \longrightarrow \frac{1}{2} \text{Cl}_{2(g)} + e^-$
Aqueous NaCl	H <sub>2</sub> gas	Cl <sub>2</sub> gas	$\text{H}_2\text{O}_{(l)} + e^- \longrightarrow \frac{1}{2} \text{H}_{2(g)} + \text{OH}^-_{(aq)}$	$\text{Cl}^-_{(aq)} \longrightarrow \frac{1}{2} \text{Cl}_{2(g)} + e^-$
Dil. H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> gas	O <sub>2</sub> gas	$\text{H}^+_{(aq)} + e^- \longrightarrow \frac{1}{2} \text{H}_{2(g)}$	$2\text{H}_2\text{O}_{(l)} \longrightarrow \text{O}_{2(g)} + 4\text{H}^+_{(aq)} + 4e^-$
Conc. H <sub>2</sub> SO <sub>4</sub>	H <sub>2</sub> gas	S <sub>2</sub> O <sub>8</sub> <sup>2-</sup>	$\text{H}^+_{(aq)} + e^- \longrightarrow \frac{1}{2} \text{H}_{2(g)}$	$2\text{SO}_4^{2-}_{(aq)} \longrightarrow \text{S}_2\text{O}_8^{2-}_{(aq)} + 2e^-$

8. The reduction potential of hydrogen half-cell will be negative if  
(a)  $p(\text{H}_2) = 1 \text{ atm}$  and  $[\text{H}^+] = 2.0 \text{ M}$   
(b)  $p(\text{H}_2) = 1 \text{ atm}$  and  $[\text{H}^+] = 1.0 \text{ M}$   
(c)  $p(\text{H}_2) = 2 \text{ atm}$  and  $[\text{H}^+] = 1.0 \text{ M}$   
(d)  $p(\text{H}_2) = 2 \text{ atm}$  and  $[\text{H}^+] = 2.0 \text{ M}$

(AIIEE 2011)

9. Given :

$$E^{\circ}_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}; E^{\circ}_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$$

$$E^{\circ}_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}; E^{\circ}_{\text{Cl}/\text{Cl}^-} = 1.36 \text{ V}$$

Based on the data given above, strongest oxidising agent will be

- (a)  $\text{MnO}_4^-$                       (b)  $\text{Cl}^-$   
(c)  $\text{Cr}^{3+}$                         (d)  $\text{Mn}^{2+}$  (JEE Main 2013)

### Electrolysis

- It is the process of decomposition of an electrolyte by passing electricity through its aqueous solution or molten state.

- Faraday's first law of electrolysis* : The amount of chemical reaction which occurs at any electrode during electrolysis by a current is proportional to the quantity of electricity passed through the electrolyte (solution or melt).  
 $w \propto Q$  or  $w = ZQ = Z \times I \times t$  where  $Z$  is electrochemical equivalent of the substance deposited and  $Z = \frac{\text{Eq. wt. of substance}}{96500}$ .

- Faraday's second law of electrolysis* : The amounts of different substances liberated by the same quantity of electricity passing through the electrolytic solution are proportional to their chemical equivalent weights.

$$\frac{w_1}{w_2} = \frac{E_1}{E_2} \quad \text{where } E \text{ is the equivalent weight.}$$

### SELF CHECK

10. Two Faradays of electricity are passed through a solution of  $\text{CuSO}_4$ . The mass of copper deposited at the cathode is (at. mass of Cu = 63.5 amu)

- (a) 2 g
- (b) 127 g
- (c) 0 g
- (d) 63.5 g

(JEE Main 2015)

#### □ Dry Cell, Lead Accumulator and Fuel Cell :

	Dry cell	Lead accumulator	Fuel cell
Anode	Zinc	Lead	Porous carbon containing catalysts ( $\text{H}_2$ passed)
Cathode	Graphite	Lead dioxide	Porous carbon containing catalysts ( $\text{O}_2$ passed)
Electrolyte	$\text{MnO}_2 + \text{C}$ (touching cathode) $\text{NH}_4\text{Cl} + \text{ZnCl}_2$ (touching anode)	$\text{H}_2\text{SO}_4$ (38%)	Conc. aqueous KOH
Anode reaction	$\text{Zn}_{(s)} \longrightarrow \text{Zn}_{(aq)}^{2+} + 2e^-$	$\text{Pb}_{(s)} + \text{SO}_4^{2-} \longrightarrow \text{PbSO}_{4(s)} + 2e^-$	$\text{H}_{2(g)} + 2\text{OH}_{(aq)}^- \longrightarrow 2\text{H}_2\text{O}_{(l)} + 2e^-$
Cathode reaction	$\text{MnO}_{2(s)} + \text{NH}_4^+_{(aq)} + e^- \longrightarrow \text{MnO}(\text{OH})_{(s)} + \text{NH}_{3(g)}$	$\text{PbO}_{2(s)} + \text{SO}_4^{2-} + 4\text{H}^+ + 2e^- \longrightarrow \text{PbSO}_{4(s)} + 2\text{H}_2\text{O}_{(l)}$	$\text{O}_{2(g)} + 2\text{H}_2\text{O}_{(l)} + 4e^- \longrightarrow 4\text{OH}_{(aq)}^-$

### CHEMICAL KINETICS

- Introduction
- Rate of Chemical Reaction
- Factors Affecting Rate of Reaction
- Elementary and Complex Reactions
- Order and Molecularity of Reaction
- Rate Law and Rate Constant
- Half Life of Reaction
- Effect of Temperature on Rate of Reaction
- Collision Theory

### TIPS TO REMEMBER

- *Chemical kinetics* is the branch of physical chemistry that deals with the study of rates of reactions and the factors governing rates of reaction.

#### Rate of Chemical Reaction

- Rate of reaction is the change in concentration of any one of the reactants or products per unit time.

- For a hypothetical reaction,  $A \rightarrow B$

$$\text{Rate of reaction} = -\frac{\Delta[A]}{\Delta t} = \frac{\Delta[B]}{\Delta t}$$

#### Some Commercial Cells

- **Primary cells** : Cells once exhausted cannot be used again e.g., dry cell and mercury cell.
- **Secondary cells** : Rechargeable cell which can be used again and again e.g., nickel-cadmium cell and lead storage battery.
- **Fuel cells** : Cells which can convert the energy of combustion of fuels such as  $\text{H}_2$ ,  $\text{CO}$ ,  $\text{CH}_4$  etc. into electrical energy e.g.,  $\text{H}_2 - \text{O}_2$  fuel cell.

- Negative sign is used while expressing the rate in terms of reactants to show that concentration of reactants is decreasing with time.

- Average rate of reaction =  $-\frac{\Delta[A]}{\Delta t}$  or  $\frac{\Delta[B]}{\Delta t}$

- Instantaneous rate =  $-\frac{d[A]}{dt} = \frac{d[B]}{dt}$

- Units of rate of reaction =  $\text{mol L}^{-1} \text{s}^{-1}$

#### Factors Affecting Rate of Reaction

- **Nature of reactants and products** :

- *Physical state* :

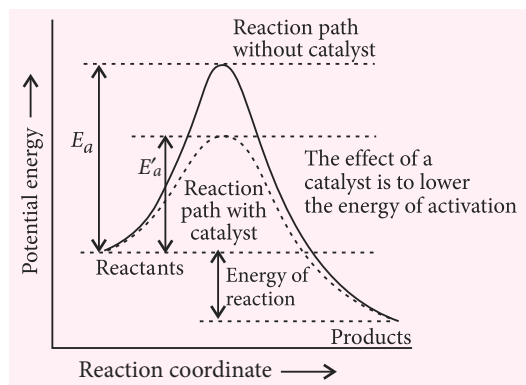
Gaseous state > Liquid state > Solid state  
 $\xrightarrow{\text{Decreasing rate of reaction}}$

- *Size of reactants* : As size of a solid reactant decreases, rate of reaction increases. Rate of reaction is maximum in powdered state because of increase in surface area.

- *Chemical nature* : Rate of reaction increases if the number of bonds broken and formed in the reaction are lesser in number.



- **Concentration of reactants** : Rate of reaction is directly proportional to the concentration of reactants.
- **Temperature** : Rate of reaction increases considerably with an increase in temperature.
- **Catalyst** : A positive catalyst increases the reaction rate by changing the path of reaction and lowering the activation energy.



- **Exposure to radiation** : The rate of chemical reaction is considerably increased by the use of radiations of certain frequency.

### ✓ SELF CHECK

11. The rate of a chemical reaction doubles for every 10°C rise of temperature. If the temperature is raised by 50°C, the rate of the reaction increases by about
- (a) 10 times                      (b) 24 times  
(c) 32 times                      (d) 64 times (AIEEE 2011)

### Elementary and Complex Reactions

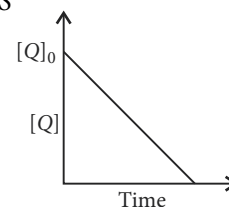
- Reaction which occurs in a single step with no experimentally detectable reaction intermediate is called *elementary reaction*.
- Reaction which involves more than one elementary reactions is called *complex* or *composite reaction*.
  - **Side or parallel path reactions** :
 
$$A \begin{cases} \rightarrow B \\ \rightarrow C \end{cases}$$
  - **Consecutive or sequential reactions** :
 
$$A \longrightarrow B \longrightarrow C$$
  - **Chain reactions** : In these reactions, the reaction intermediates formed in one step are consumed in another and regenerated in another step again.

### Order and Molecularity

Molecularity of reaction	Order of reaction
It is the total number of species taking part in a chemical reaction.	It is the sum of the powers of the concentration terms of reacting species in the rate law equation.
It is a theoretical concept.	It is an experimental quantity.
It is derived from the mechanism of reaction.	It is derived from the rate expression.
It can neither be zero nor fractional. It is always a whole number.	It may be zero, fractional or an integer (may range from 0 to 3).
It is applicable only to elementary reactions. The overall molecularity of a complex reaction has no significance.	It is applicable to elementary as well as complex reactions.

### ✓ SELF CHECK

12. Higher order (>3) reactions are rare due to
- (a) shifting of equilibrium towards reactants due to elastic collisions  
(b) loss of active species on collision  
(c) low probability of simultaneous collision of all the reacting species  
(d) increase in entropy and activation energy as more molecules are involved. (JEE Main 2015)
13. For the elementary reaction  $M \rightarrow N$ , the rate of disappearance of  $M$  increases by a factor of 8 upon doubling the concentration of  $M$ . The order of the reaction with respect to  $M$  is
- (a) 4                                      (b) 3  
(c) 2                                      (d) 1 (JEE Advanced 2014)
14. In the reaction,  $P + Q \rightarrow R + S$  the time taken for 75% reaction of  $P$  is twice the time taken for 50% reaction of  $P$ . The concentration of  $Q$  varies with reaction time as shown in the figure. The overall order of the reaction is
- (a) 2                                      (b) 3  
(c) 0                                      (d) 1 (JEE Advanced 2013)



15. For the non-stoichiometric reaction:  $2A + B \rightarrow C + D$ , the following kinetic data were obtained in three separate experiments, all at 298 K.

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

The rate law for the formation of C is

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

(JEE Main 2014)

### Rate Law and Rate Constant

- The equation that correlates the rate of reaction with concentration of reactants is known as *rate law*.

### Rate Law, Integrated Rate Law, Half-Life, Unit of Rate Constant and Graph for the Reactions of Different Orders :

Order	Rate law	Integrated rate law	Half-life	Unit of rate constant	Graph
0	Rate = $k[A]^0$	$[A]_t = -kt + [A]_0$	$t_{1/2} = [A]_0/2k$	$\text{mol L}^{-1} \text{s}^{-1}$	$[A]$ vs $t$ ; slope = $-k$
1	Rate = $k[A]^1$	$\ln[A]_t = -kt + \ln[A]_0$	$t_{1/2} = 0.693/k$	$\text{s}^{-1}$	$\ln[A]$ vs $t$ ; slope = $-k$
2	Rate = $k[A]^2$	$1/[A]_t = kt + 1/[A]_0$	$t_{1/2} = 1/k [A]_0$	$\text{L mol}^{-1} \text{s}^{-1}$	$1/[A]$ vs $t$ ; slope = $k$
2	Rate = $k[A][B]$	$kt = \frac{1}{[A]_0 - [B]_0} \ln \frac{[B]_0[A]}{[A]_0[B]}$	-	$\text{L mol}^{-1} \text{s}^{-1}$	$1/[A]$ vs $t$ ; slope = $k$
$n$	Rate = $k[A]^n$	$(n-1)kt = \frac{1}{[A]^{n-1}} - \frac{1}{[A]_0^{n-1}}$	$t_{1/2} = \frac{2^{n-1} - 1}{k(n-1)[A]_0^{n-1}}$	$(\text{mol L}^{-1})^{1-n} \text{s}^{-1}$	$\frac{1}{[A]^{n-1}}$ vs $t$ ; slope = $k$

### KEY POINT

- The rate law may not bear a simple relationship for the stoichiometric equation.
- The rate law may not depend on the concentration of every reactant or product of the reaction.
- The slowest elementary step of a complex reaction is the overall rate determining step and gives order of the reaction.
- When one of the reactants is present in large excess, the second order reaction conforms to the first order and is known as *pseudo unimolecular reaction*.
- Amount of substance left after  $n$  half lives =  $\frac{[A]_0}{2^n}$

- For a simple reaction,  $A + B \rightarrow C + D$   
 Rate =  $k[A][B]$  where  $k$  is the *rate constant* which is equal to the rate of reaction when concentration of each of the reactant is unity.

### Characteristics of rate constant :

- At a fixed temperature, the value of  $k$  is constant and characteristic of a reaction.
- It is a measure of the rate of the reaction. Larger the value of  $k$ , faster is the reaction.
- Unit of  $k$  depends upon the order of the reaction.

### Half Life of Reaction

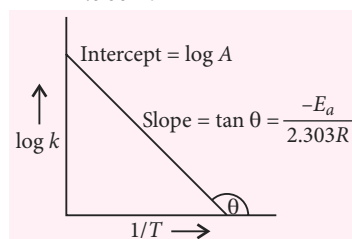
- The time in which the concentration of a reactant is reduced to one half of its initial concentration is called *half life of the reaction*.

$$t_{1/2} \propto \frac{1}{a^{n-1}} \text{ where } n \text{ is the order of the reaction.}$$

### Effect of Temperature on Rate of Reaction

- **Arrhenius equation :**  $k = Ae^{-E_a/RT}$

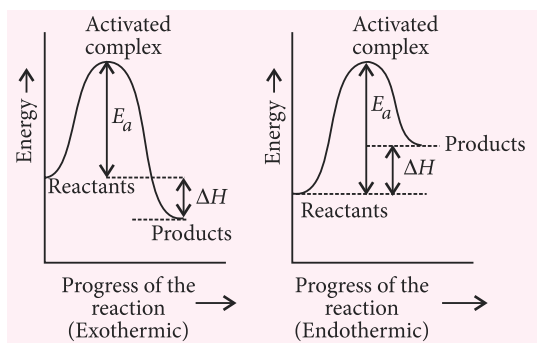
$$\log k = \log A - \frac{E_a}{2.303 RT}$$



where,  $k$  = Rate constant,  
 $A$  = Pre-exponential factor (frequency factor),  
 $E_a$  = Activation energy,  
 $T$  = Temperature

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 R} \left[ \frac{T_2 - T_1}{T_1 T_2} \right]$$

- **Activation energy** : The minimum amount of energy required by reactant molecules to participate in a reaction is called activation energy ( $E_a$ ).



- Activation energy = Threshold energy – Average kinetic energy of reacting molecules
- Activation energy ( $E_a$ )  

$$= E_{(\text{activated complex})} - E_{(\text{ground state})}$$
- $\Delta H$  = Activation energy of forward reaction – Activation energy of backward reaction

### Collision Theory

- Reactions occur when molecules collide with appropriate orientation and sufficient energy, not all molecular collisions result successfully in the formation of products.
- **For any successful collision** :
- Particles must collide.
  - They must collide with sufficient energy *i.e.*,  $E > E_a$ .
  - They need to have correct alignment (collision geometry) to keep  $E_a$  as low as possible.
  - To account for effective collision, another factor  $P$ , called orientation factor or steric factor or probability factor is introduced.

$$k = PZ_{AB} e^{-E_a/RT}$$

where,  $Z_{AB}$  represents the collision frequency of reactants  $A$  and  $B$ .

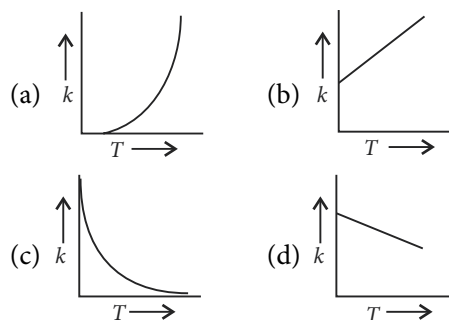
Thus, in collision theory, activation energy and proper orientation of the molecules determine the criteria for an effective collision and hence the rate of reaction.

### KEYPOINT

- Rise in rate of reaction is larger when temperature is increased in lower temperature range than in higher temperature range.
- A reaction with higher value of  $E_a$  will have smaller value of rate constant.

### SELF CHECK

16. The rate of a reaction doubles when its temperature changes from 300 K to 310 K. Activation energy of such a reaction will be ( $R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$  and  $\log 2 = 0.301$ )
- (a)  $60.5 \text{ kJ mol}^{-1}$       (b)  $53.6 \text{ kJ mol}^{-1}$   
 (c)  $48.6 \text{ kJ mol}^{-1}$       (d)  $58.5 \text{ kJ mol}^{-1}$
- (JEE Main 2013)
17. Plots showing the variation of the rate constant ( $k$ ) with temperature ( $T$ ) are given below. The plot that follows Arrhenius equation is



(IIT JEE 2010)

### SURFACE CHEMISTRY

- Adsorption
- Catalysis
- Colloidal State
- Emulsions

### TIPS TO REMEMBER

- **Adsorption** : Existence of higher concentration of any particular component (adsorbate) at the surface of liquid or solid phase (adsorbent) than in the bulk.
- In *positive adsorption* the concentration of adsorbate is high on the surface than in the bulk.
  - In *negative adsorption* the concentration of adsorbate is less on the surface than in the bulk.

❑ **Comparison of physisorption and chemisorption :**

S. No.	Physisorption	Chemisorption
1.	It arises because of 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.	It is irreversible.
4.	It depends on the nature of the gas. More easily liquefiable gases are adsorbed readily.	It also depends on the nature of the gas. Gases which can react with the adsorbent show chemisorption.
5.	Enthalpy of adsorption is low (20 - 40 kJ mol <sup>-1</sup> ).	Enthalpy of adsorption is high (80 - 240 kJ mol <sup>-1</sup> ).
6.	Low temperature is favourable for adsorption. It decreases with increase of temperature.	High temperature is favourable for adsorption. It increases with the increase of temperature.
7.	No appreciable activation energy is needed.	High activation energy is sometimes needed.
8.	It depends on the surface area and increases with increase in surface area of adsorbent.	It also depends on the surface area and increases with increase in surface area of adsorbent.
9.	It results into multimolecular layers on adsorbent surface under high pressure.	It results into unimolecular layer.

**Factors Affecting Adsorption of Gases on Solids**

- ❑ **Nature of adsorbent :** Greater are the strained forces on the surface, more is the ease with which adsorption takes place on the surface. The activated adsorbents have high adsorbing power.
- ❑ **Surface area of adsorbent :** Greater the surface area, more is the adsorption.
- ❑ **Nature of gas being adsorbed :** Easily liquefiable gases like NH<sub>3</sub>, HCl, Cl<sub>2</sub>, SO<sub>2</sub>, CO<sub>2</sub>, etc. (whose critical temperature is high) are adsorbed to greater extent.
- ❑ **Pressure :** Adsorption increases with increase in pressure. The effect of pressure is large at low temperature.

- ❑ **Temperature :** Since adsorption is an exothermic process so according to Le-Chatelier's principle adsorption decreases with increase in temperature.

**KEY POINT**

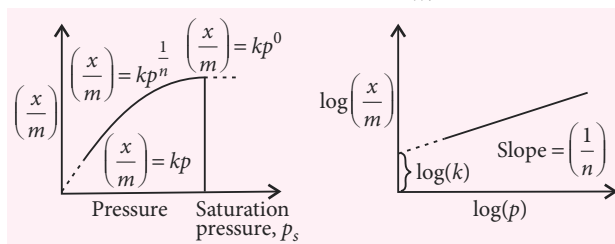
- Sorption is the term given to combined effect of adsorption and absorption.
- Occlusion refers to adsorption of gases by metals.

**SELF CHECK**

18. Methylene blue, from its aqueous solution, is adsorbed on activated charcoal at 25°C. For this process, the correct statement is
- the adsorption requires activation at 25°C
  - the adsorption is accompanied by a decrease in enthalpy
  - the adsorption increases with increase of temperature
  - the adsorption is irreversible.
- (JEE Advanced 2013)

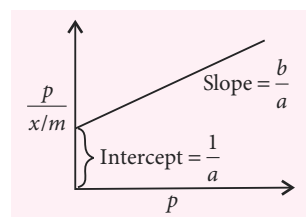
**Freundlich Adsorption Isotherm**

- ❑ The plot of  $\frac{x}{m}$  vs pressure at constant temperature is called Freundlich adsorption isotherm, where,  $m$  = Mass of the adsorbent  
 $x$  = Mass of the adsorbate
- For low pressure,  $\frac{x}{m} \propto p$
- For high pressure,  $\frac{x}{m} \propto p^0$
- For intermediate pressures,  $\frac{x}{m} \propto p^{1/n}$



**Langmuir Adsorption Isotherm**

- ❑ Assuming the formation of a monolayer of the adsorbate on the surface of the adsorbent, Langmuir derived the equation,
- $$\frac{x}{m} = \frac{ap}{1+bp}$$



where,  $a$  and  $b$  are constants whose values depend upon the nature of the gas adsorbed, nature of the adsorbent and temperature.

### For adsorption of solutes from solutions by solid adsorbents

- Freundlich equation :  $\frac{x}{m} = kC^{1/n}$
- Langmuir equation :  $\frac{x}{m} = \frac{aC}{1+bC}$

where,  $C$  is equilibrium concentration of the solute in solution.

### SELF CHECK

19. According to Freundlich adsorption isotherm, which of the following is correct?

- (a)  $\frac{x}{m} \propto p^1$                       (b)  $\frac{x}{m} \propto p^{1/n}$

(c)  $\frac{x}{m} \propto p^0$

(d) All the above are correct for different ranges of pressure.

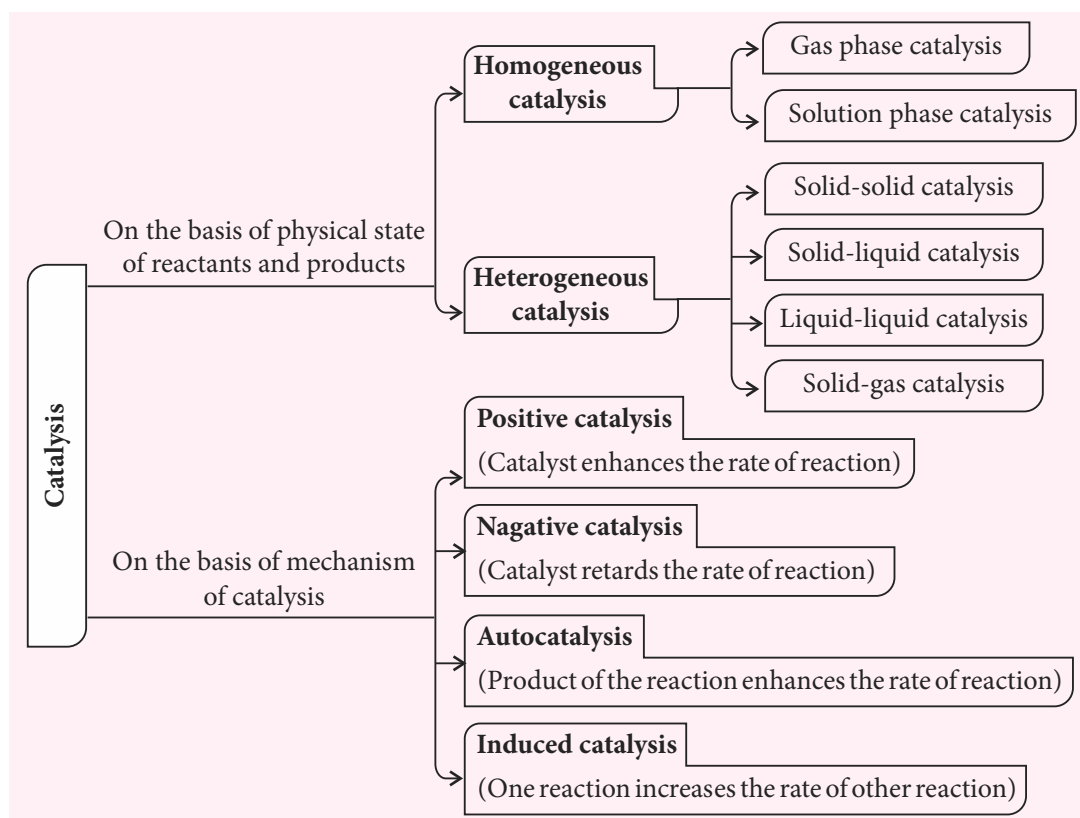
(AIEEE 2012)

### KEY POINT

- The graphs plotted  $T$  vs  $p$  for given amount of adsorption are known as *adsorption isostere*.
- For multilayered adsorption, BET isotherms (Brunauer, Emmett, Teller isotherm) are most widely used.

### Catalysis

- The process of enhancing the rate of a chemical reaction by addition of a foreign substance (catalyst) is called catalysis.



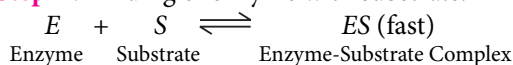
- **Activity of catalyst** : Activity of a catalyst represents its ability to accelerate the rate of a chemical reaction.
  - Extent of acceleration may be as high as  $10^{10}$  in certain reactions.
  - Extent of acceleration depends upon the strength of bond formed between reactants and

products which should not be too weak or too strong.

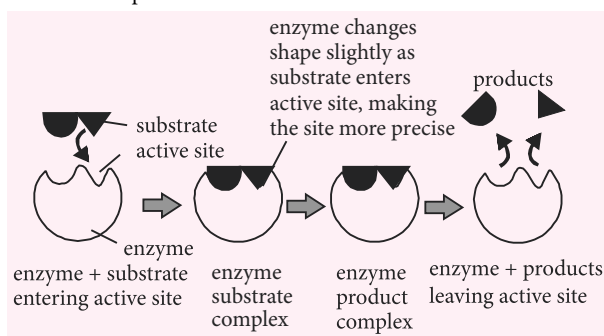
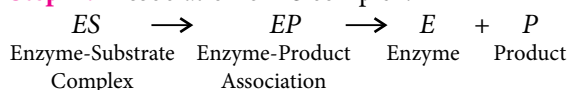
- **Selectivity of catalyst** : It is the ability of a catalyst to catalyse a particular reaction only.
- **Enzyme catalysis** : Enzymes are biological catalysts produced by living cells which catalyse the biochemical reactions in living organisms. Chemically, all enzymes are proteins.

- Enzyme catalysis mechanism : Enzyme catalysed reactions are highly specific.

**Step 1 :** Binding of enzyme with substrate.



**Step 2 :** Dissociation of ES complex.



### KEY POINT

- Catalyst lowers the activation energy.
- Catalyst does not change the value of equilibrium constant but helps in attaining the equilibrium faster.
- Substances which partially or completely destroy the activity of catalyst are called *catalytic poisons*.
- Some substances called *promoters* enhance the activity of catalyst but themselves cannot act as catalyst.

### Colloidal State

- A substance is said to be in colloidal state when it is dispersed in another medium in the form of very small particles having size in the range 1-1000 nm.
- Dispersed phase* (discontinuous phase) is the substance which has been dispersed while *dispersion medium* (continuous phase) is the medium in which the substance has been dispersed.

- Distinction between true solutions, colloids and suspensions:**

S.No.	Property	True solutions	Colloids	Suspensions
1.	Size of particles	< 1 nm	1-1000 nm	> 1000 nm
2.	Visibility	Not visible by any method	Not visible, but images may be seen with ultramicroscope	Visible with naked eye
3.	Separation (i) by filter paper (ii) by parchment membrane	Not possible Not possible	Not possible Possible	Possible Possible
4.	Nature	Homogeneous	Heterogeneous	Heterogeneous
5.	Appearance	Transparent	Turbid	Opaque
6.	Diffusion through membranes	Readily	Diffuse slowly	Do not diffuse
7.	Settling	Do not settle	Do not settle under gravity but settle under centrifugal force	Settle even under the effect of gravity

- Classification of Colloids :**

○ *On the basis of affinity of dispersed phase and dispersion medium :*

- *Lyophilic colloids* : Particles of dispersed phase have great affinity towards dispersion medium. These colloids are stable due to high hydration energy and are reversible in nature.
- *Lyophobic colloids* : Particles of dispersed phase have very less affinity for the dispersion medium. These colloids are unstable and irreversible in nature.

○ *Based on the size of colloidal particles :*

- *Macromolecular colloids* : The size of the particles of dispersed phase is of the range of colloidal particles e.g., polymers.

– *Multimolecular colloids* : Dispersed phase particles are aggregates of small molecules held together by weak or van der Waals' forces e.g., sols of gold, sulphur etc.

– *Associated colloids* : The substances which when dissolved in a medium at low concentration behave as normal strong electrolytes but at higher concentration exhibit colloidal state properties due to formation of aggregated particles called *micelles* e.g., soaps and detergents.

○ *On the basis of charge on dispersed phase :*

- *Positive colloids* : Sols of metal hydroxides, basic dyes, haemoglobin, etc.

- *Negative colloids* : Metal sulphides sols, starch, clay, charcoal, soap micelles, etc.
- *Neutral colloids* : Tween-20.
- *On the basis of nature of dispersion medium* :
  - *Aerosol* : Air is the dispersion medium.
  - *Hydrosol* : Water is the dispersion medium.
  - *Alcosol* : Alcohol is the dispersion medium.
  - *Benzosol* : Benzene is the dispersion medium.
- *On the basis of physical state of dispersed phase and dispersion medium.*

Dispersed phase	Dispersion medium	Name	Common examples
Gas	Gas	One phase system	
	Liquid	Foam	Soap, whipped cream
	Solid	Solid foam	Pumice stone, styrene rubber
Liquid	Gas	Aerosol	Fog, clouds, mist
	Liquid	Emulsion	Milk, emulsified oil
	Solid	Gel	Cheese, butter, boot polish
Solid	Gas	Aerosol	Smoke, volcanic dust
	Liquid	Sol	Paints, ink
	Solid	Solid sol	Coloured glasses, gemstones

#### □ Preparation of Colloids :

- *By mechanical disintegration*: It is done by using colloidal mill.
- *By Bredig's arc method (for metals)* : A direct current is passed through electrodes of metals suspended in a trough of ice cold water. Intense heat of the arc changes the metal into vapours which condense to form the colloidal particles.
- *Peptization* : A freshly prepared precipitate is converted into colloidal particles by adding a suitable electrolyte.

- *Ultrasonic dispersion* : Various substances such as mercury, oils, sulphur, sulphides and oxides of metals can be dispersed into colloidal state very easily with the help of ultrasonic waves. Ultrasonic vibrations which have frequency more than that of sound are made to strike a beaker containing the substance to be dispersed by using water as the dispersion medium.

#### □ Properties of Colloids :

- *Colligative properties* : The value of colligative properties of colloidal solutions are very low due to aggregation.
- *Tyndall effect* : When a beam of light is passed through a colloidal solution it becomes visible due to scattering of light by colloidal particles.
- *Brownian movement* : Brownian movement is the continuous zig-zag movement of colloidal particles which helps in providing stability to colloidal sols.
- *Electrical properties* : All the dispersed particles of colloidal sol have same charge and the particles of dispersion medium have an equal and opposite charge. Therefore, the colloidal particles repel one another and do not come close together to form large non-colloidal particles so that the sol is stable. Charge on colloidal particles may be due to frictional electrification and selective adsorption of ions.
- *Electrophoresis* : The movement of colloidal particles towards oppositely charged electrode under the influence of electric field is known as electrophoresis. The experiments of electrophoresis helps to know the charge on colloidal particles.
- *Electrophoretic mobility of colloidal particles* : It is defined as the distance travelled by colloidal particles in one second under a potential gradient of one volt per cm. It has been found that the migration velocities of colloidal particles are of the same order as those of ions under similar conditions. Since different colloidal materials have different mobilities, it is possible to separate them from one another from their mixtures.

- *Sedimentation potential or Dorn effect.* It is the reverse of electrophoresis. The sedimentation potential is set up when a particle is forced to move in a resting liquid.
- *Electro-osmosis :* It is the phenomenon in which the dispersion medium is allowed to pass through a semipermeable membrane under the influence of an electric field.
- *Coagulation and flocculation :* The precipitation of colloidal sol by the addition of electrolyte.

#### □ Purification of Colloids :

- *Dialysis :* It is the process of separating a crystalloid from a colloid by diffusion or filtration through a semipermeable membrane or dialyzing membrane. The process can be quickened by applying electric field and is called *electro-dialysis*.
- *Ultrafiltration :* It is the process of separating the colloidal particles by filtration through ultrafilter paper which is obtained by treating ordinary filter paper with gelatine solution.
- *Ultra-centrifugation :* It is based on sedimentation.
- Micelle formation takes place above a particular temperature called Kraft temperature and above a particular concentration called *Critical Micelle Concentration*.

#### □ Characteristics of Emulsions :

S. No.	Property	Water in oil	Oil in water
1.	Viscosity	More than water	Slightly more than water
2.	Appearance	Oily, opaque, and translucent	Watery, opaque and translucent
3.	Electrical conductivity	Very low	Nearly equal to water
4.	Dilution test	More oil added is soluble but not water	More water added is soluble but not oil
5.	Spreading test	Spreads easily on an oily layer	Spreads readily on watery layer
6.	Dye test : Addition of oil soluble dye like methylene blue	Dye dissolves giving a bright colour. <i>e.g., cold creams, cod liver oil</i>	Dye remains insoluble in the form of coloured droplets. <i>e.g., Milk, vanishing creams</i>

#### KEY POINT

- Gold number is the minimum number in milligrams of the protective colloid which must be added to prevent the coagulation of 10 mL of red gold solution when 1 mL of 10% solution of NaCl is added to it.

- Protective power  $\propto \frac{1}{\text{Gold number}}$

- Greater the valency of coagulating ion of the electrolyte, faster is the coagulation (Hardy-Schulze Rule).

- Flocculation value  $\propto \frac{1}{\text{Coagulating power}}$

#### Emulsions

- Emulsions are the colloidal systems in which both the dispersed phase and dispersion medium are liquids. They are stabilized by addition of substances called *emulsifiers* or *emulsifying agents*.

#### Types of Emulsions

- **Oil in Water (O/W) type :** In this type, oil is dispersed phase and water is the dispersion medium. Milk is an emulsion of O/W type, where fat globules are dispersed in water.
- **Water in Oil (W/O) type :** In this type, water is the dispersed phase and oil is the dispersion medium. Butter is an emulsion of W/O type.

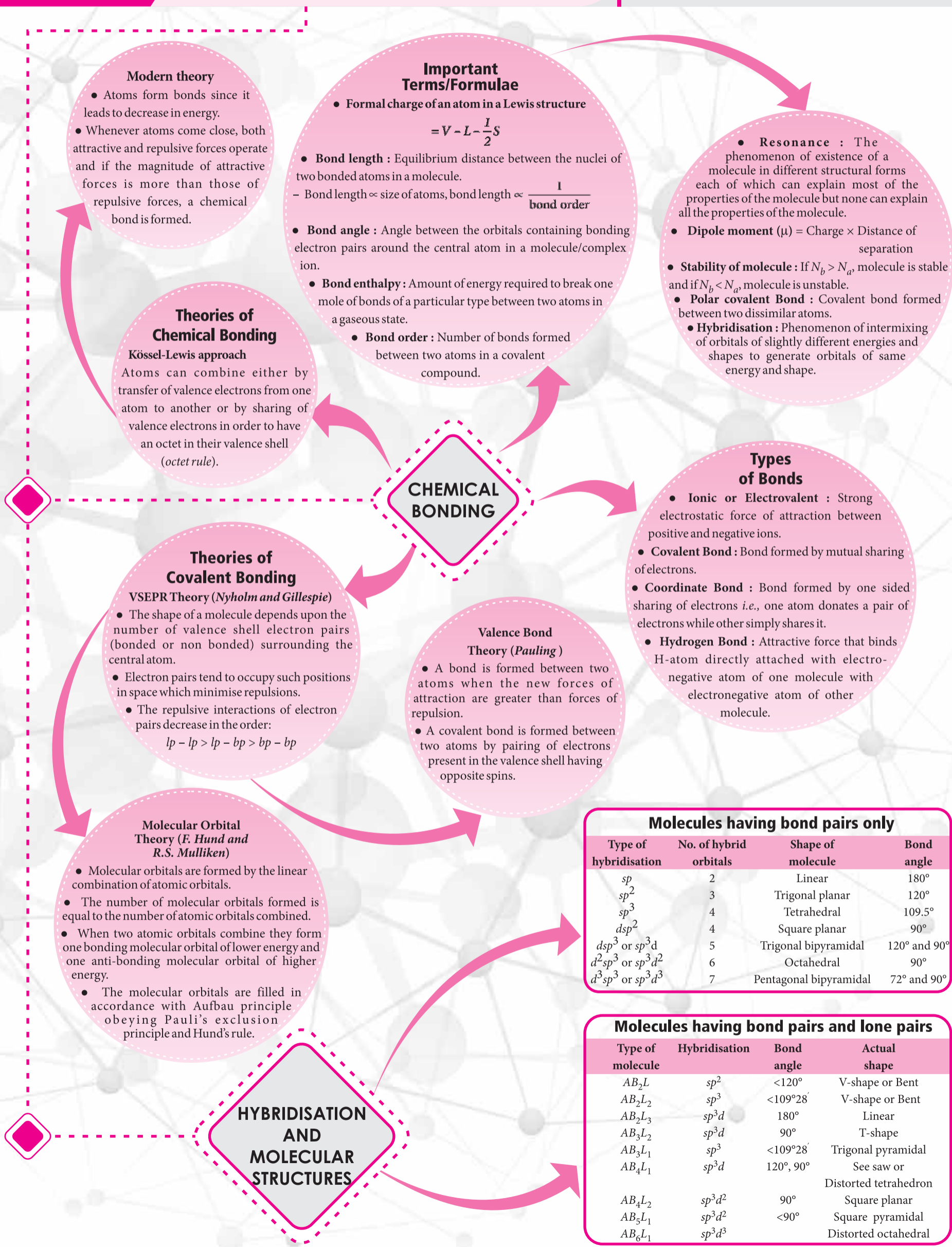
#### ANSWER KEYS (SELF CHECK)

1. (a) 2. (a) 3. (b) 4. (b) 5. (d) 6. (d) 7. (d) 8. (c) 9. (a) 10. (d)  
11. (c) 12. (c) 13. (b) 14. (d) 15. (a) 16. (b) 17. (a) 18. (b) 19. (d)



## CHEMICAL BONDING AND MOLECULAR STRUCTURE

The attractive force which holds together the constituent atoms or ions of a chemical species is known as chemical bond and different types of bonds formed between various elements govern the molecular structure and properties of compound formed.



# Exam Café

## QUESTIONS FOR PRACTICE

- Whenever a reaction between an oxidising agent and a reducing agent is carried out
  - a compound of lower oxidation state is formed if the reducing agent is in excess
  - a compound of higher oxidation state is formed if the oxidising agent is in excess
  - Both (a) and (b)
  - None of the above.
- The rate of disappearance of  $\text{Cr}_2\text{O}_7^{2-}$  ion at any instant in the following reaction :
 
$$\text{Cr}_2\text{O}_7^{2-} + 6\text{I}^- + 14\text{H}^+ \rightarrow 2\text{Cr}^{3+} + 3\text{I}_2 + 7\text{H}_2\text{O}$$
 is  $1.55 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1}$ . The rate of formation of iodine is
  - $9.3 \times 10^{-2} \text{ M s}^{-1}$
  - $4.65 \times 10^{-2} \text{ M s}^{-1}$
  - $5.0 \times 10^{-3} \text{ M s}^{-1}$
  - $2.50 \times 10^{-2} \text{ M s}^{-1}$
- Which of the following gases is expected to be adsorbed to maximum extent by the activated charcoal?
  - He
  - $\text{O}_2$
  - $\text{CH}_4$
  - $\text{SO}_2$
- The oxidation states of iodine in  $\text{HIO}_4$ ,  $\text{H}_3\text{IO}_5$  and  $\text{H}_5\text{IO}_6$  are respectively
  - +1, +3, +7
  - +7, +7, +3
  - +7, +7, +7
  - +7, +5, +3
- Which of the following statements is correct?
  - The rate of a reaction decreases with passage of time as the concentration of reactants decreases.
  - The rate of a reaction is same at any time during the reaction.
  - The rate of a reaction is independent of temperature change.
  - The rate of a reaction decreases with increase in concentration of reactants.
- In Langmuir's model of adsorption of a gas on a solid surface,
  - the rate of dissociation of adsorbed molecules from the surface does not depend on the surface covered
  - the adsorption at a single site on the surface may involve multiple molecules at the same time
  - the mass of gas striking a given area of surface is proportional to the pressure of the gas
  - the mass of gas striking a given area of surface is proportional to temperature of the gas.
- In the reaction,  $8\text{Al} + 3\text{Fe}_3\text{O}_4 \rightarrow 4\text{Al}_2\text{O}_3 + 9\text{Fe}$ , the number of electrons transferred from the reductant to the oxidant is
  - 8
  - 4
  - 16
  - 24
- Select the correct statements out of I, II and III for a zero order reaction.
  - Quantity of the product formed is directly proportional to time.
  - Larger the initial concentration of the reactant, greater is the half-life period.
  - If 50% reaction takes place in 100 minutes, 75% reaction will take place in 150 minutes.
  - I only
  - I and II only
  - II and III only
  - I, II and III
- Which of the following reactions is an example of negative catalysis?
  - $2\text{H}_2\text{O}_2(l) \xrightarrow{\text{Pt}} 2\text{H}_2\text{O}(l) + \text{O}_2(g)$
  - $\text{N}_2(g) + 3\text{H}_2(g) \xrightarrow{\text{Fe}} 2\text{NH}_3(g)$
  - $2\text{KClO}_3(s) \xrightarrow{\text{MnO}_2} 2\text{KCl}(s) + 3\text{O}_2(g)$
  - $2\text{CHCl}_3(l) + \text{O}_2(g) \xrightarrow{\text{C}_2\text{H}_5\text{OH}} 2\text{COCl}_2(g) + 2\text{HCl}(g)$
- During the passage of electricity through the solution of an electrolyte, current is carried by
  - cations only
  - anions only
  - both cations and anions, fraction of current carried being equal
  - both cations and anions, usually fraction of current carried being different.
- For the following reaction :
 
$$(\text{CH}_3)_3\text{CCl} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HCl}$$

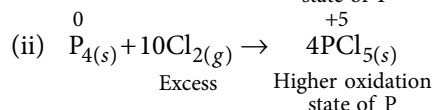
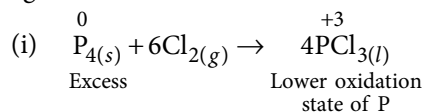
$$\left(\frac{dx}{dt}\right) = k[(\text{CH}_3)_3\text{CCl}], \text{ hence, rate determining step is}$$
  - $(\text{CH}_3)_3\text{CCl} \rightarrow (\text{CH}_3)_3\text{C}^+ + \text{Cl}^-$
  - $(\text{CH}_3)_3\text{CCl} + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{HCl}$
  - $(\text{CH}_3)_3\text{C}^+ + \text{H}_2\text{O} \rightarrow (\text{CH}_3)_3\text{COH} + \text{H}^+$
  - $\text{H}^+ + \text{Cl}^- \rightarrow \text{HCl}$
- Some properties of colloidal sol are given below :
  - Viscosity is same as that of the medium.
  - Extensive hydration takes place.

- III. Particles migrate either towards cathode or anode in an electric field.
- IV. Particles cannot be detected even under ultramicroscope.
- The properties which are specific for lyophilic colloidal sols are  
(a) I, II (b) III, IV (c) I, III (d) II, IV
13. Conductance of 0.1 M KCl (conductivity =  $x \text{ ohm}^{-1} \text{ cm}^{-1}$ ) filled in a conductivity cell is  $y \text{ ohm}^{-1}$ . If the conductance of 0.1 M NaOH filled in the same cell is  $z \text{ ohm}^{-1}$ , molar conductance of NaOH will be  
(a)  $0.1 \frac{xz}{y}$  (b)  $10 \frac{xz}{y}$  (c)  $10^3 \frac{xz}{y}$  (d)  $10^4 \frac{xz}{y}$
14. The different conditions for a gaseous reaction  $A + B \rightarrow \text{Products}$ , are given below :  
I. 1 mol of A and B each in 1 L vessel  
II. 2 mol of A and B each in 2 L vessel  
III. 0.2 mol of A and B each in 0.1 L vessel  
The formation of products and the rate of the reaction will be  
(a) fastest and greatest in III  
(b) fastest in II, greatest in III  
(c) fastest in III, greatest in II  
(d) fastest in I and II, greatest in III
15. Under the influence of an electric field, the particles in a sol migrate towards cathode. The coagulation of the same sol is studied using NaCl,  $\text{Na}_2\text{SO}_4$  and  $\text{Na}_3\text{PO}_4$  solutions. Their coagulating values will be in the order  
(a)  $\text{NaCl} > \text{Na}_2\text{SO}_4 > \text{Na}_3\text{PO}_4$   
(b)  $\text{Na}_2\text{SO}_4 > \text{Na}_3\text{PO}_4 > \text{NaCl}$   
(c)  $\text{Na}_3\text{PO}_4 > \text{Na}_2\text{SO}_4 > \text{NaCl}$   
(d)  $\text{Na}_2\text{SO}_4 > \text{NaCl} > \text{Na}_3\text{PO}_4$
16. Specific conductance of 0.1 M  $\text{CH}_3\text{COOH}$  at  $25^\circ\text{C}$  is  $3.9 \times 10^{-4} \text{ ohm}^{-1} \text{ cm}^{-1}$ . If  $\lambda^\infty(\text{H}^+)$  and  $\lambda^\infty(\text{CH}_3\text{COO}^-)$  at  $25^\circ\text{C}$  are 349.0 and  $41.0 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$  respectively, degree of ionisation of  $\text{CH}_3\text{COOH}$  at the given concentration is  
(a) 2.0% (b) 1.0% (c) 4.0% (d) 5.0%
17. What is the two-third life of a reaction having  $k = 5.48 \times 10^{-14} \text{ s}^{-1}$ ?  
(a)  $2.01 \times 10^{13} \text{ s}$  (b)  $2.01 \times 10^{12} \text{ s}$   
(c)  $4.02 \times 10^{13} \text{ s}$  (d)  $4.02 \times 10^{26} \text{ s}$
18.  $10^{-4} \text{ g}$  of gelatin is required to be added to  $100 \text{ cm}^3$  of a standard gold solution to just prevent its precipitation by addition of  $1 \text{ cm}^3$  of 10% NaCl solution to it. Hence, the gold number of gelatin in mg is  
(a) 10 (b) 1.0 (c) 0.1 (d) 0.01
19. Electrolysis is carried out in three cells :  
(A) – 1.0 M  $\text{CuSO}_4$ , Pt electrodes;  
(B) – 1.0 M  $\text{CuSO}_4$ , Copper electrodes;  
(C) – 1.0 M KCl, Pt electrodes.  
If volume of electrolytic solution is maintained constant in each of the cells, which is correct set of pH changes in (A), (B) and (C) cells respectively?  
(a) Increase in all the three  
(b) Decrease in all the three  
(c) Increase, constant, increase  
(d) Decrease, constant, increase
20. Consider the reaction  $A \rightarrow 2B + C$ ,  $\Delta H = -15 \text{ kcal}$ . The energy of activation of backward reaction is  $20 \text{ kcal mol}^{-1}$ . In presence of catalyst the energy of activation of forward reaction is  $3 \text{ kcal mol}^{-1}$ . At 400 K, the catalyst causes the rate of the reaction to increase by the number of times equal to  
(a)  $e^{3.5}$  (b)  $e^{2.5}$  (c)  $e^{-2.5}$  (d)  $e^{2.303}$
21. Protein sols at the pH less than the isoelectric pH have the colloidal particles  
(a) positively charged (b) negatively charged  
(c) with no charge  
(d) both positively and negatively charged.
22. Using the data given below, find out the correct order of reducing tendency :  
 $E^\circ_{\text{Cr}_2\text{O}_7^{2-}/\text{Cr}^{3+}} = 1.33 \text{ V}$ ;  $E^\circ_{\text{Cl}_2/\text{Cl}^-} = 1.36 \text{ V}$   
 $E^\circ_{\text{MnO}_4^-/\text{Mn}^{2+}} = 1.51 \text{ V}$ ;  $E^\circ_{\text{Cr}^{3+}/\text{Cr}} = -0.74 \text{ V}$   
(a)  $\text{Cr}^{3+} < \text{Cl}^- < \text{Mn}^{2+} < \text{Cr}$   
(b)  $\text{Mn}^{2+} < \text{Cl}^- < \text{Cr}^{3+} < \text{Cr}$   
(c)  $\text{Cr}^{3+} < \text{Cl}^- < \text{Cr}_2\text{O}_7^{2-} < \text{MnO}_4^-$   
(d)  $\text{Mn}^{2+} < \text{Cr}^{3+} < \text{Cl}^- < \text{Cr}$
23. The rate constant of a reaction is given by  $k = 2.1 \times 10^{10} \exp(-2700/RT)$   
It means that  
(a)  $\log k$  vs  $1/T$  will be a curved line with slope  $= -\frac{2700}{2.303 R}$   
(b)  $\log k$  vs  $1/T$  will be a straight line with intercept on  $\log k$  axis =  $\log 2.1 \times 10^{10}$   
(c) the number of effective collisions are  $2.1 \times 10^{10} \text{ cm}^{-3} \text{ s}^{-1}$   
(d) half-life of the reaction increases with increase in temperature.
24. To an emulsion of olive oil in water, stabilised by soap of alkali metals, a small amount of salt of bivalent or trivalent cations is added. Then  
(a) stabilisation of emulsion enhances  
(b) the emulsion breaks into the component liquids  
(c) reversal of phase to W/O type takes place  
(d) the emulsion turns into a true solution.

25. Two hydrogen electrodes (1 atm, 25°C) are set up in equimolar solutions of weak base (BOH)<sub>1</sub> and (BOH)<sub>2</sub> having pK<sub>b</sub> values 3 and 5. If the solutions are joined internally through a salt bridge, the cell potential will be  
 (a) 0.118 V (b) 0.0295 V  
 (c) 0.059 V (d) None of these.
26. If half-lives of a first order and zero order reactions are same, then the ratio of the initial rates of the first order reaction to that of zero order reaction is  
 (a) 1/0.693 (b) 2 × 0.693  
 (c) 2/0.693 (d) 6.93
27. Which of the following statements is not true about the aqueous solutions of soaps and detergents?  
 (a) Their molecules or ions have colloidal dimensions.  
 (b) Their molecules or ions aggregate spontaneously in solution to form particles of colloidal dimensions.  
 (c) In the aggregates of ions, polar ends are directed towards water and hydrocarbon ends towards the centre.  
 (d) The detergent action is due to the adsorption of grease/oil stain into the interior of the aggregates.
28. Using the following data for the electrode potentials, calculate ΔG° in kJ, for the indicated reaction.  
 $5\text{Ce}_{(aq)}^{4+} + \text{Mn}_{(aq)}^{2+} + 4\text{H}_2\text{O}_{(l)} \rightarrow 5\text{Ce}_{(aq)}^{3+} + \text{MnO}_4^{-}(aq) + 8\text{H}^{+}(aq)$   
 Given :  
 $\text{MnO}_4^{-}(aq) + 8\text{H}^{+}(aq) + 5e^{-} \rightarrow \text{Mn}_{(aq)}^{2+} + 4\text{H}_2\text{O}_{(l)}$   $E^{\circ} = +1.51 \text{ V}$   
 $\text{Ce}_{(aq)}^{4+} + e^{-} \rightarrow \text{Ce}_{(aq)}^{3+}$ ;  $E^{\circ} = +1.61 \text{ V}$   
 (a) -36.24 (b) -48.25 (c) -31.54 (d) -19.65
29. Two reactions with different activation energies have the same rate at room temperature. Which statement correctly describes the rates of these two reactions at the same higher temperature?  
 (a) The reaction with the greater activation energy will be faster.  
 (b) The reaction with the smaller activation energy will be faster.  
 (c) The two reactions will have the same rate.  
 (d) Temperature range is also required.
30. A current of 9.65 A is passed for 3 hours between nickel electrodes in 0.5 L of a 2 M solution of Ni(NO<sub>3</sub>)<sub>2</sub>. The molarity of the solution after electrolysis would be  
 (a) 0.46 M (b) 0.625 M  
 (c) 0.92 M (d) 1.25 M

## SOLUTIONS

1. (c): This can be explained by taking the example of P<sub>4</sub> as a reducing agent and Cl<sub>2</sub> as an oxidising agent.



Therefore, when P<sub>4</sub> (reducing agent) is in excess, PCl<sub>3</sub> is formed in which oxidation state of P is +3 and if Cl<sub>2</sub> (oxidising agent) is in excess, PCl<sub>5</sub> is formed in which oxidation state of P is +5.

2. (b): The rate of reaction =  $-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = \frac{1}{3} \frac{d[\text{I}_2]}{dt}$   
 or,  $\frac{d[\text{I}_2]}{dt} = 3 \times 1.55 \times 10^{-2} \text{ M s}^{-1} = 4.65 \times 10^{-2} \text{ M s}^{-1}$
3. (d): Gases having high critical temperature are readily adsorbed.

Gas	He	O <sub>2</sub>	CH <sub>4</sub>	SO <sub>2</sub>
Critical Temp. (K)	3.3	154.6	190	430

4. (c): The oxidation state of iodine in HIO<sub>4</sub> is +7 as  
 $1 + x + 4(-2) = 0$   
 $x = +7$   
 The oxidation state of iodine in H<sub>3</sub>IO<sub>5</sub> is +7 as  
 $3 + x + 5(-2) = 0$   
 $x = +7$   
 The oxidation state of iodine in H<sub>5</sub>IO<sub>6</sub> is +7 as  
 $5 + x + 6(-2) = 0$   
 $x = +7$
5. (a) 6. (c)  
 7. (d):  $8\text{Al} \rightarrow 8\text{Al}^{3+} + 24e^{-}$   
 $9\text{Fe}^{+8/3} + 24e^{-} \rightarrow 9\text{Fe}$
8. (d) 9. (d) 10. (d) 11. (a)

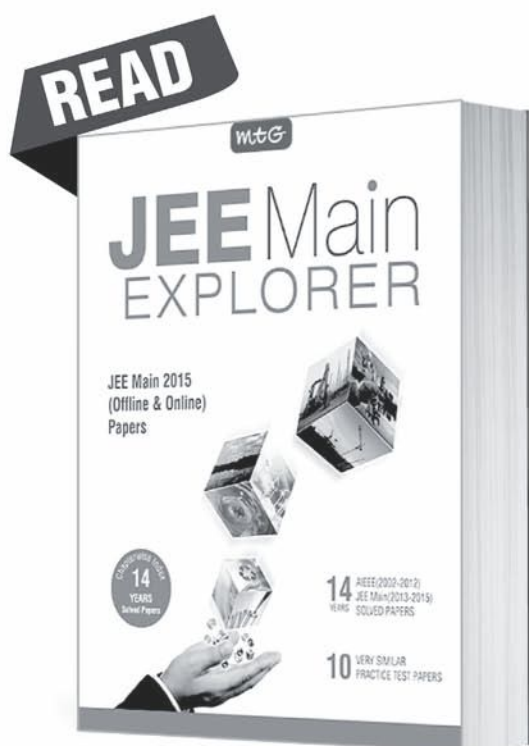
12. (d)

13. (d): Λ<sub>m</sub> for NaOH

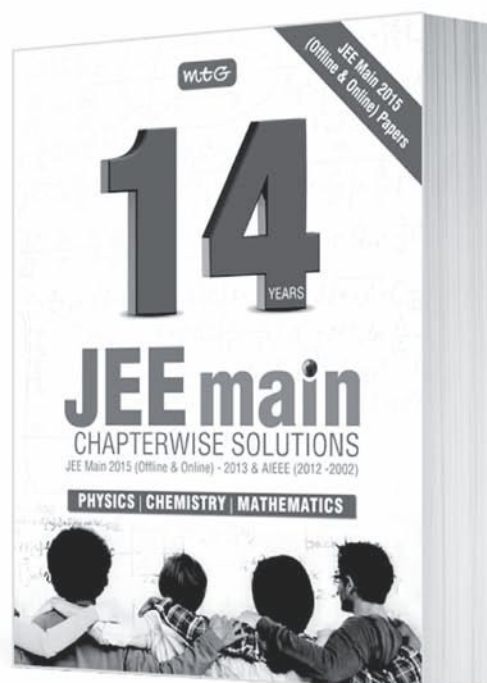
$$\begin{aligned} &= \frac{1000 \kappa}{\text{Molarity}} = \frac{1000 \times \frac{xz}{y}}{0.1} \quad \left( \because \kappa = \frac{xz}{y} \right) \\ &= 10^4 \times \frac{xz}{y} \end{aligned}$$

14. (b): (II) is fastest : Since there are more reactants present, there will be more products produced per unit time.  
 (III) has highest rate : Since concentration is greatest (2 mol L<sup>-1</sup> each) so, greatest change in concentration per unit time.

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15. (a): Since the sol particles migrate towards cathode, they are positively charged. Hence, anions would be effective in coagulation. Greater the valence of effective ion, smaller will be its coagulating value.

$$16. (b): \Lambda_m(\text{CH}_3\text{COOH}) = \frac{1000\kappa}{0.1} = \frac{1000 \times 3.9 \times 10^{-4}}{0.1}$$

$$= 3.9 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}$$

$$\alpha_{\text{CH}_3\text{COOH}} = \frac{\Lambda_m^c}{\Lambda_m^\infty} = \frac{3.9}{\lambda_{\text{CH}_3\text{COO}^-}^\infty + \lambda_{\text{H}^+}^\infty}$$

$$= \frac{3.9}{41 + 349} = 1.0 \times 10^{-2} = 1\%$$

17. (a): For 2/3 life of a reaction,

$$[A]_0 = a, [A] = a - \frac{2}{3}a = \frac{a}{3}$$

For a first order reaction,

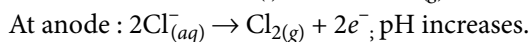
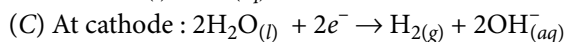
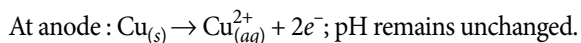
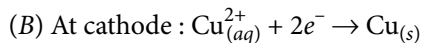
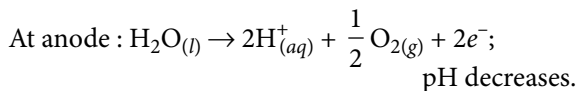
$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

$$\therefore t_{2/3} = \frac{2.303}{5.48 \times 10^{-14}} \log \frac{a}{a/3} = \frac{2.303}{5.48 \times 10^{-14}} \log 3$$

$$t_{2/3} = 2.01 \times 10^{13} \text{ s}$$

18. (d): 100 cm<sup>3</sup> of gold sol require 0.1 mg of gelatin  
(∵ 10<sup>-4</sup> g = 0.1 mg)  
∴ 10 cm<sup>3</sup> of gold sol will require 0.01 mg of gelatin  
Hence, gold number = 0.01

19. (d): (A) At cathode:  $\text{Cu}_{(aq)}^{2+} + 2e^- \rightarrow \text{Cu}_{(s)}$



20. (b):  $E_{a(f)} - E_{a(b)} = \Delta H = -15 \text{ kcal}$

$$\Rightarrow E_{a(f)} = -15 + 20 = 5 \text{ kcal}$$

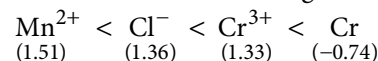
$$\frac{k(\text{catalyst})}{k} = e^{\frac{E_a - E_{a(\text{catalyst})}}{RT}} = e^{\frac{(5-3) \times 10^3}{2 \times 400}} = e^{2.5}$$

21. (a): At pH < isoelectric pH, -NH<sub>2</sub> group of protein gets protonated and the sol will be positively charged.



22. (b): More negative or less positive is the value of reduction potential, stronger is the reducing agent.

Thus, the order of reducing tendency is



23. (b):  $k = 2.1 \times 10^{10} \exp(-2700/RT)$   
i.e., log k vs 1/T will be a straight line  
Intercept on log k axis = log 2.1 × 10<sup>10</sup>

24. (c): O/W type emulsion is stabilised by soaps of alkali metals whereas W/O type emulsions are stabilised by salts of bi and trivalent cations.

25. (c): The electrode at higher value of pK<sub>b</sub> of the base will act as cathode.

$$E_{\text{cell}} = \frac{0.059}{2} \log \frac{[\text{H}^+]_{\text{cathode}}^2}{[\text{H}^+]_{\text{anode}}^2}$$

$$= \frac{0.059}{2} \log \frac{[\text{OH}^-]_{\text{anode}}^2}{[\text{OH}^-]_{\text{cathode}}^2} = \frac{0.059}{2} \log \frac{K_{b(1)} \cdot C}{K_{b(2)} \cdot C}$$

$$= \frac{0.059}{2} (\text{p}K_{b(2)} - \text{p}K_{b(1)}) = \frac{0.059}{2} \times (5 - 3) = 0.059 \text{ V}$$

26. (b): For first order reaction,  $t_{1/2} = \frac{0.693}{k}$

For zero order reaction,  $t_{1/2} = \frac{[A]_0}{2k'}$

Initial rate for first order,  $r_1 = k[A]_0$

Initial rate for zero order,  $r_0 = k'$

$$\therefore \frac{r_1}{r_0} = \frac{k[A]_0}{k'}$$

As  $\frac{0.693}{k} = \frac{[A]_0}{2k'}$

$$\therefore \frac{k[A]_0}{k'} = 2 \times 0.693$$

or  $\frac{r_1}{r_0} = 2 \times 0.693$

27. (a)

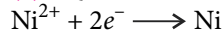
28. (b):  $E_{\text{cell}}^\circ = E_{\text{cathode}}^\circ - E_{\text{anode}}^\circ = 1.61 - 1.51 = 0.10 \text{ V}$

$$\Delta G^\circ = -nFE^\circ = -5 \times 96500 \times 0.10 \text{ J}$$

$$\Delta G^\circ = -48.25 \text{ kJ}$$

29. (a)

30. (c):  $Q = 9.65 \times 3 \times 60 \times 60 = 104220 \text{ C}$



2 × 96500 C deposit 1 mole of Ni<sup>2+</sup>

$$\therefore 104200 \text{ C will deposit Ni}^{2+} = \frac{1}{2 \times 96500} \times 104220$$

$$= 0.54 \text{ mol}$$

Now, 0.5 L of 2 M solution ≡ 1 mol Ni<sup>2+</sup>

As 0.54 mol Ni<sup>2+</sup> is deposited, solution will contain  
1 - 0.54 = 0.46 mol of Ni<sup>2+</sup>

Hence, molarity of solution =  $\frac{0.46}{0.5} = 0.92 \text{ M}$

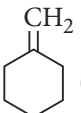


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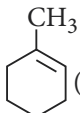
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25<sup>th</sup> July

## SOLVED PAPER 2015

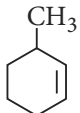
- Strong reducing behaviour of  $\text{H}_3\text{PO}_2$  is due to
  - high electron gain enthalpy of phosphorus
  - high oxidation state of phosphorus
  - presence of two  $-\text{OH}$  groups and one  $\text{P}-\text{H}$  bond
  - presence of one  $-\text{OH}$  group and two  $\text{P}-\text{H}$  bonds.
- The stability of +1 oxidation state among Al, Ga, In and Tl increases in the sequence
  - $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$
  - $\text{Tl} < \text{In} < \text{Ga} < \text{Al}$
  - $\text{In} < \text{Tl} < \text{Ga} < \text{Al}$
  - $\text{Ga} < \text{In} < \text{Al} < \text{Tl}$
- The oxidation of benzene by  $\text{V}_2\text{O}_5$  in the presence of air produces
  - maleic anhydride
  - benzoic acid
  - benzaldehyde
  - benzoic anhydride.
- If the equilibrium constant for  $\text{N}_{2(g)} + \text{O}_{2(g)} \rightleftharpoons 2\text{NO}_{(g)}$  is  $K$ , the equilibrium constant for  $\frac{1}{2}\text{N}_{2(g)} + \frac{1}{2}\text{O}_{2(g)} \rightleftharpoons \text{NO}_{(g)}$  will be
  - $\frac{1}{2}K$
  - $K$
  - $K^2$
  - $K^{1/2}$
- Gadolinium belongs to 4f series. Its atomic number is 64. Which of the following is the correct electronic configuration of gadolinium?
  - $[\text{Xe}] 4f^9 5s^1$
  - $[\text{Xe}] 4f^7 5d^1 6s^2$
  - $[\text{Xe}] 4f^6 5d^2 6s^2$
  - $[\text{Xe}] 4f^8 6d^2$
- The following reaction
 
 is known by the name
  - Perkin's reaction
  - Acetylation reaction
  - Schotten-Baumann reaction
  - Friedel-Craft's reaction.
- What is the mass of the precipitate formed when 50 mL of 16.9% solution of  $\text{AgNO}_3$  is mixed with 50 mL of 5.8%  $\text{NaCl}$  solution? ( $\text{Ag} = 107.8$ ,  $\text{N} = 14$ ,  $\text{O} = 16$ ,  $\text{Na} = 23$ ,  $\text{Cl} = 35.5$ )
  - 3.5 g
  - 7 g
  - 14 g
  - 28 g
- What is the pH of the resulting solution when equal volumes of 0.1 M  $\text{NaOH}$  and 0.01 M  $\text{HCl}$  are mixed?
  - 2.0
  - 7.0
  - 1.04
  - 12.65
- Method by which aniline cannot be prepared is
  - degradation of benzamide with bromine in alkaline solution
  - reduction of nitrobenzene with  $\text{H}_2/\text{Pd}$  in ethanol
  - potassium salt of phthalimide treated with chlorobenzene followed by hydrolysis with aqueous  $\text{NaOH}$  solution
  - hydrolysis of phenylisocyanide with acidic solution.
- If Avogadro number  $N_A$  is changed from  $6.022 \times 10^{23} \text{ mol}^{-1}$  to  $6.022 \times 10^{20} \text{ mol}^{-1}$ , this would change
  - the mass of one mole of carbon
  - the ratio of chemical species to each other in a balanced equation
  - the ratio of elements to each other in a compound
  - the definition of mass in units of grams.
- The variation of the boiling points of the hydrogen halides is in the order  $\text{HF} > \text{HI} > \text{HBr} > \text{HCl}$ . What explains the higher boiling point of hydrogen fluoride?
  - There is strong hydrogen bonding between HF molecules.
  - The bond energy of HF molecules is greater than in other hydrogen halides.
  - The effect of nuclear shielding is much reduced in fluorine which polarises the HF molecule.
  - The electronegativity of fluorine is much higher than for other elements in the group.

12. The number of structural isomers possible from the molecular formula  $C_3H_9N$  is  
 (a) 5 (b) 2  
 (c) 3 (d) 4
13. Which of the statements given below is incorrect?  
 (a)  $O_3$  molecule is bent.  
 (b) ONF is isoelectronic with  $O_2N^-$ .  
 (c)  $OF_2$  is an oxide of fluorine.  
 (d)  $Cl_2O_7$  is an anhydride of perchloric acid.
14. The formation of the oxide ion,  $O_{(g)}^{2-}$  from oxygen atom requires first an exothermic and then an endothermic step as shown below :  
 $O_{(g)} + e^- \rightarrow O_{(g)}^- ; \Delta_f H^\circ = -141 \text{ kJ mol}^{-1}$   
 $O_{(g)}^- + e^- \rightarrow O_{(g)}^{2-} ; \Delta_f H^\circ = +780 \text{ kJ mol}^{-1}$   
 Thus, process of formation of  $O^{2-}$  in gas phase is unfavourable even though  $O^{2-}$  is isoelectronic with neon. It is due to the fact that,  
 (a)  $O^-$  ion has comparatively smaller size than oxygen atom  
 (b) oxygen is more electronegative  
 (c) addition of electron in oxygen results in larger size of the ion  
 (d) electron repulsion outweighs the stability gained by achieving noble gas configuration.
15. In the reaction with HCl, an alkene reacts in accordance with the Markovnikov's rule to give a product 1-chloro-1-methylcyclohexane. The possible alkene is
- 

(a) (A)

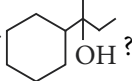
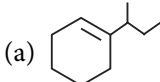
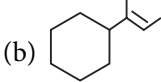
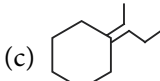
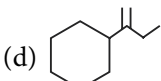


(b) (B)
- (c) (A) and (B)

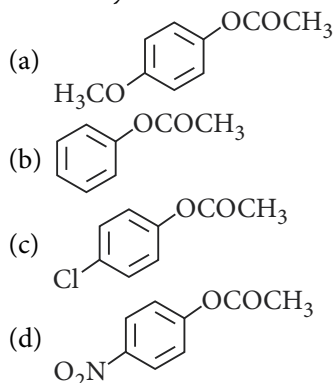


(d)
16. 2,3-Dimethyl-2-butene can be prepared by heating which of the following compounds with a strong acid?  
 (a)  $(CH_3)_3C-CH=CH_2$   
 (b)  $(CH_3)_2C=CH-CH_2-CH_3$   
 (c)  $(CH_3)_2CH-CH_2-CH=CH_2$   
 (d)  $(CH_3)_2CH-\underset{\text{CH}_3}{\text{CH}}-CH=CH_2$
17. The hybridization involved in complex  $[Ni(CN)_4]^{2-}$  is (At. No. Ni = 28)  
 (a)  $sp^3$  (b)  $d^2sp^2$   
 (c)  $d^2sp^3$  (d)  $dsp^2$
18. Reaction of a carbonyl compound with one of the following reagents involves nucleophilic addition followed by elimination of water. The reagent is  
 (a) hydrazine in presence of feebly acidic solution  
 (b) hydrocyanic acid  
 (c) sodium hydrogen sulphite  
 (d) a Grignard reagent.
19. Two possible stereo-structures of  $CH_3CHOHCOOH$ , which are optically active, are called  
 (a) atropisomers (b) enantiomers  
 (c) mesomers (d) diastereomers.
20. In the extraction of copper from its sulphide ore, the metal is finally obtained by the reduction of cuprous oxide with  
 (a) carbon monoxide (b) copper (I) sulphide  
 (c) sulphur dioxide (d) iron (II) sulphide.
21. A gas such as carbon monoxide would be most likely to obey the ideal gas law at  
 (a) low temperatures and high pressures  
 (b) high temperatures and high pressures  
 (c) low temperatures and low pressures  
 (d) high temperatures and low pressures.
22. In an  $S_N1$  reaction on chiral centres, there is  
 (a) inversion more than retention leading to partial racemisation  
 (b) 100% retention  
 (c) 100% inversion  
 (d) 100% racemisation.
23. The vacant space in bcc lattice unit cell is  
 (a) 48% (b) 23%  
 (c) 32% (d) 26%
24. The name of complex ion,  $[Fe(CN)_6]^{3-}$  is  
 (a) hexacyanoferrate (III) ion  
 (b) tricyanoferrate (III) ion  
 (c) hexacyanidoferrate (III) ion  
 (d) hexacyanoiron (III) ion.
25. The number of water molecules is maximum in  
 (a) 1.8 gram of water (b) 18 gram of water  
 (c) 18 moles of water (d) 18 molecules of water.
26. The heat of combustion of carbon to  $CO_2$  is  $-393.5 \text{ kJ/mol}$ . The heat released upon formation of 35.2 g of  $CO_2$  from carbon and oxygen gas is  
 (a) + 315 kJ (b) - 630 kJ  
 (c) - 3.15 kJ (d) - 315 kJ



27. Aqueous solution of which of the following compounds is the best conductor of electric current?  
 (a) Hydrochloric acid, HCl  
 (b) Ammonia, NH<sub>3</sub>  
 (c) Fructose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>  
 (d) Acetic acid, C<sub>2</sub>H<sub>4</sub>O<sub>2</sub>
28. In which of the following pairs, both the species are not isostructural?  
 (a) Diamond, Silicon carbide  
 (b) NH<sub>3</sub>, PH<sub>3</sub>  
 (c) XeF<sub>4</sub>, XeO<sub>4</sub>  
 (d) SiCl<sub>4</sub>, PCl<sub>4</sub><sup>+</sup>
29. What is the mole fraction of the solute in a 1.00 m aqueous solution?  
 (a) 1.770 (b) 0.0354  
 (c) 0.0177 (d) 0.177
30. Which of the following statements is not correct for a nucleophile?  
 (a) Ammonia is a nucleophile.  
 (b) Nucleophiles attack low  $e^-$  density sites.  
 (c) Nucleophiles are not electron seeking.  
 (d) Nucleophile is a Lewis acid.
31. The sum of coordination number and oxidation number of the metal  $M$  in the complex  $[M(en)_2(C_2O_4)]Cl$  (where  $en$  is ethylenediamine) is  
 (a) 6 (b) 7  
 (c) 8 (d) 9
32. Assuming complete ionisation, same moles of which of the following compounds will require the *least* amount of acidified KMnO<sub>4</sub> for complete oxidation?  
 (a) FeSO<sub>3</sub> (b) FeC<sub>2</sub>O<sub>4</sub>  
 (c) Fe(NO<sub>2</sub>)<sub>2</sub> (d) FeSO<sub>4</sub>
33. Reaction of phenol with chloroform in presence of dilute sodium hydroxide finally introduces which one of the following functional group?  
 (a) -COOH (b) -CHCl<sub>2</sub>  
 (c) -CHO (d) -CH<sub>2</sub>Cl
34. Which is the correct order of increasing energy of the listed orbitals in the atom of titanium?  
 (At. no.  $Z = 22$ )  
 (a)  $4s\ 3s\ 3p\ 3d$  (b)  $3s\ 3p\ 3d\ 4s$   
 (c)  $3s\ 3p\ 4s\ 3d$  (d)  $3s\ 4s\ 3p\ 3d$
35. Which one of the following pairs of solution is not an acidic buffer?  
 (a) CH<sub>3</sub>COOH and CH<sub>3</sub>COONa  
 (b) H<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>  
 (c) H<sub>3</sub>PO<sub>4</sub> and Na<sub>3</sub>PO<sub>4</sub>  
 (d) HClO<sub>4</sub> and NaClO<sub>4</sub>
36. Number of possible isomers for the complex  $[Co(en)_2Cl_2]Cl$  will be ( $en$  = ethylenediamine)  
 (a) 1 (b) 3  
 (c) 4 (d) 2
37. Decreasing order of stability of O<sub>2</sub>, O<sub>2</sub><sup>-</sup>, O<sub>2</sub><sup>+</sup> and O<sub>2</sub><sup>2-</sup> is  
 (a) O<sub>2</sub><sup>2-</sup> > O<sub>2</sub><sup>-</sup> > O<sub>2</sub> > O<sub>2</sub><sup>+</sup>  
 (b) O<sub>2</sub> > O<sub>2</sub><sup>+</sup> > O<sub>2</sub><sup>2-</sup> > O<sub>2</sub><sup>-</sup>  
 (c) O<sub>2</sub><sup>-</sup> > O<sub>2</sub><sup>2-</sup> > O<sub>2</sub><sup>+</sup> > O<sub>2</sub>  
 (d) O<sub>2</sub><sup>+</sup> > O<sub>2</sub> > O<sub>2</sub><sup>-</sup> > O<sub>2</sub><sup>2-</sup>
38. Which of the following is not the product of dehydration of ?  
 (a)  (b)   
 (c)  (d) 
39. The correct statement regarding defects in crystalline solids is  
 (a) Frenkel defects decrease the density of crystalline solids  
 (b) Frenkel defect is a dislocation defect  
 (c) Frenkel defect is found in halides of alkaline metals  
 (d) Schottky defects have no effect on the density of crystalline solids.
40. The rate constant of the reaction  $A \rightarrow B$  is  $0.6 \times 10^{-3} \text{ mol L}^{-1} \text{ s}^{-1}$ . If the concentration of  $A$  is 5 M, then concentration of  $B$  after 20 minutes is  
 (a) 3.60 M (b) 0.36 M  
 (c) 0.72 M (d) 1.08 M
41. On heating which of the following releases CO<sub>2</sub> most easily?  
 (a) Na<sub>2</sub>CO<sub>3</sub> (b) MgCO<sub>3</sub>  
 (c) CaCO<sub>3</sub> (d) K<sub>2</sub>CO<sub>3</sub>
42. 20.0 g of a magnesium carbonate sample decomposes on heating to give carbon dioxide and 8.0 g magnesium oxide. What will be the percentage purity of magnesium carbonate in the sample?  
 (At. wt. of Mg = 24)  
 (a) 96 (b) 60  
 (c) 84 (d) 75

43. Which one of the following esters gets hydrolysed *most easily* under alkaline conditions?



44. Caprolactam is used for the manufacture of  
 (a) teflon (b) terylene  
 (c) nylon 6, 6 (d) nylon 6.
45. Which of the following reaction(s) can be used for the preparation of alkyl halides?  
 (I)  $\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} \xrightarrow{\text{anh. ZnCl}_2}$   
 (II)  $\text{CH}_3\text{CH}_2\text{OH} + \text{HCl} \longrightarrow$   
 (III)  $(\text{CH}_3)_3\text{COH} + \text{HCl} \longrightarrow$   
 (IV)  $(\text{CH}_3)_2\text{CHOH} + \text{HCl} \xrightarrow{\text{anh. ZnCl}_2}$   
 (a) (I) and (II) only (b) (IV) only  
 (c) (III) and (IV) only (d) (I), (III) and (IV) only

### SOLUTIONS

1. (d): All oxyacids of phosphorus which have P—H bonds act as strong reducing agents.  $\text{H}_3\text{PO}_2$  has two P—H bonds hence, it acts as a strong reducing agent.
2. (a): In group 13 elements, stability of +3 oxidation state decreases down the group while that of +1 oxidation state increases due to inert pair effect. Hence, stability of +1 oxidation state increases in the sequence:  $\text{Al} < \text{Ga} < \text{In} < \text{Tl}$ .
3. (a):
4. (d): If the reaction is multiplied by  $\frac{1}{2}$ , then new equilibrium constant,  $K' = K^{1/2}$ .

5. (b)
6. (c): Benzoylation of compounds containing an active hydrogen atom such as alcohols, phenols and amines with benzoyl chloride in the presence of dilute aq. NaOH solution is called Schotten-Baumann reaction.
7. (b): 16.9% solution of  $\text{AgNO}_3$  means 16.9 g of  $\text{AgNO}_3$  in 100 mL of solution.  
 16.9 g of  $\text{AgNO}_3$  in 100 mL solution  $\equiv$  8.45 g of  $\text{AgNO}_3$  in 50 mL solution.  
 Similarly, 5.8% of NaCl in 100 mL solution  $\equiv$  2.9 g of NaCl in 50 mL solution.  
 The reaction can be represented as:
- $$\text{AgNO}_3 + \text{NaCl} \longrightarrow \text{AgCl} + \text{NaNO}_3$$
- |           |             |             |           |           |
|-----------|-------------|-------------|-----------|-----------|
| Initially | 8.45/170    | 2.9/58.5    | 0         | 0         |
|           | = 0.049 mol | = 0.049 mol |           |           |
| Finally   | 0           | 0           | 0.049 mol | 0.049 mol |
- $\therefore$  Mass of AgCl precipitated =  $0.049 \times 143.3$   
 $= 7.02 \approx 7$  g

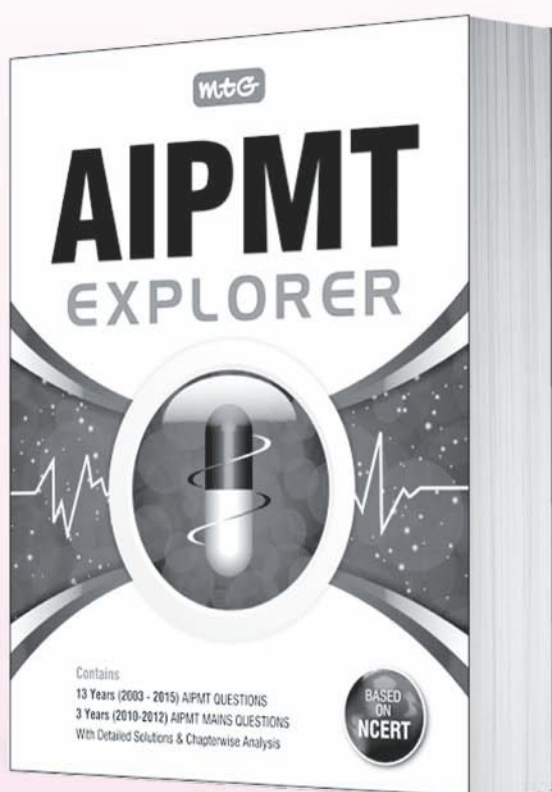
8. (d): One mole of NaOH is completely neutralised by one mole of HCl.  
 Hence, 0.01 mole of NaOH will be completely neutralised by 0.01 mole of HCl.  
 $\Rightarrow$  NaOH left unneutralised =  $0.1 - 0.01$  mol  
 $= 0.09$  mol  
 As equal volumes of two solutions are mixed,  
 $[\text{OH}]^- = \frac{0.09}{2} = 0.045$  M  
 $\Rightarrow$   $\text{pOH} = -\log(0.045) = 1.35$   
 $\therefore$   $\text{pH} = 14 - 1.35 = 12.65$
9. (c): Aniline cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution reaction with potassium phthalimide under mild conditions.

10. (a): Mass of 1 mol ( $6.022 \times 10^{23}$  atoms) of carbon = 12 g  
 If Avogadro number is changed to  $6.022 \times 10^{20}$  atoms then mass of 1 mol of carbon  
 $= \frac{12 \times 6.022 \times 10^{20}}{6.022 \times 10^{23}} = 12 \times 10^{-3}$  g

11. (a): HF forms strong intermolecular H-bonding due to high electronegativity of F. Hence, the boiling point of HF is abnormally high. Boiling points of other hydrogen halides gradually increase from HCl to HI due to increase in size of halogen atoms

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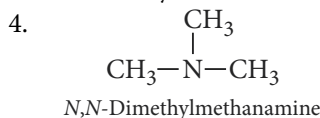
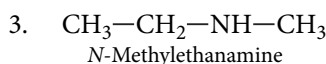
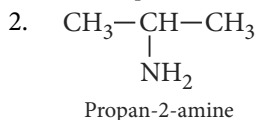
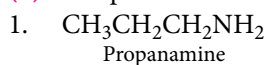


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from Cl to I which further increase the magnitude of van der Waals forces.

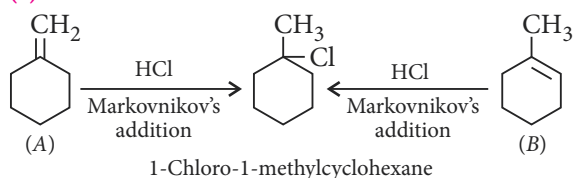
12. (d): The possible structural isomers are :



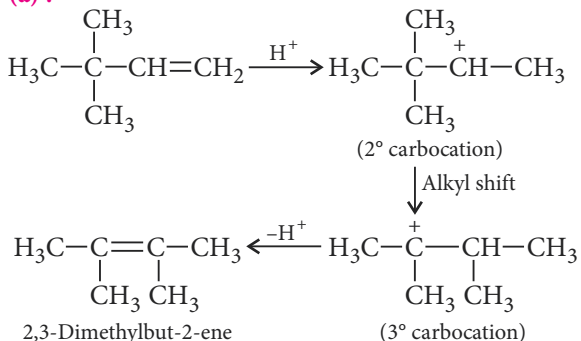
13. (c):  $\text{OF}_2$  (oxygen difluoride) is a fluoride of oxygen because fluorine is more electronegative than oxygen.

14. (d)

15. (c):



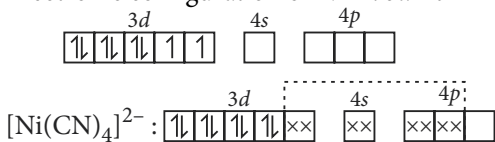
16. (a):



17. (d):  $[\text{Ni}(\text{CN})_4]^{2-}$  :

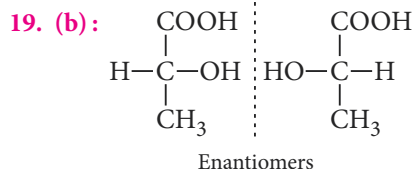
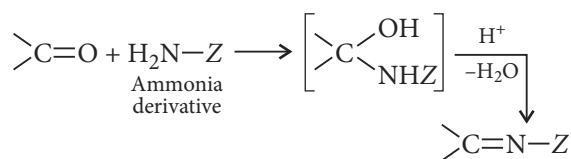
Oxidation number of Ni = +2

Electronic configuration of  $\text{Ni}^{2+}$  :  $3d^8 4s^0$



$dsp^2$  hybridization  
[Pairing of electrons in  $d$ -orbital takes place due to the presence of strong field ligand ( $\text{CN}^-$ )]

18. (a): Carbonyl compounds react with ammonia derivatives in weakly acidic medium as follows :



20. (b):  $2\text{Cu}_2\text{O} + \text{Cu}_2\text{S} \longrightarrow 6\text{Cu} + \text{SO}_2$

21. (d): Real gases show ideal gas behaviour at high temperatures and low pressures.

22. (a): In case of optically active alkyl halides,  $\text{S}_{\text{N}}1$  reaction is accompanied by racemisation. The carbocation formed in the slow step being  $sp^2$  hybridised is planar and attack of nucleophile may take place from either side resulting in a mixture of products, one having the same configuration and other having inverted configuration.

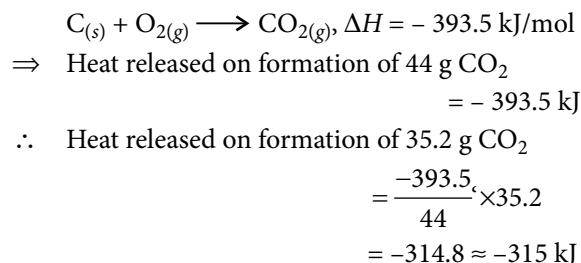
The isomer corresponding to inversion is present in slight excess because  $\text{S}_{\text{N}}1$  also depends upon the degree of shielding of the front side of the reacting carbon.

23. (c): Packing efficiency of  $bcc$  lattice = 68%  
Hence, empty space = 32%.

24. (c)

25. (c) : 1.8 gram of water =  $\frac{6.023 \times 10^{23}}{18} \times 1.8$   
=  $6.023 \times 10^{22}$  molecules  
18 gram of water =  $6.023 \times 10^{23}$  molecules  
18 moles of water =  $18 \times 6.023 \times 10^{23}$  molecules

26. (d): Given :



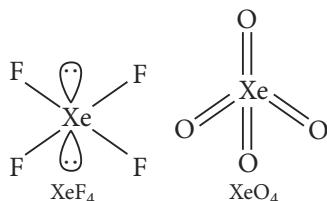
27. (a):  $\text{HCl}$  is a strong acid and dissociates completely into ions in aqueous solution.

28. (c): In diamond and silicon carbide, central atom is  $sp^3$  hybridised and hence, both are isostructural.

$\text{NH}_3$  and  $\text{PH}_3$ , both are pyramidal and central atom in both cases is  $sp^3$  hybridised.

$\text{SiCl}_4$  and  $\text{PCl}_4^+$ , both are tetrahedral and central atom in both cases is  $sp^3$  hybridised.

In  $\text{XeF}_4$ , Xe is  $sp^3d^2$  hybridised and structure is square planar while in  $\text{XeO}_4$ , Xe is  $sp^3$  hybridised and structure is tetrahedral.



29. (c) : 1 molal aqueous solution means 1 mole of solute is present in 1000 g of water.

$$\therefore x_{\text{solute}} = \frac{1}{1 + \frac{1000}{18}} = \frac{1}{56.5} = 0.0177$$

30. (d) : Nucleophiles are electron rich species hence, they are Lewis bases.

31. (d) :  $[\text{M}(\text{en})_2(\text{C}_2\text{O}_4)]\text{Cl}$  :

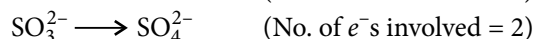
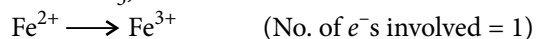
Oxidation number of metal = +3

Coordination number of metal = 6

$\therefore$  Sum of oxidation number and coordination number = 3 + 6 = 9

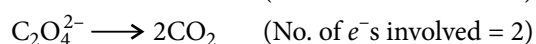
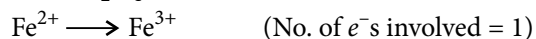
32. (d) :  $\text{KMnO}_4$  ( $\text{Mn}^{7+}$ ) changes to  $\text{Mn}^{2+}$  i.e., number of electrons involved per mole of  $\text{KMnO}_4$  is 5.

(a) For  $\text{FeSO}_3$ ,



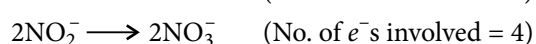
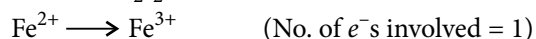
Total number of  $e^-$  s involved = 1 + 2 = 3

(b) For  $\text{FeC}_2\text{O}_4$ ,



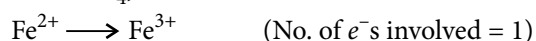
Total number of  $e^-$  s involved = 1 + 2 = 3

(c) For  $\text{Fe}(\text{NO}_2)_2$ ,



Total number of  $e^-$  s involved = 1 + 4 = 5

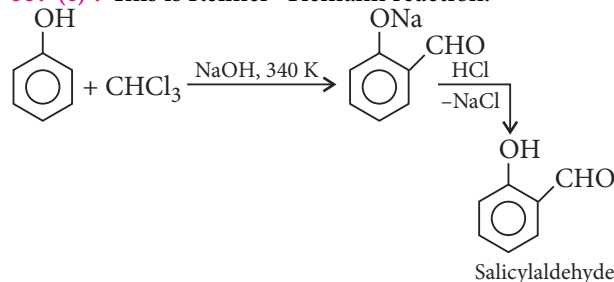
(d) For  $\text{FeSO}_4$ ,



Total number of  $e^-$  s involved = 1

As  $\text{FeSO}_4$  requires least number of electrons thus, it will require least amount of  $\text{KMnO}_4$ .

33. (c) : This is Reimer-Tiemann reaction.



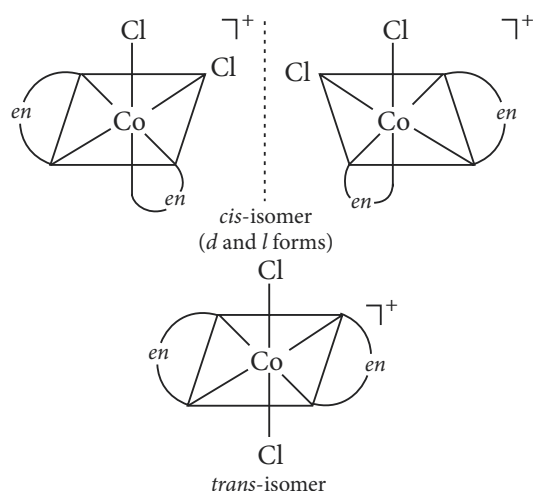
34. (c) :  $\text{Ti}(22) : 1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^2$

$\therefore$  Order of increasing energy is 3s, 3p, 4s, 3d.

35. (d) : Acidic buffer is a mixture of a weak acid and its salt with a strong base.

$\text{HClO}_4$  is a strong acid.

36. (b) : Possible isomers of  $[\text{Co}(\text{en})_2\text{Cl}_2]\text{Cl}$  :



37. (d) :  $\text{O}_2(16) : \text{KK } \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$   
 $\pi^* 2p_x^1 = \pi^* 2p_y^1$

$$\text{Bond order} = \frac{1}{2}(8 - 4) = 2$$

$$\text{O}_2^{2-}(18) : \text{KK } \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$$

$$\pi^* 2p_x^2 = \pi^* 2p_y^2$$

$$\text{Bond order} = \frac{1}{2}(8 - 6) = 1$$

$$\text{O}_2^-(17) : \text{KK } \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$$

$$\pi^* 2p_x^1 = \pi^* 2p_y^1$$

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

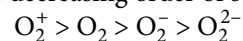
$$\text{O}_2^+(15) : \text{KK } \sigma 2s^2 \sigma^* 2s^2 \sigma 2p_z^2 \pi 2p_x^2 = \pi 2p_y^2$$

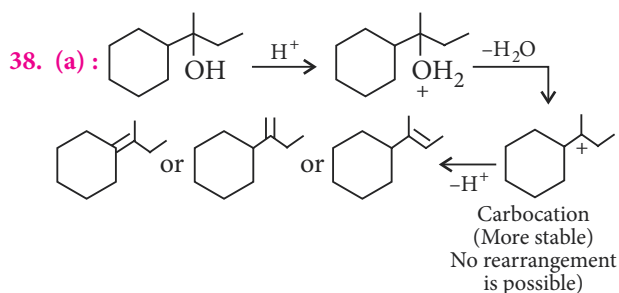
$$\pi^* 2p_x^1 = \pi^* 2p_y^1$$

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

As, bond order  $\propto$  stability

The decreasing order of stability is





39. (b): Frenkel defect is a dislocation defect as smaller ions (usually cations) are dislocated from normal sites to interstitial sites.

Frenkel defect is shown by compounds having large difference in the size of cations and anions hence, alkali metal halides do not show Frenkel defect.

Also, Schottky defect decreases the density of crystal while Frenkel defect has no effect on the density of crystal.

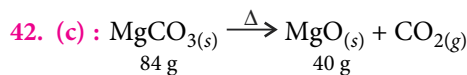
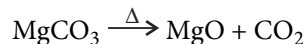
40. (c): Reaction is of zero order as the unit of rate constant is  $\text{mol L}^{-1} \text{s}^{-1}$ .

$$\begin{aligned} \therefore \text{Concentration of } B &= k \times t \\ &= 0.6 \times 10^{-3} \times 20 \times 60 \\ &= 0.72 \text{ M} \end{aligned}$$

41. (b): Stability of carbonates increases down the group with increase in the size of metal ion. Also

the alkali metal carbonates are more stable than alkaline earth metal carbonates.

Hence,  $\text{MgCO}_3$  is least stable and it releases  $\text{CO}_2$  most easily.



$$84 \text{ g} \quad \quad \quad 40 \text{ g}$$

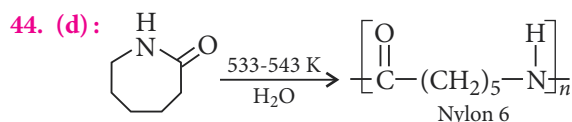
$$84 \text{ g of MgCO}_3 \equiv 40 \text{ g of MgO}$$

$$\therefore 20 \text{ g of MgCO}_3 \equiv \frac{40}{84} \times 20 = 9.52 \text{ g of MgO}$$

$$\text{Actual yield} = 8 \text{ g of MgO}$$

$$\therefore \% \text{ purity} = \frac{8}{9.52} \times 100 = 84\%$$

43. (d): Electron withdrawing groups increase the reactivity towards nucleophilic substitution reaction and  $-\text{NO}_2$  is a strong electron withdrawing group.



45. (d):  $1^\circ$  and  $2^\circ$  alcohols react with  $\text{HCl}$  in presence of anhydrous  $\text{ZnCl}_2$  as catalyst while in case of  $3^\circ$  alcohols  $\text{ZnCl}_2$  is not required.

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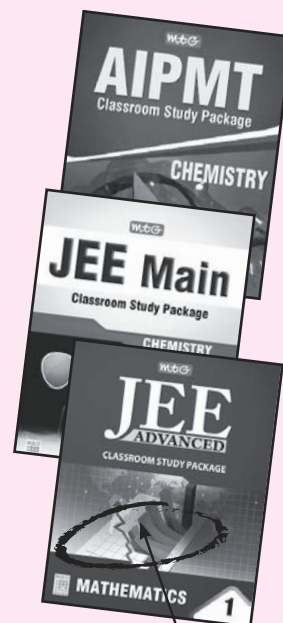
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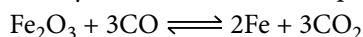
## (METALS AND METALLURGY)

Mukul C. Ray, Odisha

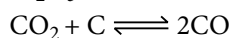
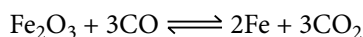
### Iron Extraction

In iron extraction, the furnace is started by heating piles of wood inside. A mixture of roasted ore, coke and limestone in the ratio of 8 : 4 : 1 is used as the 'charge' of the furnace. A blast of hot and dry air is forced through tuyeres. Coke burns raising the temperature of the furnace. The temperature increases continually from mouth (400°C) to the hearth (1500°C).

Above the boshes, at about 600-900°C, ferric oxide is reduced by carbon monoxide to spongy iron.



But the reaction being reversible, the reduction is not complete at this stage. The spongy iron absorbs sulphur from the fuel. At more than 1000°C,



The net result appears as if CO is the reducing agent. Anyway, the reduction of iron is completed in the region of 1200°C. The question generally asked is, which is the potential reducing agent of iron oxide below 700°C and which one is the reducing agent above 1000°C. For the former the answer is CO and for the latter the answer is C.

The phosphates, the manganese compounds and also a part of silica are reduced to elemental phosphorus, manganese and silicon, which readily alloy with iron. A major part of silica combines with flux forming slag.

The molten iron is tapped out at intervals to form pig iron. When the pig iron is further melted and used to cast iron products, it is generally called as the cast iron. There is not much difference between the cast and the pig iron chemically.

When carbon in cast iron is present in the form of cementite, it is called white cast iron and when it is present in the form of graphite it is called grey cast iron. Cast iron melts at 1200°C and is extremely hard and brittle. It is used in making iron pipes, railings, manhole covers etc. Cast iron expands slightly on cooling therefore, correctly reproduces the mould.

Larger part of cast iron goes to steel industry. White cast iron dissolves almost completely in dilute hydrochloric acid while grey cast iron dissolves in dilute hydrochloric acid, leaving behind a black residue of graphite.

Wrought iron is the most pure form of iron containing only 0.12 and 0.25% of carbon and melts at higher temperature than iron. It is made by melting the cast iron on the bed of reverberatory furnace with haematite lining. **The principle is impurities present in iron have higher affinity for oxygen than the metal itself.** In order to bring intimate mixing, the mixture is puddled or stirred and the operation is thus called **puddling process**.

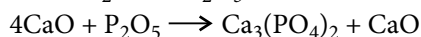
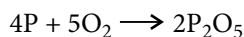
Being fibrous in structure, wrought iron has high tensile strength. It finds uses in making chains, furniture as it takes polish, cores of bar magnets etc.

### Steel Making

Steel is produced from pig iron by first removing practically all the impurities such as Mn, Si, C, P and S by oxidation and then adding the correct amount and variety of impurities according to the desired quality of steel. The operations have been upgraded over the years. The earlier method was **Bessemer process**. Presence of phosphorus develops a property in steel called **cold brittleness** and presence of sulphur develops a property called **hot brittleness**. To remove phosphorus, **basic Bessemer process** is used. The **acidic Bessemer process** is used for iron which is free from phosphorus.

The process is carried out in a converter holding molten iron at 1200°C through which hot air is passed. The acid Bessemer process has a silica lining. Manganese is oxidised to form MnO, which combines with silica to give MnSiO<sub>3</sub>. Carbon is removed as CO. After the removal of impurities, an alloy spiegeleisen is added. This is an alloy of iron, manganese and carbon. Carbon and manganese act as deoxidisers and reduce ferrous oxide if any, and the rest dissolves in iron. Manganese improves tensile strength of steel. This process (original Bessemer process) can give satisfactory quality of steel

only when the phosphorus content in iron is very less. A modified version of the above process is the basic Bessemer process that has been designed to remove phosphorus impurity. This is also known as the **Thomas Bessemer process**. The lining is limestone or dolomite. Charge contains limestone along with coke and pig iron.



The product calcium phosphate is used as Thomas slag. After the removal of impurities, desired substances like spiegeleisen is added to pure iron.

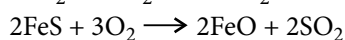
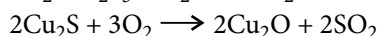
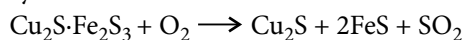
The next modern process is **Siemens-Martin open hearth process**. Basic chemistry remains almost same. Scrap steel and oxide ore of iron are added to the charge of pig iron. Towards the end of the process, after the removal of slag, a controlled amount of spiegeleisen along with other desired substances is added. The advantages include, scrap iron can be used directly; unlike Bessemer process, this process is not restricted to pig iron of certain specific composition. The process being slower as compared to Bessemer process ensures complete removal of slag from the iron. The **Linz-Donawitz (LD) or Basic Oxygen Process (BOP)** makes steel in oxygen atmosphere. Making of steel in nitrogen atmosphere develops a hard coating of iron nitride on steel. This makes cutting and welding of steel a difficult task. The advantages of the process include :

- Low capital cost and low operating cost.
- Very high production rate; large mass can be handled.
- Nitride coating is less.
- Sulphur elimination is better than the basic Bessemer process.

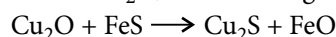
### Copper Extraction

The sulphide ores containing usually 2% of Cu are first concentrated to about 25% Cu by froth-floatation process. Very low grade ores are subjected to hydrometallurgy. Two notable points are : **at 700°C, both Cu<sub>2</sub>S and FeS have practically the same ΔG° value, but at higher temperature, Cu<sub>2</sub>S is more stable than FeS. Out of FeO and Cu<sub>2</sub>O, ΔG° for FeO is more negative than Cu<sub>2</sub>O at all temperatures.**

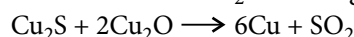
The partially roasted ore is subjected to matte smelting, in which the final percentage of copper in the matte is nearly 40.



Since Cu<sub>2</sub>S is more stable than FeS and FeO is more stable than Cu<sub>2</sub>O, the following reaction takes place.



Slowly FeO combines with silica (flux) to form slag. Matte (Cu<sub>2</sub>S + FeS) containing about 35 to 45% copper, and the slag is taken to a converter in the next stage of extraction. Slag is removed periodically. After removing the last traces of slag, air is blown into the converter. The affinity of copper towards sulphur forces Cu<sub>2</sub>O to react with unreacted Cu<sub>2</sub>S resulting in self reduction.

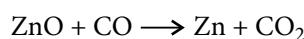
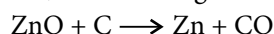


Impure copper is purified by poling, electrorefining and cupellation.

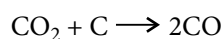
### Zinc Extraction

The principal ores of zinc are smithsonite or calamine or zinc spar (ZnCO<sub>3</sub>) and zinc blende. The concentrated ZnS ore, when roasted gives ZnO. Roasting is usually carried out at temperature 800°C. In case of calamine, calcination is done to produce ZnO.

Reduction of ZnO is carried out by Retort distillation. At 1100°C, the following reduction reactions take place.



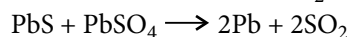
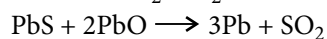
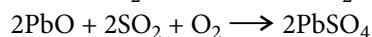
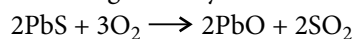
It is worth noting that in zinc extraction, excess carbon is used as carbon dioxide oxidises zinc at red hot. In presence of excess carbon, carbon dioxide becomes carbon monoxide and oxidation of zinc is prevented.



Crude zinc is mainly contaminated with cadmium and lead. Liquefaction and distillation are the two key processes of purification.

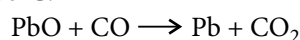
### Lead Extraction

The important ores of lead are galena (PbS) and anglesite (PbSO<sub>4</sub>). **Ore Hearth process** is suitable for high grade ores containing 70% lead or more. Air is blown into the hearth through the tuyeres.



Lead sulphate is particularly formed when sulphur dioxide concentration becomes high and temperature is slightly low (less than 500°C).

The other method called **Blast Furnace Smelting** is suitable for all types of ores. In this process, the concentrated ore is roasted and subsequently reduced by carbon. Temperature of operation is more than 1000°C.





The infusible impurities of silicon dioxide get removed by reacting with flux, CaO.

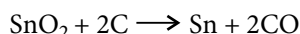
The crude lead is purified by **Parkes process**. Basically, it can be considered as desilverisation of lead. Silver is present to a little extent in lead. Being costly, a process of taking out silver from lead has been designed. This method removes silver and also ensures purification of lead. It is based on three principles :

- Molten zinc and lead are immiscible with each other.
- Molten zinc is lighter than lead.
- Silver is more soluble in molten zinc than in molten lead.

Lead is melted. Scrap zinc is added to it. Silver passes to molten zinc layer. Zinc layer is separated and distilled to get silver and, zinc obtained can be reused. Repetition of the process gives better results. Little carbon is added during distillation of zinc as it reduces ZnO formed, if any.

### Tin Extraction

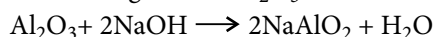
The most important mineral of tin is cassiterite or tin stone, which is SnO<sub>2</sub>. It contains about 10% tin and rest is silica and wolframite (FeWO<sub>4</sub>). Concentration is done by gravity or magnetic separation. The concentrated ore is leached with 30% solution of hydrochloric acid. Salts of copper, iron go into solution whereas tin oxide remains unaffected. Finally, leached ore is reduced by carbon.



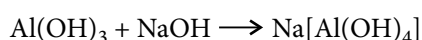
Tin is purified by liquation (melting point of tin is 232°C) or by poling.

### Aluminium Extraction

White bauxite and red bauxite are the two major ores. From red bauxite containing Fe<sub>2</sub>O<sub>3</sub> as the chief impurity, pure alumina is extracted by **Bayer's process** and **Hall's process**. **Serpeck's process** is employed for white bauxite having the major impurity as SiO<sub>2</sub>. In the ores, Al<sub>2</sub>O<sub>3</sub> content can go as high as 55%. In Bayer's process, the ore is digested with 45% NaOH solution at 160-240°C at 0.8 MPa pressure. Al<sub>2</sub>O<sub>3</sub> passes into solution leaving behind Fe<sub>2</sub>O<sub>3</sub>.



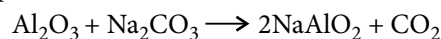
Or the equation can be written as below because, the oxide of aluminium may be in the form of hydrated one.



Ferric oxide remains insoluble. A part of silicate, if any, may also dissolve. On cooling the solution, jelly like

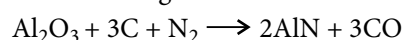
precipitate of aluminium hydroxide starts precipitating. Carbon dioxide is passed through the solution and seeding of aluminium hydroxide prepared outside is done to facilitate precipitation. The aluminium hydroxide precipitate is finally calcined to get pure aluminium oxide.

In the Hall's process, the ore is fused with Na<sub>2</sub>CO<sub>3</sub>. Al<sub>2</sub>O<sub>3</sub> dissolves leaving behind Fe<sub>2</sub>O<sub>3</sub> and SiO<sub>2</sub> as impurities.



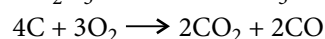
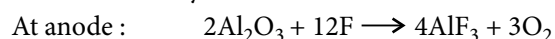
The fused mass is extracted with water where NaAlO<sub>2</sub> or the complex mentioned above dissolves.

In **Serpeck's process**, impure ore is heated with coke in a current of nitrogen at 1800°C.



The impurity silicon dioxide is reduced to silicon by carbon which being volatile passes off. Aluminium nitride is then hydrolysed to get aluminium hydroxide. All the three processes are different till Al<sub>2</sub>O<sub>3</sub> is dissolved as [(Al(OH)<sub>4</sub>]<sup>-</sup>. From the solution of this complex, separation of pure aluminium hydroxide as jelly like precipitate and subsequent calcination to get pure Al<sub>2</sub>O<sub>3</sub> method is common.

In the extraction process of aluminium, alumina is fused with cryolite and electrolyzed in a graphite tank. Pure alumina melts at 2000°C. Cryolite serves as added impurity, which lowers the melting point of bath to 950°C. CaF<sub>2</sub> is also added that helps lowering melting point. Cryolite also helps in improving the electrical conductivity of the cell. A typical electrolytic mixture contains 85% cryolite and 5 to 10% alumina.



Various products are formed at anode, including O<sub>2</sub>, CO<sub>2</sub> and carbon compounds of fluorine. They erode the anodes, which must be replaced periodically.

**Hoopes process** is followed for purification of aluminium. In this electrorefining process, the electrolytic cell contains an iron box lined inside with carbon. The middle layer is a fused mixture of fluorides of Na, Ba and Al and acts as electrolyte. The bottom layer is impure aluminium and acts as anode. The top layer is pure aluminium and is the cathode. During electrolysis, aluminium passes from middle layer to the upper layer and the middle layer takes up an equivalent amount of aluminium from the lower layer.



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**Series 4**
**CHAPTERWISE PRACTICE PAPER : THE p-BLOCK ELEMENTS (Group 15 to 18)**

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. Give a reaction to obtain dinitrogen in very pure state.
2. Which halide ion gives most stable hexahalide with group 16 elements? What is the physical state of these hexahalides?
3. Hydrogen fluoride is a liquid while other hydrogen halides are gases. Comment.
4. State two properties of helium which make it suitable for filling balloons for meteorological observations.
5. Give the resonance structures of  $N_2O_3$ .
6. Write the balanced equations for the following :
  - (i) Reduction of nitrates with  $Fe^{2+}$  to form brown coloured complex.
  - (ii) Reaction of thionyl chloride with white phosphorus.
7. Why are interhalogen compounds more reactive than halogens?
8. (i) How is  $XeO_3$  prepared? Give chemical reaction.  
(ii) Draw the structure of  $XeO_3$ .
9. Give reason : Bleaching of flowers by  $Cl_2$  is permanent while that with  $SO_2$  is temporary.
10. Explain the following observations :
  - (i) Sugar gets charred on addition of concentrated sulphuric acid.
  - (ii) Thermal stability of  $H_2O$  is much higher than that of  $H_2S$ .

**OR**

$H_2S$  acts only as reducing agent but  $SO_2$  acts both as reducing agent as well as an oxidising agent. Give reason.
11. Explain the following :
  - (i) Sulphur exhibits tendency for catenation but oxygen does not.
  - (ii)  $SF_6$  is not easily hydrolysed though thermodynamically it should be. Why?
12. (i) Why HF acid is stored in wax coated glass bottles?  
(ii) Give two examples to show the anomalous behaviour of fluorine.
13. (i) Xe forms compounds but Kr does not. Why?  
(ii) Why do noble gases form compounds with fluorine and oxygen only?  
(iii) Xenon does not form fluorides such as  $XeF_3$  and  $XeF_5$ .

14. Nitric acid forms anhydride (A) with  $P_4O_{10}$ .
- Write the reaction involved.
  - What is the role of  $P_4O_{10}$ ?
  - Write resonating structures of the anhydride (A) formed.
15. Write balanced chemical equations for the following reactions :
- $Cl_2 + NaOH \longrightarrow$   
(Cold and dil.)
  - $NaBr + \text{conc. } H_2SO_4 \longrightarrow$
  - $Cl_2 + NaOH \longrightarrow$   
(Hot and conc.)
- OR**
- Name two poisonous gases which can be prepared from chlorine gas and write reactions for their synthesis.
  - What happens when chlorine is passed over dry slaked lime.
16. What happens when  $SO_2$  is passed through
- acidified solution of  $K_2Cr_2O_7$ ?
  - acidified solution of  $KMnO_4$ ?
  - an aqueous solution of Fe (III) salts?
17. (i) Explain why fluorine forms only one oxoacid, HOF.  
(ii) Give reason for the following :
- Ferric iodide is very unstable but ferric chloride is stable.
  - $ClF_3$  molecule has a T-shaped structure and not a trigonal planar one.
18. (i) A green coloured solution turns pink when ozone is bubbled through it. The pink colour further decolourises when zinc and dilute  $H_2SO_4$  are added to it. Identify the green and pink coloured compounds giving sequence of reactions.  
(ii) Write chemical reaction when  $PtF_6$  and xenon are mixed together.
19. (i) Why has it been difficult to study the chemistry of radon?  
(ii) Draw the structure of  $H_2SO_5$ .  
(iii) Give reactions in which xenon fluoride acts as :
- fluoride donor
  - fluoride acceptor.
20. Give reasons for the following :
- Phosphinic acid behaves as a monoprotic acid.
  - When conc.  $H_2SO_4$  was added into an unknown salt present in a test tube, a brown gas (A) was evolved. This gas intensified when copper turnings were also added into this test-tube. On cooling, the gas (A) changed into a colourless gas (B).  
(a) Identify the gases A and B.  
(b) Write the equations for the reactions involved.
21. (i) Describe the favourable conditions for the manufacture of  
(a) ammonia by Haber's process  
(b) sulphuric acid by Contact process.  
(ii) Complete the following reaction :  
 $NH_3 + NaOCl \longrightarrow$
22. (i) How are  $XeF_2$  and  $XeF_4$  prepared?  
(ii) Complete the following reactions :  
(a)  $XeF_4 + O_2F_2 \longrightarrow$   
(b)  $XeF_4 + SbF_5 \longrightarrow$
23. In an adventurous sport, four teams have to cross a river. Team leader of one team carries a container having calcium carbide and calcium phosphide. He told his team members that in any emergency situation, pierce the bottom of container and throw into the river. This creates instantaneous fire and others will know that we need their help.
- What values are displayed by the team leader?
  - Which substance causes the instantaneous fire?
  - Write the chemistry behind the fire.
  - Write the chemical reaction for laboratory production of substance that causes instantaneous fire.
24. (A) is a translucent white waxy solid which on heating in inert atmosphere is converted to its allotropic form (B). When allotrope (A) reacts with very dilute, aqueous solution of KOH, it liberates a highly poisonous gas (C) having rotten fish smell. With excess of chlorine (C) forms (D) which hydrolyses to compound (E). Identify compounds (A) to (E).
- OR**
- What is the covalence of nitrogen in  $N_2O_5$ ?
  - How is nitric acid prepared in laboratory?
  - Ammonia is a stronger base than phosphine. Why?

- (iv) In the solid state,  $\text{PCl}_5$  behaves as an ionic species. Give reason.
- (v) Why does a nitric acid bottle appear yellow?
25. (i) Explain the following :
- $\text{O}_2$  and  $\text{F}_2$  both stabilize higher oxidation states of metals but  $\text{O}_2$  exceeds  $\text{F}_2$  in doing so.
  - Perchloric acid is a stronger acid than sulphuric acid.
  - The stability of +5 oxidation state decreases down the group in group 15 elements.
- (ii) Out of  $\text{PH}_3$  and  $\text{H}_2\text{S}$ , which is more acidic and why?
- (iii)  $\text{PCl}_5$  exists as  $[\text{PCl}_4]^+[\text{PCl}_6]^-$  but  $\text{PBr}_5$  exists as  $[\text{PBr}_4]^+[\text{Br}]^-$ . Explain

OR

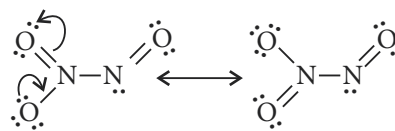
- (i) Explain the following :
- Structures of xenon fluorides cannot be explained by valence bond approach.
  - Despite having greater polarity, hydrogen fluoride boils at a lower temperature than water.
- (ii) State three important uses of neon gas.
26. (i) What is the difference between the nature of  $\pi$ -bonds present in  $\text{H}_3\text{PO}_3$  and  $\text{HNO}_3$  molecules?
- (ii) Give a chemical equation or name of the reaction to support the following statement :  
Sodium chlorate ( $\text{NaClO}_3$ ) is an oxidant.
- (iii) On being slowly passed through water,  $\text{PH}_3$  forms bubbles but  $\text{NH}_3$  dissolves. Why is it so?
- (iv) In interhalogen compounds of the type  $\text{AB}_5$  and  $\text{AB}_7$ , B is invariably fluorine. Why?
- (v) Phosphoric acid is a syrupy liquid. Explain.

OR

- (i) Two elements of the same group combine to form the compounds of the type  $\text{AA}'$ ,  $\text{AA}'_3$  and  $\text{AA}'_5$ . Draw the structure of each type, showing number of lone pairs and bond pairs?
- (ii) Explain :
- Hydrides of oxygen family are acidic in nature and acidic character increases down the group.
  - $\text{CN}^-$  is known but  $\text{CP}^-$  is not known.

## SOLUTIONS

- Very pure nitrogen can be obtained by thermal decomposition of barium azide.  
 $\text{Ba}(\text{N}_3)_2 \longrightarrow \text{Ba} + 3\text{N}_2$
- Fluoride ion ( $\text{F}^-$ ) gives most stable hexahalide with group 16 elements and these hexahalides are gaseous in nature.
- Strong intermolecular hydrogen bonding exists in HF due to high electronegativity of fluorine which causes HF to exist as a liquid.
- Helium is a non-inflammable and light gas which make it suitable for filling balloons.
- Resonance structures of  $\text{N}_2\text{O}_3$  are

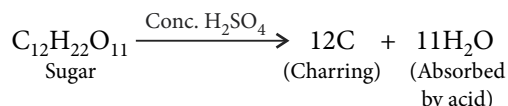


- (i)  $\text{NO}_3^- + 3\text{Fe}^{2+} + 4\text{H}^+ \longrightarrow \text{NO} + 3\text{Fe}^{3+} + 2\text{H}_2\text{O}$   
Nitrate

$[\text{Fe}(\text{H}_2\text{O})_6]^{2+} + \text{NO} \longrightarrow [\text{Fe}(\text{H}_2\text{O})_5(\text{NO})]^{2+} + \text{H}_2\text{O}$   
(Brown)

(ii)  $\text{P}_4 + 8\text{SOCl}_2 \longrightarrow 4\text{PCl}_3 + 4\text{SO}_2 + 2\text{S}_2\text{Cl}_2$   
White phosphorus      Thionyl chloride
- Interhalogen compounds are generally more reactive than halogens since  $\text{X}-\text{X}'$  bond between two dissimilar electronegative elements is weaker than  $\text{X}-\text{X}$  bond between two similar elements except  $\text{F}-\text{F}$  bond. This is due to the reason that overlapping of orbitals of two dissimilar atoms is less effective than that of two similar atoms.
- (i) Complete hydrolysis of  $\text{XeF}_6$  gives  $\text{XeO}_3$ .  
 $\text{XeF}_{6(s)} + 3\text{H}_2\text{O}_{(l)} \longrightarrow \text{XeO}_{3(s)} + 6\text{HF}_{(aq)}$

(ii)   
Pyramidal
- Chlorine bleaches by oxidation while sulphur dioxide bleaches by reduction. The reduced product when exposed to air gets oxidised again and the colour returns. That is why bleaching action of  $\text{Cl}_2$  is permanent while bleaching action of  $\text{SO}_2$  is temporary.
- (i) Sulphuric acid removes water from organic compounds and brings about charring.



- (ii) As we move down the group, the size of the central atom in  $\text{H}_2\text{M}$  increases, the H—M bond becomes weaker and breaks easily on heating. That is why thermal stability of  $\text{H}_2\text{O}$  is much higher than that of  $\text{H}_2\text{S}$ .

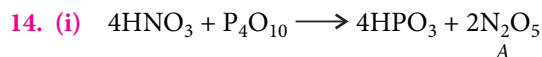
OR

Sulphur atom can have maximum oxidation state of +6 and minimum oxidation state of -2. In  $\text{SO}_2$ , the oxidation state of S is +4 therefore, it can get reduced to oxidation state of -2 as well as oxidised to oxidation state of +6 to act as oxidising agent and reducing agent respectively.

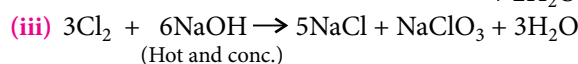
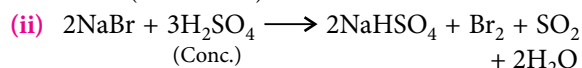
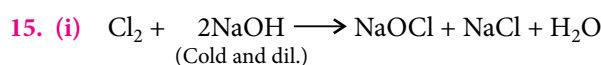
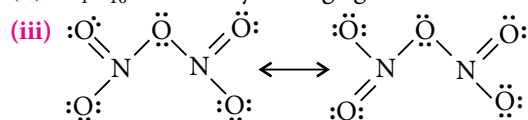
In  $\text{H}_2\text{S}$ , the oxidation state of S is -2 which is the minimum oxidation state of S hence, it can only increase its oxidation state by losing electrons and acts only as a reducing agent.

11. (i) Single O—O bond is weaker than S—S bond because of high interelectronic repulsions between the lone pair and bond pair of O—O bond, as a result catenation property is weaker in oxygen.
- (ii) In  $\text{SF}_6$  molecule, sulphur is surrounded by six fluorine atoms which protect it from attack by reagents to such an extent that even thermodynamically most favourable reactions like hydrolysis do not occur. So,  $\text{H}_2\text{O}$  cannot attack  $\text{SF}_6$  easily.
12. (i) HF does not attack wax but attacks sodium silicate which is the main constituent of glass. As a result, the glass bottles are slowly corroded or eaten up.
- $$\text{Na}_2\text{SiO}_3 + 6\text{HF} \longrightarrow \text{Na}_2\text{SiF}_6 + 3\text{H}_2\text{O}$$
- (ii) Fluorine shows only a negative oxidation state of -1 in its compounds. Other members exhibit both negative and positive oxidation states. Fluorine does not form any oxoacid while other members form a number of oxoacids.
13. (i) It is because Xe has lower ionisation enthalpy than Kr.
- (ii) Fluorine and oxygen are the most electronegative elements hence, they are very reactive and form compounds with noble gases, particularly with xenon.

- (iii) All the filled orbitals of Xe have paired electrons. The promotion of one, two or three electrons from the 5p-filled orbitals to the 5d-vacant orbitals will give rise to two, four and six half-filled orbitals. Therefore, Xe can combine with even number of F atoms but not odd. Thus, it cannot form  $\text{XeF}_3$  and  $\text{XeF}_5$ .

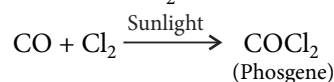


- (ii)  $\text{P}_4\text{O}_{10}$  is the dehydrating agent.

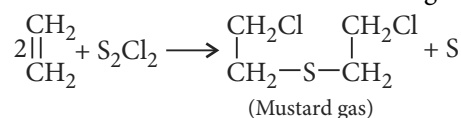


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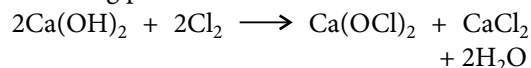
- (i) (a) **Phosgene** : It is formed by addition reaction of  $\text{Cl}_2$  and CO.



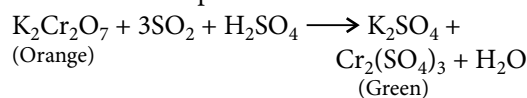
- (b) **Mustard gas** : When  $\text{Cl}_2$  is passed through boiling sulphur,  $\text{S}_2\text{Cl}_2$  is formed.  $\text{S}_2\text{Cl}_2$  is treated with ethene to form mustard gas.



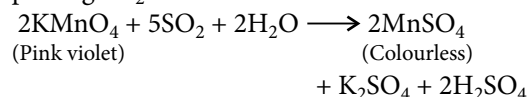
- (ii) When chlorine is passed over dry slaked lime bleaching powder is formed.



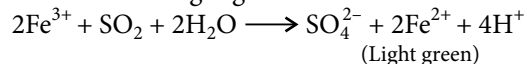
16. (i) Acidified  $\text{K}_2\text{Cr}_2\text{O}_7$  turns green due to formation of chromium sulphate.



- (ii) Acidified  $\text{KMnO}_4$  solution turns colourless on passing  $\text{SO}_2$ .



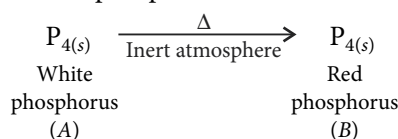
- (iii)  $\text{Fe}^{3+}$  salts are reduced to  $\text{Fe}^{2+}$  by  $\text{SO}_2$  and solution turns light green.



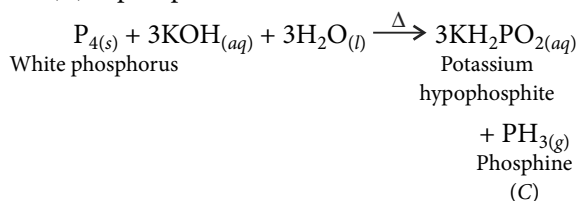


23. (i) Team leader showed responsibility and alertness.
- (ii) Phosphine,  $\text{PH}_3$  causes the instantaneous fire.
- (iii) Calcium phosphide ( $\text{Ca}_3\text{P}_2$ ) reacts with water to give  $\text{PH}_3$  which catches fire instantaneously. Also, calcium carbide ( $\text{CaC}_2$ ) on reaction with water produces acetylene which burns strongly to produce a signal.
- (iv)  $\text{P}_4 + 3\text{NaOH} + 3\text{H}_2\text{O} \longrightarrow \text{PH}_3 + 3\text{NaH}_2\text{PO}_2$   
Phosphine

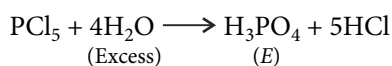
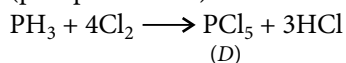
24. Since (A) is a translucent white waxy solid, which on heating in inert atmosphere is converted to its allotropic form (B) so, 'A' is white phosphorus and 'B' is red phosphorus.



When white phosphorus (A) reacts with very dilute, aqueous solution of KOH, it liberates phosphine gas which is very poisonous and has rotten fish smell. So, (C) is phosphine.

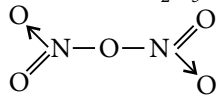


Phosphine with excess of  $\text{Cl}_2$  forms  $\text{PCl}_5$ , which hydrolyses to  $\text{H}_3\text{PO}_4$ . So, D is  $\text{PCl}_5$  and E is  $\text{H}_3\text{PO}_4$  (phosphoric acid).



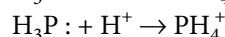
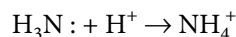
OR

- (i) The structure of  $\text{N}_2\text{O}_5$  is



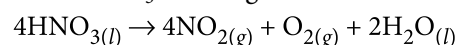
From the structure of  $\text{N}_2\text{O}_5$ , it is evident that covalence of nitrogen is four.

- (ii) Nitric acid in laboratory is prepared by heating  $\text{NaNO}_3$  and conc.  $\text{H}_2\text{SO}_4$  in a glass retort.  
 $\text{NaNO}_3 + \text{H}_2\text{SO}_4 \rightarrow \text{NaHSO}_4 + \text{HNO}_3$
- (iii) Due to the presence of lone pairs of electrons on the central atom both  $\text{NH}_3$  and  $\text{PH}_3$  are Lewis bases. When  $\text{NH}_3$  or  $\text{PH}_3$  accept a proton, an additional N—H or P—H bond is formed.

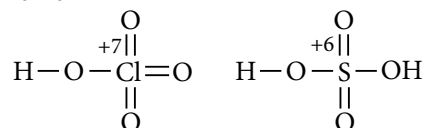


Due to smaller size of N than P, N—H bond thus formed is much stronger than P—H bond. As a result  $\text{NH}_3$  has more tendency than  $\text{PH}_3$  to accept a proton. Therefore,  $\text{NH}_3$  is stronger base than  $\text{PH}_3$ .

- (iv)  $\text{PCl}_5$  is ionic in the solid state because it exists as  $[\text{PCl}_4]^+ [\text{PCl}_6]^-$  in which the cation is tetrahedral and anion is octahedral.
- (v) The yellow colour of the concentrated nitric acid bottle is due to the partial decomposition of the  $\text{HNO}_3$  to nitrogen dioxide.



25. (i) (a) This is due to the ability of oxygen to form multiple bonds with metal atoms.
- (b) The oxidation state of Cl in perchloric acid is +7 while that of S in sulphuric acid is +6



Thus,  $\text{ClO}_3$  part of  $\text{HClO}_4$  can break the O—H bond more easily to liberate a proton than the  $\text{SO}_2$  part in  $\text{H}_2\text{SO}_4$ . Therefore, perchloric acid is a stronger acid than sulphuric acid.

- (c) In group 15 elements, the stability of +5 oxidation state decreases down the group due to inert pair effect *i.e.*, reluctance of *s*-electrons to participate in bond formation. As a result +3 oxidation state becomes more stable down the group.

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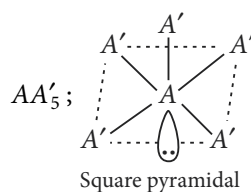
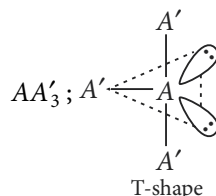
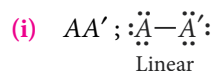
- (ii)  $\text{H}_2\text{S}$  is more acidic than  $\text{PH}_3$  because H—S bond is more polar due to higher electronegativity of sulphur.
- (iii) The splitting of  $\text{PBr}_5$  is different from  $\text{PCl}_5$  because Br atoms are large and six atoms of Br cannot be easily accommodated around smaller P atom.

OR

- (i) (a) According to the valence bond approach, orbitals containing unpaired electrons only take part in covalent bond formation. Xenon has no unpaired electrons. Hence, structure of its fluorides cannot be explained by valence bond approach.
- (b) Higher boiling point of  $\text{H}_2\text{O}$  is due to the extensive H-bonding than HF.
- (ii) (a) Neon is used in discharge tubes and fluorescent bulbs for display in advertisements.
- (b) Neon bulbs are used in botanical gardens and in green houses.
- (c) Neon is used in voltage regulators and indicators.
26. (i) In  $\text{H}_3\text{PO}_3$ , there is  $p\pi - d\pi$  bond whereas in  $\text{HNO}_3$ , there is  $p\pi - p\pi$  bond.
- (ii)  $\text{I}_2 + 2\text{NaClO}_3 \longrightarrow 2\text{NaIO}_3 + \text{Cl}_2$
- (iii)  $\text{NH}_3$  dissolves in water because it forms H-bonds whereas  $\text{PH}_3$  does not, therefore it is insoluble in water.
- (iv) Fluorine is the strongest oxidising agent therefore, it can form interhalogen compounds with other halogens in +5 and +7 oxidation states as it can provide energy for excitation of valence electrons.

- (v) Phosphoric acid is a syrupy liquid due to intermolecular H-bonding.

OR



- (ii) (a) Hydrides of oxygen family are weakly acidic in nature and acidic character increases as :  
 $\text{H}_2\text{O} < \text{H}_2\text{S} < \text{H}_2\text{Se} < \text{H}_2\text{Te}$   
 This can be explained on the basis of the size of the central atom. As the size of central atom increases, bond length ( $E-H$ ) increases and bond dissociation enthalpy decreases which further increases the acidic character of hydrides.
- (b) This is due to the reason that nitrogen can form multiple bonds ( $:\bar{\text{C}}\equiv\text{N}:$ ) while phosphorus cannot.



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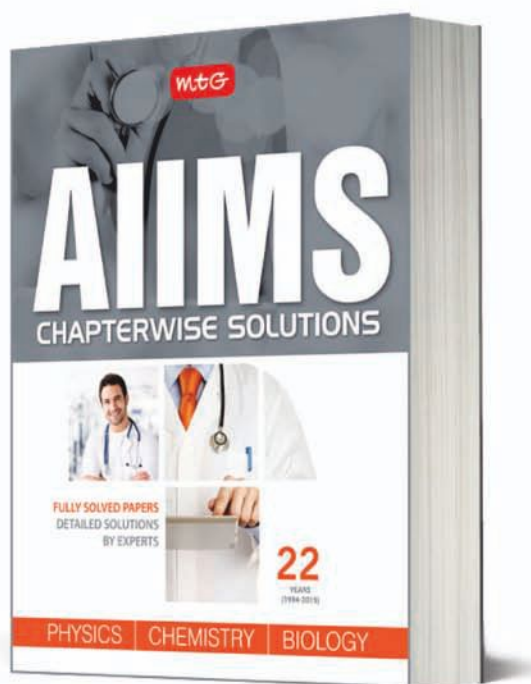
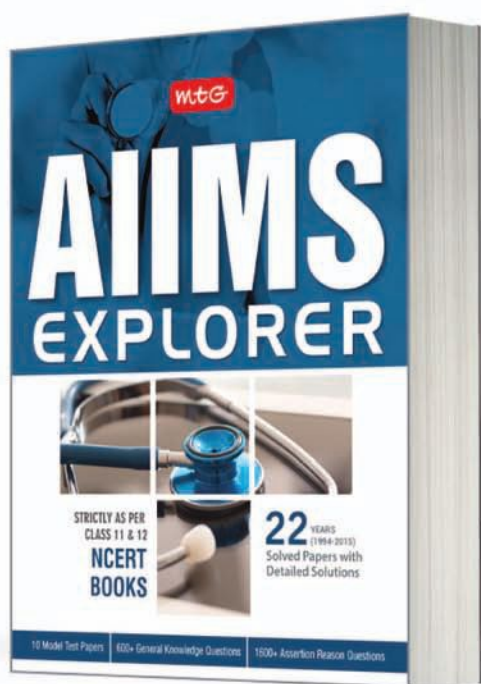
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# EXAMINER'S MIND

## CLASS XII



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

### SURFACE CHEMISTRY | GENERAL PRINCIPLES AND PROCESSES OF ISOLATION OF ELEMENTS

#### 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.

- Which of the following ores is not a sulphide ore?
  - Galena
  - Argentite
  - Malachite
  - Pyrrargyrite
- Following are the properties related to adsorption :
  - Reversible
  - Results into unimolecular layer
  - Low heat of adsorption
  - Occurs at low temperature and decreases with increasing temperature.
 Which of the above properties are for physical adsorption?
  - I, II, III only
  - I, III, IV only
  - II, III, IV only
  - I, III only
- Which of the following ores is not concentrated by electromagnetic separation?
  - Copper pyrites
  - Pyrolusite
  - Chromite
  - Cassiterite
- Lake test of aluminium ion is based on adsorption of blue litmus on solid surface of
  - Al
  - Al(OH)<sub>3</sub>
  - Al<sub>2</sub>O<sub>3</sub>
  - AlCl<sub>3</sub>
- Which of the following reaction is an example of calcination process?
  - $2\text{Ag} + 2\text{HCl} + [\text{O}] \longrightarrow 2\text{AgCl} + \text{H}_2\text{O}$
  - $2\text{Zn} + \text{O}_2 \longrightarrow 2\text{ZnO}$
  - $2\text{ZnS} + 3\text{O}_2 \longrightarrow 2\text{ZnO} + 2\text{SO}_2$
  - $\text{MgCO}_3 \longrightarrow \text{MgO} + \text{CO}_2$
- Graph between  $\log \frac{x}{m}$  and  $\log P$  is a straight line inclined at an angle,  $\theta = 45^\circ$ . When pressure of 0.5 atm and  $\log k = 0.699$ , the amount of solute adsorbed per gram of adsorbent will be
  - 1 g
  - 1.5 g
  - 2.5 g
  - 0.25 g
- During the extraction of Cu in the blast furnace at the roasting step,
  - Cu<sub>2</sub>S gets converted to Cu<sub>2</sub>O if temperature is below 800°C
  - Cu<sub>2</sub>S gets converted to Cu<sub>2</sub>O if temperature is above 800°C
  - FeS remains unaffected and gets converted to FeO only at temperature above 1000°C
  - FeSiO<sub>3</sub> is formed and removed.
- According to adsorption theory of catalysis, the speed of the reaction increases because
  - concentration of the reactant molecules at active centres of the catalyst becomes high due to adsorption
  - in the process of adsorption, the activation energy of molecules becomes large
  - adsorption produces heat which increases the speed of the reaction
  - adsorption lowers the activation energy of the reaction.
- According to Ellingham diagrams, the oxidation reaction of carbon to carbon monoxide may be used to reduce which one of the following oxides at the lowest temperature?
  - Al<sub>2</sub>O<sub>3</sub>
  - Cu<sub>2</sub>O
  - MgO
  - ZnO
- What are the products X, Y, Z (aliphatic class) in
 
$$\text{CO}_{(g)} + \text{H}_{2(g)} \xrightarrow{\text{Ni}} \text{X}$$

$$\text{CO}_{(g)} + \text{H}_{2(g)} \xrightarrow{\text{Cu}} \text{Y}$$

$$\text{CO}_{(g)} + \text{H}_{2(g)} \xrightarrow{\text{Cu/ZnO} - \text{Cr}_2\text{O}_3} \text{Z?}$$
  - CH<sub>3</sub>OH in all cases
  - CH<sub>3</sub>OH, HCHO, CH<sub>4</sub>
  - CH<sub>4</sub>, HCHO, CH<sub>3</sub>OH
  - CH<sub>4</sub>, CH<sub>3</sub>OH, HCHO

11. The method of zone refining of metals is based upon the principle of
- greater solubility of the impurity in molten state than in solid
  - greater mobility of pure metal than impurity
  - higher melting point of impurity than that of pure metal
  - greater noble character of solid metal than that of the impurity.
12. Which is not the example of coagulation?
- Curdling of milk
  - Purification of water by addition of alum
  - Rubber plating
  - Formation of deltas at the river beds
13. Chromatography is based on the general principle of
- phase rule
  - phase distribution
  - interphase separation
  - phase operation.
14. The Brownian movement is due to
- temperature fluctuations within the liquid phase
  - attraction and repulsion between charges on colloidal particles
  - impact of molecules of the dispersion medium on colloidal particles
  - none of these.
15. A coupled reaction takes place as follows :
- $$A + B \longrightarrow C + D, \quad \Delta G^\circ = +x \text{ kJ}$$
- $$D + E \longrightarrow F \quad \Delta G^\circ = -y \text{ kJ}$$
- For the spontaneity of reaction  $A + B + E \longrightarrow C + F$ , which of the following relations is correct?
- $2x = y$
  - $x < y$
  - $x > y$
  - $x = y$
16. Identify the correct statement regarding enzymes.
- Enzymes are specific inorganic catalysts that possess well-defined active sites.
  - Enzymes are specific biological catalysts that can normally function at very high temperature ( $T \approx 1000 \text{ K}$ ).
  - Enzymes are normally heterogeneous catalysts that are very specific in action.
  - Enzymes are specific biological catalysts that cannot be poisoned.
17. Which of the following forms of iron has the highest carbon content?
- Cast iron
  - Wrought iron
  - Stainless steel
  - Powerful magnet
18. Compared to common colloidal solution micelles have
- higher colligative property
  - lower colligative property
  - same colligative property
  - none of these.
19. Which of the following reactions is not taking place during the extraction of Ag from  $\text{Ag}_2\text{S}$  by cyanide process?
- $\text{Ag}_2\text{S} + \text{CN}^- \longrightarrow [\text{Ag}(\text{CN})_2]^- + \text{S}^{2-}$
  - $\text{Zn} + 2[\text{Ag}(\text{CN})_2]^- \longrightarrow [\text{Zn}(\text{CN})_4]^{2-} + 2\text{Ag}\downarrow$
  - $\text{Cu} + 2[\text{Ag}(\text{CN})_2]^- \longrightarrow [\text{Cu}(\text{CN})_4]^{2-} + 2\text{Ag}\downarrow$
  - None of these
20. Milk can be preserved by adding a few drops of
- formic acid solution
  - formaldehyde solution
  - acetic acid solution
  - acetaldehyde solution.

## 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. On adding  $\text{AgNO}_3$  solution into KI solution, a negatively charged colloidal sol is obtained on mixing
- 100 mL of 0.1 M  $\text{AgNO}_3$  + 100 mL of 0.1 M KI
  - 100 mL of 0.1 M  $\text{AgNO}_3$  + 100 mL of 0.2 M KI
  - 100 mL of 0.2 M  $\text{AgNO}_3$  + 100 mL of 0.1 M KI
  - 100 mL of 0.15 M  $\text{AgNO}_3$  + 100 mL of 0.25 M KI
22. Which of the following is/are correct?
- $\text{Fe}_2\text{O}_3 + \text{CO} \xrightarrow[\Delta]{\text{Blast furnace}} \text{Fe}$
  - $\text{ZnO} + \text{C} \xrightarrow{1200^\circ\text{C}} \text{Zn}$
  - $\text{Ca}_3(\text{PO}_4)_2 + \text{C} \xrightarrow{\Delta} \text{P}$
  - $\text{MgO} + \text{C} \xrightarrow[\Delta]{2000^\circ\text{C}} \text{Mg}$
23. Choose the correct reason(s) for the stability of lyophobic colloidal particles.
- Preferential adsorption of ions on their surface from the solution.
  - Preferential adsorption of solvent on their surface from the solution.
  - Attraction between different particles having opposite charges on their surface.
  - Potential difference between the fixed layer and the diffused layer of opposite charges around the colloidal particles.

24. Which of the following is/are not method(s) for refining metals?
- Poling
  - Cupellation
  - Goldschmidt aluminothermic process
  - Smelting
25. Colloidal solutions of gold prepared by different methods are of different colours because of
- different diameters of colloidal gold particles
  - variable valency of gold
  - different concentration of gold particles
  - impurities produced by different methods.

### 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

It is quite easy to reduce oxide ores of copper directly to the metal by heating with coke (the lines of C, CO and C, CO<sub>2</sub> are at much lower positions in the Ellingham diagram particularly after 500 – 600 K). However most of the ores are sulphide and some may also contain iron. The sulphide ores are roasted/smelted to give oxides. The oxide can then be easily reduced to metallic copper using coke.

26. Smelting process is carried at about 1400°C. Two layers are formed
- bottom layer contains copper matte
  - upper layer contains copper matte
  - copper matte remains in both the layers
  - copper matte is not present in any of the layers.
27. When copper pyrites is roasted in excess of air, a mixture of CuO + FeO is formed. FeO is present as impurity. This can be removed as slag during reduction of CuO. The flux added to form slag is
- SiO<sub>2</sub>, which is an acidic flux
  - limestone, which is a basic flux
  - SiO<sub>2</sub>, which is a basic flux
  - CaO, which is a basic flux.
28. Blister copper is
- impure copper
  - obtained in self-reduction process during bessemerisation
  - both (a) and (b) are correct
  - none of the above is correct.

#### Paragraph for Questions 29 to 31

There are certain colloids which behave as normal strong electrolytes at low concentrations, but exhibit colloidal properties at higher concentrations due to the formation of aggregated particles. These are known as micelles or associated colloids. Surface active agents like soaps and synthetic detergents belong to this class.

29. Select the incorrect statement(s).
- Surface active agents like soaps and synthetic detergents are micelles.
  - Soaps are emulsifying agents.
  - C<sub>17</sub>H<sub>35</sub> (hydrocarbon part) and —COO<sup>−</sup> (carboxylate) part of stearate ion (C<sub>17</sub>H<sub>35</sub>COO<sup>−</sup>) both are hydrophobic.
  - All the above statements are incorrect.
30. Which part of the soap (RCOO<sup>−</sup>) dissolves grease and forms micelle?
- R part (called tail of the anion)
  - COO<sup>−</sup> part (called head of the anion)
  - Both (a) and (b)
  - None of the above
31. In multimolecular colloidal sols, atoms or molecules are held together by
- H-bonding
  - van der Waals forces
  - ionic bonding
  - polar covalent bonding.

### 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 with List II and select the correct answer using the code given below the lists :

List I				List II	
P.	CaO + SiO <sub>2</sub> → CaSiO <sub>3</sub>			1.	850°C
Q.	C + CO <sub>2</sub> → 2CO			2.	1900°C
R.	FeO + C → Fe + CO			3.	250°C
S.	Fe <sub>2</sub> O <sub>3</sub> + CO → Fe <sub>3</sub> O <sub>4</sub> + CO <sub>2</sub>			4.	1500°C
	<b>P</b>	<b>Q</b>	<b>R</b>	<b>S</b>	
(a)	1	4	2	3	
(b)	4	2	3	1	
(c)	1	2	4	3	
(d)	3	2	1	4	

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

List I		List II	
	<b>X (Colloids)</b>		<b>Y (Classification)</b>
P.	Rain cloud	1.	Sol
Q.	Milk of magnesia	2.	Aerosol
R.	Soap suds	3.	Gel
S.	Butter	4.	Foam

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

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.	Carnallite	1.	Zinc
Q.	Calamine	2.	Titanium
R.	Ilmenite	3.	Magnesium
S.	Chalcopyrite	4.	Copper

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

### SECTION - V

#### Assertion-Reason Type

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

- (a) If both assertion and reason are true and reason is the correct explanation of assertion.  
 (b) If both assertion and reason are true but reason is not the correct explanation of assertion.  
 (c) If assertion is true but reason is false.  
 (d) If both assertion and reason are false.

35. **Assertion :** In the presence of promoter, the activity of the catalyst is enhanced.

**Reason :** The promoter increases the surface area of the catalyst and thus, enhancing the number of active centres.

36. **Assertion :** Levigation is used for the separation of oxide ores from impurities.

**Reason :** Ore particles are removed by washing in a current of water.

37. **Assertion :** The adsorption of hydrogen on the surface of glass is an endothermic process.

**Reason :** Change in the entropy of the process is highly positive.

38. **Assertion :** Aluminium is used as a reducing agent in aluminothermy.

**Reason :** Aluminium has lower melting point than Fe, Cr and Mn.

39. **Assertion :** A colloidal sol of  $\text{Fe}(\text{OH})_3$  formed by peptisation carries positive charge.

**Reason :** During formation of  $\text{Fe}(\text{OH})_3$  sol, electrons are lost by the particles.

40. **Assertion :** Pb, Sn and Bi are purified by liquation method.

**Reason :** Pb, Sn and Bi have low melting point as compared to impurities.

### 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.  $\text{KClO}_3$  decomposition is catalysed by  $\text{MnO}_2$ . A green coloured intermediate of Mn is formed. What is the oxidation number of Mn in this intermediate?

42. Among the following, how many are oxide ores? Zincite, siderite, magnetite, tin stone, malachite

43. Positively charged colloidal sol is formed by hydrolysis of  $\text{FeCl}_3$ . How many total ions are present in fixed layer and diffused layer.

44. How many of the following metals can be refined by vapour phase refining?

Zn, Cd, Ti, Pt, Zr, Th, Ni

45. How many of the following are colloidal systems having solid dispersed in liquid?

Fog, cloud, foam, proteins, gold sol, ink, paint, arsenic sulphide sol

46. The formula of carnallite is  $\text{KCl} \cdot \text{MgCl}_2 \cdot x\text{H}_2\text{O}$ . The value of  $x$  is

47. 0.008 g of starch is required to prevent coagulation of 10 mL of gold sol when 1 mL of 10% NaCl solution is present. What is gold number of starch sol?

48. How many of the following are aerosols?

Smoke, cheese, butter, duststorm, milk, whipped cream

49. During adsorption of acetic acid vapour by 1 g of charcoal, the following observations are obtained :

	(i) Observation	(ii) Observation
$x$	0.726	0.438
$P$	0.576	0.210

What is the value of  $k$ ?

50. How many of the following metals are obtained by leaching the ore with a cyanide solution?

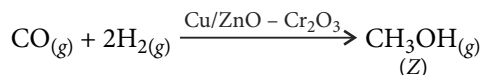
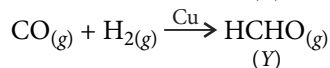
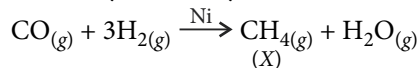
Au, Ag, Fe, Cu, Co

## SOLUTIONS

1. (c) : Malachite is  $\text{CuCO}_3 \cdot \text{Cu}(\text{OH})_2$ .  
 (a) Galena is  $\text{PbS}$ .  
 (b) Argentite is  $\text{Ag}_2\text{S}$ .  
 (d) Pyrargyrite is  $\text{Ag}_3\text{SbS}_3$ .
2. (b) : Physical adsorption results into multimolecular layers on adsorbent surface under high pressure. While chemical adsorption results into unimolecular layer.
3. (a) : Copper pyrites is a non-magnetic ore while (b), (c) and (d) are magnetic ores, therefore, it cannot be concentrated by electromagnetic separation.
4. (b) : Aluminium hydroxide formed in the lake test is a good adsorbent. Therefore, it adsorbs the blue litmus solution and gives blue lake test.
5. (d) : During calcination process, the concentrated ore is heated in the absence of air or limited supply of air. Thus,  $\text{MgCO}_3$  when heated in absence of air it gives  $\text{MgO}$  and volatile  $\text{CO}_2$  is removed.
6. (c) :  $\frac{x}{m} = k \cdot P^{1/n}$   
 $\log \frac{x}{m} = \log k + \frac{1}{n} \log P$   
 Plot of  $\log \frac{x}{m}$  vs  $\log P$  is a straight line, with slope =  $\frac{1}{n}$  and intercept  $\log k$ .  
 Since  $\log k = 0.699$ , hence  $k = 5$   
 Slope =  $\frac{1}{n} = \tan 45^\circ = 1$ , hence  $n = 1$ ,  $P = 0.5$  atm  
 Thus,  $\frac{x}{m} = 5 \times (0.5)^1 = 2.5$  g per gram of adsorbent
7. (b) : (b) is correct as very high energy is required for the conversion of  $\text{CuS}$  to  $\text{CuO}$ . It follows (a) is wrong.  
 (c) is wrong as  $\text{FeS}$  gets converted to  $\text{FeO}$  even at low temperature below  $800^\circ\text{C}$ .  
 (d) is wrong as  $\text{FeSiO}_3$  is formed at  $1400^\circ\text{C}$  during smelting and not during roasting.
8. (a) : The increased concentration of the reactants on the surface influences the rate of reaction.
9. (b) : Carbon is used as the reducing agent. It combines with oxygen of the metal oxide to form carbon monoxide.  
 $M_xO_y + yC \longrightarrow xM + yCO$   
 Ellingham diagram consists of plots of  $\Delta_f G^\circ$  vs  $T$  for formation of oxides of elements.  
 A point, where the  $\Delta G^\circ$  value becomes more negative for the combined process results in the reduction of metal oxide.

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

10. (c) : The given sequence of reactions shows the selectivity of a catalyst.



11. (a) : Zone refining is based on the principle that the impurities are more soluble in the melt than in the solid state of the metal.

12. (c) : Rubber plating does not involve coagulation process.

13. (c)

14. (c)

15. (b) : For a spontaneous reaction,  $\Delta G^\circ$  must be negative and it can only be possible when  $x < y$ .

16. (c)

17. (a) : Cast iron – 2.5 – 5% carbon, stainless steel ~ 0.25 – 2.0% carbon, wrought iron – 0.1–0.21% carbon.

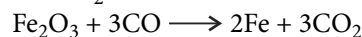
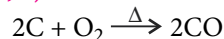
18. (b) : Micelles have lower colligative property than colloids.

19. (c) : Only highly reactive metals can displace Ag. Here though copper has less reduction potential than Ag still its oxidation potential is not very high that the yields are very good. Hence, only Zn is used.

20. (b) : Milk can be preserved by adding formaldehyde.

21. (b, d) : Solutions having higher concentration of  $\text{I}^-$  ions than  $\text{Ag}^+$  ions will result in the formation of a negatively charged colloidal sol.

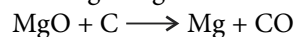
22. (a, b, d) : In a blast furnace



When  $\text{ZnO}$  is heated with carbon, Zn is obtained.



While when  $\text{MgO}$  is heated at  $2000^\circ\text{C}$  in electric furnace we get Mg.



23. (a, d) : Adsorption of same type of ions on their surface causes repulsion between them and thus stabilise the colloid. Also, the potential difference between the fixed and diffused layer of opposite charges results in stabilisation of colloid.



# YOU ASK WE ANSWER

Do you have a question that you just can't get answered?

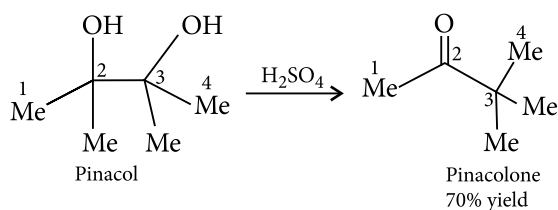
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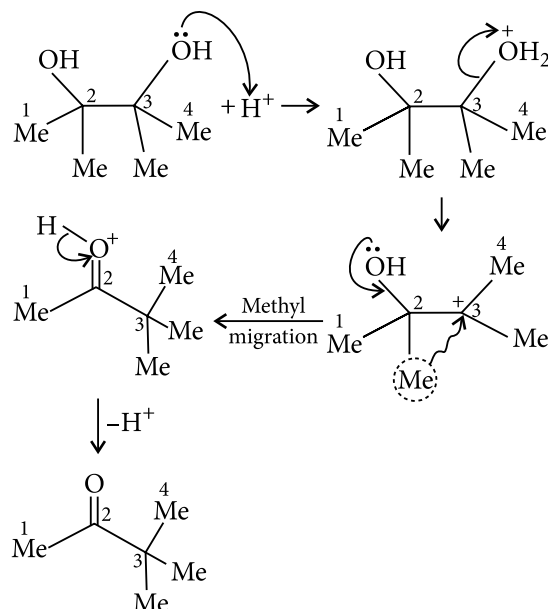
**Q1. I want to know more about Pinacol-Pinacolone rearrangement mechanism and its importance.**

*Rishikiran Devajyoti Sahoo (Bhubaneswar, Odisha)*

**Ans.** When the 1,2-diol pinacol is treated with acid, a rearrangement takes place.

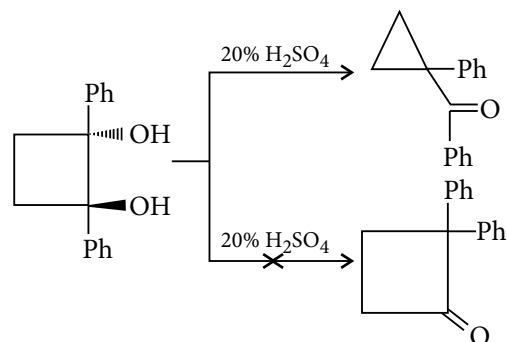


The reaction proceeds via carbocation intermediate which undergoes methyl migration and subsequent loss of proton to give a stable ketone.



Other important aspects of Pinacol-Pinacolone rearrangement :

- (i) Epoxides rearrange with Lewis acids in a Pinacol fashion.
- (ii) In case of an unsymmetrical diol or epoxide, the formation of product occurs via the formation of more stable carbocation.
- (iii) Strain factors decide the product formed as illustrated below :



Phenyl group has a high migratory aptitude still isomeric cyclobutanone does not form as the carbocation that results from a phenyl shift would be just as strained as its precursor. Whereas, the shift of methylene group of the ring generates an unstrained cation stabilised by phenyl and oxygen.

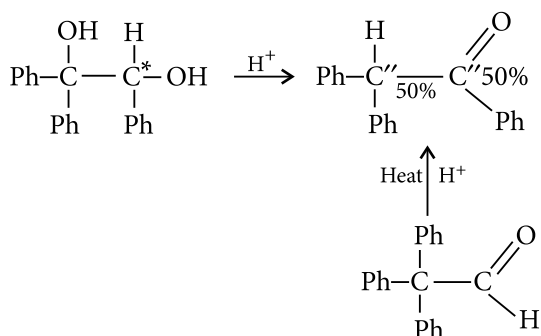
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(iv) Additional information from stereochemical and isotopic labeling viewpoints :



Rate of racemisation = Rate of rearrangement  
Loss of water from the tertiary carbinol site, followed by a reversible 1,2-hydride shift, generates a conjugate acid of the ketone product. A corresponding phenyl shift to the initially formed tertiary carbocation generates the aldehyde conjugate acid and the aldehyde itself isomerises to the same rearranged ketone. An isotopic carbon label ( $C^*$ ) in either the diol or aldehyde is scrambled ( $C''$ ) in the course of these reactions, thus, indicating an epoxide intermediate.

(v) Pinacol rearrangement is used in the biosynthesis of valine and isoleucine.

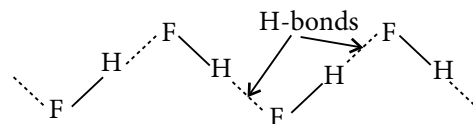
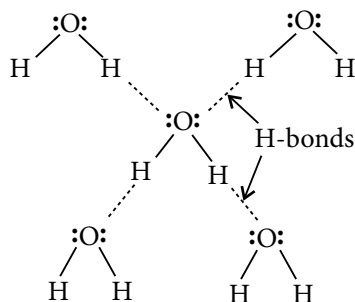
(vi) Pinacol rearrangement is used in the synthesis of bicyclic alkene.

**Q2. Though water has lesser molecular mass than HF, it has higher boiling point. Why?**

*A. Sai Krishna*

**Ans.** Boiling point of water ( $100^\circ\text{C}$ ) is much higher than HF ( $19.5^\circ\text{C}$ ).

As we know, more the intermolecular attractions, higher is the boiling point. There is extensive H-bonding in  $\text{H}_2\text{O}$  as compared to HF. There are four hydrogen bonds in  $\text{H}_2\text{O}$  and two in HF since oxygen atom in  $\text{H}_2\text{O}$  has two lone pairs of electrons which also participate in H-bonding.



**Q3. Ligands capable of forming very strong bonds (strong field ligands) give low spin complexes whereas those forming weak bonds (weak field ligands) give high spin complexes. Why?**

*Kanika Sharma (Maharashtra)*

**Ans.** In low spin complexes,  $d$ -electrons are forcefully paired up to generate inner vacant  $d$ -orbitals so that inner orbital hybridization ( $d^2sp^3$ ,  $dsp^2$ ) can take place. This activity requires energy. Only ligands capable of forming very strong bonds release enough energy to cause this action. On the other hand, weak field ligands do not have that much of strength to pair the  $d$ -electrons and hence form high spin complexes.



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#### SET 25

1. Harpreet Singh (Ambala)
2. Swayangdipta Bera
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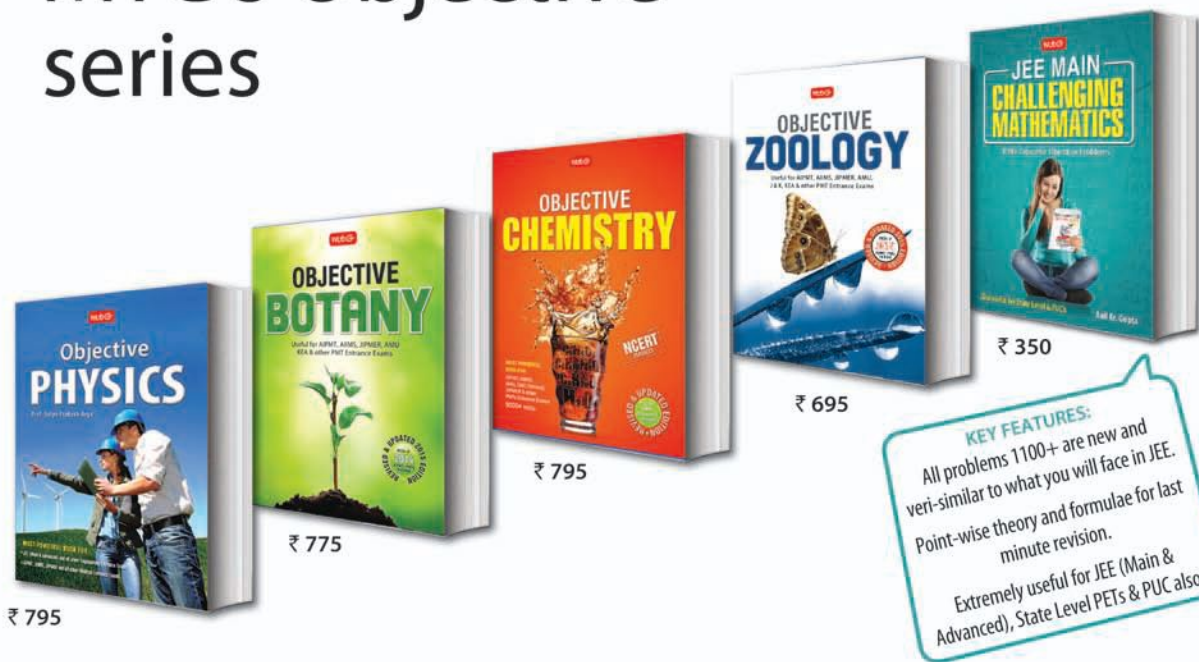
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# OLYMPIAD PROBLEMS



- In hexagonal close packing of spheres in three dimensions
  - in one unit cell there are 12 octahedral voids and all are completely inside the unit cell
  - in one unit cell there are six octahedral voids and all are completely inside the unit cell
  - in one unit cell there are six octahedral voids of which, three are completely inside the unit cell and other three are from contributions of octahedral voids which are partially inside the unit cell
  - in one unit cell there are 12 tetrahedral voids and all are completely inside the unit cell.
- An element has atomic number 79. Predict the group and period in which the element is placed.
  - 2<sup>nd</sup> group, 7<sup>th</sup> period
  - 11<sup>th</sup> group, 6<sup>th</sup> period
  - 13<sup>th</sup> group, 6<sup>th</sup> period
  - 12<sup>th</sup> group, 6<sup>th</sup> period
- Which of the following is also known as “fools” gold?
  - wurtzite
  - iron pyrites
  - chalcocite
  - silver glance
- In the nitration of benzene with concentrated HNO<sub>3</sub> and concentrated H<sub>2</sub>SO<sub>4</sub>, the electrophile is
  - NO<sub>2</sub><sup>+</sup>
  - NO<sub>2</sub><sup>-</sup>
  - NO<sub>2</sub>
  - nitric oxide
- At constant volume and temperature conditions, the rates of diffusion  $D_A$  and  $D_B$  of gases  $A$  and  $B$  having densities  $\rho_A$  and  $\rho_B$  are related by the expression
  - $D_A = \left[ D_B \cdot \frac{\rho_A}{\rho_B} \right]^{1/2}$
  - $D_A = \left[ D_B \cdot \frac{\rho_B}{\rho_A} \right]^{1/2}$
  - $D_A = D_B \left( \frac{\rho_A}{\rho_B} \right)^{1/2}$
  - $D_A = D_B \left( \frac{\rho_B}{\rho_A} \right)^{1/2}$
- A compound C<sub>4</sub>H<sub>8</sub> decolourises a KMnO<sub>4</sub> solution. How many structures are possible for this compound?
  - 3
  - 4
  - 2
  - 5
- Which of the following molecules shows  $p\pi-p\pi$  bonding?
  - P<sub>4</sub>
  - As<sub>4</sub>
  - Sb<sub>4</sub>
  - N<sub>2</sub>
- Among the following compounds, the one which will not show keto-enol tautomerism is
  - 
  - 
  - 
  -
- Carbon suboxide C<sub>3</sub>O<sub>2</sub> has
  - linear structure
  - bent structure
  - trigonal planar structure
  - distorted tetrahedral structure.
- [Cr(H<sub>2</sub>O)<sub>6</sub>]Cl<sub>3</sub> (At. no. of Cr = 24) has a magnetic moment of 3.83 B.M. The correct distribution of 3d electrons in the central atom of the complex is
  - 3d<sub>xy</sub><sup>1</sup>, 3d<sub>yz</sub><sup>1</sup>, 3d<sub>z<sup>2</sup></sub><sup>1</sup>
  - 3d<sub>(x<sup>2</sup>-y<sup>2</sup>)</sub><sup>1</sup>, 3d<sub>z<sup>2</sup></sub><sup>1</sup>, 3d<sub>xz</sub><sup>1</sup>
  - 3d<sub>xy</sub><sup>1</sup>, 3d<sub>(x<sup>2</sup>-y<sup>2</sup>)</sub><sup>1</sup>, 3d<sub>yz</sub><sup>1</sup>
  - 3d<sub>xy</sub><sup>1</sup>, 3d<sub>yz</sub><sup>1</sup>, 3d<sub>xz</sub><sup>1</sup>

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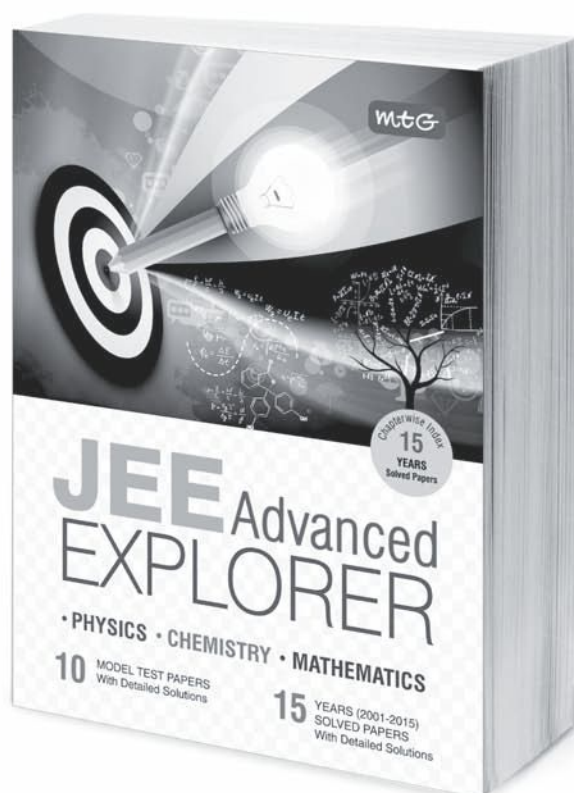
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11. A bottle completely filled with conc.  $\text{H}_2\text{SO}_4$  is left unstoppered for several days and we observe spontaneous overflow of acid. It is due to
- change in temperature
  - dehydration of  $\text{H}_2\text{SO}_4$
  - hygroscopic nature of  $\text{H}_2\text{SO}_4$
  - absorption of air by  $\text{H}_2\text{SO}_4$ .
12. Novolac is
- linear condensation product of phenol and formaldehyde
  - cross linked condensation product of urea and formaldehyde
  - cross linked condensation product of phenol and formaldehyde
  - linear condensation product of urea and formaldehyde.
13. Consider the following reactions at 300 K.  
 $A \longrightarrow B$  (uncatalysed reaction)  
 $A \xrightarrow{\text{catalyst}} B$  (catalysed reaction)  
 The activation energy is lowered by  $8.314 \text{ kJ mol}^{-1}$  for the catalysed reaction. The rate of this reaction is \_\_\_\_\_ that of the uncatalysed reaction.
- 15 times
  - 38 times
  - 22 times
  - 28 times
14. An acid-base indicator has a  $K_a = 1.0 \times 10^{-5}$ . The acid form of the indicator is red and the basic form is blue. Calculate the pH change required to change the colour of the indicator from 80% red to 80% blue.
- 1.20
  - 0.80
  - 0.20
  - 1.40
15. Which pair has most similar geometry?
- $\text{SO}_3$  and  $\text{SO}_3^{2-}$
  - $\text{SO}_3$  and  $\text{CO}_3^{2-}$
  - $\text{SO}_3$  and  $\text{SO}_4^{2-}$
  - $\text{SO}_4^{2-}$  and  $\text{CO}_3^{2-}$
16. The vapour pressure of a liquid in a closed container depends upon
- temperature of the liquid
  - quantity of the liquid
  - surface area of the liquid
- (i) only
  - (ii) only
  - (i) and (iii) only
  - (i), (ii) and (iii).
17. For compounds with the same anion, the hydration energies of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$  and  $\text{Li}^+$  follow the order
- $\text{Cs}^+ > \text{Rb}^+ > \text{K}^+ > \text{Na}^+ > \text{Li}^+$
  - $\text{Li}^+ > \text{Na}^+ > \text{K}^+ > \text{Rb}^+ > \text{Cs}^+$
  - $\text{K}^+ > \text{Na}^+ > \text{Li}^+ > \text{Cs}^+ > \text{Rb}^+$
  - $\text{Li}^+ > \text{K}^+ > \text{Na}^+ > \text{Cs}^+ > \text{Rb}^+$
18. Milk can be preserved by adding a few drops of
- formic acid solution
  - formaldehyde solution
  - acetic acid solution
  - acetaldehyde solution.
19. The atomic weights of two elements  $A$  and  $B$  are 40 and 80 respectively. If  $x$  g of  $A$  contains  $y$  atoms, how many atoms are present in  $2x$  g of  $B$ ?
- $\frac{y}{2}$
  - $\frac{y}{4}$
  - $y$
  - $2y$
20. Protein responsible for blood clotting is
- albumin
  - globulin
  - fibroin
  - fibrinogen.
21. In which of the following reactions will there be no change in the oxidation number of nitrogen?
- $\text{HNO}_3 + 2\text{H}_2\text{SO}_4 \longrightarrow \text{NO}_2^+ + \text{H}_3\text{O}^+ + 2\text{HSO}_4^-$
  - $2\text{N}_2\text{O}_4 + 2\text{KI} \longrightarrow 2\text{KNO}_3 + 2\text{NO} + \text{I}_2$
  - $2\text{KNH}_2 + \text{N}_2\text{O} \longrightarrow \text{KN}_3 + \text{KOH} + \text{NH}_3$
  - $4\text{NO}_2 + \text{O}_2 + 2\text{H}_2\text{O} \longrightarrow 4\text{HNO}_3$
22. When a Cu-Zn galvanic cell operates under standard conditions,
- the concentration of  $\text{Zn}^{2+}$  ions in the zinc half-cell gradually decreases
  - the concentration of  $\text{Cu}^{2+}$  ions in the copper half-cell gradually increases
  - negative ions migrate from the zinc half-cell to the copper half-cell
  - the intensity of the colour of the electrolyte in the copper half-cell gradually decreases.
23. The ligand tetraethylenepentamine forms \_\_\_\_\_ with central metal.
- four 5-membered rings
  - five 4-membered rings
  - four 4-membered rings
  - five 5-membered rings
24. A gel is
- a liquid mass of a lyophilic sol in which all the dispersion medium has penetrated into the sol particles
  - like an emulsion which is stabilized by adding emulsifying agent

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- (c) a semi-rigid mass of a lyophobic sol in which all the dispersion medium has penetrated into the sol particles
- (d) a semi-rigid mass of a lyophilic sol in which all the dispersion medium has penetrated into the sol particles.
25. A solution of (-)-1-chloro-1-phenylethane in toluene racemises slowly in the presence of small amount of  $\text{SbCl}_5$  due to the formation of
- (a) carbanion (b) carbene  
(c) free radical (d) carbocation.
26. Equal volumes of 1 M HCl and 1 M  $\text{H}_2\text{SO}_4$  are neutralised by a 1 M NaOH solution, and  $x$  and  $y$  kJ/equivalent of heat are liberated respectively. Which of the following relations is correct?
- (a)  $x = 2y$  (b)  $x = 3y$   
(c)  $x = 4y$  (d)  $x = \frac{1}{2}y$
27. In which of the following compounds B atoms are in  $sp^2$  and  $sp^3$  hybridisation states?
- (a) borax (b) diborane  
(c) borazole (d) sodium metaborate
28. Among the following, the latent heats of fusion and vapourisation are maximum in
- (a)  $\text{H}_2$  (b)  $\text{D}_2$   
(c)  $\text{T}_2$  (d)  $\text{H}_2^+$
29. What is the order of increasing tendency for dehydrohalogenation for the following compounds?
- (I)  $\text{CH}_3\text{CH}_2-\overset{\text{Br}}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$
- (II)  $\text{CH}_3\text{CH}_2\underset{\text{Br}}{\text{CH}}\text{CH}_2\text{CH}_3$
- (III)  $\text{CH}_3\text{CH}_2\text{CH}_2\underset{\text{Br}}{\text{CH}}\text{CH}_3$
- (IV)  $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Br}$   
(V)  $\text{CH}_3\text{CH}_2\text{Br}$
- (a)  $\text{V} < \text{IV} < \text{III} < \text{II} < \text{I}$   
(b)  $\text{V} < \text{I} < \text{II} < \text{III} < \text{IV}$   
(c)  $\text{I} < \text{II} < \text{III} < \text{IV} < \text{V}$   
(d)  $\text{I} < \text{III} < \text{II} < \text{IV} < \text{V}$
30. In the period October 2004-2006, the South African newspaper group, The Independent, published over 30 articles on vioxx. Vioxx (also called Refexicob)

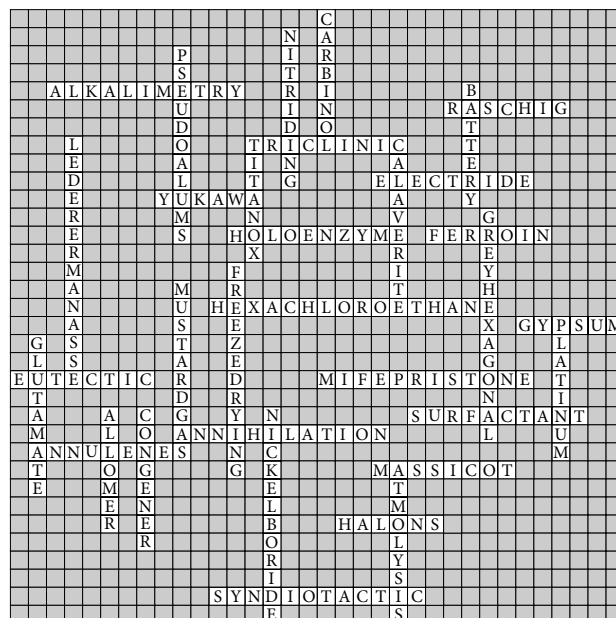
was the drug manufactured by Merck and approved by the FDA as a nonsteroidal anti-inflammatory drug to treat arthritis. The drug was withdrawn on September 30, 2004, leading to several lawsuits against Merck. The reason for the drug's withdrawal was

- (a) vioxx was not particularly effective and fared much worse than aspirin  
(b) Merck falsified clinical data and misled the FDA into approving vioxx  
(c) vioxx increased patient's risks of getting heart attacks  
(d) vioxx was too expensive to make and very little profit could be made from its sales.

## ANSWER KEYS

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

## SOLUTIONS TO AUGUST 2015 CROSSWORD



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- Prag Mukherjee (West Bengal)
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# CROSSWORD



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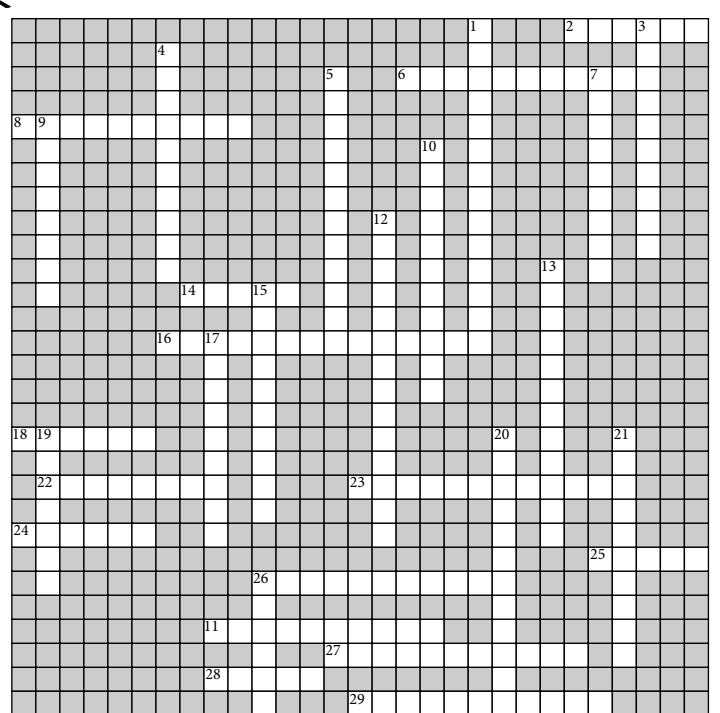
## ACROSS

2. A general name used for aromatic hydrocarbons. (6)
6. The compounds which when combine with the moisture in atmosphere are converted into hydroxides or hydrates. (11)
8. The law which explains the expansion of air on heating. (10)
11. A reaction with positive  $\Delta G$ . (11)
14. A subatomic particle having either a positive or negative charge equal to that of an electron. (5)
16. A reaction that yields only one (or a predominance of one) constitutional isomer as the product when two or more constitutional isomers are possible products. (14)
18. The metal used in making gold paint. (6)
22. Sols having very high viscosity than that of the solvent. (8)
23. The crystalline parts of the amorphous solids. (12)
24. The formation of an oxide film on the surface of bronze, iron, etc., resulting in a decorative and corrosion resistant surface. (6)
25. A brand name for medicinal liquid paraffin. (5)
26. Elements present in warm superconductors. (11)
27. Other name of halo alcohols. (11)
28. A neutral molecule having a negative carbon adjacent to a positive heteroatom. (5)
29. The reciprocal of disintegration constant. (11)

## DOWN

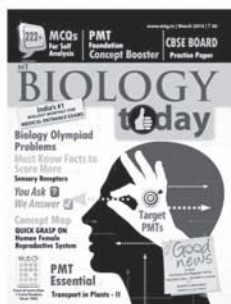
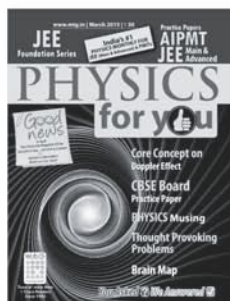
1. Compound used specifically in X-ray imaging of the stomach. (14)
3. A five-carbon monosaccharide bonded at the 1' position to a purine or pyrimidine. (10)
4. Thermosetting plastics have strong supporting \_\_\_\_\_. (10)
5. An electrical apparatus used commercially to make chlorine and sodium hydroxide. (12)
7. The ions present in plant fertilizers used for flowering. (9)

Cut Here



9. The product obtained at cathode by the electrolysis of aqueous NaCl. (8)
10. Process of removing alkenes from light petroleum fractions. (11)
12. Titration which can be used for coloured solutions and will work where no indicator is found to be satisfactory. (14)
13. The process in which the magnetic iron oxide is reduced to iron by the action of water gas. (12)
15. A chemical species with an oxygen atom that bears a formal positive charge. (10)
17. A mixture of  $\text{KNO}_3$ , sulphur and charcoal. (9)
19. A four membered ether. (7)
20. The colloidal system where the sizes of dispersed particles are widely different. (12)
21. Process by which the enantiomers of a racemic form are separated. (10)
26. The German chemist who discovered Mond's process for purification of Ni. (6)

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